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STABILITY CONSTANTS OF COMPLEXES OF METAL IONS WITH PEATSOIL HUMIC ACIDS UNDER NON-ACID-CONDITIONS

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ABSTRACT

Stability constants of complexes of four divalent metal ions viz. Cu^{2+}, Pb^{2+},Mg^{2+} and Cd^{2+} with humic acids (HA) were determined by potentiometric titration of humic acids with the corresponding salt of the divalent metals in aqueous media under non-acid-condition. The log K (logarithm of the stability constant) ranged from 1.0942 to 2.7471 for metal-humic acid complexes were determined using point-wise computational method. The order of stability constants were obtained as follows: Cu >Pb> Cd > Mg for metal -HA complexes respectively, indicating a higher degree of complexation with Cu metal ion.

Keywords: stability constant, humic acid, potentiometric titration, divalent metals, acid hydrolysis.

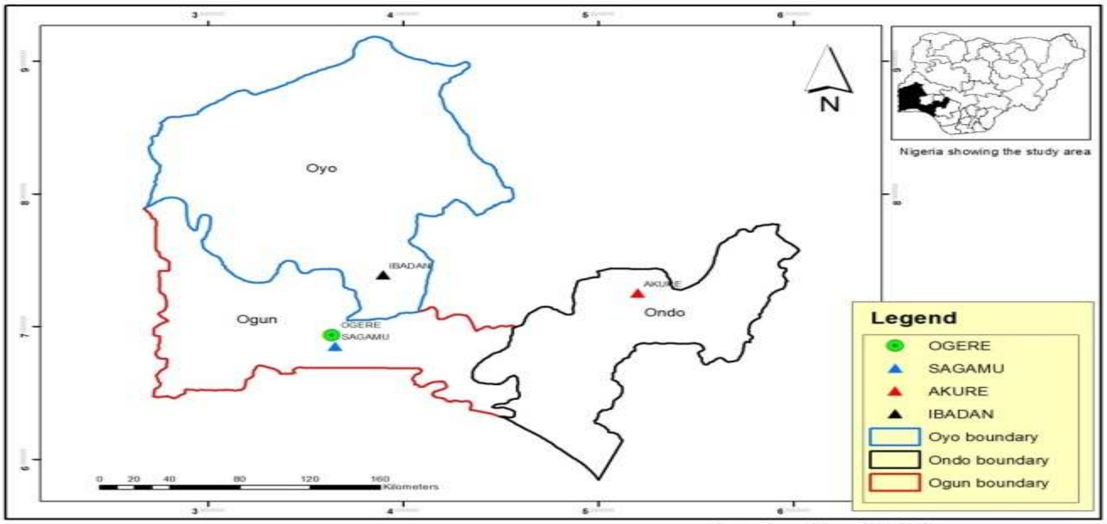
NTRODUCTION

The stability constant of a complex is the numerical expression of its stability and provides a quantitative measure of affinity of the metal ion to the complexing agent. An understanding of the relative stability of metal-complexes helps in predicting the behavior of metal ions in the soil (Ram and Raman, 1982). Extensive researches has been done to determine the stability constants of the complexes formed between humic acid (HA) with a number of metal ions. Ashok *et al*., (2000) reported that humic acid with hydroxyl, phenoxyl and carboxyl reactive groups can form coordination compound with metal ions at pH 3.5. The stability constants(Log K) for different metal-humic acid complexes indicated the following order of the stabilities of complexes formed between humic acid and metal ion, Cu >Fe >Pb> Ni > Co > Ca > Cd > Zn >Mn> Mg. Andelkovic *et al*., (2010) investigated the binding of Cd(II) to soil humic acid at pH 6.5 and in 0.1M KNO_3 ionic medium. The stability constant for binding indicating greater stability in the case when carboxyl groups are involved in complexation reaction. Kostic *et al*.,(2012) investigated the complexation of humic acid with certain heavy metal ions (Co(II), Ni(II),Cu(II), Zn(II), and Pb(II). The experiment was performed at 25°C, at pH 4.0 and ionic strength of 0.01M. Stability constant of complex between Pb(II) ions and humic acid is greater than stability constants of other investigated metal-humate complexes. Bogata and Sokolowska (2016) analyses the interaction between humic acids from different soils and Zn (II) ions at wide concentration ranges and at pH 5. Studies have showed significant impact of Zn concentration, pH and some properties of humic acids with zinc.But all of these studies were limited to acidic pH range. Therefore, the present study was carried out to determine and compare the stability constants of complexes of metal ions with hydrolysed peat soil humic acid and unhydrolysed peat soil humic under non-acid conditions.

MATERIALS AND METHODS

Analytical grade chemicals used includes hydrochloric acid (HCl), nitric acid (HNO_3), sodium hydroxide (NaOH), lead nitrate $Pb(NO_3)_2$, copper nitrate $Cu(NO_3)_2.3H_2O$, cadmium nitrate $Cd(NO_3)_2.4H_2O$, magnesium nitrate $Mg(NO_3)_2.6H_2O$, potassium nitrate (KNO_3), calcium chloride ($CaCl_2$), (sigma-Aldrich). Dowex 50WX8, (20-50 mesh) from Fluka.

Area of study



Source: Dept. of Geog. BUK (2016)

Figure 1: Map showing the sampling point at Sagamu Town, Ogun State.

Description of Sampling Area

Sagamu has geographical coordinates between 6°50′ north; 3° 38′ east is located in south western region of Nigeria. The region has tropical wet and dry climate with a lengthy wet season and relatively constant temperatures throughout the course of the year. Wet season runs from March to October, November to December forms the region dry season. The vegetation type of the region is savannah which is really grassland with small bushes and occasional big trees. Grassland soils have substantially higher organic matter content than forest soils (Novackova, 2011).

Sample Collection

The Peatsoil samples were collected from four different sampling points (0-10cm depth) in Sagamu into polyethylene bag with plastic spoons. Samples were taken to the laboratory, extraneous materials were removed; the samples were air-dried, crushed and ground to a fine powder in a mortar passed through a 0.20mm sieve. The samples were kept for analysis.

Isolation and purification of humic acid from peat soil sample

Peatsoil sample (100g) was mixed with 1000 cm^3 of 0.1M NaOH solution, shaken for 3hours and left to stand overnight. Dark-coloured supernatant was obtained and decanted from solid residue. The dark-coloured supernatant was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 6 hours. Yellowish brown supernatant and dark-brown precipitate were obtained. The yellowish brown supernatant was decanted followed by centrifuge and discarded. The dark-brown precipitate was mixed with $500cm^3$of 0.1M NaOH solution followed by passing through dowex resin. The dark-brown solution was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 3 hours. The dark-brown precipitate was washed several times with deionized water. The supernatant was treated with $AgNO_3$ solution until no white precipitate observed. The humic acid was transferred to weighed crucible and dried at 60°C in an oven for 12 hours. The humic acid was cooled and dried in the desiccator, weighed and recorded. The obtained humic acid was dried again at 60°C for additional 6 hours cooled and dried in the desiccator, weighed and recorded constant weight was obtained (Baruah *et al.*, 2015).

FT-IR analysis

FT-IR spectra of humic acid sample was analysed using Carry 630 FT-IR Agilent Technologies.

Unhydrolysed compost humic acid

The unhydrolysed humic acid was obtained after isolation and purification of compost humic acid and kept for investigation.

Acid hydrolysis of Peatsoil acid

Peatsoil humic acid sample (1g) was refluxed for 12 hours at (160°C) with $50cm^3$ of 6M HCl. The mixture was allowed to cool, decanted, and centrifuged after hydrolysis. The insoluble residues were washed with distilled water via centrifugation several times, and the supernatant was treated with $AgNO_3$ solution until no white precipitate was observed. The residue was thoroughly dried over $CaCl_2$ in a desiccator at room temperature (Chefetz *et al.*, 2002). Finally, the obtained hydrolysed humic acid was kept for investigation.

Potentiometric Titrations

Potentiometric measurements were carried out using a pH-meter Jenway (model 3510) with combine electrode, the sensitivity of the pH - meter is 0.01 units. The pH meter was switched on half an hour before starting the titration for initial warm up of the instrument. The instrument was calibrated with an aqueous standard buffer solution of pH 4.00 and 10.0 (borate buffer) prepared from a "Qualigens" buffer tablets.

The following sets of solutions were prepared in a 250cm^3 volumetric flask separately for pH metric titrations.

(i) 5 cm^3 0.1 M HCl + 40 cm^3 deionized water

(ii) 5 cm^3 0.1 M HCl + 39 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid

(iii) 5 cm^3 0.1 M HCl + 37 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid + 2 cm^3 0.01 M Cu(II)

The solutions were titrated against standardized 0.110MNaOH separately. The total volume of each mixture was adjusted to 50 cm^3 and the ionic strength of the solutions was maintained constant at by adding appropriate amount of stock solution of 1M KNO_3 (Gamal, 2015; Omar and Ali, 2015). A magnetic stirrer was used to achieve thorough mixing of the interacting solutions at 550 rpm. The same set of experimental conditions was applied for potentiometric titration of remaining samples.

Evaluation of pKa of Hydrolysed peat soil Humic Acids

The proton-ligand formation number $n_{\mathbf{A}}$ were calculated by Irving and Rossotti expression (Omar and Ali, 2015).

$$nA = Y - \frac{(V2-V1)(No-Eo)}{(Vo+V1)TcL} \text{ ....1}$$

Where: Y is number of dissociable proton, (V_2-V_1) is the measure of displacement of the ligand curve relative to acid curve, N^o and E^o are the resultant concentration of alkali solution, free acid solution, $T_{cL}{}^o$ is the total ligand concentration, V^o is the total volume of titration solution,V_1 is the volume of alkali added to acid solution,V_2 is the volume of alkali added to acid solution + ligand solution, acid dissociation constants (pKa - values) of ligand were calculated by algebraic method point wise calculation (Tables 1). The dissociation constants (pKa) were calculated according to the following relation:

$$pKa = pH + \log\left(\frac{nA}{1-nA}\right) \text{ ....2}$$

Where: pKa is the acid dissociation constant, $n_A$is the Proton-ligand formation number and pH is the pH-values (Omar and Ali, 2015).

Determination of metal-ligand stability constants (log K) of complexes

The potentiometric measurement for the determination of stability constant of a complex in solution is based on the fact that the redox potential of the couple $\frac{M^{+(m-n)}}{M^{+m}}$ is shifted significantly on complexation of the metal ion with the ligand. This method involves change in hydrogen ion concentration [H$^+$] due to the displacement or association of one or more protons taking place during complexation reaction. This change can be found out by titrating the solutions containing free acid, acid with ligand, and acid with ligand and metal ion, individually against a standard alkali solution at a constant ionic strength or temperature. Either ionic strength or temperature may be varied for different sets of solutions. In all the cases, the change in the pH of the solution is measured after each addition of a known amount of alkali to the reaction cell which contains the reaction mixture. The titration curves are then drawn by plotting the measured pH values against the corresponding volume of alkali added and the stability constants of the complexes are determined from the titration curves by employing pH-metric titration technique given by (Irving and Rossoti).

Metal-ligand stability constants (Log K) were determined by using the following relations:

$$\bar{n} = \frac{(V_3 - V_2)(E^0 + N^0)}{(V^0 + V_2)\bar{n}_A T_m^0} \text{ ....3}$$

and

$$PL = \log_{10}\left\{\frac{1 + \beta_n^H \dfrac{1}{[anti\ \log \mathrm{pH}]^n}}{T_L^0 - \bar{n}T_m^0} \mathrm{X} \frac{(V^0 + V_3)}{V^0}\right\} \text{ ....4}$$

Where $T_{L,}$ T^o, E°, and V^ohavethe same significance as in equation (1) above, T_m denotes the total concentration of metal present in solution, V_3 is the volume of metal ions present in solution and β^H is the overall proton ligand stability constant. The metal-ligand stability constants (log K) were determined by employing point wise computational Method (eq. 5 and 6).

$$\text{Log}K_1 = \log\left(\frac{n}{1-n}\right) + pL \quad ....5$$

$$\text{Log}K_2 = \log\left(\frac{1-n}{2-n}\right) + pL.......................6$$

Where: Log K is the metal-ligand stability constant, pL is the Free ligand exponent function, **n** is the Average number of ligand attached with metal ion (Janrao*et al.*, 2014).The results obtained were analyzed by an ORIGIN 2016 program using titration data and then the proton-ligand stability constants (pKa) and Metal-ligand stability constant (LogK) calculated (Omar and Ali, 2015).

RESULTS AND DISCUSSION

Fourier transformed infrared (FT-IR) spectra of isolated humic acid from peat soils Figure 2 had distinct clear absorption bands indicating the presence of major humic acid structural elemental groups such as H bonded OH ($3680cm^{-1}$ peak), C=O of carbonyl ($1721cm^{-1}$ peak), functional groups of aliphatic components CH_2 ($2918cm^{-1}$ peak) and C-O stretching of polysaccharide ($1168cm^{-1}$ peak). The positions of the absorption bands of the spectra fell within typical major absorption bands of humic acid which is at frequencies 3680, 2918, 1721, 1168 cm^{-1}. The first peak centred in the vicinity of 3680 cm^{-1} region is attributed to phenol OH group bounded by intermolecular H bonds. The $2918cm^{-1}$ band usually has absorption maximum at 2918 cm^{-1} which is due to C–H stretching of alkane group (CH_2). The next major absorption band is 1721 cm^{-1}. This band has been commonly ascribed to C=O stretching of mainly carboxyl group (COOH) with trace amount of ketones. The last peak was observed at 1168 cm^{-1} due to C–O stretching of polysaccharides and this peak appeared also in the spectra of humic acid from peat soil. The FTIR spectra of the isolated humic acid contained all major characteristic absorption peaks of humic acid. These absorption peaks indicated the presence of the major structural elements of humic acid namely H bonded OH, C=C of aromatic ring, C=O of carbonyl group (both carboxyl and ketonic), CH_2 group. This strongly supports the presence of humic acid.

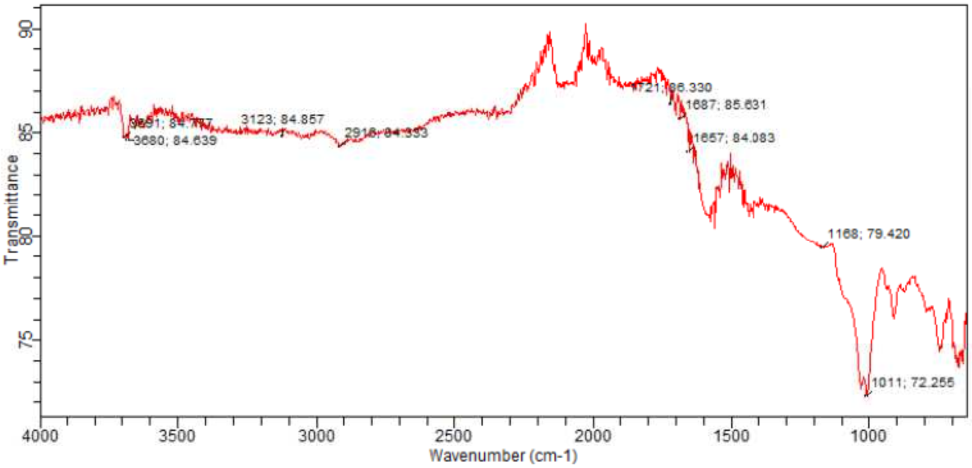


Fig. 2 : FT-IR spectraof peatsoilhumic acid (PSHA)

Evaluation of acid dissociation constant (pka) of acid hydrolysed peat soil humicacid at phenolic group

The value of the dissociation constant of the peat soil humic acid (PSHA) that underwent acidhydrolysis studied was found to be 8.9299 as shown Table 1, which is lower than the literaturevalues reported by Almeida and Szpoganics, (2015), Borges *et al.*, (2005); Badr *et al.*, (2012)and Fernandes *et al,*.(2009) of 9.73, 9.47 and 10.30. The difference between the obtained valuesand the reported values in this study might be probably as a result of acid hydrolysis of humicacid.

Table 1: PKa of (Hydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	$\log(\frac{nA}{1-nA})$	pKa
8.50	5.30	6.29	0.99	0.3594	-0.2510	8.2490
8.72	5.35	6.37	1.02	0.3400	-0.2880	8.4320
9.00	5.40	6.46	1.06	0.3141	-0.3391	8.6609
9.22	5.45	6.55	1.10	0.2882	-0.3927	8.8273
9.51	5.50	6.66	1.16	0.2494	-0.4786	9.0314
9.73	5.55	6.78	1.23	0.2041	-0.5910	9.1390
10.00	5.60	6.90	1.30	0.1589	-0.7238	9.2762
10.23	5.65	7.05	1.40	0.0941	-0.9835	9.2465
10.49	5.70	7.10	1.40	0.0941	-0.9835	9.5065

Average pKa = 8.9299 ± 0.4186

Table 2: PKa of (Unhydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	$\text{Log}(\frac{nA}{1-n})$	pKa
8.50	5.30	5.81	0.51	0.6619	0.2919	8.7919
8.72	5.35	5.90	0.55	0.6357	0.2418	8.9618
9.00	5.40	6.00	0.60	0.6029	0.1813	9.1813
9.22	5.45	6.10	0.65	0.5701	0.1226	9.3426
9.51	5.50	6.20	0.70	0.5376	0.0654	9.5754
9.73	5.55	6.33	0.78	0.4851	-0.0259	9.7041
10.00	5.60	6.47	0.87	0.4262	-0.1291	9.8709
10.23	5.65	6.62	0.99	0.3609	-0.2481	9.9819
10.49	5.70	6.80	1.10	0.2759	-0.4690	10.0210

Average pKa = 9.4923± 0.4410

Metal-ligand stability constant (Log K)

The stabilityconstants require the accurate values of proton-ligand stability constants (Anil and Maroti, 2008). Metal titration curves crossed over ligand titration curve indicated the formation of complex upon proton release (Santosh, *et al.*, 2011). If the values of n- are within range 0.2-0.8 and 1.2-18 this indicates the formation of 1:1 and 1:2 complexes (Sayyed and Mazahar, 2012).

The metal (II)-humate stepwise stability constants (log k) at phenolic group (Tables 3-18)

Table 3: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$\log(\frac{n}{1-n})$	LogK_1
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

LogK_1 (Average value) = 2.4788± 0.2203

Table 4: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$\text{Log}(\frac{n-1}{2-n})$	LogK_2
9.51	5.50	6.66	6.73	0.07	1.3509	1.70	-0.2671	1.4329
9.73	5.55	6.78	6.85	0.07	1.6383	1.51	0.2467	1.7567
10.00	5.60	6.90	6.98	0.08	2.1783	1.31	-0.2158	1.0942
10.23	5.65	7.05	7.13	0.08	4.1904	1.27		
10.49	5.70	7.10	7.19	0.09	4.6920			

LogK_2(Average value) = 1.4280 ± 0.3312

Table 5:Point-wise method,Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	Log($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430

$LogK_1$ **(Average value)** = 2.3059± 0.6153

Table 6:Point-wise method, Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
9.73	5.55	6.33	6.42	0.09	0.9000	1.69		
10.00	5.60	6.47	6.58	0.11	1.2578	1.44	-0.4592	0.9808
10.23	5.65	6.62	6.84	0.12	1.6137	1.26	-0.2010	1.4610
10.49	5.70	6.80	6.92	0.12	2.1052	1.03		

$LogK_2$ **(Average value)** = 1.2209± 0.3398

Table 7:Point-wise method,Pb (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n}{1-n}$)	$LogK_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.60	0.05	0.8333	1.96	0.6989	2.6589

$LogK_1$ (Average value) = 2.5832 ±0.1614

Table 8:Point-wise method,Pb-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n-1}{2-n}$)	$logK_2$
9.51	5.50	6.66	6.71	0.05	0.9650	1.67	-0.0237	1.1963
9.73	5.55	6.78	6.83	0.05	1.1702	1.44		
10.00	5.60	6.90	6.90	0.05	1.4864	1.22		
10.23	5.65	7.05	7.10	0.05	2.0190	1.09		
10.49	5.70	7.10	7.17	0.07	3.6492	1.00		

$LogK_2$(Average value) = 1.1963

Table 9:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log ($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.5477	2.3123
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	0.0272	2.2072
9.51	5.50	6.20	6.26	0.07	0.6417	1.89	0.2530	2.1430
9.73	5.55	6.40	6.40	0.07	0.7000	1.67	0.3680	2.0380

$LogK_1$ **(Average value)** = 2.2364 ± 0.1602

Table 10:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
10.00	5.60	6.47	6.55	0.08	1.9503	1.41		
10.23	5.65	6.62	6.72	0.11	1.4792	1.26	-0.0361	1.2239

$LogK_2$ **(Average value)** = 1.2239

Table 11:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n}{n-1}$)	$LogK_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4290	2.2110
8.72	5.35	6.37	6.39	0.02	0.2858	2.42	-0.3978	2.0222
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

$LogK_1$ (Average value)=2.1382**±**0.1046

Table 12:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	log$(\frac{n-1}{2-n})$	LogK$_2$
9.51	5.55	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.84	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.93	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.10		
10.49	5.70	7.10	7.18	0.07	3.6492	0.83		

LogK$_2$(Average value) = 1.5453 **±** 0.3450

Table 13:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	V$_3$-V$_2$	n	pL	Log$(\frac{n}{n-1})$	Log K$_1$
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.3477	2.3123
9.00	5.40	6.00	6.04	0.04	0.3236	2.38	-0.3202	2.0598
9.22	5.45	6.10	6.15	0.05	0.4297	2.17	-0.1230	2.0470
9.51	5.50	6.20	6.26	0.06	0.5500	1.89	0.0871	1.9771
9.73	5.55	6.33	6.40	0.07	0.7000	1.67	0.3680	2.0380

LogK$_1$ **(Average value)** = 2.1568 ± 0.2069

Table 14:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	V$_3$-V$_2$	n	pL	Log$(\frac{n-1}{2-n})$	Log K$_2$
10.00	5.60	6.47	6.55	0.08	0.9148	1.41		
10.23	5.65	6.62	6.71	0.09	1.2102	1.20	-0.5749	0.6251
10.49	5.70	6.80	6.92	0.09	1.5968	1.03	0.1703	1.2003

LogK$_2$ **(Average value)** = 0.9127± 0.4070

Table15:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	Log$(\frac{n}{1-n})$	LogK$_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4210	2.2190
8.72	5.35	6.37	6.40	0.03	0.4286	2.42	-0.1249	2.2951
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.96	0.3010	2.2610
9.51	5.55	6.66	6.70	0.04	0.7720	1.67	0.5297	2.1997

LogK$_1$ (Average value) = 2.2108± 0.0825

Table 16:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	Log$(\frac{n-1}{2-n})$	Log K$_2$
9.73	5.55	6.78	6.83	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.95	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.09		
10.49	5.70	7.10	7.16	0.06	3.1429	0.89		

LogK$_2$ **(Average value)** = 1.5453± 0.3450

Table 17:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	V$_3$-V$_2$	n	pL	Log$(\frac{n}{n-1})$	Log K$_1$
8.50	5.30	5.81	5.86	0.05	0.3717	2.88	-0.2280	2.6520
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.06	0.06	0.4853	2.38	-0.0255	2.3545
9.22	5.45	6.10	6.16	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430
9.73	5.55	6.33	6.41	0.08	0.8000	1.69	0.6020	2.2920

LogK$_1$ **(Average value)** = 2.2516± 0.5380

Table 18:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$\text{Log}(\frac{n-1}{2-n})$	Log K_2
10.00	5.60	6.47	6.57	0.10	1.1434	1.43		
10.23	5.65	6.62	6.72	0.10	1.3448	1.23	-0.2788	0.9512
10.49	5.70	6.80	6.90	0.10	1.7742	1.03	0.5351	1.5651

LogK_2 **(Average value)** = 1.2581± 0.4340

Table 19: Stepwise and overall Stability constants of thehydrolysed and unhydrolysed divalent metal (II) complexes

Chelates	**LogK_1**	**LogK_2**	**Logβ**
[Cu (Hydrolysed PSHA-1)$_2$]	2.4788	1.4280	3.9068
[Pb (Hydrolysed PSHA-1)$_2$]	2.5832	1.1963	3.7795
[Cd (Hydrolysed PSHA-1)$_2$]	2.2108	1.5453	3.7561
[Mg (Hydrolysed PSHA-1)$_2$]	2.1382	1.5453	3.6835
[Cu (Unhydrolysed PSHA-1)$_2$]	2.3059	1.2209	3.5268
[Pb (Unhydrolysed PSHA-1)$_2$]	2.2364	1.2239	3.4603
[Cd (Unhydrolysed PSHA-1)$_2$]	2.2516	1.2581	3.5097
[Mg (Unydrolysed PSHA-1)$_2$]	2.1568	0.9127	3.0695

The results obtained (Table19) shows the stepwise and overall stability constants to be not high indicating low stability of the complexes, because the solubility of most metal ions in the basic pH range is minimal due to metal hydroxide precipitation (Karimi, 2017). In general, the stepwise stability constants (K_1 and K_2) follow the order $K_1 > K_2$ for the copper, lead, magnesium and cadmium complexes respectively. The steady decrease of the values with increasing number of ligands is in agreement with the prediction made by researchers (Na'aliya, 2013). The decrease could be attributed to the fact that as the number of the ligands (Humate ions) that enters the coordination zone increases the aqua molecules available for replacement by the ligands become less. Thus, the metal ions become less electron loving with progressive intake of the ligand and this results in the decrease in the values of the constants (Na'aliya, 2013). Also the stability of the complexes is influenced by the size and number of the chelate rings(Mackay and Mackay,2002).All the complexes form rings in their structure as humate, a bidentate ligand, bond the metal ions in the ratio 1:2 (Boguta and Sokolowska, 2016) forming chelate rings. The values of the overall stability constants (logβ) obtained for humate complexes are not high indicating low stability as the values are not high. LogK values for copper-humates (Table 3 to 6) obtained in this study are lower than those reported for the complexes of humic acids (Pandey *et al.*, 2015; Dinu, 2013; Kaschl *et al.*, 2010 and Gilbeto and Jorg, 2001). The values of LogK(Table 7 to 10) forlead-humates are lower than those reported for the lead in the literature (Dinu, 2013; Gilbeto and Jorg 2001). Log K values(Table 11 to 14) for magnesium-humates obtained in this study are close to those reported by (Pandey *et al.*, 2015). Log K values of cadmium-humates (Table 15 to 18) obtained in this work near to the one reported by (Dinu, 2013 and Pandey *et al.*, 2015).The difference between the reported values and the values obtained in this study might be probably as a result of acid hydrolysis of humic acid. The values of the overall stability constants (log β) of the copper humates complexes presented in Table 19 is high than that of other metal humate complexes, show relatively high stability of Cu-HA complexes, show the following order of stability: Cu >Pb> Cd > Mg; which are in close agreement to the findings of (Dinu, 2013 and Pandey *et al.*, 2015).The high stability of Cu-humate chelate could be attributed to the existence of coordinate covalent bond between the complexing agents and the Cu^{2+} ions. Since, Cu^{2+} being a metal of the transitional series with $3d^9$ electronic configurations can accept the electrons from the complexing agents. Similarly,the low stabilities of Pb,Cd and Mg -complexes could be explained by that Pb^{2+} with $6s^2$, Cd^{2+} with $4d^{10}$ and Mg^{2+} with $2p^6$ their electronic configuration has a completely filled d,p and s orbitals. Moreover, the stabilities of metal ions with hydrolysed humic acid from peat soil were higher than those with unhydrolysed humic acid from peat soil; which is ascribed to the high content of acidity in hydrolysed humic acid than unhydrolysed humic acid.

CONCLUSION

The values of logK for Cu(II) hydrolysed humic acid complex was higher followed by Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes as compared with metal(II) unhydrolysed humic acid complexes . This indicates acid hydrolysis of humic acid can enhance the complexation behavior of humic acid with metal (II) ions. However, the higher values of logβ for Cu(II), Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes indicates more stable stepwise complexes formed as compared with Cu(II), Pb(II), Cd(II) and Mg(II) unhydrolysed humic acid complexes.

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STABILITY CONSTANTS OF COMPLEXES OF METAL IONS WITH PEATSOIL HUMIC ACIDS UNDER NON-ACID-CONDITIONS

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ABSTRACT

Stability constants of complexes of four divalent metal ions viz. Cu^{2+}, Pb^{2+},Mg^{2+} and Cd^{2+} with humic acids (HA) were determined by potentiometric titration of humic acids with the corresponding salt of the divalent metals in aqueous media under non-acid-condition. The log K (logarithm of the stability constant) ranged from 1.0942 to 2.7471 for metal-humic acid complexes were determined using point-wise computational method. The order of stability constants were obtained as follows: Cu >Pb> Cd > Mg for metal -HA complexes respectively, indicating a higher degree of complexation with Cu metal ion.

Keywords: stability constant, humic acid, potentiometric titration, divalent metals, acid hydrolysis.

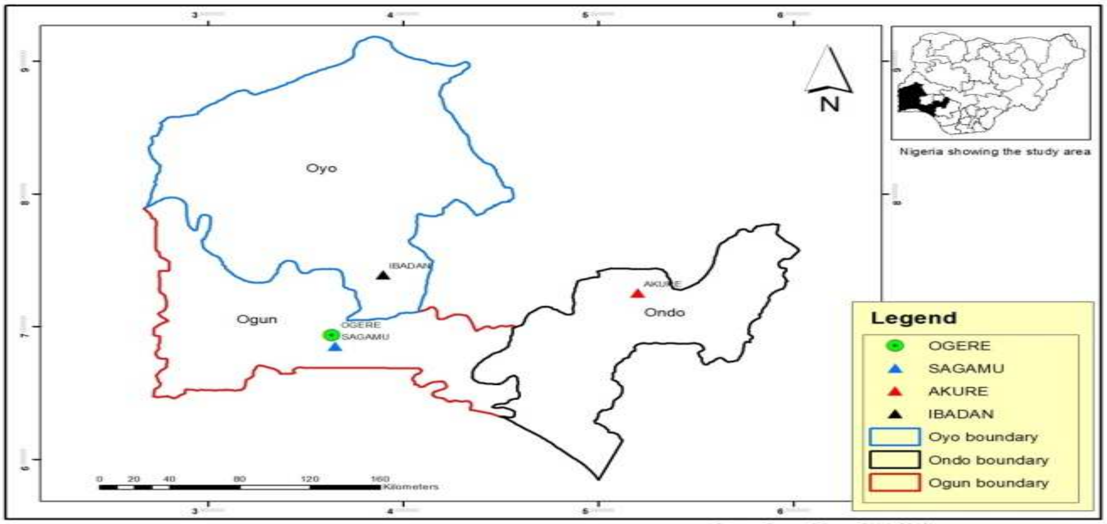
NTRODUCTION

The stability constant of a complex is the numerical expression of its stability and provides a quantitative measure of affinity of the metal ion to the complexing agent. An understanding of the relative stability of metal-complexes helps in predicting the behavior of metal ions in the soil (Ram and Raman, 1982). Extensive researches has been done to determine the stability constants of the complexes formed between humic acid (HA) with a number of metal ions. Ashok *et al.*, (2000) reported that humic acid with hydroxyl, phenoxyl and carboxyl reactive groups can form coordination compound with metal ions at pH 3.5. The stability constants(Log K) for different metal-humic acid complexes indicated the following order of the stabilities of complexes formed between humic acid and metal ion, Cu >Fe >Pb> Ni > Co > Ca > Cd > Zn >Mn> Mg. Andelkovic *et al.*, (2010) investigated the binding of Cd(II) to soil humic acid at pH 6.5 and in 0.1M KNO$_3$ ionic medium. The stability constant for binding indicating greater stability in the case when carboxyl groups are involved in complexation reaction. Kostic *et al.*,(2012) investigated the complexation of humic acid with certain heavy metal ions (Co(II), Ni(II),Cu(II), Zn(II), and Pb(II). The experiment was performed at 25°C, at pH 4.0 and ionic strength of 0.01M. Stability constant of complex between Pb(II) ions and humic acid is greater than stability constants of other investigated metal-humate complexes. Bogata and Sokolowska (2016) analyses the interaction between humic acids from different soils and Zn (II) ions at wide concentration ranges and at pH 5. Studies have showed significant impact of Zn concentration, pH and some properties of humic acids with zinc.But all of these studies were limited to acidic pH range. Therefore, the present study was carried out to determine and compare the stability constants of complexes of metal ions with hydrolysed peat soil humic acid and unhydrolysed peat soil humic under non-acid conditions.

MATERIALS AND METHODS

Analytical grade chemicals used includes hydrochloric acid (HCl), nitric acid (HNO$_3$), sodium hydroxide (NaOH), lead nitrate Pb(NO$_3$)$_2$, copper nitrate Cu(NO$_3$)$_2$.3H$_2$O, cadmium nitrate Cd(NO$_3$)$_2$.4H$_2$O, magnesium nitrate Mg(NO$_3$)$_2$.6H$_2$O, potassium nitrate (KNO$_3$), calcium chloride (CaCl$_2$), (sigma-Aldrich). Dowex 50WX8, (20-50 mesh) from Fluka.

Area of study



Source: Dept. of Geog. BUK (2016)

Figure 1: Map showing the sampling point at Sagamu Town, Ogun State.

Description of Sampling Area

Sagamu has geographical coordinates between 6°50′ north; 3° 38′ east is located in south western region of Nigeria. The region has tropical wet and dry climate with a lengthy wet season and relatively constant temperatures throughout the course of the year. Wet season runs from March to October, November to December forms the region dry season. The vegetation type of the region is savannah which is really grassland with small bushes and occasional big trees. Grassland soils have substantially higher organic matter content than forest soils (Novackova, 2011).

Sample Collection

The Peatsoil samples were collected from four different sampling points (0-10cm depth) in Sagamu into polyethylene bag with plastic spoons. Samples were taken to the laboratory, extraneous materials were removed; the samples were air-dried, crushed and ground to a fine powder in a mortar passed through a 0.20mm sieve. The samples were kept for analysis.

Isolation and purification of humic acid from peat soil sample

Peatsoil sample (100g) was mixed with 1000 cm^3 of 0.1M NaOH solution, shaken for 3hours and left to stand overnight. Dark-coloured supernatant was obtained and decanted from solid residue. The dark-coloured supernatant was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 6 hours. Yellowish brown supernatant and dark-brown precipitate were obtained. The yellowish brown supernatant was decanted followed by centrifuge and discarded. The dark-brown precipitate was mixed with $500cm^3$of 0.1M NaOH solution followed by passing through dowex resin. The dark-brown solution was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 3 hours. The dark-brown precipitate was washed several times with deionized water. The supernatant was treated with $AgNO_3$ solution until no white precipitate observed. The humic acid was transferred to weighed crucible and dried at 60°C in an oven for 12 hours. The humic acid was cooled and dried in the desiccator, weighed and recorded. The obtained humic acid was dried again at 60°C for additional 6 hours cooled and dried in the desiccator, weighed and recorded constant weight was obtained (Baruah *et al*., 2015).

FT-IR analysis

FT-IR spectra of humic acid sample was analysed using Carry 630 FT-IR Agilent Technologies.

Unhydrolysed compost humic acid

The unhydrolysed humic acid was obtained after isolation and purification of compost humic acid and kept for investigation.

Acid hydrolysis of Peatsoil acid

Peatsoil humic acid sample (1g) was refluxed for 12 hours at (160°C) with $50cm^3$ of 6M HCl. The mixture was allowed to cool, decanted, and centrifuged after hydrolysis. The insoluble residues were washed with distilled water via centrifugation several times, and the supernatant was treated with $AgNO_3$ solution until no white precipitate was observed. The residue was thoroughly dried over $CaCl_2$ in a desiccator at room temperature (Chefetz *et al*., 2002). Finally, the obtained hydrolysed humic acid was kept for investigation.

Potentiometric Titrations

Potentiometric measurements were carried out using a pH-meter Jenway (model 3510) with combine electrode, the sensitivity of the pH - meter is 0.01 units. The pH meter was switched on half an hour before starting the titration for initial warm up of the instrument. The instrument was calibrated with an aqueous standard buffer solution of pH 4.00 and 10.0 (borate buffer) prepared from a "Qualigens" buffer tablets.

The following sets of solutions were prepared in a 250cm^3 volumetric flask separately for pH metric titrations.

(i) 5 cm^3 0.1 M HCl + 40 cm^3 deionized water

(ii) 5 cm^3 0.1 M HCl + 39 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid

(iii) 5 cm^3 0.1 M HCl + 37 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid + 2 cm^3 0.01 M Cu(II)

The solutions were titrated against standardized 0.110MNaOH separately. The total volume of each mixture was adjusted to 50 cm^3 and the ionic strength of the solutions was maintained constant at by adding appropriate amount of stock solution of 1M KNO_3 (Gamal, 2015; Omar and Ali, 2015). A magnetic stirrer was used to achieve thorough mixing of the interacting solutions at 550 rpm. The same set of experimental conditions was applied for potentiometric titration of remaining samples.

Evaluation of pKa of Hydrolysed peat soil Humic Acids

The proton-ligand formation number $n_{\mathbf{A}}$ were calculated by Irving and Rossotti expression (Omar and Ali, 2015).

$$nA = Y - \frac{(V2-V1)(No-Eo)}{(Vo+V1)TcL} \quad \text{..................................} 1$$

Where: Y is number of dissociable proton, (V_2-V_1) is the measure of displacement of the ligand curve relative to acid curve, N^o and E^o are the resultant concentration of alkali solution, free acid solution, $T_{cL}{}^o$ is the total ligand concentration, V^o is the total volume of titration solution,V_1 is the volume of alkali added to acid solution,V_2 is the volume of alkali added to acid solution + ligand solution, acid dissociation constants (pKa - values) of ligand were calculated by algebraic method point wise calculation (Tables 1). The dissociation constants (pKa) were calculated according to the following relation:

$$pKa = pH + \log(\frac{nA}{1-nA}) \quad \text{.............................} 2$$

Where: pKa is the acid dissociation constant, $n_A$is the Proton-ligand formation number and pH is the pH-values (Omar and Ali, 2015).

Determination of metal-ligand stability constants (log K) of complexes

The potentiometric measurement for the determination of stability constant of a complex in solution is based on the fact that the redox potential of the couple $\frac{M^{+(m-n)}}{M^{+m}}$ is shifted significantly on complexation of the metal ion with the ligand. This method involves change in hydrogen ion concentration [H$^+$] due to the displacement or association of one or more protons taking place during complexation reaction. This change can be found out by titrating the solutions containing free acid, acid with ligand, and acid with ligand and metal ion, individually against a standard alkali solution at a constant ionic strength or temperature. Either ionic strength or temperature may be varied for different sets of solutions. In all the cases, the change in the pH of the solution is measured after each addition of a known amount of alkali to the reaction cell which contains the reaction mixture. The titration curves are then drawn by plotting the measured pH values against the corresponding volume of alkali added and the stability constants of the complexes are determined from the titration curves by employing pH-metric titration technique given by (Irving and Rossoti).

Metal-ligand stability constants (Log K) were determined by using the following relations:

$$\bar{n} = \frac{(V_3 - V_2)(E^0 + N^0)}{(V^0 + V_2)\bar{n}_A T_m^0} \quad \text{..} 3$$

and

$$PL = \log_{10}\{\frac{1 + \beta_n^H \frac{1}{[anti\ \log pH]^n}}{T_L^0 - \bar{n}T_m^0} X \frac{(V^0 + V_3)}{V^0}\} \quad \text{...} 4$$

Where $T_{L,}$ T^o, E°, and V^ohavethe same significance as in equation (1) above, T_m denotes the total concentration of metal present in solution, V_3 is the volume of metal ions present in solution and β^H is the overall proton ligand stability constant. The metal-ligand stability constants (log K) were determined by employing point wise computational Method (eq. 5 and 6).

$$\text{Log}K_1 = \log\left(\frac{n}{1-n}\right) + pL \quad \ldots\ldots\ldots\ldots.5$$

$$\text{Log}K_2 = \log\left(\frac{1-n}{2-n}\right) + pL\ldots\ldots\ldots\ldots\ldots\ldots\ldots.6$$

Where: Log K is the metal-ligand stability constant, pL is the Free ligand exponent function, **n** is the Average number of ligand attached with metal ion (Janrao*et al*., 2014).The results obtained were analyzed by an ORIGIN 2016 program using titration data and then the proton-ligand stability constants (pKa) and Metal-ligand stability constant (LogK) calculated (Omar and Ali, 2015).

RESULTS AND DISCUSSION

Fourier transformed infrared (FT-IR) spectra of isolated humic acid from peat soils Figure 2 had distinct clear absorption bands indicating the presence of major humic acid structural elemental groups such as H bonded OH ($3680cm^{-1}$ peak), C=O of carbonyl ($1721cm^{-1}$ peak), functional groups of aliphatic components CH_2 ($2918cm^{-1}$ peak) and C-O stretching of polysaccharide ($1168cm^{-1}$ peak). The positions of the absorption bands of the spectra fell within typical major absorption bands of humic acid which is at frequencies 3680, 2918, 1721, 1168 cm^{-1}. The first peak centred in the vicinity of 3680 cm^{-1} region is attributed to phenol OH group bounded by intermolecular H bonds. The $2918cm^{-1}$ band usually has absorption maximum at 2918 cm^{-1} which is due to C–H stretching of alkane group (CH_2). The next major absorption band is 1721 cm^{-1}. This band has been commonly ascribed to C=O stretching of mainly carboxyl group (COOH) with trace amount of ketones. The last peak was observed at 1168 cm^{-1} due to C–O stretching of polysaccharides and this peak appeared also in the spectra of humic acid from peat soil. The FTIR spectra of the isolated humic acid contained all major characteristic absorption peaks of humic acid. These absorption peaks indicated the presence of the major structural elements of humic acid namely H bonded OH, C=C of aromatic ring, C=O of carbonyl group (both carboxyl and ketonic), CH_2 group. This strongly supports the presence of humic acid.

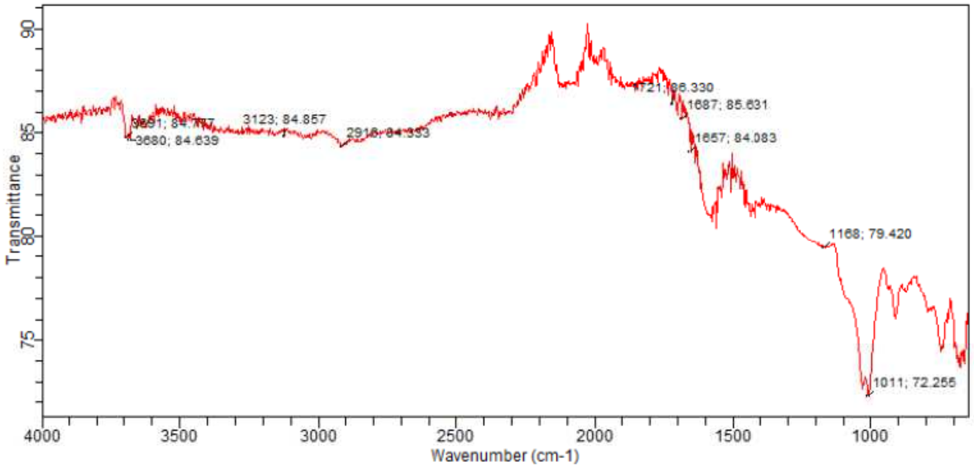


Fig. 2 : FT-IR spectraof peatsoilhumic acid (PSHA)

Evaluation of acid dissociation constant (pka) of acid hydrolysed peat soil humicacid at phenolic group

The value of the dissociation constant of the peat soil humic acid (PSHA) that underwent acidhydrolysis studied was found to be 8.9299 as shown Table 1, which is lower than the literaturevalues reported by Almeida and Szpoganics, (2015), Borges *et al*., (2005); Badr *et al*., (2012)and Fernandes *et al*,.(2009) of 9.73, 9.47 and 10.30. The difference between the obtained valuesand the reported values in this study might be probably as a result of acid hydrolysis of humicacid.

Table 1: PKa of (Hydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	$\log(\frac{nA}{1-nA})$	pKa
8.50	5.30	6.29	0.99	0.3594	-0.2510	8.2490
8.72	5.35	6.37	1.02	0.3400	-0.2880	8.4320
9.00	5.40	6.46	1.06	0.3141	-0.3391	8.6609
9.22	5.45	6.55	1.10	0.2882	-0.3927	8.8273
9.51	5.50	6.66	1.16	0.2494	-0.4786	9.0314
9.73	5.55	6.78	1.23	0.2041	-0.5910	9.1390
10.00	5.60	6.90	1.30	0.1589	-0.7238	9.2762
10.23	5.65	7.05	1.40	0.0941	-0.9835	9.2465
10.49	5.70	7.10	1.40	0.0941	-0.9835	9.5065

Average pKa = 8.9299 ± 0.4186

Table 2: PKa of (Unhydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	$\text{Log}(\frac{nA}{1-n})$	pKa
8.50	5.30	5.81	0.51	0.6619	0.2919	8.7919
8.72	5.35	5.90	0.55	0.6357	0.2418	8.9618
9.00	5.40	6.00	0.60	0.6029	0.1813	9.1813
9.22	5.45	6.10	0.65	0.5701	0.1226	9.3426
9.51	5.50	6.20	0.70	0.5376	0.0654	9.5754
9.73	5.55	6.33	0.78	0.4851	-0.0259	9.7041
10.00	5.60	6.47	0.87	0.4262	-0.1291	9.8709
10.23	5.65	6.62	0.99	0.3609	-0.2481	9.9819
10.49	5.70	6.80	1.10	0.2759	-0.4690	10.0210

Average pKa = 9.4923± 0.4410

Metal-ligand stability constant (Log K)

The stabilityconstants require the accurate values of proton-ligand stability constants (Anil and Maroti, 2008). Metal titration curves crossed over ligand titration curve indicated the formation of complex upon proton release (Santosh, *et al.*, 2011). If the values of n- are within range 0.2-0.8 and 1.2-18 this indicates the formation of 1:1 and 1:2 complexes (Sayyed and Mazahar, 2012).

The metal (II)-humate stepwise stability constants (log k) at phenolic group (Tables 3-18)

Table 3: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$\log(\frac{n}{1-n})$	LogK_1
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

LogK_1 (Average value) = 2.4788± 0.2203

Table 4: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$\text{Log}(\frac{n-1}{2-n})$	LogK_2
9.51	5.50	6.66	6.73	0.07	1.3509	1.70	-0.2671	1.4329
9.73	5.55	6.78	6.85	0.07	1.6383	1.51	0.2467	1.7567
10.00	5.60	6.90	6.98	0.08	2.1783	1.31	-0.2158	1.0942
10.23	5.65	7.05	7.13	0.08	4.1904	1.27		
10.49	5.70	7.10	7.19	0.09	4.6920			

LogK_2(Average value) = 1.4280 ± 0.3312

Table 5:Point-wise method,Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$\text{Log}(\frac{n}{n-1})$	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430

$\text{Log}K_1$ **(Average value)** = 2.3059± 0.6153

Table 6:Point-wise method, Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$\text{Log}(\frac{n-1}{2-n})$	Log K_2
9.73	5.55	6.33	6.42	0.09	0.9000	1.69		
10.00	5.60	6.47	6.58	0.11	1.2578	1.44	-0.4592	0.9808
10.23	5.65	6.62	6.84	0.12	1.6137	1.26	-0.2010	1.4610
10.49	5.70	6.80	6.92	0.12	2.1052	1.03		

$\text{Log}K_2$ **(Average value)** = 1.2209± 0.3398

Table 7:Point-wise method,Pb (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$\log(\frac{n}{1-n})$	$\text{Log}K_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.60	0.05	0.8333	1.96	0.6989	2.6589

$\text{Log}K_1$ (Average value) = 2.5832 ±0.1614

Table 8:Point-wise method,Pb-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$\log(\frac{n-1}{2-n})$	$\log K_2$
9.51	5.50	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.83	0.05	1.1702	1.44		
10.00	5.60	6.90	6.90	0.05	1.4864	1.22	-0.0237	1.1963
10.23	5.65	7.05	7.10	0.05	2.0190	1.09		
10.49	5.70	7.10	7.17	0.07	3.6492	1.00		

$\text{Log}K_2$(Average value) = 1.1963

Table 9:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$\text{Log}(\frac{n}{n-1})$	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.5477	2.3123
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	0.0272	2.2072
9.51	5.50	6.20	6.26	0.07	0.6417	1.89	0.2530	2.1430
9.73	5.55	6.40	6.40	0.07	0.7000	1.67	0.3680	2.0380

$\text{Log}K_1$ **(Average value)** = 2.2364 ± 0.1602

Table 10:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$\text{Log}(\frac{n-1}{2-n})$	Log K_2
10.00	5.60	6.47	6.55	0.08	1.9503	1.41		
10.23	5.65	6.62	6.72	0.11	1.4792	1.26	-0.0361	1.2239

$\text{Log}K_2$ **(Average value)** = 1.2239

Table 11:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$\log(\frac{n}{n-1})$	$\text{Log}K_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4290	2.2110
8.72	5.35	6.37	6.39	0.02	0.2858	2.42	-0.3978	2.0222
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

$\text{Log}K_1$ (Average value)=2.1382±0.1046

Table 12:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n-1}{2-n}$)	$LogK_2$
9.51	5.55	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.84	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.93	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.10		
10.49	5.70	7.10	7.18	0.07	3.6492	0.83		

$LogK_2$(Average value) = 1.5453 **±** 0.3450

Table 13:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.3477	2.3123
9.00	5.40	6.00	6.04	0.04	0.3236	2.38	-0.3202	2.0598
9.22	5.45	6.10	6.15	0.05	0.4297	2.17	-0.1230	2.0470
9.51	5.50	6.20	6.26	0.06	0.5500	1.89	0.0871	1.9771
9.73	5.55	6.33	6.40	0.07	0.7000	1.67	0.3680	2.0380

$LogK_1$ **(Average value)** = 2.1568 ± 0.2069

Table 14:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
10.00	5.60	6.47	6.55	0.08	0.9148	1.41		
10.23	5.65	6.62	6.71	0.09	1.2102	1.20	-0.5749	0.6251
10.49	5.70	6.80	6.92	0.09	1.5968	1.03	0.1703	1.2003

$LogK_2$ **(Average value)** = 0.9127± 0.4070

Table15:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	Log($\frac{n}{1-n}$)	$LogK_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4210	2.2190
8.72	5.35	6.37	6.40	0.03	0.4286	2.42	-0.1249	2.2951
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.96	0.3010	2.2610
9.51	5.55	6.66	6.70	0.04	0.7720	1.67	0.5297	2.1997

$LogK_1$ (Average value) = 2.2108± 0.0825

Table 16:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
9.73	5.55	6.78	6.83	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.95	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.09		
10.49	5.70	7.10	7.16	0.06	3.1429	0.89		

$LogK_2$ **(Average value)** = 1.5453± 0.3450

Table 17:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.86	0.05	0.3717	2.88	-0.2280	2.6520
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.06	0.06	0.4853	2.38	-0.0255	2.3545
9.22	5.45	6.10	6.16	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430
9.73	5.55	6.33	6.41	0.08	0.8000	1.69	0.6020	2.2920

$LogK_1$ **(Average value)** = 2.2516± 0.5380

Table 18:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$\mathrm{Log}(\frac{n-1}{2-n})$	Log K_2
10.00	5.60	6.47	6.57	0.10	1.1434	1.43		
10.23	5.65	6.62	6.72	0.10	1.3448	1.23	-0.2788	0.9512
10.49	5.70	6.80	6.90	0.10	1.7742	1.03	0.5351	1.5651

LogK_2 **(Average value)** = 1.2581± 0.4340

Table 19: Stepwise and overall Stability constants of thehydrolysed and unhydrolysed divalent metal (II) complexes

Chelates	**LogK_1**	**LogK_2**	**Logβ**
[Cu (Hydrolysed PSHA-1)$_2$]	2.4788	1.4280	3.9068
[Pb (Hydrolysed PSHA-1)$_2$]	2.5832	1.1963	3.7795
[Cd (Hydrolysed PSHA-1)$_2$]	2.2108	1.5453	3.7561
[Mg (Hydrolysed PSHA-1)$_2$]	2.1382	1.5453	3.6835
[Cu (Unhydrolysed PSHA-1)$_2$]	2.3059	1.2209	3.5268
[Pb (Unhydrolysed PSHA-1)$_2$]	2.2364	1.2239	3.4603
[Cd (Unhydrolysed PSHA-1)$_2$]	2.2516	1.2581	3.5097
[Mg (Unydrolysed PSHA-1)$_2$]	2.1568	0.9127	3.0695

The results obtained (Table19) shows the stepwise and overall stability constants to be not high indicating low stability of the complexes, because the solubility of most metal ions in the basic pH range is minimal due to metal hydroxide precipitation (Karimi, 2017). In general, the stepwise stability constants (K_1 and K_2) follow the order $K_1 > K_2$ for the copper, lead, magnesium and cadmium complexes respectively. The steady decrease of the values with increasing number of ligands is in agreement with the prediction made by researchers (Na'aliya, 2013). The decrease could be attributed to the fact that as the number of the ligands (Humate ions) that enters the coordination zone increases the aqua molecules available for replacement by the ligands become less. Thus, the metal ions become less electron loving with progressive intake of the ligand and this results in the decrease in the values of the constants (Na'aliya, 2013). Also the stability of the complexes is influenced by the size and number of the chelate rings(Mackay and Mackay,2002).All the complexes form rings in their structure as humate, a bidentate ligand, bond the metal ions in the ratio 1:2 (Boguta and Sokolowska, 2016) forming chelate rings. The values of the overall stability constants (logβ) obtained for humate complexes are not high indicating low stability as the values are not high. LogK values for copper-humates (Table 3 to 6) obtained in this study are lower than those reported for the complexes of humic acids (Pandey *et al.*, 2015; Dinu, 2013; Kaschl *et al.*, 2010 and Gilbeto and Jorg, 2001). The values of LogK(Table 7 to 10) forlead-humates are lower than those reported for the lead in the literature (Dinu, 2013; Gilbeto and Jorg 2001). Log K values(Table 11 to 14) for magnesium-humates obtained in this study are close to those reported by (Pandey *et al.*, 2015). Log K values of cadmium-humates (Table 15 to 18) obtained in this work near to the one reported by (Dinu, 2013 and Pandey *et al.*, 2015).The difference between the reported values and the values obtained in this study might be probably as a result of acid hydrolysis of humic acid. The values of the overall stability constants (log β) of the copper humates complexes presented in Table 19 is high than that of other metal humate complexes, show relatively high stability of Cu-HA complexes, show the following order of stability: Cu >Pb> Cd > Mg; which are in close agreement to the findings of (Dinu, 2013 and Pandey *et al.*, 2015).The high stability of Cu-humate chelate could be attributed to the existence of coordinate covalent bond between the complexing agents and the Cu^{2+} ions. Since, Cu^{2+} being a metal of the transitional series with $3d^9$ electronic configurations can accept the electrons from the complexing agents. Similarly,the low stabilities of Pb,Cd and Mg - complexes could be explained by that Pb^{2+} with $6s^2$, Cd^{2+} with $4d^{10}$ and Mg^{2+} with $2p^6$ their electronic configuration has a completely filled d,p and s orbitals. Moreover, the stabilities of metal ions with hydrolysed humic acid from peat soil were higher than those with unhydrolysed humic acid from peat soil; which is ascribed to the high content of acidity in hydrolysed humic acid than unhydrolysed humic acid.

CONCLUSION

The values of logK for Cu(II) hydrolysed humic acid complex was higher followed by Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes as compared with metal(II) unhydrolysed humic acid complexes . This indicates acid hydrolysis of humic acid can enhance the complexation behavior of humic acid with metal (II) ions. However, the higher values of logβ for Cu(II), Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes indicates more stable stepwise complexes formed as compared with Cu(II), Pb(II), Cd(II) and Mg(II) unhydrolysed humic acid complexes.

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STABILITY CONSTANTS OF COMPLEXES OF METAL IONS WITH PEATSOIL HUMIC ACIDS UNDER NON-ACID-CONDITIONS

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ABSTRACT

Stability constants of complexes of four divalent metal ions viz. Cu^{2+}, Pb^{2+},Mg^{2+} and Cd^{2+} with humic acids (HA) were determined by potentiometric titration of humic acids with the corresponding salt of the divalent metals in aqueous media under non-acid-condition. The log K (logarithm of the stability constant) ranged from 1.0942 to 2.7471 for metal-humic acid complexes were determined using point-wise computational method. The order of stability constants were obtained as follows: Cu >Pb> Cd > Mg for metal -HA complexes respectively, indicating a higher degree of complexation with Cu metal ion.

Keywords: stability constant, humic acid, potentiometric titration, divalent metals, acid hydrolysis.

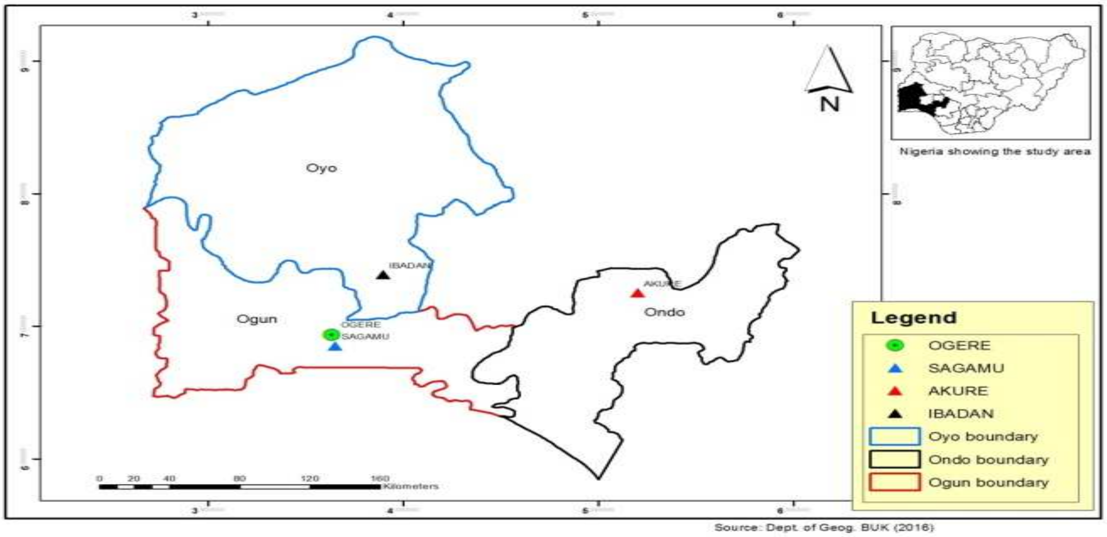
NTRODUCTION

The stability constant of a complex is the numerical expression of its stability and provides a quantitative measure of affinity of the metal ion to the complexing agent. An understanding of the relative stability of metal-complexes helps in predicting the behavior of metal ions in the soil (Ram and Raman, 1982). Extensive researches has been done to determine the stability constants of the complexes formed between humic acid (HA) with a number of metal ions. Ashok *et al.*, (2000) reported that humic acid with hydroxyl, phenoxyl and carboxyl reactive groups can form coordination compound with metal ions at pH 3.5. The stability constants(Log K) for different metal-humic acid complexes indicated the following order of the stabilities of complexes formed between humic acid and metal ion, Cu >Fe >Pb> Ni > Co > Ca > Cd > Zn >Mn> Mg. Andelkovic *et al.*, (2010) investigated the binding of Cd(II) to soil humic acid at pH 6.5 and in 0.1M KNO_3 ionic medium. The stability constant for binding indicating greater stability in the case when carboxyl groups are involved in complexation reaction. Kostic *et al.*,(2012) investigated the complexation of humic acid with certain heavy metal ions (Co(II), Ni(II),Cu(II), Zn(II), and Pb(II). The experiment was performed at 25°C, at pH 4.0 and ionic strength of 0.01M. Stability constant of complex between Pb(II) ions and humic acid is greater than stability constants of other investigated metal-humate complexes. Bogata and Sokolowska (2016) analyses the interaction between humic acids from different soils and Zn (II) ions at wide concentration ranges and at pH 5. Studies have showed significant impact of Zn concentration, pH and some properties of humic acids with zinc.But all of these studies were limited to acidic pH range. Therefore, the present study was carried out to determine and compare the stability constants of complexes of metal ions with hydrolysed peat soil humic acid and unhydrolysed peat soil humic under non-acid conditions.

MATERIALS AND METHODS

Analytical grade chemicals used includes hydrochloric acid (HCl), nitric acid (HNO_3), sodium hydroxide (NaOH), lead nitrate $Pb(NO_3)_2$, copper nitrate $Cu(NO_3)_2.3H_2O$, cadmium nitrate $Cd(NO_3)_2.4H_2O$, magnesium nitrate $Mg(NO_3)_2.6H_2O$, potassium nitrate (KNO_3), calcium chloride ($CaCl_2$), (sigma-Aldrich). Dowex 50WX8, (20-50 mesh) from Fluka.

Area of study



Source: Dept. of Geog. BUK (2016)

Figure 1: Map showing the sampling point at Sagamu Town, Ogun State.

Description of Sampling Area

Sagamu has geographical coordinates between 6°50′ north; 3° 38′ east is located in south western region of Nigeria. The region has tropical wet and dry climate with a lengthy wet season and relatively constant temperatures throughout the course of the year. Wet season runs from March to October, November to December forms the region dry season. The vegetation type of the region is savannah which is really grassland with small bushes and occasional big trees. Grassland soils have substantially higher organic matter content than forest soils (Novackova, 2011).

Sample Collection

The Peatsoil samples were collected from four different sampling points (0-10cm depth) in Sagamu into polyethylene bag with plastic spoons. Samples were taken to the laboratory, extraneous materials were removed; the samples were air-dried, crushed and ground to a fine powder in a mortar passed through a 0.20mm sieve. The samples were kept for analysis.

Isolation and purification of humic acid from peat soil sample

Peatsoil sample (100g) was mixed with 1000 cm^3 of 0.1M NaOH solution, shaken for 3hours and left to stand overnight. Dark-coloured supernatant was obtained and decanted from solid residue. The dark-coloured supernatant was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 6 hours. Yellowish brown supernatant and dark-brown precipitate were obtained. The yellowish brown supernatant was decanted followed by centrifuge and discarded. The dark-brown precipitate was mixed with $500cm^3$of 0.1M NaOH solution followed by passing through dowex resin. The dark-brown solution was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 3 hours. The dark-brown precipitate was washed several times with deionized water. The supernatant was treated with $AgNO_3$ solution until no white precipitate observed. The humic acid was transferred to weighed crucible and dried at 60°C in an oven for 12 hours. The humic acid was cooled and dried in the desiccator, weighed and recorded. The obtained humic acid was dried again at 60°C for additional 6 hours cooled and dried in the desiccator, weighed and recorded constant weight was obtained (Baruah *et al*., 2015).

FT-IR analysis

FT-IR spectra of humic acid sample was analysed using Carry 630 FT-IR Agilent Technologies.

Unhydrolysed compost humic acid

The unhydrolysed humic acid was obtained after isolation and purification of compost humic acid and kept for investigation.

Acid hydrolysis of Peatsoil acid

Peatsoil humic acid sample (1g) was refluxed for 12 hours at (160°C) with $50cm^3$ of 6M HCl. The mixture was allowed to cool, decanted, and centrifuged after hydrolysis. The insoluble residues were washed with distilled water via centrifugation several times, and the supernatant was treated with $AgNO_3$ solution until no white precipitate was observed. The residue was thoroughly dried over $CaCl_2$ in a desiccator at room temperature (Chefetz *et al*., 2002). Finally, the obtained hydrolysed humic acid was kept for investigation.

Potentiometric Titrations

Potentiometric measurements were carried out using a pH-meter Jenway (model 3510) with combine electrode, the sensitivity of the pH - meter is 0.01 units. The pH meter was switched on half an hour before starting the titration for initial warm up of the instrument. The instrument was calibrated with an aqueous standard buffer solution of pH 4.00 and 10.0 (borate buffer) prepared from a "Qualigens" buffer tablets.

The following sets of solutions were prepared in a 250cm^3 volumetric flask separately for pH metric titrations.

(i) 5 cm^3 0.1 M HCl + 40 cm^3 deionized water
(ii) 5 cm^3 0.1 M HCl + 39 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid
(iii) 5 cm^3 0.1 M HCl + 37 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid + 2 cm^3 0.01 M Cu(II)

The solutions were titrated against standardized 0.110MNaOH separately. The total volume of each mixture was adjusted to 50 cm^3 and the ionic strength of the solutions was maintained constant at by adding appropriate amount of stock solution of 1M KNO_3 (Gamal, 2015; Omar and Ali, 2015). A magnetic stirrer was used to achieve thorough mixing of the interacting solutions at 550 rpm. The same set of experimental conditions was applied for potentiometric titration of remaining samples.

Evaluation of pKa of Hydrolysed peat soil Humic Acids

The proton-ligand formation number n_A were calculated by Irving and Rossotti expression (Omar and Ali, 2015).

$nA = Y- \frac{(V2-V1)(No-Eo)}{(Vo+V1)TcL}$ ………………………………1

Where: Y is number of dissociable proton, (V_2-V_1) is the measure of displacement of the ligand curve relative to acid curve, N^o and E^o are the resultant concentration of alkali solution, free acid solution, $T_{cL}{}^o$ is the total ligand concentration, V^o is the total volume of titration solution,V_1 is the volume of alkali added to acid solution,V_2 is the volume of alkali added to acid solution + ligand solution, acid dissociation constants (pKa - values) of ligand were calculated by algebraic method point wise calculation (Tables 1). The dissociation constants (pKa) were calculated according to the following relation:

$pKa = pH + \log(\frac{nA}{1-nA})$ …………………………2

Where: pKa is the acid dissociation constant, $n_A$is the Proton-ligand formation number and pH is the pH-values (Omar and Ali, 2015).

Determination of metal-ligand stability constants (log K) of complexes

The potentiometric measurement for the determination of stability constant of a complex in solution is based on the fact that the redox potential of the couple $\frac{M^{+(m-n)}}{M^{+m}}$ is shifted significantly on complexation of the metal ion with the ligand. This method involves change in hydrogen ion concentration [H$^+$] due to the displacement or association of one or more protons taking place during complexation reaction. This change can be found out by titrating the solutions containing free acid, acid with ligand, and acid with ligand and metal ion, individually against a standard alkali solution at a constant ionic strength or temperature. Either ionic strength or temperature may be varied for different sets of solutions. In all the cases, the change in the pH of the solution is measured after each addition of a known amount of alkali to the reaction cell which contains the reaction mixture. The titration curves are then drawn by plotting the measured pH values against the corresponding volume of alkali added and the stability constants of the complexes are determined from the titration curves by employing pH-metric titration technique given by (Irving and Rossoti).

Metal-ligand stability constants (Log K) were determined by using the following relations:

$$\bar{n} = \frac{(V_3 - V_2)(E^0 + N^0)}{(V^0 + V_2)\bar{n}_A T_m^0}$$

………………………………………………………………………3

and

$$PL = \log_{10}\{\frac{1 + \beta_n^H \frac{1}{[anti\ \log pH]^n}}{T_L^0 - \bar{n} T_m^0} X \frac{(V^0 + V_3)}{V^0}\}$$

………………………………………………………4

Where $T_{L,}$ T^o, E°, and V^ohavethe same significance as in equation (1) above, T_m denotes the total concentration of metal present in solution, V_3 is the volume of metal ions present in solution and β^H is the overall proton ligand stability constant. The metal-ligand stability constants (log K) were determined by employing point wise computational Method (eq. 5 and 6).

$\text{Log}K_1 = \log\left(\frac{n}{1-n}\right) + pL$ 5

$\text{Log}K_2 = \log\left(\frac{1-n}{2-n}\right) + pL$........................6

Where: Log K is the metal-ligand stability constant, pL is the Free ligand exponent function, **n** is the Average number of ligand attached with metal ion (Janrao*et al*., 2014).The results obtained were analyzed by an ORIGIN 2016 program using titration data and then the proton-ligand stability constants (pKa) and Metal-ligand stability constant (LogK) calculated (Omar and Ali, 2015).

RESULTS AND DISCUSSION

Fourier transformed infrared (FT-IR) spectra of isolated humic acid from peat soils Figure 2 had distinct clear absorption bands indicating the presence of major humic acid structural elemental groups such as H bonded OH ($3680cm^{-1}$ peak), C=O of carbonyl ($1721cm^{-1}$ peak), functional groups of aliphatic components CH_2 ($2918cm^{-1}$ peak) and C-O stretching of polysaccharide ($1168cm^{-1}$ peak). The positions of the absorption bands of the spectra fell within typical major absorption bands of humic acid which is at frequencies 3680, 2918, 1721, 1168 cm^{-1}. The first peak centred in the vicinity of 3680 cm^{-1} region is attributed to phenol OH group bounded by intermolecular H bonds. The $2918cm^{-1}$ band usually has absorption maximum at 2918 cm^{-1} which is due to C–H stretching of alkane group (CH_2). The next major absorption band is 1721 cm^{-1}. This band has been commonly ascribed to C=O stretching of mainly carboxyl group (COOH) with trace amount of ketones. The last peak was observed at 1168 cm^{-1} due to C–O stretching of polysaccharides and this peak appeared also in the spectra of humic acid from peat soil. The FTIR spectra of the isolated humic acid contained all major characteristic absorption peaks of humic acid. These absorption peaks indicated the presence of the major structural elements of humic acid namely H bonded OH, C=C of aromatic ring, C=O of carbonyl group (both carboxyl and ketonic), CH_2 group. This strongly supports the presence of humic acid.

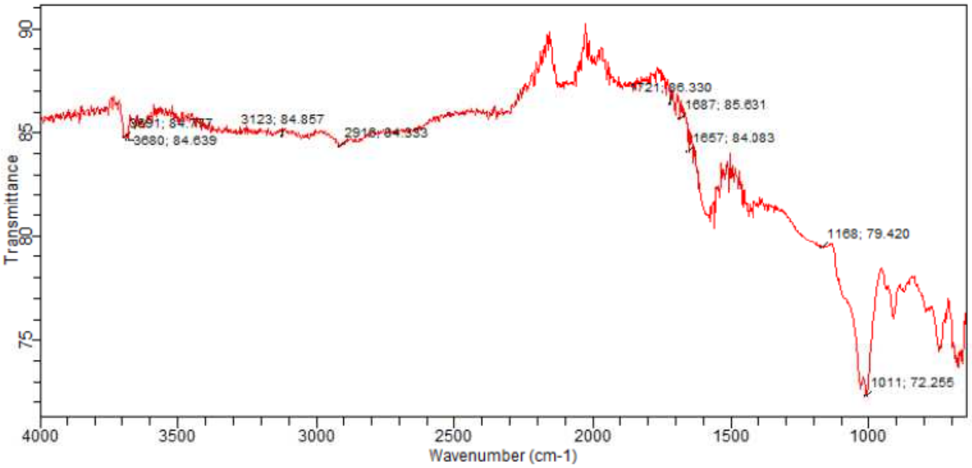


Fig. 2 : FT-IR spectraof peatsoilhumic acid (PSHA)

Evaluation of acid dissociation constant (pka) of acid hydrolysed peat soil humicacid at phenolic group

The value of the dissociation constant of the peat soil humic acid (PSHA) that underwent acidhydrolysis studied was found to be 8.9299 as shown Table 1, which is lower than the literaturevalues reported by Almeida and Szpoganics, (2015), Borges *et al*., (2005); Badr *et al*., (2012)and Fernandes *et al*,.(2009) of 9.73, 9.47 and 10.30. The difference between the obtained valuesand the reported values in this study might be probably as a result of acid hydrolysis of humicacid.

Table 1: PKa of (Hydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	$\log(\frac{nA}{1-nA})$	pKa
8.50	5.30	6.29	0.99	0.3594	-0.2510	8.2490
8.72	5.35	6.37	1.02	0.3400	-0.2880	8.4320
9.00	5.40	6.46	1.06	0.3141	-0.3391	8.6609
9.22	5.45	6.55	1.10	0.2882	-0.3927	8.8273
9.51	5.50	6.66	1.16	0.2494	-0.4786	9.0314
9.73	5.55	6.78	1.23	0.2041	-0.5910	9.1390
10.00	5.60	6.90	1.30	0.1589	-0.7238	9.2762
10.23	5.65	7.05	1.40	0.0941	-0.9835	9.2465
10.49	5.70	7.10	1.40	0.0941	-0.9835	9.5065

Average pKa = 8.9299 ± 0.4186

Table 2: PKa of (Unhydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	$\mathrm{Log}(\frac{nA}{1-n})$	pKa
8.50	5.30	5.81	0.51	0.6619	0.2919	8.7919
8.72	5.35	5.90	0.55	0.6357	0.2418	8.9618
9.00	5.40	6.00	0.60	0.6029	0.1813	9.1813
9.22	5.45	6.10	0.65	0.5701	0.1226	9.3426
9.51	5.50	6.20	0.70	0.5376	0.0654	9.5754
9.73	5.55	6.33	0.78	0.4851	-0.0259	9.7041
10.00	5.60	6.47	0.87	0.4262	-0.1291	9.8709
10.23	5.65	6.62	0.99	0.3609	-0.2481	9.9819
10.49	5.70	6.80	1.10	0.2759	-0.4690	10.0210

Average pKa = 9.4923± 0.4410

Metal-ligand stability constant (Log K)

The stabilityconstants require the accurate values of proton-ligand stability constants (Anil and Maroti, 2008). Metal titration curves crossed over ligand titration curve indicated the formation of complex upon proton release (Santosh, *et al.*, 2011). If the values of n- are within range 0.2-0.8 and 1.2-18 this indicates the formation of 1:1 and 1:2 complexes (Sayyed and Mazahar, 2012).

The metal (II)-humate stepwise stability constants (log k) at phenolic group (Tables 3-18)

Table 3: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$\log(\frac{n}{1-n})$	LogK_1
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

LogK_1 (Average value) = 2.4788± 0.2203

Table 4: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$\mathrm{Log}(\frac{n-1}{2-n})$	LogK_2
9.51	5.50	6.66	6.73	0.07	1.3509	1.70	-0.2671	1.4329
9.73	5.55	6.78	6.85	0.07	1.6383	1.51	0.2467	1.7567
10.00	5.60	6.90	6.98	0.08	2.1783	1.31	-0.2158	1.0942
10.23	5.65	7.05	7.13	0.08	4.1904	1.27		
10.49	5.70	7.10	7.19	0.09	4.6920			

LogK_2(Average value) = 1.4280 ± 0.3312

Table 5:Point-wise method,Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	Log($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430

$LogK_1$ **(Average value)** = 2.3059± 0.6153

Table 6:Point-wise method, Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
9.73	5.55	6.33	6.42	0.09	0.9000	1.69		
10.00	5.60	6.47	6.58	0.11	1.2578	1.44	-0.4592	0.9808
10.23	5.65	6.62	6.84	0.12	1.6137	1.26	-0.2010	1.4610
10.49	5.70	6.80	6.92	0.12	2.1052	1.03		

$LogK_2$ **(Average value)** = 1.2209± 0.3398

Table 7:Point-wise method,Pb (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n}{1-n}$)	$LogK_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.60	0.05	0.8333	1.96	0.6989	2.6589

$LogK_1$ (Average value) = 2.5832 ±0.1614

Table 8:Point-wise method,Pb-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n-1}{2-n}$)	$logK_2$
9.51	5.50	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.83	0.05	1.1702	1.44		
10.00	5.60	6.90	6.90	0.05	1.4864	1.22	-0.0237	1.1963
10.23	5.65	7.05	7.10	0.05	2.0190	1.09		
10.49	5.70	7.10	7.17	0.07	3.6492	1.00		

$LogK_2$(Average value) = 1.1963

Table 9:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log ($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.5477	2.3123
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	0.0272	2.2072
9.51	5.50	6.20	6.26	0.07	0.6417	1.89	0.2530	2.1430
9.73	5.55	6.40	6.40	0.07	0.7000	1.67	0.3680	2.0380

$LogK_1$ **(Average value)** = 2.2364 ± 0.1602

Table 10:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
10.00	5.60	6.47	6.55	0.08	1.9503	1.41		
10.23	5.65	6.62	6.72	0.11	1.4792	1.26	-0.0361	1.2239

$LogK_2$ **(Average value)** = 1.2239

Table 11:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n}{n-1}$)	$LogK_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4290	2.2110
8.72	5.35	6.37	6.39	0.02	0.2858	2.42	-0.3978	2.0222
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

$LogK_1$ (Average value)=2.1382±0.1046

Table 12:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	log($\frac{n-1}{2-n}$)	LogK$_2$
9.51	5.55	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.84	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.93	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.10		
10.49	5.70	7.10	7.18	0.07	3.6492	0.83		

LogK$_2$(Average value) = 1.5453 **±** 0.3450

Table 13:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	V$_3$-V$_2$	n	pL	Log($\frac{n}{n-1}$)	Log K$_1$
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.3477	2.3123
9.00	5.40	6.00	6.04	0.04	0.3236	2.38	-0.3202	2.0598
9.22	5.45	6.10	6.15	0.05	0.4297	2.17	-0.1230	2.0470
9.51	5.50	6.20	6.26	0.06	0.5500	1.89	0.0871	1.9771
9.73	5.55	6.33	6.40	0.07	0.7000	1.67	0.3680	2.0380

LogK$_1$ **(Average value)** = 2.1568 ± 0.2069

Table 14:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	V$_3$-V$_2$	n	pL	Log($\frac{n-1}{2-n}$)	Log K$_2$
10.00	5.60	6.47	6.55	0.08	0.9148	1.41		
10.23	5.65	6.62	6.71	0.09	1.2102	1.20	-0.5749	0.6251
10.49	5.70	6.80	6.92	0.09	1.5968	1.03	0.1703	1.2003

LogK$_2$ **(Average value)** = 0.9127± 0.4070

Table15:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	Log($\frac{n}{1-n}$)	LogK$_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4210	2.2190
8.72	5.35	6.37	6.40	0.03	0.4286	2.42	-0.1249	2.2951
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.96	0.3010	2.2610
9.51	5.55	6.66	6.70	0.04	0.7720	1.67	0.5297	2.1997

LogK$_1$ (Average value) = 2.2108± 0.0825

Table 16:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	Log($\frac{n-1}{2-n}$)	Log K$_2$
9.73	5.55	6.78	6.83	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.95	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.09		
10.49	5.70	7.10	7.16	0.06	3.1429	0.89		

LogK$_2$ **(Average value)** = 1.5453± 0.3450

Table 17:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	V$_3$-V$_2$	n	pL	Log($\frac{n}{n-1}$)	Log K$_1$
8.50	5.30	5.81	5.86	0.05	0.3717	2.88	-0.2280	2.6520
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.06	0.06	0.4853	2.38	-0.0255	2.3545
9.22	5.45	6.10	6.16	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430
9.73	5.55	6.33	6.41	0.08	0.8000	1.69	0.6020	2.2920

LogK$_1$ **(Average value)** = 2.2516± 0.5380

Table 18:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log$(\frac{n-1}{2-n})$	Log K_2
10.00	5.60	6.47	6.57	0.10	1.1434	1.43		
10.23	5.65	6.62	6.72	0.10	1.3448	1.23	-0.2788	0.9512
10.49	5.70	6.80	6.90	0.10	1.7742	1.03	0.5351	1.5651

LogK_2 **(Average value)** = 1.2581± 0.4340

Table 19: Stepwise and overall Stability constants of thehydrolysed and unhydrolysed divalent metal (II) complexes

Chelates	**LogK_1**	**LogK_2**	**Logβ**
[Cu (Hydrolysed PSHA-1)$_2$]	2.4788	1.4280	3.9068
[Pb (Hydrolysed PSHA-1)$_2$]	2.5832	1.1963	3.7795
[Cd (Hydrolysed PSHA-1)$_2$]	2.2108	1.5453	3.7561
[Mg (Hydrolysed PSHA-1)$_2$]	2.1382	1.5453	3.6835
[Cu (Unhydrolysed PSHA-1)$_2$]	2.3059	1.2209	3.5268
[Pb (Unhydrolysed PSHA-1)$_2$]	2.2364	1.2239	3.4603
[Cd (Unhydrolysed PSHA-1)$_2$]	2.2516	1.2581	3.5097
[Mg (Unydrolysed PSHA-1)$_2$]	2.1568	0.9127	3.0695

The results obtained (Table19) shows the stepwise and overall stability constants to be not high indicating low stability of the complexes, because the solubility of most metal ions in the basic pH range is minimal due to metal hydroxide precipitation (Karimi, 2017). In general, the stepwise stability constants (K_1 and K_2) follow the order $K_1 > K_2$ for the copper, lead, magnesium and cadmium complexes respectively. The steady decrease of the values with increasing number of ligands is in agreement with the prediction made by researchers (Na'aliya, 2013). The decrease could be attributed to the fact that as the number of the ligands (Humate ions) that enters the coordination zone increases the aqua molecules available for replacement by the ligands become less. Thus, the metal ions become less electron loving with progressive intake of the ligand and this results in the decrease in the values of the constants (Na'aliya, 2013). Also the stability of the complexes is influenced by the size and number of the chelate rings(Mackay and Mackay,2002).All the complexes form rings in their structure as humate, a bidentate ligand, bond the metal ions in the ratio 1:2 (Boguta and Sokolowska, 2016) forming chelate rings. The values of the overall stability constants (logβ) obtained for humate complexes are not high indicating low stability as the values are not high. LogK values for copper-humates (Table 3 to 6) obtained in this study are lower than those reported for the complexes of humic acids (Pandey *et al*., 2015; Dinu, 2013; Kaschl *et al*., 2010 and Gilbeto and Jorg, 2001). The values of LogK(Table 7 to 10) forlead-humates are lower than those reported for the lead in the literature (Dinu, 2013; Gilbeto and Jorg 2001). Log K values(Table 11 to 14) for magnesium-humates obtained in this study are close to those reported by (Pandey *et al*., 2015). Log K values of cadmium-humates (Table 15 to 18) obtained in this work near to the one reported by (Dinu, 2013 and Pandey *et al*., 2015).The difference between the reported values and the values obtained in this study might be probably as a result of acid hydrolysis of humic acid. The values of the overall stability constants (log β) of the copper humates complexes presented in Table 19 is high than that of other metal humate complexes, show relatively high stability of Cu-HA complexes, show the following order of stability: Cu >Pb> Cd > Mg; which are in close agreement to the findings of (Dinu, 2013 and Pandey *et al*., 2015).The high stability of Cu-humate chelate could be attributed to the existence of coordinate covalent bond between the complexing agents and the Cu^{2+} ions. Since, Cu^{2+} being a metal of the transitional series with $3d^9$ electronic configurations can accept the electrons from the complexing agents. Similarly,the low stabilities of Pb,Cd and Mg -complexes could be explained by that Pb^{2+} with $6s^2$, Cd^{2+} with $4d^{10}$ and Mg^{2+} with $2p^6$ their electronic configuration has a completely filled d,p and s orbitals. Moreover, the stabilities of metal ions with hydrolysed humic acid from peat soil were higher than those with unhydrolysed humic acid from peat soil; which is ascribed to the high content of acidity in hydrolysed humic acid than unhydrolysed humic acid.

CONCLUSION

The values of logK for Cu(II) hydrolysed humic acid complex was higher followed by Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes as compared with metal(II) unhydrolysed humic acid complexes . This indicates acid hydrolysis of humic acid can enhance the complexation behavior of humic acid with metal (II) ions. However, the higher values of logβ for Cu(II), Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes indicates more stable stepwise complexes formed as compared with Cu(II), Pb(II), Cd(II) and Mg(II) unhydrolysed humic acid complexes.

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STABILITY CONSTANTS OF COMPLEXES OF METAL IONS WITH PEATSOIL HUMIC ACIDS UNDER NON-ACID-CONDITIONS

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ABSTRACT

Stability constants of complexes of four divalent metal ions viz. Cu^{2+}, Pb^{2+},Mg^{2+} and Cd^{2+} with humic acids (HA) were determined by potentiometric titration of humic acids with the corresponding salt of the divalent metals in aqueous media under non-acid-condition. The log K (logarithm of the stability constant) ranged from 1.0942 to 2.7471 for metal-humic acid complexes were determined using point-wise computational method. The order of stability constants were obtained as follows: Cu >Pb> Cd > Mg for metal -HA complexes respectively, indicating a higher degree of complexation with Cu metal ion.

Keywords: stability constant, humic acid, potentiometric titration, divalent metals, acid hydrolysis.

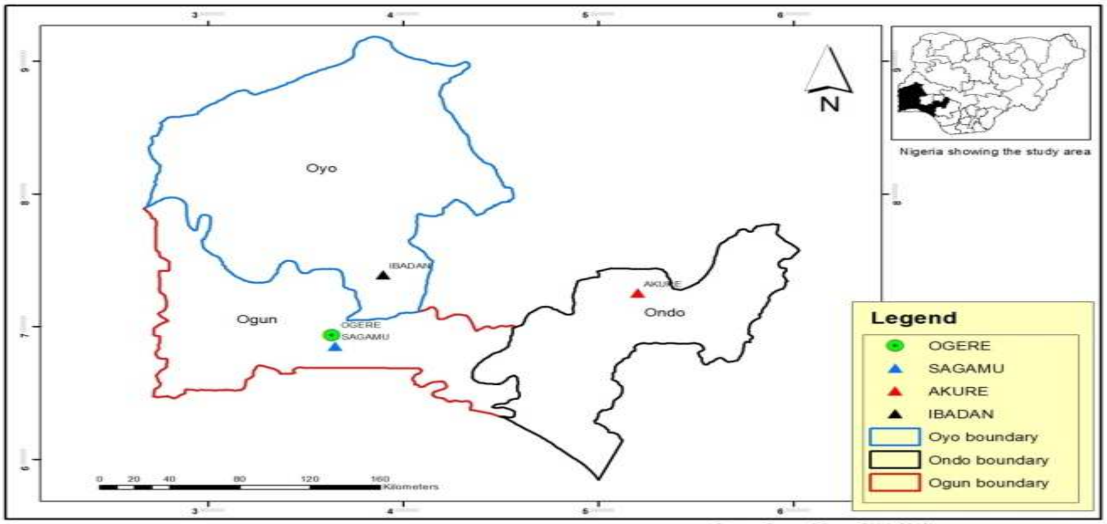
NTRODUCTION

The stability constant of a complex is the numerical expression of its stability and provides a quantitative measure of affinity of the metal ion to the complexing agent. An understanding of the relative stability of metal-complexes helps in predicting the behavior of metal ions in the soil (Ram and Raman, 1982). Extensive researches has been done to determine the stability constants of the complexes formed between humic acid (HA) with a number of metal ions. Ashok *et al*., (2000) reported that humic acid with hydroxyl, phenoxyl and carboxyl reactive groups can form coordination compound with metal ions at pH 3.5. The stability constants(Log K) for different metal-humic acid complexes indicated the following order of the stabilities of complexes formed between humic acid and metal ion, Cu >Fe >Pb> Ni > Co > Ca > Cd > Zn >Mn> Mg. Andelkovic *et al*., (2010) investigated the binding of Cd(II) to soil humic acid at pH 6.5 and in 0.1M KNO_3 ionic medium. The stability constant for binding indicating greater stability in the case when carboxyl groups are involved in complexation reaction. Kostic *et al*.,(2012) investigated the complexation of humic acid with certain heavy metal ions (Co(II), Ni(II),Cu(II), Zn(II), and Pb(II). The experiment was performed at 25°C, at pH 4.0 and ionic strength of 0.01M. Stability constant of complex between Pb(II) ions and humic acid is greater than stability constants of other investigated metal-humate complexes. Bogata and Sokolowska (2016) analyses the interaction between humic acids from different soils and Zn (II) ions at wide concentration ranges and at pH 5. Studies have showed significant impact of Zn concentration, pH and some properties of humic acids with zinc.But all of these studies were limited to acidic pH range. Therefore, the present study was carried out to determine and compare the stability constants of complexes of metal ions with hydrolysed peat soil humic acid and unhydrolysed peat soil humic under non-acid conditions.

MATERIALS AND METHODS

Analytical grade chemicals used includes hydrochloric acid (HCl), nitric acid (HNO_3), sodium hydroxide (NaOH), lead nitrate $Pb(NO_3)_2$, copper nitrate $Cu(NO_3)_2.3H_2O$, cadmium nitrate $Cd(NO_3)_2.4H_2O$, magnesium nitrate $Mg(NO_3)_2.6H_2O$, potassium nitrate (KNO_3), calcium chloride ($CaCl_2$), (sigma-Aldrich). Dowex 50WX8, (20-50 mesh) from Fluka.

Area of study



Source: Dept. of Geog. BUK (2016)

Figure 1: Map showing the sampling point at Sagamu Town, Ogun State.

Description of Sampling Area

Sagamu has geographical coordinates between 6°50′ north; 3° 38′ east is located in south western region of Nigeria. The region has tropical wet and dry climate with a lengthy wet season and relatively constant temperatures throughout the course of the year. Wet season runs from March to October, November to December forms the region dry season. The vegetation type of the region is savannah which is really grassland with small bushes and occasional big trees. Grassland soils have substantially higher organic matter content than forest soils (Novackova, 2011).

Sample Collection

The Peatsoil samples were collected from four different sampling points (0-10cm depth) in Sagamu into polyethylene bag with plastic spoons. Samples were taken to the laboratory, extraneous materials were removed; the samples were air-dried, crushed and ground to a fine powder in a mortar passed through a 0.20mm sieve. The samples were kept for analysis.

Isolation and purification of humic acid from peat soil sample

Peatsoil sample (100g) was mixed with 1000 cm^3 of 0.1M NaOH solution, shaken for 3hours and left to stand overnight. Dark-coloured supernatant was obtained and decanted from solid residue. The dark-coloured supernatant was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 6 hours. Yellowish brown supernatant and dark-brown precipitate were obtained. The yellowish brown supernatant was decanted followed by centrifuge and discarded. The dark-brown precipitate was mixed with $500cm^3$of 0.1M NaOH solution followed by passing through dowex resin. The dark-brown solution was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 3 hours. The dark-brown precipitate was washed several times with deionized water. The supernatant was treated with $AgNO_3$ solution until no white precipitate observed. The humic acid was transferred to weighed crucible and dried at 60°C in an oven for 12 hours. The humic acid was cooled and dried in the desiccator, weighed and recorded. The obtained humic acid was dried again at 60°C for additional 6 hours cooled and dried in the desiccator, weighed and recorded constant weight was obtained (Baruah *et al.*, 2015).

FT-IR analysis

FT-IR spectra of humic acid sample was analysed using Carry 630 FT-IR Agilent Technologies.

Unhydrolysed compost humic acid

The unhydrolysed humic acid was obtained after isolation and purification of compost humic acid and kept for investigation.

Acid hydrolysis of Peatsoil acid

Peatsoil humic acid sample (1g) was refluxed for 12 hours at (160°C) with $50cm^3$ of 6M HCl. The mixture was allowed to cool, decanted, and centrifuged after hydrolysis. The insoluble residues were washed with distilled water via centrifugation several times, and the supernatant was treated with $AgNO_3$ solution until no white precipitate was observed. The residue was thoroughly dried over $CaCl_2$ in a desiccator at room temperature (Chefetz *et al.*, 2002). Finally, the obtained hydrolysed humic acid was kept for investigation.

Potentiometric Titrations

Potentiometric measurements were carried out using a pH-meter Jenway (model 3510) with combine electrode, the sensitivity of the pH - meter is 0.01 units. The pH meter was switched on half an hour before starting the titration for initial warm up of the instrument. The instrument was calibrated with an aqueous standard buffer solution of pH 4.00 and 10.0 (borate buffer) prepared from a "Qualigens" buffer tablets.

The following sets of solutions were prepared in a 250cm^3 volumetric flask separately for pH metric titrations.

(i) 5 cm^3 0.1 M HCl + 40 cm^3 deionized water

(ii) 5 cm^3 0.1 M HCl + 39 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid

(iii) 5 cm^3 0.1 M HCl + 37 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid + 2 cm^3 0.01 M Cu(II)

The solutions were titrated against standardized 0.110MNaOH separately. The total volume of each mixture was adjusted to 50 cm^3 and the ionic strength of the solutions was maintained constant at by adding appropriate amount of stock solution of 1M KNO_3 (Gamal, 2015; Omar and Ali, 2015). A magnetic stirrer was used to achieve thorough mixing of the interacting solutions at 550 rpm. The same set of experimental conditions was applied for potentiometric titration of remaining samples.

Evaluation of pKa of Hydrolysed peat soil Humic Acids

The proton-ligand formation number n_A were calculated by Irving and Rossotti expression (Omar and Ali, 2015).

$$nA = Y- \frac{(V2-V1)(No-Eo)}{(Vo+V1)TcL} \quad \text{.................................}1$$

Where: Y is number of dissociable proton, (V_2-V_1) is the measure of displacement of the ligand curve relative to acid curve, N^o and E^o are the resultant concentration of alkali solution, free acid solution, $T_{cL}{}^o$ is the total ligand concentration, V^o is the total volume of titration solution,V_1 is the volume of alkali added to acid solution,V_2 is the volume of alkali added to acid solution + ligand solution, acid dissociation constants (pKa - values) of ligand were calculated by algebraic method point wise calculation (Tables 1). The dissociation constants (pKa) were calculated according to the following relation:

$$pKa = pH + \log(\frac{nA}{1-nA}) \quad \text{...........................}2$$

Where: pKa is the acid dissociation constant, $n_A$is the Proton-ligand formation number and pH is the pH-values (Omar and Ali, 2015).

Determination of metal-ligand stability constants (log K) of complexes

The potentiometric measurement for the determination of stability constant of a complex in solution is based on the fact that the redox potential of the couple $\frac{M^{+(m-n)}}{M^{+m}}$ is shifted significantly on complexation of the metal ion with the ligand. This method involves change in hydrogen ion concentration [H$^+$] due to the displacement or association of one or more protons taking place during complexation reaction. This change can be found out by titrating the solutions containing free acid, acid with ligand, and acid with ligand and metal ion, individually against a standard alkali solution at a constant ionic strength or temperature. Either ionic strength or temperature may be varied for different sets of solutions. In all the cases, the change in the pH of the solution is measured after each addition of a known amount of alkali to the reaction cell which contains the reaction mixture. The titration curves are then drawn by plotting the measured pH values against the corresponding volume of alkali added and the stability constants of the complexes are determined from the titration curves by employing pH-metric titration technique given by (Irving and Rossoti).

Metal-ligand stability constants (Log K) were determined by using the following relations:

$$\bar{n} = \frac{(V_3 - V_2)(E^0 + N^0)}{(V^0 + V_2)\bar{n}_A T_m^0} \quad \text{..}3$$

and

$$PL = \log_{10}\{\frac{1+\beta_n^H \frac{1}{[anti\ \log pH]^n}}{T_L^0 - \bar{n}T_m^0} X \frac{(V^0+V_3)}{V^0}\} \quad \text{..}4$$

Where $T_{L,}$ T^{o}, E°, and V^{o}havethe same significance as in equation (1) above, T_m denotes the total concentration of metal present in solution, V_3 is the volume of metal ions present in solution and β^H is the overall proton ligand stability constant. The metal-ligand stability constants (log K) were determined by employing point wise computational Method (eq. 5 and 6).

$$\mathrm{Log}K_1 = \log\left(\frac{n}{1-n}\right) + pL \quad ....5$$

$$\mathrm{Log}K_2 = \log\left(\frac{1-n}{2-n}\right) + pL......................6$$

Where: Log K is the metal-ligand stability constant, pL is the Free ligand exponent function, **n** is the Average number of ligand attached with metal ion (Janrao*et al.*, 2014).The results obtained were analyzed by an ORIGIN 2016 program using titration data and then the proton-ligand stability constants (pKa) and Metal-ligand stability constant (LogK) calculated (Omar and Ali, 2015).

RESULTS AND DISCUSSION

Fourier transformed infrared (FT-IR) spectra of isolated humic acid from peat soils Figure 2 had distinct clear absorption bands indicating the presence of major humic acid structural elemental groups such as H bonded OH ($3680cm^{-1}$ peak), C=O of carbonyl ($1721cm^{-1}$ peak), functional groups of aliphatic components CH_2 ($2918cm^{-1}$ peak) and C-O stretching of polysaccharide ($1168cm^{-1}$ peak). The positions of the absorption bands of the spectra fell within typical major absorption bands of humic acid which is at frequencies 3680, 2918, 1721, 1168 cm^{-1}. The first peak centred in the vicinity of 3680 cm^{-1} region is attributed to phenol OH group bounded by intermolecular H bonds. The $2918cm^{-1}$ band usually has absorption maximum at 2918 cm^{-1} which is due to C–H stretching of alkane group (CH_2). The next major absorption band is 1721 cm^{-1}. This band has been commonly ascribed to C=O stretching of mainly carboxyl group (COOH) with trace amount of ketones. The last peak was observed at 1168 cm^{-1} due to C–O stretching of polysaccharides and this peak appeared also in the spectra of humic acid from peat soil. The FTIR spectra of the isolated humic acid contained all major characteristic absorption peaks of humic acid. These absorption peaks indicated the presence of the major structural elements of humic acid namely H bonded OH, C=C of aromatic ring, C=O of carbonyl group (both carboxyl and ketonic), CH_2 group. This strongly supports the presence of humic acid.

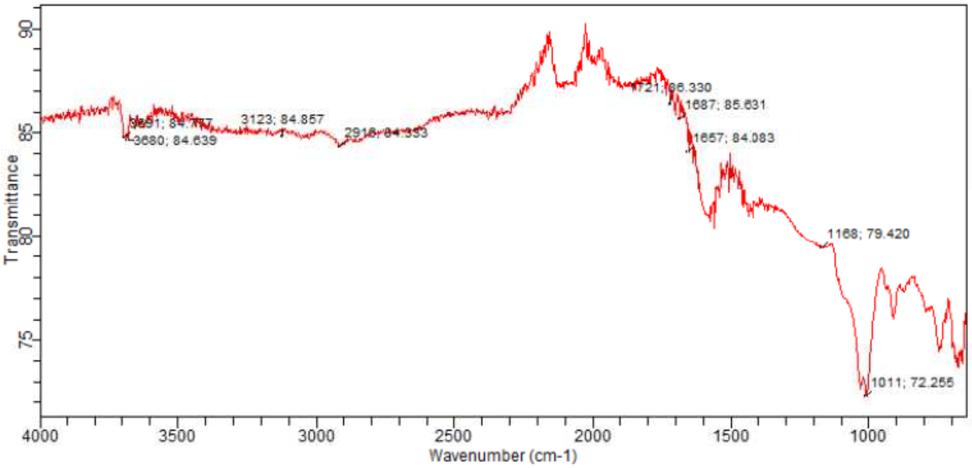


Fig. 2 : FT-IR spectraof peatsoilhumic acid (PSHA)

Evaluation of acid dissociation constant (pka) of acid hydrolysed peat soil humicacid at phenolic group

The value of the dissociation constant of the peat soil humic acid (PSHA) that underwent acidhydrolysis studied was found to be 8.9299 as shown Table 1, which is lower than the literaturevalues reported by Almeida and Szpoganics, (2015), Borges *et al.*, (2005); Badr *et al.*, (2012)and Fernandes *et al*,.(2009) of 9.73, 9.47 and 10.30. The difference between the obtained valuesand the reported values in this study might be probably as a result of acid hydrolysis of humicacid.

Table 1: PKa of (Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	V_2-V_1	nA	log($\frac{nA}{1-nA}$)	pKa
8.50	5.30	6.29	0.99	0.3594	-0.2510	8.2490
8.72	5.35	6.37	1.02	0.3400	-0.2880	8.4320
9.00	5.40	6.46	1.06	0.3141	-0.3391	8.6609
9.22	5.45	6.55	1.10	0.2882	-0.3927	8.8273
9.51	5.50	6.66	1.16	0.2494	-0.4786	9.0314
9.73	5.55	6.78	1.23	0.2041	-0.5910	9.1390
10.00	5.60	6.90	1.30	0.1589	-0.7238	9.2762
10.23	5.65	7.05	1.40	0.0941	-0.9835	9.2465
10.49	5.70	7.10	1.40	0.0941	-0.9835	9.5065

Average pKa = 8.9299 ± 0.4186

Table 2: PKa of (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	V_2-V_1	nA	Log($\frac{nA}{1-n}$)	pKa
8.50	5.30	5.81	0.51	0.6619	0.2919	8.7919
8.72	5.35	5.90	0.55	0.6357	0.2418	8.9618
9.00	5.40	6.00	0.60	0.6029	0.1813	9.1813
9.22	5.45	6.10	0.65	0.5701	0.1226	9.3426
9.51	5.50	6.20	0.70	0.5376	0.0654	9.5754
9.73	5.55	6.33	0.78	0.4851	-0.0259	9.7041
10.00	5.60	6.47	0.87	0.4262	-0.1291	9.8709
10.23	5.65	6.62	0.99	0.3609	-0.2481	9.9819
10.49	5.70	6.80	1.10	0.2759	-0.4690	10.0210

Average pKa = 9.4923± 0.4410

Metal-ligand stability constant (Log K)

The stabilityconstants require the accurate values of proton-ligand stability constants (Anil and Maroti, 2008). Metal titration curves crossed over ligand titration curve indicated the formation of complex upon proton release (Santosh, *et al.*, 2011). If the values of n- are within range 0.2-0.8 and 1.2-18 this indicates the formation of 1:1 and 1:2 complexes (Sayyed and Mazahar, 2012).

The metal (II)-humate stepwise stability constants (log k) at phenolic group (Tables 3-18)

Table 3: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V_3-V_2)	n	pL	log($\frac{n}{1-n}$)	LogK$_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

LogK$_1$ (Average value) = 2.4788± 0.2203

Table 4: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V_3-V_2)	n	pL	Log($\frac{n-1}{2-n}$)	LogK$_2$
9.51	5.50	6.66	6.73	0.07	1.3509	1.70	-0.2671	1.4329
9.73	5.55	6.78	6.85	0.07	1.6383	1.51	0.2467	1.7567
10.00	5.60	6.90	6.98	0.08	2.1783	1.31	-0.2158	1.0942
10.23	5.65	7.05	7.13	0.08	4.1904	1.27		
10.49	5.70	7.10	7.19	0.09	4.6920			

LogK$_2$(Average value) = 1.4280 ± 0.3312

Table 5:Point-wise method,Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	Log($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430

$LogK_1$ **(Average value)** = 2.3059± 0.6153

Table 6:Point-wise method, Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$V_3\text{-}V_2$	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
9.73	5.55	6.33	6.42	0.09	0.9000	1.69		
10.00	5.60	6.47	6.58	0.11	1.2578	1.44	-0.4592	0.9808
10.23	5.65	6.62	6.84	0.12	1.6137	1.26	-0.2010	1.4610
10.49	5.70	6.80	6.92	0.12	2.1052	1.03		

$LogK_2$ **(Average value)** = 1.2209± 0.3398

Table 7:Point-wise method,Pb (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	log($\frac{n}{1-n}$)	$LogK_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.60	0.05	0.8333	1.96	0.6989	2.6589

$LogK_1$ (Average value) = 2.5832 ±0.1614

Table 8:Point-wise method,Pb-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	log($\frac{n-1}{2-n}$)	$logK_2$
9.51	5.50	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.83	0.05	1.1702	1.44		
10.00	5.60	6.90	6.90	0.05	1.4864	1.22	-0.0237	1.1963
10.23	5.65	7.05	7.10	0.05	2.0190	1.09		
10.49	5.70	7.10	7.17	0.07	3.6492	1.00		

$LogK_2$(Average value) = 1.1963

Table 9:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$V_3\text{-}V_2$	n	pL	Log ($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.5477	2.3123
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	0.0272	2.2072
9.51	5.50	6.20	6.26	0.07	0.6417	1.89	0.2530	2.1430
9.73	5.55	6.40	6.40	0.07	0.7000	1.67	0.3680	2.0380

$LogK_1$ **(Average value)** = 2.2364 ± 0.1602

Table 10:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$V_3\text{-}V_2$	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
10.00	5.60	6.47	6.55	0.08	1.9503	1.41		
10.23	5.65	6.62	6.72	0.11	1.4792	1.26	-0.0361	1.2239

$LogK_2$ **(Average value)** = 1.2239

Table 11:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	log($\frac{n}{n-1}$)	$LogK_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4290	2.2110
8.72	5.35	6.37	6.39	0.02	0.2858	2.42	-0.3978	2.0222
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

$LogK_1$ (Average value)=2.1382**±**0.1046

Table 12:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$\log(\frac{n-1}{2-n})$	$\log K_2$
9.51	5.55	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.84	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.93	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.10		
10.49	5.70	7.10	7.18	0.07	3.6492	0.83		

$\log K_2$(Average value) = 1.5453 **±** 0.3450

Table 13:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$\log(\frac{n}{n-1})$	$\log K_1$
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.3477	2.3123
9.00	5.40	6.00	6.04	0.04	0.3236	2.38	-0.3202	2.0598
9.22	5.45	6.10	6.15	0.05	0.4297	2.17	-0.1230	2.0470
9.51	5.50	6.20	6.26	0.06	0.5500	1.89	0.0871	1.9771
9.73	5.55	6.33	6.40	0.07	0.7000	1.67	0.3680	2.0380

$\log K_1$ **(Average value)** = 2.1568 ± 0.2069

Table 14:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$\log(\frac{n-1}{2-n})$	$\log K_2$
10.00	5.60	6.47	6.55	0.08	0.9148	1.41		
10.23	5.65	6.62	6.71	0.09	1.2102	1.20	-0.5749	0.6251
10.49	5.70	6.80	6.92	0.09	1.5968	1.03	0.1703	1.2003

$\log K_2$ **(Average value)** = 0.9127± 0.4070

Table15:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$\log(\frac{n}{1-n})$	$\log K_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4210	2.2190
8.72	5.35	6.37	6.40	0.03	0.4286	2.42	-0.1249	2.2951
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.96	0.3010	2.2610
9.51	5.55	6.66	6.70	0.04	0.7720	1.67	0.5297	2.1997

$\log K_1$ (Average value) = 2.2108± 0.0825

Table 16:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$\log(\frac{n-1}{2-n})$	$\log K_2$
9.73	5.55	6.78	6.83	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.95	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.09		
10.49	5.70	7.10	7.16	0.06	3.1429	0.89		

$\log K_2$ **(Average value)** = 1.5453± 0.3450

Table 17:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$\log(\frac{n}{n-1})$	$\log K_1$
8.50	5.30	5.81	5.86	0.05	0.3717	2.88	-0.2280	2.6520
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.06	0.06	0.4853	2.38	-0.0255	2.3545
9.22	5.45	6.10	6.16	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430
9.73	5.55	6.33	6.41	0.08	0.8000	1.69	0.6020	2.2920

$\log K_1$ **(Average value)** = 2.2516± 0.5380

Table 18:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
10.00	5.60	6.47	6.57	0.10	1.1434	1.43		
10.23	5.65	6.62	6.72	0.10	1.3448	1.23	-0.2788	0.9512
10.49	5.70	6.80	6.90	0.10	1.7742	1.03	0.5351	1.5651

LogK_2 **(Average value)** = 1.2581± 0.4340

Table 19: Stepwise and overall Stability constants of thehydrolysed and unhydrolysed divalent metal (II) complexes

Chelates	**LogK_1**	**LogK_2**	**Logβ**
[Cu (Hydrolysed PSHA-1)$_2$]	2.4788	1.4280	3.9068
[Pb (Hydrolysed PSHA-1)$_2$]	2.5832	1.1963	3.7795
[Cd (Hydrolysed PSHA-1)$_2$]	2.2108	1.5453	3.7561
[Mg (Hydrolysed PSHA-1)$_2$]	2.1382	1.5453	3.6835
[Cu (Unhydrolysed PSHA-1)$_2$]	2.3059	1.2209	3.5268
[Pb (Unhydrolysed PSHA-1)$_2$]	2.2364	1.2239	3.4603
[Cd (Unhydrolysed PSHA-1)$_2$]	2.2516	1.2581	3.5097
[Mg (Unydrolysed PSHA-1)$_2$]	2.1568	0.9127	3.0695

The results obtained (Table19) shows the stepwise and overall stability constants to be not high indicating low stability of the complexes, because the solubility of most metal ions in the basic pH range is minimal due to metal hydroxide precipitation (Karimi, 2017). In general, the stepwise stability constants (K_1 and K_2) follow the order $K_1 > K_2$ for the copper, lead, magnesium and cadmium complexes respectively. The steady decrease of the values with increasing number of ligands is in agreement with the prediction made by researchers (Na'aliya, 2013). The decrease could be attributed to the fact that as the number of the ligands (Humate ions) that enters the coordination zone increases the aqua molecules available for replacement by the ligands become less. Thus, the metal ions become less electron loving with progressive intake of the ligand and this results in the decrease in the values of the constants (Na'aliya, 2013). Also the stability of the complexes is influenced by the size and number of the chelate rings(Mackay and Mackay,2002).All the complexes form rings in their structure as humate, a bidentate ligand, bond the metal ions in the ratio 1:2 (Boguta and Sokolowska, 2016) forming chelate rings. The values of the overall stability constants (logβ) obtained for humate complexes are not high indicating low stability as the values are not high. LogK values for copper-humates (Table 3 to 6) obtained in this study are lower than those reported for the complexes of humic acids (Pandey *et al.*, 2015; Dinu, 2013; Kaschl *et al.*, 2010 and Gilbeto and Jorg, 2001). The values of LogK(Table 7 to 10) forlead-humates are lower than those reported for the lead in the literature (Dinu, 2013; Gilbeto and Jorg 2001). Log K values(Table 11 to 14) for magnesium-humates obtained in this study are close to those reported by (Pandey *et al.*, 2015). Log K values of cadmium-humates (Table 15 to 18) obtained in this work near to the one reported by (Dinu, 2013 and Pandey *et al.*, 2015).The difference between the reported values and the values obtained in this study might be probably as a result of acid hydrolysis of humic acid. The values of the overall stability constants (log β) of the copper humates complexes presented in Table 19 is high than that of other metal humate complexes, show relatively high stability of Cu-HA complexes, show the following order of stability: Cu >Pb> Cd > Mg; which are in close agreement to the findings of (Dinu, 2013 and Pandey *et al.*, 2015).The high stability of Cu-humate chelate could be attributed to the existence of coordinate covalent bond between the complexing agents and the Cu^{2+} ions. Since, Cu^{2+} being a metal of the transitional series with $3d^9$ electronic configurations can accept the electrons from the complexing agents. Similarly,the low stabilities of Pb,Cd and Mg - complexes could be explained by that Pb^{2+} with $6s^2$, Cd^{2+} with $4d^{10}$ and Mg^{2+} with $2p^6$ their electronic configuration has a completely filled d,p and s orbitals. Moreover, the stabilities of metal ions with hydrolysed humic acid from peat soil were higher than those with unhydrolysed humic acid from peat soil; which is ascribed to the high content of acidity in hydrolysed humic acid than unhydrolysed humic acid.

CONCLUSION

The values of logK for Cu(II) hydrolysed humic acid complex was higher followed by Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes as compared with metal(II) unhydrolysed humic acid complexes . This indicates acid hydrolysis of humic acid can enhance the complexation behavior of humic acid with metal (II) ions. However, the higher values of logβ for Cu(II), Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes indicates more stable stepwise complexes formed as compared with Cu(II), Pb(II), Cd(II) and Mg(II) unhydrolysed humic acid complexes.

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STABILITY CONSTANTS OF COMPLEXES OF METAL IONS WITH PEATSOIL HUMIC ACIDS UNDER NON-ACID-CONDITIONS

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ABSTRACT

Stability constants of complexes of four divalent metal ions viz. Cu^{2+}, Pb^{2+},Mg^{2+} and Cd^{2+} with humic acids (HA) were determined by potentiometric titration of humic acids with the corresponding salt of the divalent metals in aqueous media under non-acid-condition. The log K (logarithm of the stability constant) ranged from 1.0942 to 2.7471 for metal-humic acid complexes were determined using point-wise computational method. The order of stability constants were obtained as follows: Cu >Pb> Cd > Mg for metal -HA complexes respectively, indicating a higher degree of complexation with Cu metal ion.

Keywords: stability constant, humic acid, potentiometric titration, divalent metals, acid hydrolysis.

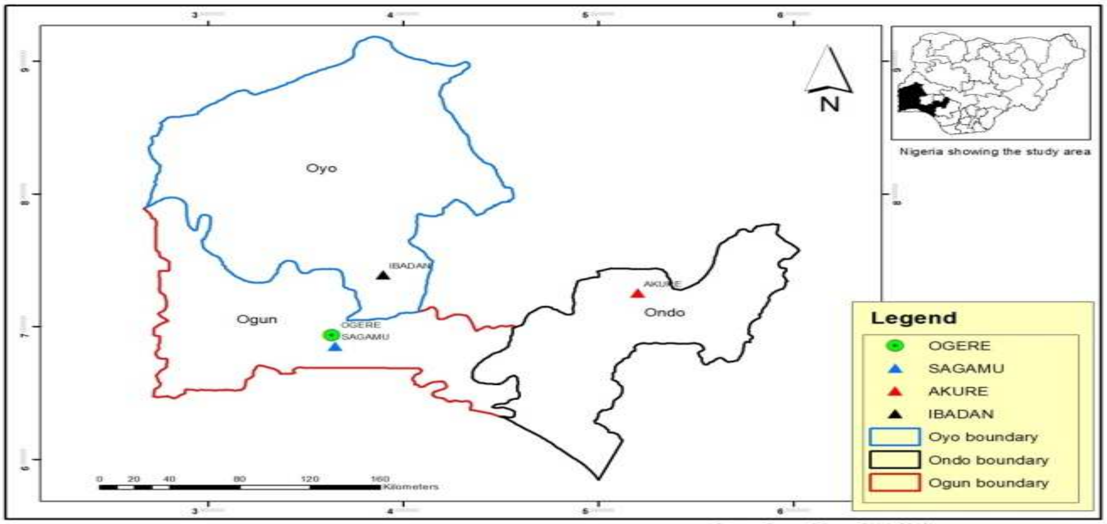
NTRODUCTION

The stability constant of a complex is the numerical expression of its stability and provides a quantitative measure of affinity of the metal ion to the complexing agent. An understanding of the relative stability of metal-complexes helps in predicting the behavior of metal ions in the soil (Ram and Raman, 1982). Extensive researches has been done to determine the stability constants of the complexes formed between humic acid (HA) with a number of metal ions. Ashok *et al*., (2000) reported that humic acid with hydroxyl, phenoxyl and carboxyl reactive groups can form coordination compound with metal ions at pH 3.5. The stability constants(Log K) for different metal-humic acid complexes indicated the following order of the stabilities of complexes formed between humic acid and metal ion, Cu >Fe >Pb> Ni > Co > Ca > Cd > Zn >Mn> Mg. Andelkovic *et al*., (2010) investigated the binding of Cd(II) to soil humic acid at pH 6.5 and in 0.1M KNO_3 ionic medium. The stability constant for binding indicating greater stability in the case when carboxyl groups are involved in complexation reaction. Kostic *et al*.,(2012) investigated the complexation of humic acid with certain heavy metal ions (Co(II), Ni(II),Cu(II), Zn(II), and Pb(II). The experiment was performed at 25°C, at pH 4.0 and ionic strength of 0.01M. Stability constant of complex between Pb(II) ions and humic acid is greater than stability constants of other investigated metal-humate complexes. Bogata and Sokolowska (2016) analyses the interaction between humic acids from different soils and Zn (II) ions at wide concentration ranges and at pH 5. Studies have showed significant impact of Zn concentration, pH and some properties of humic acids with zinc.But all of these studies were limited to acidic pH range. Therefore, the present study was carried out to determine and compare the stability constants of complexes of metal ions with hydrolysed peat soil humic acid and unhydrolysed peat soil humic under non-acid conditions.

MATERIALS AND METHODS

Analytical grade chemicals used includes hydrochloric acid (HCl), nitric acid (HNO_3), sodium hydroxide (NaOH), lead nitrate $Pb(NO_3)_2$, copper nitrate $Cu(NO_3)_2.3H_2O$, cadmium nitrate $Cd(NO_3)_2.4H_2O$, magnesium nitrate $Mg(NO_3)_2.6H_2O$, potassium nitrate (KNO_3), calcium chloride ($CaCl_2$), (sigma-Aldrich). Dowex 50WX8, (20-50 mesh) from Fluka.

Area of study



Source: Dept. of Geog. BUK (2016)

Figure 1: Map showing the sampling point at Sagamu Town, Ogun State.

Description of Sampling Area

Sagamu has geographical coordinates between 6°50′ north; 3° 38′ east is located in south western region of Nigeria. The region has tropical wet and dry climate with a lengthy wet season and relatively constant temperatures throughout the course of the year. Wet season runs from March to October, November to December forms the region dry season. The vegetation type of the region is savannah which is really grassland with small bushes and occasional big trees. Grassland soils have substantially higher organic matter content than forest soils (Novackova, 2011).

Sample Collection

The Peatsoil samples were collected from four different sampling points (0-10cm depth) in Sagamu into polyethylene bag with plastic spoons. Samples were taken to the laboratory, extraneous materials were removed; the samples were air-dried, crushed and ground to a fine powder in a mortar passed through a 0.20mm sieve. The samples were kept for analysis.

Isolation and purification of humic acid from peat soil sample

Peatsoil sample (100g) was mixed with 1000 cm^3 of 0.1M NaOH solution, shaken for 3hours and left to stand overnight. Dark-coloured supernatant was obtained and decanted from solid residue. The dark-coloured supernatant was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 6 hours. Yellowish brown supernatant and dark-brown precipitate were obtained. The yellowish brown supernatant was decanted followed by centrifuge and discarded. The dark-brown precipitate was mixed with $500cm^3$of 0.1M NaOH solution followed by passing through dowex resin. The dark-brown solution was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 3 hours. The dark-brown precipitate was washed several times with deionized water. The supernatant was treated with $AgNO_3$ solution until no white precipitate observed. The humic acid was transferred to weighed crucible and dried at 60°C in an oven for 12 hours. The humic acid was cooled and dried in the desiccator, weighed and recorded. The obtained humic acid was dried again at 60°C for additional 6 hours cooled and dried in the desiccator, weighed and recorded constant weight was obtained (Baruah *et al*., 2015).

FT-IR analysis

FT-IR spectra of humic acid sample was analysed using Carry 630 FT-IR Agilent Technologies.

Unhydrolysed compost humic acid

The unhydrolysed humic acid was obtained after isolation and purification of compost humic acid and kept for investigation.

Acid hydrolysis of Peatsoil acid

Peatsoil humic acid sample (1g) was refluxed for 12 hours at (160°C) with $50cm^3$ of 6M HCl. The mixture was allowed to cool, decanted, and centrifuged after hydrolysis. The insoluble residues were washed with distilled water via centrifugation several times, and the supernatant was treated with $AgNO_3$ solution until no white precipitate was observed. The residue was thoroughly dried over $CaCl_2$ in a desiccator at room temperature (Chefetz *et al*., 2002). Finally, the obtained hydrolysed humic acid was kept for investigation.

Potentiometric Titrations

Potentiometric measurements were carried out using a pH-meter Jenway (model 3510) with combine electrode, the sensitivity of the pH - meter is 0.01 units. The pH meter was switched on half an hour before starting the titration for initial warm up of the instrument. The instrument was calibrated with an aqueous standard buffer solution of pH 4.00 and 10.0 (borate buffer) prepared from a "Qualigens" buffer tablets.

The following sets of solutions were prepared in a 250cm^3 volumetric flask separately for pH metric titrations.

(i) 5 cm^3 0.1 M HCl + 40 cm^3 deionized water

(ii) 5 cm^3 0.1 M HCl + 39 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid

(iii) 5 cm^3 0.1 M HCl + 37 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid + 2 cm^3 0.01 M Cu(II)

The solutions were titrated against standardized 0.110MNaOH separately. The total volume of each mixture was adjusted to 50 cm^3 and the ionic strength of the solutions was maintained constant at by adding appropriate amount of stock solution of 1M KNO$_3$ (Gamal, 2015; Omar and Ali, 2015). A magnetic stirrer was used to achieve thorough mixing of the interacting solutions at 550 rpm. The same set of experimental conditions was applied for potentiometric titration of remaining samples.

Evaluation of pKa of Hydrolysed peat soil Humic Acids

The proton-ligand formation number n$_\mathbf{A}$ were calculated by Irving and Rossotti expression (Omar and Ali, 2015).

$$nA = Y - \frac{(V2-V1)(No-Eo)}{(Vo+V1)TcL} \quad \text{.................................1}$$

Where: Y is number of dissociable proton, (V$_2$-V$_1$) is the measure of displacement of the ligand curve relative to acid curve, N^o and E^o are the resultant concentration of alkali solution, free acid solution, T$_{cL}$^{o} is the total ligand concentration, V^o is the total volume of titration solution,V$_1$ is the volume of alkali added to acid solution,V$_2$ is the volume of alkali added to acid solution + ligand solution, acid dissociation constants (pKa - values) of ligand were calculated by algebraic method point wise calculation (Tables 1). The dissociation constants (pKa) were calculated according to the following relation:

$$pKa = pH + \log\left(\frac{nA}{1-nA}\right) \quad \text{............................2}$$

Where: pKa is the acid dissociation constant, n$_A$is the Proton-ligand formation number and pH is the pH-values (Omar and Ali, 2015).

Determination of metal-ligand stability constants (log K) of complexes

The potentiometric measurement for the determination of stability constant of a complex in solution is based on the fact that the redox potential of the couple $\frac{M^{+(m-n)}}{M^{+m}}$ is shifted significantly on complexation of the metal ion with the ligand. This method involves change in hydrogen ion concentration [H$^+$] due to the displacement or association of one or more protons taking place during complexation reaction. This change can be found out by titrating the solutions containing free acid, acid with ligand, and acid with ligand and metal ion, individually against a standard alkali solution at a constant ionic strength or temperature. Either ionic strength or temperature may be varied for different sets of solutions. In all the cases, the change in the pH of the solution is measured after each addition of a known amount of alkali to the reaction cell which contains the reaction mixture. The titration curves are then drawn by plotting the measured pH values against the corresponding volume of alkali added and the stability constants of the complexes are determined from the titration curves by employing pH-metric titration technique given by (Irving and Rossoti).

Metal-ligand stability constants (Log K) were determined by using the following relations:

$$\bar{n} = \frac{(V_3 - V_2)(E^0 + N^0)}{(V^0 + V_2)\bar{n}_A T_m^0} \quad \text{..3}$$

and

$$PL = \log_{10}\{\frac{1+\beta_n^H \frac{1}{[anti\ \log pH]^n}}{T_L^0 - \bar{n}T_m^0} X \frac{(V^0+V_3)}{V^0}\} \quad \text{...4}$$

Where $T_{L,}$ T^{o}, E°, and V^{o}havethe same significance as in equation (1) above, T_m denotes the total concentration of metal present in solution, V_3 is the volume of metal ions present in solution and β^{H} is the overall proton ligand stability constant. The metal-ligand stability constants (log K) were determined by employing point wise computational Method (eq. 5 and 6).

$$\text{Log}K_1 = \log\left(\frac{n}{1-n}\right) + pL \qquad \ldots\ldots\ldots\ldots.5$$

$$\text{Log}K_2 = \log\left(\frac{1-n}{2-n}\right) + pL\ldots\ldots\ldots\ldots\ldots\ldots\ldots..6$$

Where: Log K is the metal-ligand stability constant, pL is the Free ligand exponent function, **n** is the Average number of ligand attached with metal ion (Janrao*et al.*, 2014).The results obtained were analyzed by an ORIGIN 2016 program using titration data and then the proton-ligand stability constants (pKa) and Metal-ligand stability constant (LogK) calculated (Omar and Ali, 2015).

RESULTS AND DISCUSSION

Fourier transformed infrared (FT-IR) spectra of isolated humic acid from peat soils Figure 2 had distinct clear absorption bands indicating the presence of major humic acid structural elemental groups such as H bonded OH ($3680cm^{-1}$ peak), C=O of carbonyl ($1721cm^{-1}$ peak), functional groups of aliphatic components CH_2 ($2918cm^{-1}$ peak) and C-O stretching of polysaccharide ($1168cm^{-1}$ peak). The positions of the absorption bands of the spectra fell within typical major absorption bands of humic acid which is at frequencies 3680, 2918, 1721, 1168 cm^{-1}. The first peak centred in the vicinity of 3680 cm^{-1} region is attributed to phenol OH group bounded by intermolecular H bonds. The $2918cm^{-1}$ band usually has absorption maximum at 2918 cm^{-1} which is due to C–H stretching of alkane group (CH_2). The next major absorption band is 1721 cm^{-1}. This band has been commonly ascribed to C=O stretching of mainly carboxyl group (COOH) with trace amount of ketones. The last peak was observed at 1168 cm^{-1} due to C–O stretching of polysaccharides and this peak appeared also in the spectra of humic acid from peat soil. The FTIR spectra of the isolated humic acid contained all major characteristic absorption peaks of humic acid. These absorption peaks indicated the presence of the major structural elements of humic acid namely H bonded OH, C=C of aromatic ring, C=O of carbonyl group (both carboxyl and ketonic), CH_2 group. This strongly supports the presence of humic acid.

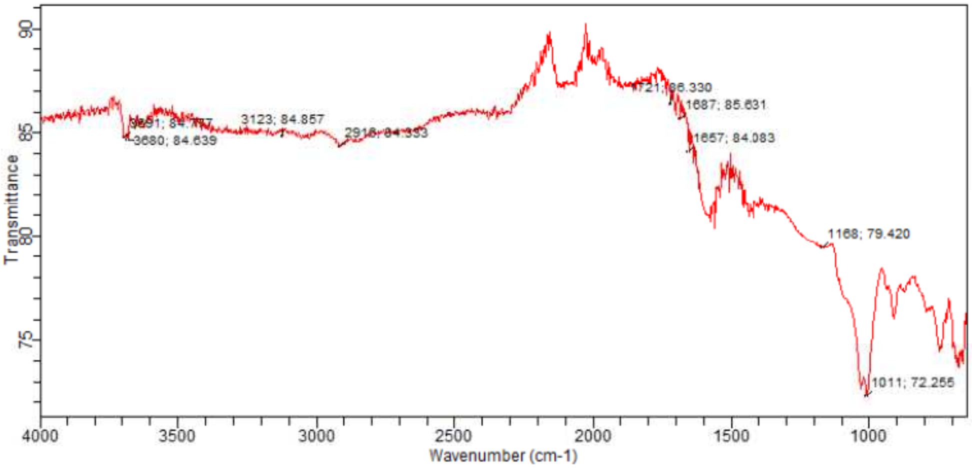


Fig. 2 : FT-IR spectraof peatsoilhumic acid (PSHA)

Evaluation of acid dissociation constant (pka) of acid hydrolysed peat soil humicacid at phenolic group

The value of the dissociation constant of the peat soil humic acid (PSHA) that underwent acidhydrolysis studied was found to be 8.9299 as shown Table 1, which is lower than the literaturevalues reported by Almeida and Szpoganics, (2015), Borges *et al.*, (2005); Badr *et al.*, (2012)and Fernandes *et al*,.(2009) of 9.73, 9.47 and 10.30. The difference between the obtained valuesand the reported values in this study might be probably as a result of acid hydrolysis of humicacid.

Table 1: PKa of (Hydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	$\log(\frac{nA}{1-nA})$	pKa
8.50	5.30	6.29	0.99	0.3594	-0.2510	8.2490
8.72	5.35	6.37	1.02	0.3400	-0.2880	8.4320
9.00	5.40	6.46	1.06	0.3141	-0.3391	8.6609
9.22	5.45	6.55	1.10	0.2882	-0.3927	8.8273
9.51	5.50	6.66	1.16	0.2494	-0.4786	9.0314
9.73	5.55	6.78	1.23	0.2041	-0.5910	9.1390
10.00	5.60	6.90	1.30	0.1589	-0.7238	9.2762
10.23	5.65	7.05	1.40	0.0941	-0.9835	9.2465
10.49	5.70	7.10	1.40	0.0941	-0.9835	9.5065

Average pKa = 8.9299 ± 0.4186

Table 2: PKa of (Unhydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	$\mathrm{Log}(\frac{nA}{1-n})$	pKa
8.50	5.30	5.81	0.51	0.6619	0.2919	8.7919
8.72	5.35	5.90	0.55	0.6357	0.2418	8.9618
9.00	5.40	6.00	0.60	0.6029	0.1813	9.1813
9.22	5.45	6.10	0.65	0.5701	0.1226	9.3426
9.51	5.50	6.20	0.70	0.5376	0.0654	9.5754
9.73	5.55	6.33	0.78	0.4851	-0.0259	9.7041
10.00	5.60	6.47	0.87	0.4262	-0.1291	9.8709
10.23	5.65	6.62	0.99	0.3609	-0.2481	9.9819
10.49	5.70	6.80	1.10	0.2759	-0.4690	10.0210

Average pKa = 9.4923± 0.4410

Metal-ligand stability constant (Log K)

The stabilityconstants require the accurate values of proton-ligand stability constants (Anil and Maroti, 2008). Metal titration curves crossed over ligand titration curve indicated the formation of complex upon proton release (Santosh, *et al.*, 2011). If the values of n- are within range 0.2-0.8 and 1.2-18 this indicates the formation of 1:1 and 1:2 complexes (Sayyed and Mazahar, 2012).

The metal (II)-humate stepwise stability constants (log k) at phenolic group (Tables 3-18)

Table 3: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$\log(\frac{n}{1-n})$	$\mathrm{Log}K_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

$\mathrm{Log}K_1$ (Average value) = 2.4788± 0.2203

Table 4: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$\mathrm{Log}(\frac{n-1}{2-n})$	$\mathrm{Log}K_2$
9.51	5.50	6.66	6.73	0.07	1.3509	1.70	-0.2671	1.4329
9.73	5.55	6.78	6.85	0.07	1.6383	1.51	0.2467	1.7567
10.00	5.60	6.90	6.98	0.08	2.1783	1.31	-0.2158	1.0942
10.23	5.65	7.05	7.13	0.08	4.1904	1.27		
10.49	5.70	7.10	7.19	0.09	4.6920			

$\mathrm{Log}K_2$(Average value) = 1.4280 ± 0.3312

Table 5:Point-wise method,Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	Log$(\frac{n}{n-1})$	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430

$LogK_1$ **(Average value)** = 2.3059± 0.6153

Table 6:Point-wise method, Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log$(\frac{n-1}{2-n})$	Log K_2
9.73	5.55	6.33	6.42	0.09	0.9000	1.69		
10.00	5.60	6.47	6.58	0.11	1.2578	1.44	-0.4592	0.9808
10.23	5.65	6.62	6.84	0.12	1.6137	1.26	-0.2010	1.4610
10.49	5.70	6.80	6.92	0.12	2.1052	1.03		

$LogK_2$ **(Average value)** = 1.2209± 0.3398

Table 7:Point-wise method,Pb (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log$(\frac{n}{1-n})$	$LogK_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.60	0.05	0.8333	1.96	0.6989	2.6589

$\mathbf{LogK_1}$ **(Average value)** = 2.5832 ±0.1614

Table 8:Point-wise method,Pb-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log$(\frac{n-1}{2-n})$	$logK_2$
9.51	5.50	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.83	0.05	1.1702	1.44		
10.00	5.60	6.90	6.90	0.05	1.4864	1.22	-0.0237	1.1963
10.23	5.65	7.05	7.10	0.05	2.0190	1.09		
10.49	5.70	7.10	7.17	0.07	3.6492	1.00		

$\mathbf{LogK_2}$**(Average value)** = 1.1963

Table 9:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log $(\frac{n}{n-1})$	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.5477	2.3123
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	0.0272	2.2072
9.51	5.50	6.20	6.26	0.07	0.6417	1.89	0.2530	2.1430
9.73	5.55	6.40	6.40	0.07	0.7000	1.67	0.3680	2.0380

$LogK_1$ **(Average value)** = 2.2364 ± 0.1602

Table 10:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log$(\frac{n-1}{2-n})$	Log K_2
10.00	5.60	6.47	6.55	0.08	1.9503	1.41		
10.23	5.65	6.62	6.72	0.11	1.4792	1.26	-0.0361	1.2239

$LogK_2$ **(Average value)** = 1.2239

Table 11:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log$(\frac{n}{n-1})$	$LogK_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4290	2.2110
8.72	5.35	6.37	6.39	0.02	0.2858	2.42	-0.3978	2.0222
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

$\mathbf{LogK_1}$ **(Average value)=**2.1382**±**0.1046

Table 12:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n-1}{2-n}$)	LogK_2
9.51	5.55	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.84	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.93	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.10		
10.49	5.70	7.10	7.18	0.07	3.6492	0.83		

LogK_2(Average value) = 1.5453 **±** 0.3450

Table 13:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.3477	2.3123
9.00	5.40	6.00	6.04	0.04	0.3236	2.38	-0.3202	2.0598
9.22	5.45	6.10	6.15	0.05	0.4297	2.17	-0.1230	2.0470
9.51	5.50	6.20	6.26	0.06	0.5500	1.89	0.0871	1.9771
9.73	5.55	6.33	6.40	0.07	0.7000	1.67	0.3680	2.0380

LogK_1 **(Average value)** = 2.1568 ± 0.2069

Table 14:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
10.00	5.60	6.47	6.55	0.08	0.9148	1.41		
10.23	5.65	6.62	6.71	0.09	1.2102	1.20	-0.5749	0.6251
10.49	5.70	6.80	6.92	0.09	1.5968	1.03	0.1703	1.2003

LogK_2 **(Average value)** = 0.9127± 0.4070

Table15:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	Log($\frac{n}{1-n}$)	LogK_1
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4210	2.2190
8.72	5.35	6.37	6.40	0.03	0.4286	2.42	-0.1249	2.2951
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.96	0.3010	2.2610
9.51	5.55	6.66	6.70	0.04	0.7720	1.67	0.5297	2.1997

LogK_1 (Average value) = 2.2108± 0.0825

Table 16:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
9.73	5.55	6.78	6.83	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.95	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.09		
10.49	5.70	7.10	7.16	0.06	3.1429	0.89		

LogK_2 **(Average value)** = 1.5453± 0.3450

Table 17:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.86	0.05	0.3717	2.88	-0.2280	2.6520
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.06	0.06	0.4853	2.38	-0.0255	2.3545
9.22	5.45	6.10	6.16	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430
9.73	5.55	6.33	6.41	0.08	0.8000	1.69	0.6020	2.2920

LogK_1 **(Average value)** = 2.2516± 0.5380

Table 18:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log$(\frac{n-1}{2-n})$	Log K_2
10.00	5.60	6.47	6.57	0.10	1.1434	1.43		
10.23	5.65	6.62	6.72	0.10	1.3448	1.23	-0.2788	0.9512
10.49	5.70	6.80	6.90	0.10	1.7742	1.03	0.5351	1.5651

LogK_2 **(Average value)** = 1.2581± 0.4340

Table 19: Stepwise and overall Stability constants of thehydrolysed and unhydrolysed divalent metal (II) complexes

Chelates	**LogK_1**	**LogK_2**	**Logβ**
[Cu (Hydrolysed PSHA-1)$_2$]	2.4788	1.4280	3.9068
[Pb (Hydrolysed PSHA-1)$_2$]	2.5832	1.1963	3.7795
[Cd (Hydrolysed PSHA-1)$_2$]	2.2108	1.5453	3.7561
[Mg (Hydrolysed PSHA-1)$_2$]	2.1382	1.5453	3.6835
[Cu (Unhydrolysed PSHA-1)$_2$]	2.3059	1.2209	3.5268
[Pb (Unhydrolysed PSHA-1)$_2$]	2.2364	1.2239	3.4603
[Cd (Unhydrolysed PSHA-1)$_2$]	2.2516	1.2581	3.5097
[Mg (Unydrolysed PSHA-1)$_2$]	2.1568	0.9127	3.0695

The results obtained (Table19) shows the stepwise and overall stability constants to be not high indicating low stability of the complexes, because the solubility of most metal ions in the basic pH range is minimal due to metal hydroxide precipitation (Karimi, 2017). In general, the stepwise stability constants (K_1 and K_2) follow the order $K_1 > K_2$ for the copper, lead, magnesium and cadmium complexes respectively. The steady decrease of the values with increasing number of ligands is in agreement with the prediction made by researchers (Na'aliya, 2013). The decrease could be attributed to the fact that as the number of the ligands (Humate ions) that enters the coordination zone increases the aqua molecules available for replacement by the ligands become less. Thus, the metal ions become less electron loving with progressive intake of the ligand and this results in the decrease in the values of the constants (Na'aliya, 2013). Also the stability of the complexes is influenced by the size and number of the chelate rings(Mackay and Mackay,2002).All the complexes form rings in their structure as humate, a bidentate ligand, bond the metal ions in the ratio 1:2 (Boguta and Sokolowska, 2016) forming chelate rings. The values of the overall stability constants (logβ) obtained for humate complexes are not high indicating low stability as the values are not high. LogK values for copper-humates (Table 3 to 6) obtained in this study are lower than those reported for the complexes of humic acids (Pandey *et al.*, 2015; Dinu, 2013; Kaschl *et al.*, 2010 and Gilbeto and Jorg, 2001). The values of LogK(Table 7 to 10) forlead-humates are lower than those reported for the lead in the literature (Dinu, 2013; Gilbeto and Jorg 2001). Log K values(Table 11 to 14) for magnesium-humates obtained in this study are close to those reported by (Pandey *et al.*, 2015). Log K values of cadmium-humates (Table 15 to 18) obtained in this work near to the one reported by (Dinu, 2013 and Pandey *et al.*, 2015).The difference between the reported values and the values obtained in this study might be probably as a result of acid hydrolysis of humic acid. The values of the overall stability constants (log β) of the copper humates complexes presented in Table 19 is high than that of other metal humate complexes, show relatively high stability of Cu-HA complexes, show the following order of stability: Cu >Pb> Cd > Mg; which are in close agreement to the findings of (Dinu, 2013 and Pandey *et al.*, 2015).The high stability of Cu-humate chelate could be attributed to the existence of coordinate covalent bond between the complexing agents and the Cu^{2+} ions. Since, Cu^{2+} being a metal of the transitional series with $3d^9$ electronic configurations can accept the electrons from the complexing agents. Similarly,the low stabilities of Pb,Cd and Mg -complexes could be explained by that Pb^{2+} with $6s^2$, Cd^{2+} with $4d^{10}$ and Mg^{2+} with $2p^6$ their electronic configuration has a completely filled d,p and s orbitals. Moreover, the stabilities of metal ions with hydrolysed humic acid from peat soil were higher than those with unhydrolysed humic acid from peat soil; which is ascribed to the high content of acidity in hydrolysed humic acid than unhydrolysed humic acid.

CONCLUSION

The values of logK for Cu(II) hydrolysed humic acid complex was higher followed by Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes as compared with metal(II) unhydrolysed humic acid complexes . This indicates acid hydrolysis of humic acid can enhance the complexation behavior of humic acid with metal (II) ions. However, the higher values of logβ for Cu(II), Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes indicates more stable stepwise complexes formed as compared with Cu(II), Pb(II), Cd(II) and Mg(II) unhydrolysed humic acid complexes.

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STABILITY CONSTANTS OF COMPLEXES OF METAL IONS WITH PEATSOIL HUMIC ACIDS UNDER NON-ACID-CONDITIONS

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ABSTRACT

Stability constants of complexes of four divalent metal ions viz. Cu^{2+}, Pb^{2+},Mg^{2+} and Cd^{2+} with humic acids (HA) were determined by potentiometric titration of humic acids with the corresponding salt of the divalent metals in aqueous media under non-acid-condition. The log K (logarithm of the stability constant) ranged from 1.0942 to 2.7471 for metal-humic acid complexes were determined using point-wise computational method. The order of stability constants were obtained as follows: Cu >Pb> Cd > Mg for metal -HA complexes respectively, indicating a higher degree of complexation with Cu metal ion.

Keywords: stability constant, humic acid, potentiometric titration, divalent metals, acid hydrolysis.

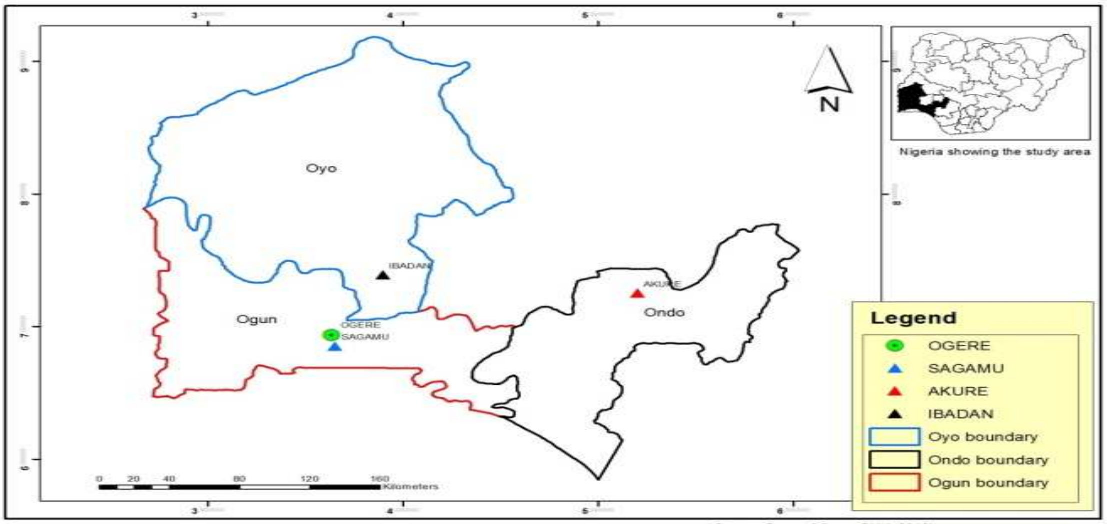
NTRODUCTION

The stability constant of a complex is the numerical expression of its stability and provides a quantitative measure of affinity of the metal ion to the complexing agent. An understanding of the relative stability of metal-complexes helps in predicting the behavior of metal ions in the soil (Ram and Raman, 1982). Extensive researches has been done to determine the stability constants of the complexes formed between humic acid (HA) with a number of metal ions. Ashok *et al.*, (2000) reported that humic acid with hydroxyl, phenoxyl and carboxyl reactive groups can form coordination compound with metal ions at pH 3.5. The stability constants(Log K) for different metal-humic acid complexes indicated the following order of the stabilities of complexes formed between humic acid and metal ion, Cu >Fe >Pb> Ni > Co > Ca > Cd > Zn >Mn> Mg. Andelkovic *et al.*, (2010) investigated the binding of Cd(II) to soil humic acid at pH 6.5 and in 0.1M KNO_3 ionic medium. The stability constant for binding indicating greater stability in the case when carboxyl groups are involved in complexation reaction. Kostic *et al.*,(2012) investigated the complexation of humic acid with certain heavy metal ions (Co(II), Ni(II),Cu(II), Zn(II), and Pb(II). The experiment was performed at 25°C, at pH 4.0 and ionic strength of 0.01M. Stability constant of complex between Pb(II) ions and humic acid is greater than stability constants of other investigated metal-humate complexes. Bogata and Sokolowska (2016) analyses the interaction between humic acids from different soils and Zn (II) ions at wide concentration ranges and at pH 5. Studies have showed significant impact of Zn concentration, pH and some properties of humic acids with zinc.But all of these studies were limited to acidic pH range. Therefore, the present study was carried out to determine and compare the stability constants of complexes of metal ions with hydrolysed peat soil humic acid and unhydrolysed peat soil humic under non-acid conditions.

MATERIALS AND METHODS

Analytical grade chemicals used includes hydrochloric acid (HCl), nitric acid (HNO_3), sodium hydroxide (NaOH), lead nitrate $Pb(NO_3)_2$, copper nitrate $Cu(NO_3)_2.3H_2O$, cadmium nitrate $Cd(NO_3)_2.4H_2O$, magnesium nitrate $Mg(NO_3)_2.6H_2O$, potassium nitrate (KNO_3), calcium chloride ($CaCl_2$), (sigma-Aldrich). Dowex 50WX8, (20-50 mesh) from Fluka.

Area of study



Source: Dept. of Geog. BUK (2016)

Figure 1: Map showing the sampling point at Sagamu Town, Ogun State.

Description of Sampling Area

Sagamu has geographical coordinates between 6°50′ north; 3° 38′ east is located in south western region of Nigeria. The region has tropical wet and dry climate with a lengthy wet season and relatively constant temperatures throughout the course of the year. Wet season runs from March to October, November to December forms the region dry season. The vegetation type of the region is savannah which is really grassland with small bushes and occasional big trees. Grassland soils have substantially higher organic matter content than forest soils (Novackova, 2011).

Sample Collection

The Peatsoil samples were collected from four different sampling points (0-10cm depth) in Sagamu into polyethylene bag with plastic spoons. Samples were taken to the laboratory, extraneous materials were removed; the samples were air-dried, crushed and ground to a fine powder in a mortar passed through a 0.20mm sieve. The samples were kept for analysis.

Isolation and purification of humic acid from peat soil sample

Peatsoil sample (100g) was mixed with 1000 cm^3 of 0.1M NaOH solution, shaken for 3hours and left to stand overnight. Dark-coloured supernatant was obtained and decanted from solid residue. The dark-coloured supernatant was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 6 hours. Yellowish brown supernatant and dark-brown precipitate were obtained. The yellowish brown supernatant was decanted followed by centrifuge and discarded. The dark-brown precipitate was mixed with $500cm^3$of 0.1M NaOH solution followed by passing through dowex resin. The dark-brown solution was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 3 hours. The dark-brown precipitate was washed several times with deionized water. The supernatant was treated with $AgNO_3$ solution until no white precipitate observed. The humic acid was transferred to weighed crucible and dried at 60°C in an oven for 12 hours. The humic acid was cooled and dried in the desiccator, weighed and recorded. The obtained humic acid was dried again at 60°C for additional 6 hours cooled and dried in the desiccator, weighed and recorded constant weight was obtained (Baruah *et al.*, 2015).

FT-IR analysis

FT-IR spectra of humic acid sample was analysed using Carry 630 FT-IR Agilent Technologies.

Unhydrolysed compost humic acid

The unhydrolysed humic acid was obtained after isolation and purification of compost humic acid and kept for investigation.

Acid hydrolysis of Peatsoil acid

Peatsoil humic acid sample (1g) was refluxed for 12 hours at (160°C) with $50cm^3$ of 6M HCl. The mixture was allowed to cool, decanted, and centrifuged after hydrolysis. The insoluble residues were washed with distilled water via centrifugation several times, and the supernatant was treated with $AgNO_3$ solution until no white precipitate was observed. The residue was thoroughly dried over $CaCl_2$ in a desiccator at room temperature (Chefetz *et al.*, 2002). Finally, the obtained hydrolysed humic acid was kept for investigation.

Potentiometric Titrations

Potentiometric measurements were carried out using a pH-meter Jenway (model 3510) with combine electrode, the sensitivity of the pH - meter is 0.01 units. The pH meter was switched on half an hour before starting the titration for initial warm up of the instrument. The instrument was calibrated with an aqueous standard buffer solution of pH 4.00 and 10.0 (borate buffer) prepared from a "Qualigens" buffer tablets.

The following sets of solutions were prepared in a 250cm^3 volumetric flask separately for pH metric titrations.

(i) 5 cm^3 0.1 M HCl + 40 cm^3 deionized water
(ii) 5 cm^3 0.1 M HCl + 39 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid
(iii) 5 cm^3 0.1 M HCl + 37 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid + 2 cm^3 0.01 M Cu(II)

The solutions were titrated against standardized 0.110MNaOH separately. The total volume of each mixture was adjusted to 50 cm^3 and the ionic strength of the solutions was maintained constant at by adding appropriate amount of stock solution of 1M KNO_3 (Gamal, 2015; Omar and Ali, 2015). A magnetic stirrer was used to achieve thorough mixing of the interacting solutions at 550 rpm. The same set of experimental conditions was applied for potentiometric titration of remaining samples.

Evaluation of pKa of Hydrolysed peat soil Humic Acids

The proton-ligand formation number $n_{\mathbf{A}}$ were calculated by Irving and Rossotti expression (Omar and Ali, 2015).

nA = Y- $\frac{(V2-V1)(No-Eo)}{(Vo+V1)TcL}$ 1

Where: Y is number of dissociable proton, (V_2-V_1) is the measure of displacement of the ligand curve relative to acid curve, N^o and E^o are the resultant concentration of alkali solution, free acid solution, $T_{cL}{}^o$ is the total ligand concentration, V^o is the total volume of titration solution,V_1 is the volume of alkali added to acid solution,V_2 is the volume of alkali added to acid solution + ligand solution, acid dissociation constants (pKa - values) of ligand were calculated by algebraic method point wise calculation (Tables 1). The dissociation constants (pKa) were calculated according to the following relation:

pKa = pH + log($\frac{nA}{1-nA}$) 2

Where: pKa is the acid dissociation constant, $n_A$is the Proton-ligand formation number and pH is the pH-values (Omar and Ali, 2015).

Determination of metal-ligand stability constants (log K) of complexes

The potentiometric measurement for the determination of stability constant of a complex in solution is based on the fact that the redox potential of the couple $\frac{M^{+(m-n)}}{M^{+m}}$ is shifted significantly on complexation of the metal ion with the ligand. This method involves change in hydrogen ion concentration [H$^+$] due to the displacement or association of one or more protons taking place during complexation reaction. This change can be found out by titrating the solutions containing free acid, acid with ligand, and acid with ligand and metal ion, individually against a standard alkali solution at a constant ionic strength or temperature. Either ionic strength or temperature may be varied for different sets of solutions. In all the cases, the change in the pH of the solution is measured after each addition of a known amount of alkali to the reaction cell which contains the reaction mixture. The titration curves are then drawn by plotting the measured pH values against the corresponding volume of alkali added and the stability constants of the complexes are determined from the titration curves by employing pH-metric titration technique given by (Irving and Rossoti).

Metal-ligand stability constants (Log K) were determined by using the following relations:

$$\bar{n} = \frac{(V_3 - V_2)(E^0 + N^0)}{(V^0 + V_2)\bar{n}_A T_m^0}$$ 3

and

$$PL = \log_{10}\{\frac{1 + \beta_n^H \frac{1}{[anti\ \log \mathrm{pH}]^n}}{T_L^0 - \bar{n}T_m^0} X \frac{(V^0 + V_3)}{V^0}\}$$ 4

Where $T_{L,}$ T^{o}, E°, and V^{o}havethe same significance as in equation (1) above, T_m denotes the total concentration of metal present in solution, V_3 is the volume of metal ions present in solution and β^{H} is the overall proton ligand stability constant. The metal-ligand stability constants (log K) were determined by employing point wise computational Method (eq. 5 and 6).

$$\text{LogK}_1 = \log\left(\frac{n}{1-n}\right) + \text{pL} \quad \text{.............5}$$

$$\text{LogK}_2 = \log\left(\frac{1-n}{2-n}\right) + \text{pL}\text{.......................6}$$

Where: Log K is the metal-ligand stability constant, pL is the Free ligand exponent function, **n** is the Average number of ligand attached with metal ion (Janrao*et al*., 2014).The results obtained were analyzed by an ORIGIN 2016 program using titration data and then the proton-ligand stability constants (pKa) and Metal-ligand stability constant (LogK) calculated (Omar and Ali, 2015).

RESULTS AND DISCUSSION

Fourier transformed infrared (FT-IR) spectra of isolated humic acid from peat soils Figure 2 had distinct clear absorption bands indicating the presence of major humic acid structural elemental groups such as H bonded OH ($3680cm^{-1}$ peak), C=O of carbonyl ($1721cm^{-1}$ peak), functional groups of aliphatic components CH_2 ($2918cm^{-1}$ peak) and C-O stretching of polysaccharide ($1168cm^{-1}$ peak). The positions of the absorption bands of the spectra fell within typical major absorption bands of humic acid which is at frequencies 3680, 2918, 1721, 1168 cm^{-1}. The first peak centred in the vicinity of 3680 cm^{-1} region is attributed to phenol OH group bounded by intermolecular H bonds. The $2918cm^{-1}$ band usually has absorption maximum at 2918 cm^{-1} which is due to C–H stretching of alkane group (CH_2). The next major absorption band is 1721 cm^{-1}. This band has been commonly ascribed to C=O stretching of mainly carboxyl group (COOH) with trace amount of ketones. The last peak was observed at 1168 cm^{-1} due to C–O stretching of polysaccharides and this peak appeared also in the spectra of humic acid from peat soil. The FTIR spectra of the isolated humic acid contained all major characteristic absorption peaks of humic acid. These absorption peaks indicated the presence of the major structural elements of humic acid namely H bonded OH, C=C of aromatic ring, C=O of carbonyl group (both carboxyl and ketonic), CH_2 group. This strongly supports the presence of humic acid.

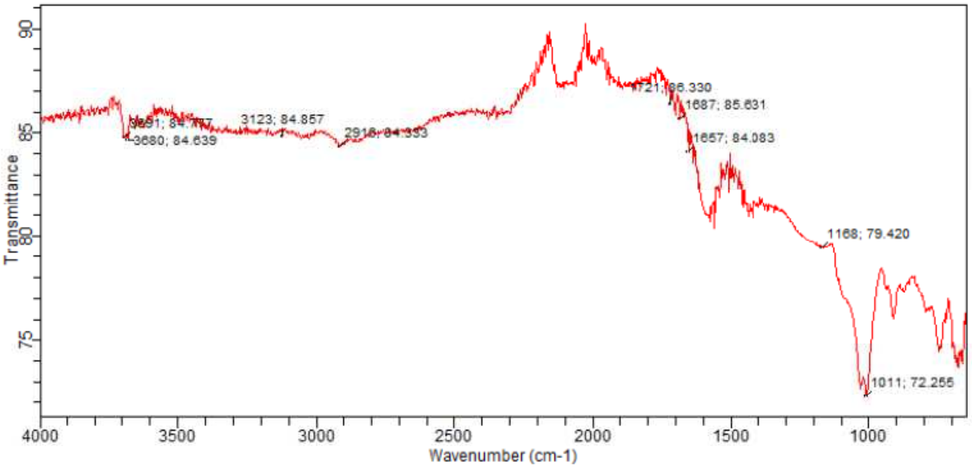


Fig. 2 : FT-IR spectraof peatsoilhumic acid (PSHA)

Evaluation of acid dissociation constant (pka) of acid hydrolysed peat soil humicacid at phenolic group

The value of the dissociation constant of the peat soil humic acid (PSHA) that underwent acidhydrolysis studied was found to be 8.9299 as shown Table 1, which is lower than the literaturevalues reported by Almeida and Szpoganics, (2015), Borges *et al*., (2005); Badr *et al*., (2012)and Fernandes *et al*,.(2009) of 9.73, 9.47 and 10.30. The difference between the obtained valuesand the reported values in this study might be probably as a result of acid hydrolysis of humicacid.

Table 1: PKa of (Hydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	log($\frac{nA}{1-nA}$)	pKa
8.50	5.30	6.29	0.99	0.3594	-0.2510	8.2490
8.72	5.35	6.37	1.02	0.3400	-0.2880	8.4320
9.00	5.40	6.46	1.06	0.3141	-0.3391	8.6609
9.22	5.45	6.55	1.10	0.2882	-0.3927	8.8273
9.51	5.50	6.66	1.16	0.2494	-0.4786	9.0314
9.73	5.55	6.78	1.23	0.2041	-0.5910	9.1390
10.00	5.60	6.90	1.30	0.1589	-0.7238	9.2762
10.23	5.65	7.05	1.40	0.0941	-0.9835	9.2465
10.49	5.70	7.10	1.40	0.0941	-0.9835	9.5065

Average pKa = 8.9299 ± 0.4186

Table 2: PKa of (Unhydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	Log($\frac{nA}{1-n}$)	pKa
8.50	5.30	5.81	0.51	0.6619	0.2919	8.7919
8.72	5.35	5.90	0.55	0.6357	0.2418	8.9618
9.00	5.40	6.00	0.60	0.6029	0.1813	9.1813
9.22	5.45	6.10	0.65	0.5701	0.1226	9.3426
9.51	5.50	6.20	0.70	0.5376	0.0654	9.5754
9.73	5.55	6.33	0.78	0.4851	-0.0259	9.7041
10.00	5.60	6.47	0.87	0.4262	-0.1291	9.8709
10.23	5.65	6.62	0.99	0.3609	-0.2481	9.9819
10.49	5.70	6.80	1.10	0.2759	-0.4690	10.0210

Average pKa = 9.4923± 0.4410

Metal-ligand stability constant (Log K)

The stabilityconstants require the accurate values of proton-ligand stability constants (Anil and Maroti, 2008). Metal titration curves crossed over ligand titration curve indicated the formation of complex upon proton release (Santosh, *et al.*, 2011). If the values of n- are within range 0.2-0.8 and 1.2-18 this indicates the formation of 1:1 and 1:2 complexes (Sayyed and Mazahar, 2012).

The metal (II)-humate stepwise stability constants (log k) at phenolic group (Tables 3-18)

Table 3: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n}{1-n}$)	$LogK_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

$LogK_1$ (Average value) = 2.4788± 0.2203

Table 4: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	Log($\frac{n-1}{2-n}$)	$LogK_2$
9.51	5.50	6.66	6.73	0.07	1.3509	1.70	-0.2671	1.4329
9.73	5.55	6.78	6.85	0.07	1.6383	1.51	0.2467	1.7567
10.00	5.60	6.90	6.98	0.08	2.1783	1.31	-0.2158	1.0942
10.23	5.65	7.05	7.13	0.08	4.1904	1.27		
10.49	5.70	7.10	7.19	0.09	4.6920			

$LogK_2$(Average value) = 1.4280 ± 0.3312

Table 5:Point-wise method,Cu (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	Log($\frac{n}{n-1}$)	Log K$_1$
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430

LogK$_1$ **(Average value)** = 2.3059± 0.6153

Table 6:Point-wise method, Cu (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	V$_3$-V$_2$	n	pL	Log($\frac{n-1}{2-n}$)	Log K$_2$
9.73	5.55	6.33	6.42	0.09	0.9000	1.69		
10.00	5.60	6.47	6.58	0.11	1.2578	1.44	-0.4592	0.9808
10.23	5.65	6.62	6.84	0.12	1.6137	1.26	-0.2010	1.4610
10.49	5.70	6.80	6.92	0.12	2.1052	1.03		

LogK$_2$ **(Average value)** = 1.2209± 0.3398

Table 7:Point-wise method,Pb (Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	log($\frac{n}{1-n}$)	LogK$_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.60	0.05	0.8333	1.96	0.6989	2.6589

LogK$_1$ (Average value) = 2.5832 ±0.1614

Table 8:Point-wise method,Pb-(Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	log($\frac{n-1}{2-n}$)	logK$_2$
9.51	5.50	6.66	6.71	0.05	0.9650	1.67	-0.0237	1.1963
9.73	5.55	6.78	6.83	0.05	1.1702	1.44		
10.00	5.60	6.90	6.90	0.05	1.4864	1.22		
10.23	5.65	7.05	7.10	0.05	2.0190	1.09		
10.49	5.70	7.10	7.17	0.07	3.6492	1.00		

LogK$_2$(Average value) = 1.1963

Table 9:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	V$_3$-V$_2$	n	pL	Log ($\frac{n}{n-1}$)	Log K$_1$
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.5477	2.3123
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	0.0272	2.2072
9.51	5.50	6.20	6.26	0.07	0.6417	1.89	0.2530	2.1430
9.73	5.55	6.40	6.40	0.07	0.7000	1.67	0.3680	2.0380

LogK$_1$ **(Average value)** = 2.2364 ± 0.1602

Table 10:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	V$_3$-V$_2$	n	pL	Log($\frac{n-1}{2-n}$)	Log K$_2$
10.00	5.60	6.47	6.55	0.08	1.9503	1.41		
10.23	5.65	6.62	6.72	0.11	1.4792	1.26	-0.0361	1.2239

LogK$_2$ **(Average value)** = 1.2239

Table 11:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	log($\frac{n}{n-1}$)	LogK$_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4290	2.2110
8.72	5.35	6.37	6.39	0.02	0.2858	2.42	-0.3978	2.0222
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

LogK$_1$ (Average value)=2.1382±0.1046

Table 12:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$\log(\frac{n-1}{2-n})$	$LogK_2$
9.51	5.55	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.84	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.93	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.10		
10.49	5.70	7.10	7.18	0.07	3.6492	0.83		

$LogK_2$(Average value) = 1.5453 **±** 0.3450

Table 13:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$Log(\frac{n}{n-1})$	$Log\ K_1$
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.3477	2.3123
9.00	5.40	6.00	6.04	0.04	0.3236	2.38	-0.3202	2.0598
9.22	5.45	6.10	6.15	0.05	0.4297	2.17	-0.1230	2.0470
9.51	5.50	6.20	6.26	0.06	0.5500	1.89	0.0871	1.9771
9.73	5.55	6.33	6.40	0.07	0.7000	1.67	0.3680	2.0380

$LogK_1$ **(Average value)** = 2.1568 ± 0.2069

Table 14:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$Log(\frac{n-1}{2-n})$	$Log\ K_2$
10.00	5.60	6.47	6.55	0.08	0.9148	1.41		
10.23	5.65	6.62	6.71	0.09	1.2102	1.20	-0.5749	0.6251
10.49	5.70	6.80	6.92	0.09	1.5968	1.03	0.1703	1.2003

$LogK_2$ **(Average value)** = 0.9127± 0.4070

Table15:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$Log(\frac{n}{1-n})$	$LogK_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4210	2.2190
8.72	5.35	6.37	6.40	0.03	0.4286	2.42	-0.1249	2.2951
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.96	0.3010	2.2610
9.51	5.55	6.66	6.70	0.04	0.7720	1.67	0.5297	2.1997

$LogK_1$ (Average value) = 2.2108± 0.0825

Table 16:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$Log(\frac{n-1}{2-n})$	$Log\ K_2$
9.73	5.55	6.78	6.83	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.95	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.09		
10.49	5.70	7.10	7.16	0.06	3.1429	0.89		

$LogK_2$ **(Average value)** = 1.5453± 0.3450

Table 17:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$Log(\frac{n}{n-1})$	$Log\ K_1$
8.50	5.30	5.81	5.86	0.05	0.3717	2.88	-0.2280	2.6520
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.06	0.06	0.4853	2.38	-0.0255	2.3545
9.22	5.45	6.10	6.16	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430
9.73	5.55	6.33	6.41	0.08	0.8000	1.69	0.6020	2.2920

$LogK_1$ **(Average value)** = 2.2516± 0.5380

Table 18:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$\text{Log}(\frac{n-1}{2-n})$	Log K_2
10.00	5.60	6.47	6.57	0.10	1.1434	1.43		
10.23	5.65	6.62	6.72	0.10	1.3448	1.23	-0.2788	0.9512
10.49	5.70	6.80	6.90	0.10	1.7742	1.03	0.5351	1.5651

LogK_2 **(Average value)** = 1.2581± 0.4340

Table 19: Stepwise and overall Stability constants of thehydrolysed and unhydrolysed divalent metal (II) complexes

Chelates	**LogK$_1$**	**LogK$_2$**	**Logβ**
[Cu (Hydrolysed PSHA-1)$_2$]	2.4788	1.4280	3.9068
[Pb (Hydrolysed PSHA-1)$_2$]	2.5832	1.1963	3.7795
[Cd (Hydrolysed PSHA-1)$_2$]	2.2108	1.5453	3.7561
[Mg (Hydrolysed PSHA-1)$_2$]	2.1382	1.5453	3.6835
[Cu (Unhydrolysed PSHA-1)$_2$]	2.3059	1.2209	3.5268
[Pb (Unhydrolysed PSHA-1)$_2$]	2.2364	1.2239	3.4603
[Cd (Unhydrolysed PSHA-1)$_2$]	2.2516	1.2581	3.5097
[Mg (Unydrolysed PSHA-1)$_2$]	2.1568	0.9127	3.0695

The results obtained (Table19) shows the stepwise and overall stability constants to be not high indicating low stability of the complexes, because the solubility of most metal ions in the basic pH range is minimal due to metal hydroxide precipitation (Karimi, 2017). In general, the stepwise stability constants (K_1 and K_2) follow the order $K_1 > K_2$ for the copper, lead, magnesium and cadmium complexes respectively. The steady decrease of the values with increasing number of ligands is in agreement with the prediction made by researchers (Na'aliya, 2013). The decrease could be attributed to the fact that as the number of the ligands (Humate ions) that enters the coordination zone increases the aqua molecules available for replacement by the ligands become less. Thus, the metal ions become less electron loving with progressive intake of the ligand and this results in the decrease in the values of the constants (Na'aliya, 2013). Also the stability of the complexes is influenced by the size and number of the chelate rings(Mackay and Mackay,2002).All the complexes form rings in their structure as humate, a bidentate ligand, bond the metal ions in the ratio 1:2 (Boguta and Sokolowska, 2016) forming chelate rings. The values of the overall stability constants (logβ) obtained for humate complexes are not high indicating low stability as the values are not high. LogK values for copper-humates (Table 3 to 6) obtained in this study are lower than those reported for the complexes of humic acids (Pandey *et al.*, 2015; Dinu, 2013; Kaschl *et al.*, 2010 and Gilbeto and Jorg, 2001). The values of LogK(Table 7 to 10) forlead-humates are lower than those reported for the lead in the literature (Dinu, 2013; Gilbeto and Jorg 2001). Log K values(Table 11 to 14) for magnesium-humates obtained in this study are close to those reported by (Pandey *et al.*, 2015). Log K values of cadmium-humates (Table 15 to 18) obtained in this work near to the one reported by (Dinu, 2013 and Pandey *et al.*, 2015).The difference between the reported values and the values obtained in this study might be probably as a result of acid hydrolysis of humic acid. The values of the overall stability constants (log β) of the copper humates complexes presented in Table 19 is high than that of other metal humate complexes, show relatively high stability of Cu-HA complexes, show the following order of stability: Cu >Pb> Cd > Mg; which are in close agreement to the findings of (Dinu, 2013 and Pandey *et al.*, 2015).The high stability of Cu-humate chelate could be attributed to the existence of coordinate covalent bond between the complexing agents and the Cu^{2+} ions. Since, Cu^{2+} being a metal of the transitional series with $3d^9$ electronic configurations can accept the electrons from the complexing agents. Similarly,the low stabilities of Pb,Cd and Mg - complexes could be explained by that Pb^{2+} with $6s^2$, Cd^{2+} with $4d^{10}$ and Mg^{2+} with $2p^6$ their electronic configuration has a completely filled d,p and s orbitals. Moreover, the stabilities of metal ions with hydrolysed humic acid from peat soil were higher than those with unhydrolysed humic acid from peat soil; which is ascribed to the high content of acidity in hydrolysed humic acid than unhydrolysed humic acid.

CONCLUSION

The values of logK for Cu(II) hydrolysed humic acid complex was higher followed by Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes as compared with metal(II) unhydrolysed humic acid complexes . This indicates acid hydrolysis of humic acid can enhance the complexation behavior of humic acid with metal (II) ions. However, the higher values of logβ for Cu(II), Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes indicates more stable stepwise complexes formed as compared with Cu(II), Pb(II), Cd(II) and Mg(II) unhydrolysed humic acid complexes.

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STABILITY CONSTANTS OF COMPLEXES OF METAL IONS WITH PEATSOIL HUMIC ACIDS UNDER NON-ACID-CONDITIONS

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ABSTRACT

Stability constants of complexes of four divalent metal ions viz. Cu^{2+}, Pb^{2+},Mg^{2+} and Cd^{2+} with humic acids (HA) were determined by potentiometric titration of humic acids with the corresponding salt of the divalent metals in aqueous media under non-acid-condition. The log K (logarithm of the stability constant) ranged from 1.0942 to 2.7471 for metal-humic acid complexes were determined using point-wise computational method. The order of stability constants were obtained as follows: Cu >Pb> Cd > Mg for metal -HA complexes respectively, indicating a higher degree of complexation with Cu metal ion.

Keywords: stability constant, humic acid, potentiometric titration, divalent metals, acid hydrolysis.

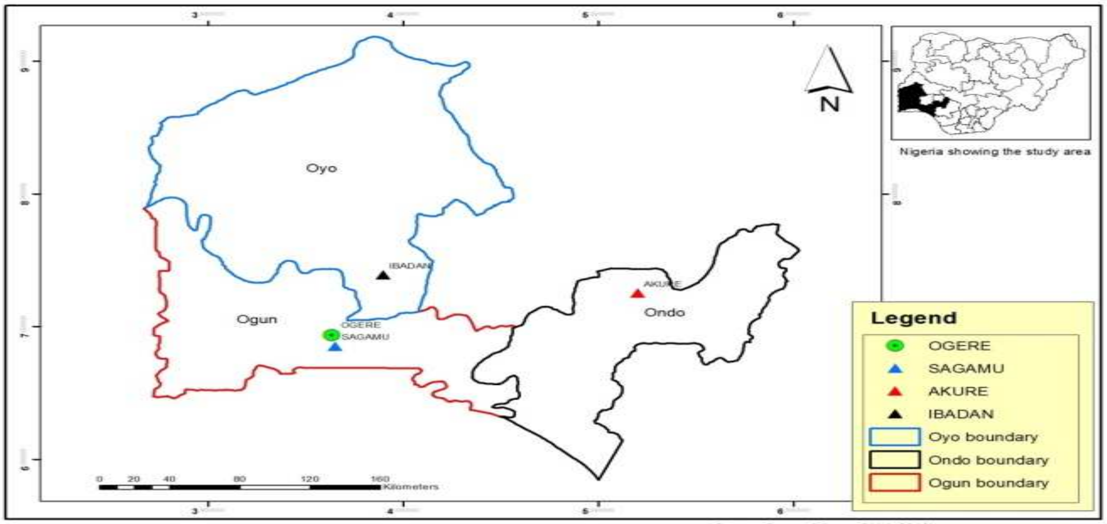
NTRODUCTION

The stability constant of a complex is the numerical expression of its stability and provides a quantitative measure of affinity of the metal ion to the complexing agent. An understanding of the relative stability of metal-complexes helps in predicting the behavior of metal ions in the soil (Ram and Raman, 1982). Extensive researches has been done to determine the stability constants of the complexes formed between humic acid (HA) with a number of metal ions. Ashok *et al*., (2000) reported that humic acid with hydroxyl, phenoxyl and carboxyl reactive groups can form coordination compound with metal ions at pH 3.5. The stability constants(Log K) for different metal-humic acid complexes indicated the following order of the stabilities of complexes formed between humic acid and metal ion, Cu >Fe >Pb> Ni > Co > Ca > Cd > Zn >Mn> Mg. Andelkovic *et al*., (2010) investigated the binding of Cd(II) to soil humic acid at pH 6.5 and in 0.1M KNO_3 ionic medium. The stability constant for binding indicating greater stability in the case when carboxyl groups are involved in complexation reaction. Kostic *et al*.,(2012) investigated the complexation of humic acid with certain heavy metal ions (Co(II), Ni(II),Cu(II), Zn(II), and Pb(II). The experiment was performed at 25°C, at pH 4.0 and ionic strength of 0.01M. Stability constant of complex between Pb(II) ions and humic acid is greater than stability constants of other investigated metal-humate complexes. Bogata and Sokolowska (2016) analyses the interaction between humic acids from different soils and Zn (II) ions at wide concentration ranges and at pH 5. Studies have showed significant impact of Zn concentration, pH and some properties of humic acids with zinc.But all of these studies were limited to acidic pH range. Therefore, the present study was carried out to determine and compare the stability constants of complexes of metal ions with hydrolysed peat soil humic acid and unhydrolysed peat soil humic under non-acid conditions.

MATERIALS AND METHODS

Analytical grade chemicals used includes hydrochloric acid (HCl), nitric acid (HNO_3), sodium hydroxide (NaOH), lead nitrate $Pb(NO_3)_2$, copper nitrate $Cu(NO_3)_2.3H_2O$, cadmium nitrate $Cd(NO_3)_2.4H_2O$, magnesium nitrate $Mg(NO_3)_2.6H_2O$, potassium nitrate (KNO_3), calcium chloride ($CaCl_2$), (sigma-Aldrich). Dowex 50WX8, (20-50 mesh) from Fluka.

Area of study



Source: Dept. of Geog. BUK (2016)

Figure 1: Map showing the sampling point at Sagamu Town, Ogun State.

Description of Sampling Area

Sagamu has geographical coordinates between 6°50′ north; 3° 38′ east is located in south western region of Nigeria. The region has tropical wet and dry climate with a lengthy wet season and relatively constant temperatures throughout the course of the year. Wet season runs from March to October, November to December forms the region dry season. The vegetation type of the region is savannah which is really grassland with small bushes and occasional big trees. Grassland soils have substantially higher organic matter content than forest soils (Novackova, 2011).

Sample Collection

The Peatsoil samples were collected from four different sampling points (0-10cm depth) in Sagamu into polyethylene bag with plastic spoons. Samples were taken to the laboratory, extraneous materials were removed; the samples were air-dried, crushed and ground to a fine powder in a mortar passed through a 0.20mm sieve. The samples were kept for analysis.

Isolation and purification of humic acid from peat soil sample

Peatsoil sample (100g) was mixed with 1000 cm^3 of 0.1M NaOH solution, shaken for 3hours and left to stand overnight. Dark-coloured supernatant was obtained and decanted from solid residue. The dark-coloured supernatant was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 6 hours. Yellowish brown supernatant and dark-brown precipitate were obtained. The yellowish brown supernatant was decanted followed by centrifuge and discarded. The dark-brown precipitate was mixed with 500$cm^3$of 0.1M NaOH solution followed by passing through dowex resin. The dark-brown solution was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 3 hours. The dark-brown precipitate was washed several times with deionized water. The supernatant was treated with $AgNO_3$ solution until no white precipitate observed. The humic acid was transferred to weighed crucible and dried at 60°C in an oven for 12 hours. The humic acid was cooled and dried in the desiccator, weighed and recorded. The obtained humic acid was dried again at 60°C for additional 6 hours cooled and dried in the desiccator, weighed and recorded constant weight was obtained (Baruah *et al*., 2015).

FT-IR analysis

FT-IR spectra of humic acid sample was analysed using Carry 630 FT-IR Agilent Technologies.

Unhydrolysed compost humic acid

The unhydrolysed humic acid was obtained after isolation and purification of compost humic acid and kept for investigation.

Acid hydrolysis of Peatsoil acid

Peatsoil humic acid sample (1g) was refluxed for 12 hours at (160°C) with 50cm^3 of 6M HCl. The mixture was allowed to cool, decanted, and centrifuged after hydrolysis. The insoluble residues were washed with distilled water via centrifugation several times, and the supernatant was treated with $AgNO_3$ solution until no white precipitate was observed. The residue was thoroughly dried over $CaCl_2$ in a desiccator at room temperature (Chefetz *et al.*, 2002). Finally, the obtained hydrolysed humic acid was kept for investigation.

Potentiometric Titrations

Potentiometric measurements were carried out using a pH-meter Jenway (model 3510) with combine electrode, the sensitivity of the pH - meter is 0.01 units. The pH meter was switched on half an hour before starting the titration for initial warm up of the instrument. The instrument was calibrated with an aqueous standard buffer solution of pH 4.00 and 10.0 (borate buffer) prepared from a "Qualigens" buffer tablets.

The following sets of solutions were prepared in a 250cm^3 volumetric flask separately for pH metric titrations.

(i) 5 cm^3 0.1 M HCl + 40 cm^3 deionized water

(ii) 5 cm^3 0.1 M HCl + 39 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid

(iii) 5 cm^3 0.1 M HCl + 37 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid + 2 cm^3 0.01 M Cu(II)

The solutions were titrated against standardized 0.110MNaOH separately. The total volume of each mixture was adjusted to 50 cm^3 and the ionic strength of the solutions was maintained constant at by adding appropriate amount of stock solution of 1M KNO_3 (Gamal, 2015; Omar and Ali, 2015). A magnetic stirrer was used to achieve thorough mixing of the interacting solutions at 550 rpm. The same set of experimental conditions was applied for potentiometric titration of remaining samples.

Evaluation of pKa of Hydrolysed peat soil Humic Acids

The proton-ligand formation number $n_{\mathbf{A}}$ were calculated by Irving and Rossotti expression (Omar and Ali, 2015).

$$nA = Y- \frac{(V2-V1)(No-Eo)}{(Vo+V1)TcL} \quad ....1$$

Where: Y is number of dissociable proton, (V_2-V_1) is the measure of displacement of the ligand curve relative to acid curve, N^o and E^o are the resultant concentration of alkali solution, free acid solution, $T_{cL}{}^o$ is the total ligand concentration, V^o is the total volume of titration solution,V_1 is the volume of alkali added to acid solution,V_2 is the volume of alkali added to acid solution + ligand solution, acid dissociation constants (pKa - values) of ligand were calculated by algebraic method point wise calculation (Tables 1). The dissociation constants (pKa) were calculated according to the following relation:

$$pKa = pH + \log(\frac{nA}{1-nA}) \quad ....2$$

Where: pKa is the acid dissociation constant, $n_A$is the Proton-ligand formation number and pH is the pH-values (Omar and Ali, 2015).

Determination of metal-ligand stability constants (log K) of complexes

The potentiometric measurement for the determination of stability constant of a complex in solution is based on the fact that the redox potential of the couple $\frac{M^{+(m-n)}}{M^{+m}}$ is shifted significantly on complexation of the metal ion with the ligand. This method involves change in hydrogen ion concentration [H$^+$] due to the displacement or association of one or more protons taking place during complexation reaction. This change can be found out by titrating the solutions containing free acid, acid with ligand, and acid with ligand and metal ion, individually against a standard alkali solution at a constant ionic strength or temperature. Either ionic strength or temperature may be varied for different sets of solutions. In all the cases, the change in the pH of the solution is measured after each addition of a known amount of alkali to the reaction cell which contains the reaction mixture. The titration curves are then drawn by plotting the measured pH values against the corresponding volume of alkali added and the stability constants of the complexes are determined from the titration curves by employing pH-metric titration technique given by (Irving and Rossoti).

Metal-ligand stability constants (Log K) were determined by using the following relations:

$$\bar{n} = \frac{(V_3 - V_2)(E^0 + N^0)}{(V^0 + V_2)\bar{n}_A T_m^0} \quad ....3$$

and

$$PL = \log_{10}\{\frac{1+\beta_n^H \frac{1}{[anti\ \log pH]^n}}{T_L^0 - \bar{n}T_m^0} X \frac{(V^0 + V_3)}{V^0}\} \quad ....4$$

Where $T_{L,}$ T^{o}, E°, and V^{o}havethe same significance as in equation (1) above, T_m denotes the total concentration of metal present in solution, V_3 is the volume of metal ions present in solution and β^H is the overall proton ligand stability constant. The metal-ligand stability constants (log K) were determined by employing point wise computational Method (eq. 5 and 6).

$$\mathrm{Log}K_1 = \log\left(\frac{n}{1-n}\right) + pL \qquad \ldots\ldots\ldots\ldots.5$$

$$\mathrm{Log}K_2 = \log\left(\frac{1-n}{2-n}\right) + pL\ldots\ldots\ldots\ldots\ldots\ldots\ldots.6$$

Where: Log K is the metal-ligand stability constant, pL is the Free ligand exponent function, **n** is the Average number of ligand attached with metal ion (Janrao*et al*., 2014).The results obtained were analyzed by an ORIGIN 2016 program using titration data and then the proton-ligand stability constants (pKa) and Metal-ligand stability constant (LogK) calculated (Omar and Ali, 2015).

RESULTS AND DISCUSSION

Fourier transformed infrared (FT-IR) spectra of isolated humic acid from peat soils Figure 2 had distinct clear absorption bands indicating the presence of major humic acid structural elemental groups such as H bonded OH (3680cm^{-1} peak), C=O of carbonyl (1721cm^{-1} peak), functional groups of aliphatic components CH_2 (2918cm^{-1} peak) and C-O stretching of polysaccharide (1168cm^{-1} peak). The positions of the absorption bands of the spectra fell within typical major absorption bands of humic acid which is at frequencies 3680, 2918, 1721, 1168 cm^{-1}. The first peak centred in the vicinity of 3680 cm^{-1} region is attributed to phenol OH group bounded by intermolecular H bonds. The 2918cm^{-1} band usually has absorption maximum at 2918 cm^{-1} which is due to C–H stretching of alkane group (CH_2). The next major absorption band is 1721 cm^{-1}. This band has been commonly ascribed to C=O stretching of mainly carboxyl group (COOH) with trace amount of ketones. The last peak was observed at 1168 cm^{-1} due to C–O stretching of polysaccharides and this peak appeared also in the spectra of humic acid from peat soil. The FTIR spectra of the isolated humic acid contained all major characteristic absorption peaks of humic acid. These absorption peaks indicated the presence of the major structural elements of humic acid namely H bonded OH, C=C of aromatic ring, C=O of carbonyl group (both carboxyl and ketonic), CH_2 group. This strongly supports the presence of humic acid.

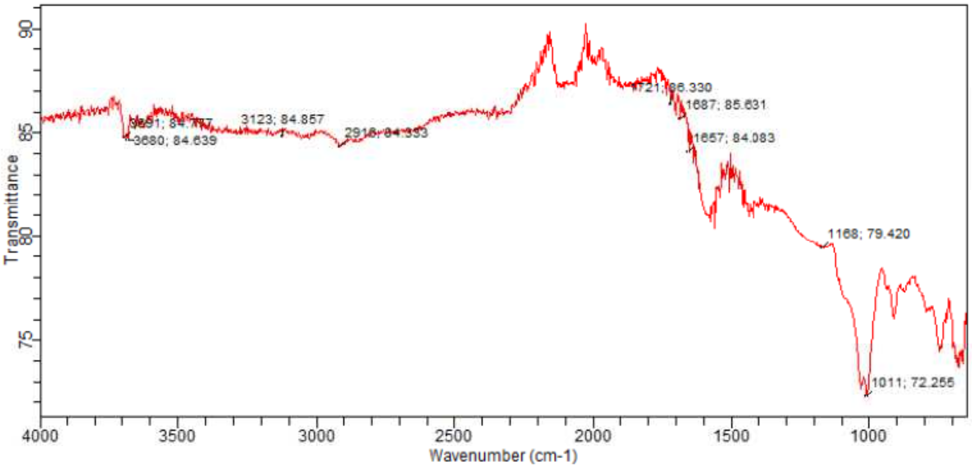


Fig. 2 : FT-IR spectraof peatsoilhumic acid (PSHA)

Evaluation of acid dissociation constant (pka) of acid hydrolysed peat soil humicacid at phenolic group

The value of the dissociation constant of the peat soil humic acid (PSHA) that underwent acidhydrolysis studied was found to be 8.9299 as shown Table 1, which is lower than the literaturevalues reported by Almeida and Szpoganics, (2015), Borges *et al*., (2005); Badr *et al*., (2012)and Fernandes *et al*,.(2009) of 9.73, 9.47 and 10.30. The difference between the obtained valuesand the reported values in this study might be probably as a result of acid hydrolysis of humicacid.

Table 1: PKa of (Hydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	log($\frac{nA}{1-nA}$)	pKa
8.50	5.30	6.29	0.99	0.3594	-0.2510	8.2490
8.72	5.35	6.37	1.02	0.3400	-0.2880	8.4320
9.00	5.40	6.46	1.06	0.3141	-0.3391	8.6609
9.22	5.45	6.55	1.10	0.2882	-0.3927	8.8273
9.51	5.50	6.66	1.16	0.2494	-0.4786	9.0314
9.73	5.55	6.78	1.23	0.2041	-0.5910	9.1390
10.00	5.60	6.90	1.30	0.1589	-0.7238	9.2762
10.23	5.65	7.05	1.40	0.0941	-0.9835	9.2465
10.49	5.70	7.10	1.40	0.0941	-0.9835	9.5065

Average pKa = 8.9299 ± 0.4186

Table 2: PKa of (Unhydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	Log($\frac{nA}{1-n}$)	pKa
8.50	5.30	5.81	0.51	0.6619	0.2919	8.7919
8.72	5.35	5.90	0.55	0.6357	0.2418	8.9618
9.00	5.40	6.00	0.60	0.6029	0.1813	9.1813
9.22	5.45	6.10	0.65	0.5701	0.1226	9.3426
9.51	5.50	6.20	0.70	0.5376	0.0654	9.5754
9.73	5.55	6.33	0.78	0.4851	-0.0259	9.7041
10.00	5.60	6.47	0.87	0.4262	-0.1291	9.8709
10.23	5.65	6.62	0.99	0.3609	-0.2481	9.9819
10.49	5.70	6.80	1.10	0.2759	-0.4690	10.0210

Average pKa = 9.4923± 0.4410

Metal-ligand stability constant (Log K)

The stabilityconstants require the accurate values of proton-ligand stability constants (Anil and Maroti, 2008). Metal titration curves crossed over ligand titration curve indicated the formation of complex upon proton release (Santosh, *et al.*, 2011). If the values of n- are within range 0.2-0.8 and 1.2-18 this indicates the formation of 1:1 and 1:2 complexes (Sayyed and Mazahar, 2012).

The metal (II)-humate stepwise stability constants (log k) at phenolic group (Tables 3-18)

Table 3: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n}{1-n}$)	$LogK_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

$LogK_1$ (Average value) = 2.4788± 0.2203

Table 4: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	Log($\frac{n-1}{2-n}$)	$LogK_2$
9.51	5.50	6.66	6.73	0.07	1.3509	1.70	-0.2671	1.4329
9.73	5.55	6.78	6.85	0.07	1.6383	1.51	0.2467	1.7567
10.00	5.60	6.90	6.98	0.08	2.1783	1.31	-0.2158	1.0942
10.23	5.65	7.05	7.13	0.08	4.1904	1.27		
10.49	5.70	7.10	7.19	0.09	4.6920			

$LogK_2$(Average value) = 1.4280 ± 0.3312

Table 5:Point-wise method,Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	Log($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430

$LogK_1$ **(Average value)** = 2.3059± 0.6153

Table 6:Point-wise method, Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
9.73	5.55	6.33	6.42	0.09	0.9000	1.69		
10.00	5.60	6.47	6.58	0.11	1.2578	1.44	-0.4592	0.9808
10.23	5.65	6.62	6.84	0.12	1.6137	1.26	-0.2010	1.4610
10.49	5.70	6.80	6.92	0.12	2.1052	1.03		

$LogK_2$ **(Average value)** = 1.2209± 0.3398

Table 7:Point-wise method,Pb (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n}{1-n}$)	$LogK_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.60	0.05	0.8333	1.96	0.6989	2.6589

$LogK_1$ (Average value) = 2.5832 ±0.1614

Table 8:Point-wise method,Pb-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n-1}{2-n}$)	$logK_2$
9.51	5.50	6.66	6.71	0.05	0.9650	1.67	-0.0237	1.1963
9.73	5.55	6.78	6.83	0.05	1.1702	1.44		
10.00	5.60	6.90	6.90	0.05	1.4864	1.22		
10.23	5.65	7.05	7.10	0.05	2.0190	1.09		
10.49	5.70	7.10	7.17	0.07	3.6492	1.00		

$LogK_2$(Average value) = 1.1963

Table 9:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log ($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.5477	2.3123
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	0.0272	2.2072
9.51	5.50	6.20	6.26	0.07	0.6417	1.89	0.2530	2.1430
9.73	5.55	6.40	6.40	0.07	0.7000	1.67	0.3680	2.0380

$LogK_1$ **(Average value)** = 2.2364 ± 0.1602

Table 10:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
10.00	5.60	6.47	6.55	0.08	1.9503	1.41	-0.0361	1.2239
10.23	5.65	6.62	6.72	0.11	1.4792	1.26		

$LogK_2$ **(Average value)** = 1.2239

Table 11:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n}{n-1}$)	$LogK_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4290	2.2110
8.72	5.35	6.37	6.39	0.02	0.2858	2.42	-0.3978	2.0222
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

$LogK_1$ (Average value)=2.1382**±**0.1046

Table 12:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log$(\frac{n-1}{2-n})$	LogK_2
9.51	5.55	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.84	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.93	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.10		
10.49	5.70	7.10	7.18	0.07	3.6492	0.83		

LogK_2(Average value) = 1.5453 **±** 0.3450

Table 13:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log$(\frac{n}{n-1})$	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.3477	2.3123
9.00	5.40	6.00	6.04	0.04	0.3236	2.38	-0.3202	2.0598
9.22	5.45	6.10	6.15	0.05	0.4297	2.17	-0.1230	2.0470
9.51	5.50	6.20	6.26	0.06	0.5500	1.89	0.0871	1.9771
9.73	5.55	6.33	6.40	0.07	0.7000	1.67	0.3680	2.0380

LogK_1 **(Average value)** = 2.1568 ± 0.2069

Table 14:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log$(\frac{n-1}{2-n})$	Log K_2
10.00	5.60	6.47	6.55	0.08	0.9148	1.41		
10.23	5.65	6.62	6.71	0.09	1.2102	1.20	-0.5749	0.6251
10.49	5.70	6.80	6.92	0.09	1.5968	1.03	0.1703	1.2003

LogK_2 **(Average value)** = 0.9127± 0.4070

Table15:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	Log$(\frac{n}{1-n})$	LogK_1
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4210	2.2190
8.72	5.35	6.37	6.40	0.03	0.4286	2.42	-0.1249	2.2951
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.96	0.3010	2.2610
9.51	5.55	6.66	6.70	0.04	0.7720	1.67	0.5297	2.1997

LogK_1 (Average value) = 2.2108± 0.0825

Table 16:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	Log$(\frac{n-1}{2-n})$	Log K_2
9.73	5.55	6.78	6.83	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.95	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.09		
10.49	5.70	7.10	7.16	0.06	3.1429	0.89		

LogK_2 **(Average value)** = 1.5453± 0.3450

Table 17:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log$(\frac{n}{n-1})$	Log K_1
8.50	5.30	5.81	5.86	0.05	0.3717	2.88	-0.2280	2.6520
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.06	0.06	0.4853	2.38	-0.0255	2.3545
9.22	5.45	6.10	6.16	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430
9.73	5.55	6.33	6.41	0.08	0.8000	1.69	0.6020	2.2920

LogK_1 **(Average value)** = 2.2516± 0.5380

Table 18:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
10.00	5.60	6.47	6.57	0.10	1.1434	1.43		
10.23	5.65	6.62	6.72	0.10	1.3448	1.23	-0.2788	0.9512
10.49	5.70	6.80	6.90	0.10	1.7742	1.03	0.5351	1.5651

LogK_2 **(Average value)** = 1.2581± 0.4340

Table 19: Stepwise and overall Stability constants of thehydrolysed and unhydrolysed divalent metal (II) complexes

Chelates	$LogK_1$	$LogK_2$	Logβ
[Cu (Hydrolysed PSHA-1)$_2$]	2.4788	1.4280	3.9068
[Pb (Hydrolysed PSHA-1)$_2$]	2.5832	1.1963	3.7795
[Cd (Hydrolysed PSHA-1)$_2$]	2.2108	1.5453	3.7561
[Mg (Hydrolysed PSHA-1)$_2$]	2.1382	1.5453	3.6835
[Cu (Unhydrolysed PSHA-1)$_2$]	2.3059	1.2209	3.5268
[Pb (Unhydrolysed PSHA-1)$_2$]	2.2364	1.2239	3.4603
[Cd (Unhydrolysed PSHA-1)$_2$]	2.2516	1.2581	3.5097
[Mg (Unydrolysed PSHA-1)$_2$]	2.1568	0.9127	3.0695

The results obtained (Table19) shows the stepwise and overall stability constants to be not high indicating low stability of the complexes, because the solubility of most metal ions in the basic pH range is minimal due to metal hydroxide precipitation (Karimi, 2017). In general, the stepwise stability constants (K_1 and K_2) follow the order $K_1 > K_2$ for the copper, lead, magnesium and cadmium complexes respectively. The steady decrease of the values with increasing number of ligands is in agreement with the prediction made by researchers (Na'aliya, 2013). The decrease could be attributed to the fact that as the number of the ligands (Humate ions) that enters the coordination zone increases the aqua molecules available for replacement by the ligands become less. Thus, the metal ions become less electron loving with progressive intake of the ligand and this results in the decrease in the values of the constants (Na'aliya, 2013). Also the stability of the complexes is influenced by the size and number of the chelate rings(Mackay and Mackay,2002).All the complexes form rings in their structure as humate, a bidentate ligand, bond the metal ions in the ratio 1:2 (Boguta and Sokolowska, 2016) forming chelate rings. The values of the overall stability constants (logβ) obtained for humate complexes are not high indicating low stability as the values are not high. LogK values for copper-humates (Table 3 to 6) obtained in this study are lower than those reported for the complexes of humic acids (Pandey *et al.*, 2015; Dinu, 2013; Kaschl *et al.*, 2010 and Gilbeto and Jorg, 2001). The values of LogK(Table 7 to 10) forlead-humates are lower than those reported for the lead in the literature (Dinu, 2013; Gilbeto and Jorg 2001). Log K values(Table 11 to 14) for magnesium-humates obtained in this study are close to those reported by (Pandey *et al.*, 2015). Log K values of cadmium-humates (Table 15 to 18) obtained in this work near to the one reported by (Dinu, 2013 and Pandey *et al.*, 2015).The difference between the reported values and the values obtained in this study might be probably as a result of acid hydrolysis of humic acid. The values of the overall stability constants (log β) of the copper humates complexes presented in Table 19 is high than that of other metal humate complexes, show relatively high stability of Cu-HA complexes, show the following order of stability: Cu >Pb> Cd > Mg; which are in close agreement to the findings of (Dinu, 2013 and Pandey *et al.*, 2015).The high stability of Cu-humate chelate could be attributed to the existence of coordinate covalent bond between the complexing agents and the Cu^{2+} ions. Since, Cu^{2+} being a metal of the transitional series with $3d^9$ electronic configurations can accept the electrons from the complexing agents. Similarly,the low stabilities of Pb,Cd and Mg - complexes could be explained by that Pb^{2+} with $6s^2$, Cd^{2+} with $4d^{10}$ and Mg^{2+} with $2p^6$ their electronic configuration has a completely filled d,p and s orbitals. Moreover, the stabilities of metal ions with hydrolysed humic acid from peat soil were higher than those with unhydrolysed humic acid from peat soil; which is ascribed to the high content of acidity in hydrolysed humic acid than unhydrolysed humic acid.

CONCLUSION

The values of logK for Cu(II) hydrolysed humic acid complex was higher followed by Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes as compared with metal(II) unhydrolysed humic acid complexes . This indicates acid hydrolysis of humic acid can enhance the complexation behavior of humic acid with metal (II) ions. However, the higher values of logβ for Cu(II), Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes indicates more stable stepwise complexes formed as compared with Cu(II), Pb(II), Cd(II) and Mg(II) unhydrolysed humic acid complexes.

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STABILITY CONSTANTS OF COMPLEXES OF METAL IONS WITH PEATSOIL HUMIC ACIDS UNDER NON-ACID-CONDITIONS

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ABSTRACT

Stability constants of complexes of four divalent metal ions viz. Cu^{2+}, Pb^{2+},Mg^{2+} and Cd^{2+} with humic acids (HA) were determined by potentiometric titration of humic acids with the corresponding salt of the divalent metals in aqueous media under non-acid-condition. The log K (logarithm of the stability constant) ranged from 1.0942 to 2.7471 for metal-humic acid complexes were determined using point-wise computational method. The order of stability constants were obtained as follows: Cu >Pb> Cd > Mg for metal -HA complexes respectively, indicating a higher degree of complexation with Cu metal ion.

Keywords: stability constant, humic acid, potentiometric titration, divalent metals, acid hydrolysis.

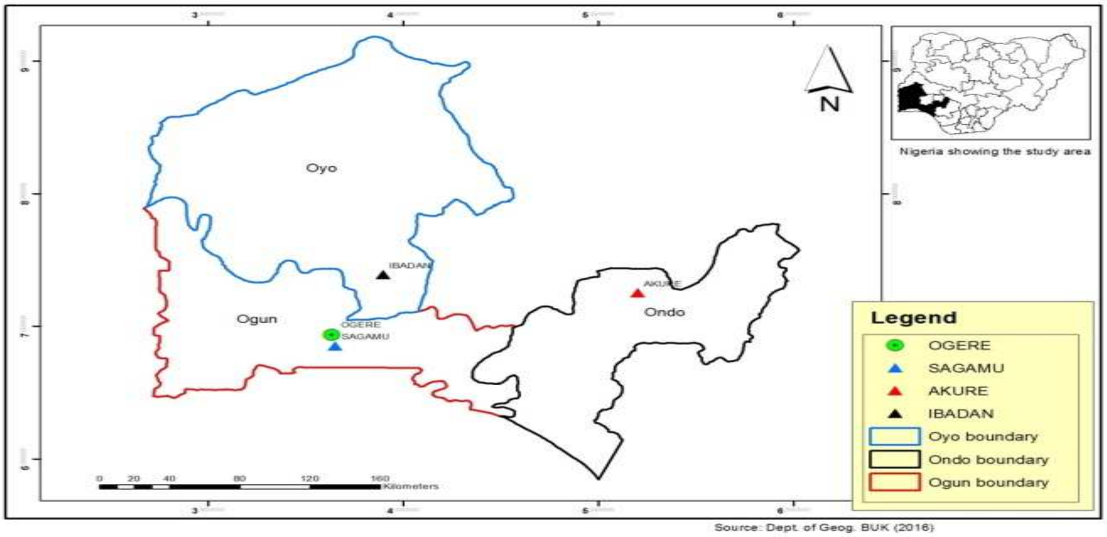
NTRODUCTION

The stability constant of a complex is the numerical expression of its stability and provides a quantitative measure of affinity of the metal ion to the complexing agent. An understanding of the relative stability of metal-complexes helps in predicting the behavior of metal ions in the soil (Ram and Raman, 1982). Extensive researches has been done to determine the stability constants of the complexes formed between humic acid (HA) with a number of metal ions. Ashok *et al*., (2000) reported that humic acid with hydroxyl, phenoxyl and carboxyl reactive groups can form coordination compound with metal ions at pH 3.5. The stability constants(Log K) for different metal-humic acid complexes indicated the following order of the stabilities of complexes formed between humic acid and metal ion, Cu >Fe >Pb> Ni > Co > Ca > Cd > Zn >Mn> Mg. Andelkovic *et al*., (2010) investigated the binding of Cd(II) to soil humic acid at pH 6.5 and in 0.1M KNO_3 ionic medium. The stability constant for binding indicating greater stability in the case when carboxyl groups are involved in complexation reaction. Kostic *et al*.,(2012) investigated the complexation of humic acid with certain heavy metal ions (Co(II), Ni(II),Cu(II), Zn(II), and Pb(II). The experiment was performed at 25°C, at pH 4.0 and ionic strength of 0.01M. Stability constant of complex between Pb(II) ions and humic acid is greater than stability constants of other investigated metal-humate complexes. Bogata and Sokolowska (2016) analyses the interaction between humic acids from different soils and Zn (II) ions at wide concentration ranges and at pH 5. Studies have showed significant impact of Zn concentration, pH and some properties of humic acids with zinc.But all of these studies were limited to acidic pH range. Therefore, the present study was carried out to determine and compare the stability constants of complexes of metal ions with hydrolysed peat soil humic acid and unhydrolysed peat soil humic under non-acid conditions.

MATERIALS AND METHODS

Analytical grade chemicals used includes hydrochloric acid (HCl), nitric acid (HNO_3), sodium hydroxide (NaOH), lead nitrate $Pb(NO_3)_2$, copper nitrate $Cu(NO_3)_2.3H_2O$, cadmium nitrate $Cd(NO_3)_2.4H_2O$, magnesium nitrate $Mg(NO_3)_2.6H_2O$, potassium nitrate (KNO_3), calcium chloride ($CaCl_2$), (sigma-Aldrich). Dowex 50WX8, (20-50 mesh) from Fluka.

Area of study



Source: Dept. of Geog. BUK (2016)

Figure 1: Map showing the sampling point at Sagamu Town, Ogun State.

Description of Sampling Area

Sagamu has geographical coordinates between 6°50′ north; 3° 38′ east is located in south western region of Nigeria. The region has tropical wet and dry climate with a lengthy wet season and relatively constant temperatures throughout the course of the year. Wet season runs from March to October, November to December forms the region dry season. The vegetation type of the region is savannah which is really grassland with small bushes and occasional big trees. Grassland soils have substantially higher organic matter content than forest soils (Novackova, 2011).

Sample Collection

The Peatsoil samples were collected from four different sampling points (0-10cm depth) in Sagamu into polyethylene bag with plastic spoons. Samples were taken to the laboratory, extraneous materials were removed; the samples were air-dried, crushed and ground to a fine powder in a mortar passed through a 0.20mm sieve. The samples were kept for analysis.

Isolation and purification of humic acid from peat soil sample

Peatsoil sample (100g) was mixed with 1000 cm^3 of 0.1M NaOH solution, shaken for 3hours and left to stand overnight. Dark-coloured supernatant was obtained and decanted from solid residue. The dark-coloured supernatant was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 6 hours. Yellowish brown supernatant and dark-brown precipitate were obtained. The yellowish brown supernatant was decanted followed by centrifuge and discarded. The dark-brown precipitate was mixed with $500cm^3$of 0.1M NaOH solution followed by passing through dowex resin. The dark-brown solution was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 3 hours. The dark-brown precipitate was washed several times with deionized water. The supernatant was treated with $AgNO_3$ solution until no white precipitate observed. The humic acid was transferred to weighed crucible and dried at 60°C in an oven for 12 hours. The humic acid was cooled and dried in the desiccator, weighed and recorded. The obtained humic acid was dried again at 60°C for additional 6 hours cooled and dried in the desiccator, weighed and recorded constant weight was obtained (Baruah *et al.*, 2015).

FT-IR analysis

FT-IR spectra of humic acid sample was analysed using Carry 630 FT-IR Agilent Technologies.

Unhydrolysed compost humic acid

The unhydrolysed humic acid was obtained after isolation and purification of compost humic acid and kept for investigation.

Acid hydrolysis of Peatsoil acid

Peatsoil humic acid sample (1g) was refluxed for 12 hours at (160°C) with $50cm^3$ of 6M HCl. The mixture was allowed to cool, decanted, and centrifuged after hydrolysis. The insoluble residues were washed with distilled water via centrifugation several times, and the supernatant was treated with $AgNO_3$ solution until no white precipitate was observed. The residue was thoroughly dried over $CaCl_2$ in a desiccator at room temperature (Chefetz *et al.*, 2002). Finally, the obtained hydrolysed humic acid was kept for investigation.

Potentiometric Titrations

Potentiometric measurements were carried out using a pH-meter Jenway (model 3510) with combine electrode, the sensitivity of the pH -meter is 0.01 units. The pH meter was switched on half an hour before starting the titration for initial warm up of the instrument. The instrument was calibrated with an aqueous standard buffer solution of pH 4.00 and 10.0 (borate buffer) prepared from a "Qualigens" buffer tablets.

The following sets of solutions were prepared in a 250cm^3 volumetric flask separately for pH metric titrations.

(i) 5 cm^3 0.1 M HCl + 40 cm^3 deionized water

(ii) 5 cm^3 0.1 M HCl + 39 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid

(iii) 5 cm^3 0.1 M HCl + 37 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid + 2 cm^3 0.01 M Cu(II)

The solutions were titrated against standardized 0.110MNaOH separately. The total volume of each mixture was adjusted to 50 cm^3 and the ionic strength of the solutions was maintained constant at by adding appropriate amount of stock solution of 1M KNO$_3$ (Gamal, 2015; Omar and Ali, 2015). A magnetic stirrer was used to achieve thorough mixing of the interacting solutions at 550 rpm. The same set of experimental conditions was applied for potentiometric titration of remaining samples.

Evaluation of pKa of Hydrolysed peat soil Humic Acids

The proton-ligand formation number n$_{\mathbf{A}}$ were calculated by Irving and Rossotti expression (Omar and Ali, 2015).

$$nA = Y- \frac{(V2-V1)(No-Eo)}{(Vo+V1)TcL} \quad \text{....................................1}$$

Where: Y is number of dissociable proton, (V$_2$-V$_1$) is the measure of displacement of the ligand curve relative to acid curve, N^o and E^o are the resultant concentration of alkali solution, free acid solution, T$_{cL}$^{o} is the total ligand concentration, V^o is the total volume of titration solution,V$_1$ is the volume of alkali added to acid solution,V$_2$ is the volume of alkali added to acid solution + ligand solution, acid dissociation constants (pKa - values) of ligand were calculated by algebraic method point wise calculation (Tables 1). The dissociation constants (pKa) were calculated according to the following relation:

$$\text{pKa} = \text{pH} + \log\left(\frac{nA}{1-nA}\right) \quad \text{..............................2}$$

Where: pKa is the acid dissociation constant, n$_A$is the Proton-ligand formation number and pH is the pH-values (Omar and Ali, 2015).

Determination of metal-ligand stability constants (log K) of complexes

The potentiometric measurement for the determination of stability constant of a complex in solution is based on the fact that the redox potential of the couple $\frac{M^{+(m-n)}}{M^{+m}}$ is shifted significantly on complexation of the metal ion with the ligand. This method involves change in hydrogen ion concentration [H$^+$] due to the displacement or association of one or more protons taking place during complexation reaction. This change can be found out by titrating the solutions containing free acid, acid with ligand, and acid with ligand and metal ion, individually against a standard alkali solution at a constant ionic strength or temperature. Either ionic strength or temperature may be varied for different sets of solutions. In all the cases, the change in the pH of the solution is measured after each addition of a known amount of alkali to the reaction cell which contains the reaction mixture. The titration curves are then drawn by plotting the measured pH values against the corresponding volume of alkali added and the stability constants of the complexes are determined from the titration curves by employing pH-metric titration technique given by (Irving and Rossoti).

Metal-ligand stability constants (Log K) were determined by using the following relations:

$$\bar{n} = \frac{(V_3 - V_2)(E^0 + N^0)}{(V^0 + V_2)\bar{n}_A T_m^0} \quad \text{...3}$$

and

$$PL = \log_{10}\{\frac{1 + \beta_n^H \frac{1}{[anti\ \log \text{pH}]^n}}{\text{T}_\text{L}^0 - \bar{n}T_m^0} \text{X} \frac{(V^0 + V_3)}{V^0}\} \quad \text{...4}$$

Where $T_{L,}$ T^o, E°, and V^ohavethe same significance as in equation (1) above, T_m denotes the total concentration of metal present in solution, V_3 is the volume of metal ions present in solution and β^H is the overall proton ligand stability constant. The metal-ligand stability constants (log K) were determined by employing point wise computational Method (eq. 5 and 6).

$$\text{Log}K_1 = \log\left(\frac{n}{1-n}\right) + pL \qquad \text{.............}5$$

$$\text{Log}K_2 = \log\left(\frac{1-n}{2-n}\right) + pL\text{.......................}6$$

Where: Log K is the metal-ligand stability constant, pL is the Free ligand exponent function, **n** is the Average number of ligand attached with metal ion (Janrao*et al.*, 2014).The results obtained were analyzed by an ORIGIN 2016 program using titration data and then the proton-ligand stability constants (pKa) and Metal-ligand stability constant (LogK) calculated (Omar and Ali, 2015).

RESULTS AND DISCUSSION

Fourier transformed infrared (FT-IR) spectra of isolated humic acid from peat soils Figure 2 had distinct clear absorption bands indicating the presence of major humic acid structural elemental groups such as H bonded OH (3680cm^{-1} peak), C=O of carbonyl (1721cm^{-1} peak), functional groups of aliphatic components CH_2 (2918cm^{-1} peak) and C-O stretching of polysaccharide (1168cm^{-1} peak). The positions of the absorption bands of the spectra fell within typical major absorption bands of humic acid which is at frequencies 3680, 2918, 1721, 1168 cm^{-1}. The first peak centred in the vicinity of 3680 cm^{-1} region is attributed to phenol OH group bounded by intermolecular H bonds. The 2918cm^{-1} band usually has absorption maximum at 2918 cm^{-1} which is due to C–H stretching of alkane group (CH_2). The next major absorption band is 1721 cm^{-1}. This band has been commonly ascribed to C=O stretching of mainly carboxyl group (COOH) with trace amount of ketones. The last peak was observed at 1168 cm^{-1} due to C–O stretching of polysaccharides and this peak appeared also in the spectra of humic acid from peat soil. The FTIR spectra of the isolated humic acid contained all major characteristic absorption peaks of humic acid. These absorption peaks indicated the presence of the major structural elements of humic acid namely H bonded OH, C=C of aromatic ring, C=O of carbonyl group (both carboxyl and ketonic), CH_2 group. This strongly supports the presence of humic acid.

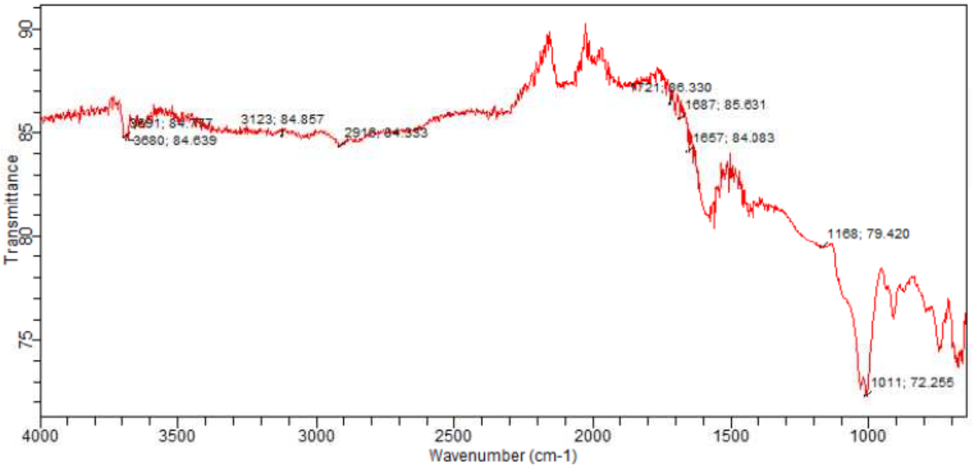


Fig. 2 : FT-IR spectraof peatsoilhumic acid (PSHA)

Evaluation of acid dissociation constant (pka) of acid hydrolysed peat soil humicacid at phenolic group

The value of the dissociation constant of the peat soil humic acid (PSHA) that underwent acidhydrolysis studied was found to be 8.9299 as shown Table 1, which is lower than the literaturevalues reported by Almeida and Szpoganics, (2015), Borges *et al.*, (2005); Badr *et al.*, (2012)and Fernandes *et al*,.(2009) of 9.73, 9.47 and 10.30. The difference between the obtained valuesand the reported values in this study might be probably as a result of acid hydrolysis of humicacid.

Table 1: PKa of (Hydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	$\log(\frac{nA}{1-nA})$	pKa
8.50	5.30	6.29	0.99	0.3594	-0.2510	8.2490
8.72	5.35	6.37	1.02	0.3400	-0.2880	8.4320
9.00	5.40	6.46	1.06	0.3141	-0.3391	8.6609
9.22	5.45	6.55	1.10	0.2882	-0.3927	8.8273
9.51	5.50	6.66	1.16	0.2494	-0.4786	9.0314
9.73	5.55	6.78	1.23	0.2041	-0.5910	9.1390
10.00	5.60	6.90	1.30	0.1589	-0.7238	9.2762
10.23	5.65	7.05	1.40	0.0941	-0.9835	9.2465
10.49	5.70	7.10	1.40	0.0941	-0.9835	9.5065

Average pKa = 8.9299 ± 0.4186

Table 2: PKa of (Unhydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	$\text{Log}(\frac{nA}{1-n})$	pKa
8.50	5.30	5.81	0.51	0.6619	0.2919	8.7919
8.72	5.35	5.90	0.55	0.6357	0.2418	8.9618
9.00	5.40	6.00	0.60	0.6029	0.1813	9.1813
9.22	5.45	6.10	0.65	0.5701	0.1226	9.3426
9.51	5.50	6.20	0.70	0.5376	0.0654	9.5754
9.73	5.55	6.33	0.78	0.4851	-0.0259	9.7041
10.00	5.60	6.47	0.87	0.4262	-0.1291	9.8709
10.23	5.65	6.62	0.99	0.3609	-0.2481	9.9819
10.49	5.70	6.80	1.10	0.2759	-0.4690	10.0210

Average pKa = 9.4923± 0.4410

Metal-ligand stability constant (Log K)

The stabilityconstants require the accurate values of proton-ligand stability constants (Anil and Maroti, 2008). Metal titration curves crossed over ligand titration curve indicated the formation of complex upon proton release (Santosh, *et al.*, 2011). If the values of n- are within range 0.2-0.8 and 1.2-18 this indicates the formation of 1:1 and 1:2 complexes (Sayyed and Mazahar, 2012).

The metal (II)-humate stepwise stability constants (log k) at phenolic group (Tables 3-18)

Table 3: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$\log(\frac{n}{1-n})$	$\text{Log}K_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

LogK_1 (Average value) = 2.4788± 0.2203

Table 4: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$\text{Log}(\frac{n-1}{2-n})$	$\text{Log}K_2$
9.51	5.50	6.66	6.73	0.07	1.3509	1.70	-0.2671	1.4329
9.73	5.55	6.78	6.85	0.07	1.6383	1.51	0.2467	1.7567
10.00	5.60	6.90	6.98	0.08	2.1783	1.31	-0.2158	1.0942
10.23	5.65	7.05	7.13	0.08	4.1904	1.27		
10.49	5.70	7.10	7.19	0.09	4.6920			

LogK_2(Average value) = 1.4280 ± 0.3312

Table 5:Point-wise method,Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	Log$(\frac{n}{n-1})$	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430

$LogK_1$ **(Average value)** = 2.3059± 0.6153

Table 6:Point-wise method, Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log$(\frac{n-1}{2-n})$	Log K_2
9.73	5.55	6.33	6.42	0.09	0.9000	1.69		
10.00	5.60	6.47	6.58	0.11	1.2578	1.44	-0.4592	0.9808
10.23	5.65	6.62	6.84	0.12	1.6137	1.26	-0.2010	1.4610
10.49	5.70	6.80	6.92	0.12	2.1052	1.03		

$LogK_2$ **(Average value)** = 1.2209± 0.3398

Table 7:Point-wise method,Pb (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log$(\frac{n}{1-n})$	$LogK_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.60	0.05	0.8333	1.96	0.6989	2.6589

$\mathbf{LogK_1}$ **(Average value)** = 2.5832 ±0.1614

Table 8:Point-wise method,Pb-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log$(\frac{n-1}{2-n})$	$logK_2$
9.51	5.50	6.66	6.71	0.05	0.9650	1.67	-0.0237	1.1963
9.73	5.55	6.78	6.83	0.05	1.1702	1.44		
10.00	5.60	6.90	6.90	0.05	1.4864	1.22		
10.23	5.65	7.05	7.10	0.05	2.0190	1.09		
10.49	5.70	7.10	7.17	0.07	3.6492	1.00		

$\mathbf{LogK_2}$**(Average value)** = 1.1963

Table 9:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log $(\frac{n}{n-1})$	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.5477	2.3123
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	0.0272	2.2072
9.51	5.50	6.20	6.26	0.07	0.6417	1.89	0.2530	2.1430
9.73	5.55	6.40	6.40	0.07	0.7000	1.67	0.3680	2.0380

$LogK_1$ **(Average value)** = 2.2364 ± 0.1602

Table 10:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log$(\frac{n-1}{2-n})$	Log K_2
10.00	5.60	6.47	6.55	0.08	1.9503	1.41		
10.23	5.65	6.62	6.72	0.11	1.4792	1.26	-0.0361	1.2239

$LogK_2$ **(Average value)** = 1.2239

Table 11:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log$(\frac{n}{n-1})$	$LogK_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4290	2.2110
8.72	5.35	6.37	6.39	0.02	0.2858	2.42	-0.3978	2.0222
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

$\mathbf{LogK_1}$ **(Average value)=**2.1382**±**0.1046

Table 12:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$\log(\frac{n-1}{2-n})$	$LogK_2$
9.51	5.55	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.84	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.93	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.10		
10.49	5.70	7.10	7.18	0.07	3.6492	0.83		

$LogK_2$(Average value) = 1.5453 **±** 0.3450

Table 13:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$Log(\frac{n}{n-1})$	$Log\ K_1$
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.3477	2.3123
9.00	5.40	6.00	6.04	0.04	0.3236	2.38	-0.3202	2.0598
9.22	5.45	6.10	6.15	0.05	0.4297	2.17	-0.1230	2.0470
9.51	5.50	6.20	6.26	0.06	0.5500	1.89	0.0871	1.9771
9.73	5.55	6.33	6.40	0.07	0.7000	1.67	0.3680	2.0380

$LogK_1$ **(Average value)** = 2.1568 ± 0.2069

Table 14:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$Log(\frac{n-1}{2-n})$	$Log\ K_2$
10.00	5.60	6.47	6.55	0.08	0.9148	1.41		
10.23	5.65	6.62	6.71	0.09	1.2102	1.20	-0.5749	0.6251
10.49	5.70	6.80	6.92	0.09	1.5968	1.03	0.1703	1.2003

$LogK_2$ **(Average value)** = 0.9127± 0.4070

Table15:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$Log(\frac{n}{1-n})$	$LogK_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4210	2.2190
8.72	5.35	6.37	6.40	0.03	0.4286	2.42	-0.1249	2.2951
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.96	0.3010	2.2610
9.51	5.55	6.66	6.70	0.04	0.7720	1.67	0.5297	2.1997

$LogK_1$ (Average value) = 2.2108± 0.0825

Table 16:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$Log(\frac{n-1}{2-n})$	$Log\ K_2$
9.73	5.55	6.78	6.83	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.95	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.09		
10.49	5.70	7.10	7.16	0.06	3.1429	0.89		

$LogK_2$ **(Average value)** = 1.5453± 0.3450

Table 17:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$Log(\frac{n}{n-1})$	$Log\ K_1$
8.50	5.30	5.81	5.86	0.05	0.3717	2.88	-0.2280	2.6520
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.06	0.06	0.4853	2.38	-0.0255	2.3545
9.22	5.45	6.10	6.16	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430
9.73	5.55	6.33	6.41	0.08	0.8000	1.69	0.6020	2.2920

$LogK_1$ **(Average value)** = 2.2516± 0.5380

Table 18:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$\text{Log}(\frac{n-1}{2-n})$	Log K_2
10.00	5.60	6.47	6.57	0.10	1.1434	1.43		
10.23	5.65	6.62	6.72	0.10	1.3448	1.23	-0.2788	0.9512
10.49	5.70	6.80	6.90	0.10	1.7742	1.03	0.5351	1.5651

LogK_2 **(Average value)** = 1.2581± 0.4340

Table 19: Stepwise and overall Stability constants of thehydrolysed and unhydrolysed divalent metal (II) complexes

Chelates	**LogK₁**	**LogK₂**	**Logβ**
[Cu (Hydrolysed PSHA-1)$_2$]	2.4788	1.4280	3.9068
[Pb (Hydrolysed PSHA-1)$_2$]	2.5832	1.1963	3.7795
[Cd (Hydrolysed PSHA-1)$_2$]	2.2108	1.5453	3.7561
[Mg (Hydrolysed PSHA-1)$_2$]	2.1382	1.5453	3.6835
[Cu (Unhydrolysed PSHA-1)$_2$]	2.3059	1.2209	3.5268
[Pb (Unhydrolysed PSHA-1)$_2$]	2.2364	1.2239	3.4603
[Cd (Unhydrolysed PSHA-1)$_2$]	2.2516	1.2581	3.5097
[Mg (Unydrolysed PSHA-1)$_2$]	2.1568	0.9127	3.0695

The results obtained (Table19) shows the stepwise and overall stability constants to be not high indicating low stability of the complexes, because the solubility of most metal ions in the basic pH range is minimal due to metal hydroxide precipitation (Karimi, 2017). In general, the stepwise stability constants (K_1 and K_2) follow the order $K_1 > K_2$ for the copper, lead, magnesium and cadmium complexes respectively. The steady decrease of the values with increasing number of ligands is in agreement with the prediction made by researchers (Na'aliya, 2013). The decrease could be attributed to the fact that as the number of the ligands (Humate ions) that enters the coordination zone increases the aqua molecules available for replacement by the ligands become less. Thus, the metal ions become less electron loving with progressive intake of the ligand and this results in the decrease in the values of the constants (Na'aliya, 2013). Also the stability of the complexes is influenced by the size and number of the chelate rings(Mackay and Mackay,2002).All the complexes form rings in their structure as humate, a bidentate ligand, bond the metal ions in the ratio 1:2 (Boguta and Sokolowska, 2016) forming chelate rings. The values of the overall stability constants (logβ) obtained for humate complexes are not high indicating low stability as the values are not high. LogK values for copper-humates (Table 3 to 6) obtained in this study are lower than those reported for the complexes of humic acids (Pandey *et al*., 2015; Dinu, 2013; Kaschl *et al*., 2010 and Gilbeto and Jorg, 2001). The values of LogK(Table 7 to 10) forlead-humates are lower than those reported for the lead in the literature (Dinu, 2013; Gilbeto and Jorg 2001). Log K values(Table 11 to 14) for magnesium-humates obtained in this study are close to those reported by (Pandey *et al*., 2015). Log K values of cadmium-humates (Table 15 to 18) obtained in this work near to the one reported by (Dinu, 2013 and Pandey *et al*., 2015).The difference between the reported values and the values obtained in this study might be probably as a result of acid hydrolysis of humic acid. The values of the overall stability constants (log β) of the copper humates complexes presented in Table 19 is high than that of other metal humate complexes, show relatively high stability of Cu-HA complexes, show the following order of stability: Cu >Pb> Cd > Mg; which are in close agreement to the findings of (Dinu, 2013 and Pandey *et al*., 2015).The high stability of Cu-humate chelate could be attributed to the existence of coordinate covalent bond between the complexing agents and the Cu^{2+} ions. Since, Cu^{2+} being a metal of the transitional series with $3d^9$ electronic configurations can accept the electrons from the complexing agents. Similarly,the low stabilities of Pb,Cd and Mg -complexes could be explained by that Pb^{2+} with $6s^2$, Cd^{2+} with $4d^{10}$ and Mg^{2+} with $2p^6$ their electronic configuration has a completely filled d,p and s orbitals. Moreover, the stabilities of metal ions with hydrolysed humic acid from peat soil were higher than those with unhydrolysed humic acid from peat soil; which is ascribed to the high content of acidity in hydrolysed humic acid than unhydrolysed humic acid.

CONCLUSION

The values of logK for Cu(II) hydrolysed humic acid complex was higher followed by Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes as compared with metal(II) unhydrolysed humic acid complexes . This indicates acid hydrolysis of humic acid can enhance the complexation behavior of humic acid with metal (II) ions. However, the higher values of logβ for Cu(II), Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes indicates more stable stepwise complexes formed as compared with Cu(II), Pb(II), Cd(II) and Mg(II) unhydrolysed humic acid complexes.

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STABILITY CONSTANTS OF COMPLEXES OF METAL IONS WITH PEATSOIL HUMIC ACIDS UNDER NON-ACID-CONDITIONS

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ABSTRACT

Stability constants of complexes of four divalent metal ions viz. Cu^{2+}, Pb^{2+},Mg^{2+} and Cd^{2+} with humic acids (HA) were determined by potentiometric titration of humic acids with the corresponding salt of the divalent metals in aqueous media under non-acid-condition. The log K (logarithm of the stability constant) ranged from 1.0942 to 2.7471 for metal-humic acid complexes were determined using point-wise computational method. The order of stability constants were obtained as follows: Cu >Pb> Cd > Mg for metal -HA complexes respectively, indicating a higher degree of complexation with Cu metal ion.

Keywords: stability constant, humic acid, potentiometric titration, divalent metals, acid hydrolysis.

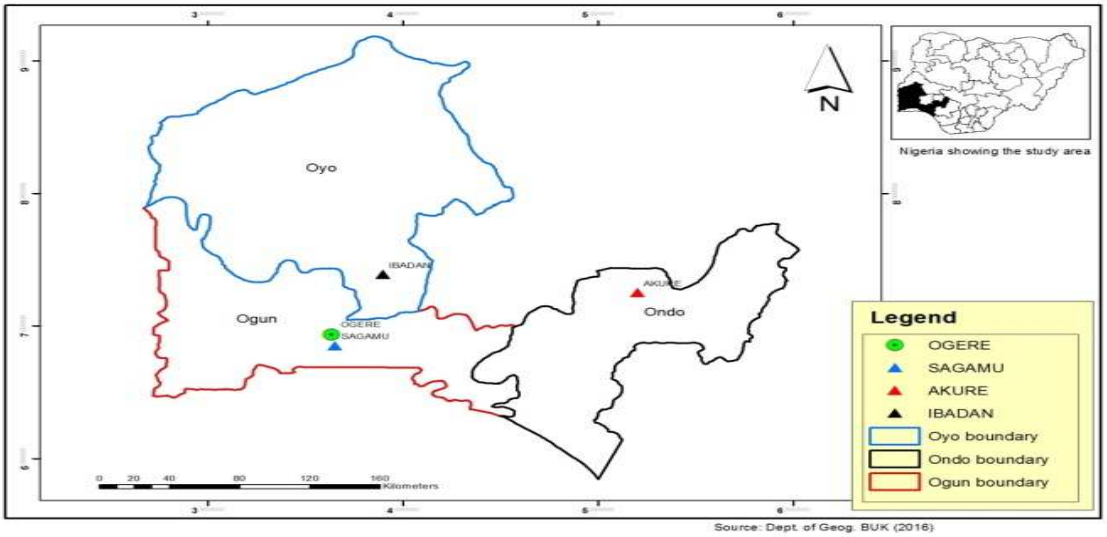
NTRODUCTION

The stability constant of a complex is the numerical expression of its stability and provides a quantitative measure of affinity of the metal ion to the complexing agent. An understanding of the relative stability of metal-complexes helps in predicting the behavior of metal ions in the soil (Ram and Raman, 1982). Extensive researches has been done to determine the stability constants of the complexes formed between humic acid (HA) with a number of metal ions. Ashok *et al*., (2000) reported that humic acid with hydroxyl, phenoxyl and carboxyl reactive groups can form coordination compound with metal ions at pH 3.5. The stability constants(Log K) for different metal-humic acid complexes indicated the following order of the stabilities of complexes formed between humic acid and metal ion, Cu >Fe >Pb> Ni > Co > Ca > Cd > Zn >Mn> Mg. Andelkovic *et al*., (2010) investigated the binding of Cd(II) to soil humic acid at pH 6.5 and in 0.1M KNO_3 ionic medium. The stability constant for binding indicating greater stability in the case when carboxyl groups are involved in complexation reaction. Kostic *et al*.,(2012) investigated the complexation of humic acid with certain heavy metal ions (Co(II), Ni(II),Cu(II), Zn(II), and Pb(II). The experiment was performed at 25°C, at pH 4.0 and ionic strength of 0.01M. Stability constant of complex between Pb(II) ions and humic acid is greater than stability constants of other investigated metal-humate complexes. Bogata and Sokolowska (2016) analyses the interaction between humic acids from different soils and Zn (II) ions at wide concentration ranges and at pH 5. Studies have showed significant impact of Zn concentration, pH and some properties of humic acids with zinc.But all of these studies were limited to acidic pH range. Therefore, the present study was carried out to determine and compare the stability constants of complexes of metal ions with hydrolysed peat soil humic acid and unhydrolysed peat soil humic under non-acid conditions.

MATERIALS AND METHODS

Analytical grade chemicals used includes hydrochloric acid (HCl), nitric acid (HNO_3), sodium hydroxide (NaOH), lead nitrate $Pb(NO_3)_2$, copper nitrate $Cu(NO_3)_2.3H_2O$, cadmium nitrate $Cd(NO_3)_2.4H_2O$, magnesium nitrate $Mg(NO_3)_2.6H_2O$, potassium nitrate (KNO_3), calcium chloride ($CaCl_2$), (sigma-Aldrich). Dowex 50WX8, (20-50 mesh) from Fluka.

Area of study



Source: Dept. of Geog. BUK (2016)

Figure 1: Map showing the sampling point at Sagamu Town, Ogun State.

Description of Sampling Area

Sagamu has geographical coordinates between 6°50′ north; 3° 38′ east is located in south western region of Nigeria. The region has tropical wet and dry climate with a lengthy wet season and relatively constant temperatures throughout the course of the year. Wet season runs from March to October, November to December forms the region dry season. The vegetation type of the region is savannah which is really grassland with small bushes and occasional big trees. Grassland soils have substantially higher organic matter content than forest soils (Novackova, 2011).

Sample Collection

The Peatsoil samples were collected from four different sampling points (0-10cm depth) in Sagamu into polyethylene bag with plastic spoons. Samples were taken to the laboratory, extraneous materials were removed; the samples were air-dried, crushed and ground to a fine powder in a mortar passed through a 0.20mm sieve. The samples were kept for analysis.

Isolation and purification of humic acid from peat soil sample

Peatsoil sample (100g) was mixed with 1000 cm^3 of 0.1M NaOH solution, shaken for 3hours and left to stand overnight. Dark-coloured supernatant was obtained and decanted from solid residue. The dark-coloured supernatant was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 6 hours. Yellowish brown supernatant and dark-brown precipitate were obtained. The yellowish brown supernatant was decanted followed by centrifuge and discarded. The dark-brown precipitate was mixed with $500cm^3$of 0.1M NaOH solution followed by passing through dowex resin. The dark-brown solution was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 3 hours. The dark-brown precipitate was washed several times with deionized water. The supernatant was treated with $AgNO_3$ solution until no white precipitate observed. The humic acid was transferred to weighed crucible and dried at 60°C in an oven for 12 hours. The humic acid was cooled and dried in the desiccator, weighed and recorded. The obtained humic acid was dried again at 60°C for additional 6 hours cooled and dried in the desiccator, weighed and recorded constant weight was obtained (Baruah *et al*., 2015).

FT-IR analysis

FT-IR spectra of humic acid sample was analysed using Carry 630 FT-IR Agilent Technologies.

Unhydrolysed compost humic acid

The unhydrolysed humic acid was obtained after isolation and purification of compost humic acid and kept for investigation.

Acid hydrolysis of Peatsoil acid

Peatsoil humic acid sample (1g) was refluxed for 12 hours at (160°C) with $50cm^3$ of 6M HCl. The mixture was allowed to cool, decanted, and centrifuged after hydrolysis. The insoluble residues were washed with distilled water via centrifugation several times, and the supernatant was treated with $AgNO_3$ solution until no white precipitate was observed. The residue was thoroughly dried over $CaCl_2$ in a desiccator at room temperature (Chefetz *et al*., 2002). Finally, the obtained hydrolysed humic acid was kept for investigation.

Potentiometric Titrations

Potentiometric measurements were carried out using a pH-meter Jenway (model 3510) with combine electrode, the sensitivity of the pH - meter is 0.01 units. The pH meter was switched on half an hour before starting the titration for initial warm up of the instrument. The instrument was calibrated with an aqueous standard buffer solution of pH 4.00 and 10.0 (borate buffer) prepared from a "Qualigens" buffer tablets.

The following sets of solutions were prepared in a 250cm^3 volumetric flask separately for pH metric titrations.

(i) 5 cm^3 0.1 M HCl + 40 cm^3 deionized water

(ii) 5 cm^3 0.1 M HCl + 39 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid

(iii) 5 cm^3 0.1 M HCl + 37 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid + 2 cm^3 0.01 M Cu(II)

The solutions were titrated against standardized 0.110MNaOH separately. The total volume of each mixture was adjusted to 50 cm^3 and the ionic strength of the solutions was maintained constant at by adding appropriate amount of stock solution of 1M KNO$_3$ (Gamal, 2015; Omar and Ali, 2015). A magnetic stirrer was used to achieve thorough mixing of the interacting solutions at 550 rpm. The same set of experimental conditions was applied for potentiometric titration of remaining samples.

Evaluation of pKa of Hydrolysed peat soil Humic Acids

The proton-ligand formation number n$_\mathbf{A}$ were calculated by Irving and Rossotti expression (Omar and Ali, 2015).

$$nA = Y - \frac{(V2-V1)(No-Eo)}{(Vo+V1)TcL} \quad \text{......................................1}$$

Where: Y is number of dissociable proton, (V$_2$-V$_1$) is the measure of displacement of the ligand curve relative to acid curve, N^o and E^o are the resultant concentration of alkali solution, free acid solution, T$_{cL}$^{o} is the total ligand concentration, V^o is the total volume of titration solution,V$_1$ is the volume of alkali added to acid solution,V$_2$ is the volume of alkali added to acid solution + ligand solution, acid dissociation constants (pKa - values) of ligand were calculated by algebraic method point wise calculation (Tables 1). The dissociation constants (pKa) were calculated according to the following relation:

$$pKa = pH + \log\left(\frac{nA}{1-nA}\right) \quad \text{..............................2}$$

Where: pKa is the acid dissociation constant, n$_A$is the Proton-ligand formation number and pH is the pH-values (Omar and Ali, 2015).

Determination of metal-ligand stability constants (log K) of complexes

The potentiometric measurement for the determination of stability constant of a complex in solution is based on the fact that the redox potential of the couple $\frac{M^{+(m-n)}}{M^{+m}}$ is shifted significantly on complexation of the metal ion with the ligand. This method involves change in hydrogen ion concentration [H$^+$] due to the displacement or association of one or more protons taking place during complexation reaction. This change can be found out by titrating the solutions containing free acid, acid with ligand, and acid with ligand and metal ion, individually against a standard alkali solution at a constant ionic strength or temperature. Either ionic strength or temperature may be varied for different sets of solutions. In all the cases, the change in the pH of the solution is measured after each addition of a known amount of alkali to the reaction cell which contains the reaction mixture. The titration curves are then drawn by plotting the measured pH values against the corresponding volume of alkali added and the stability constants of the complexes are determined from the titration curves by employing pH-metric titration technique given by (Irving and Rossoti).

Metal-ligand stability constants (Log K) were determined by using the following relations:

$$\bar{n} = \frac{(V_3 - V_2)(E^0 + N^0)}{(V^0 + V_2)\bar{n}_A T_m^0} \quad \text{..3}$$

and

$$PL = \log_{10}\left\{\frac{1 + \beta_n^H \dfrac{1}{[anti\ \log pH]^n}}{T_L^0 - \bar{n}T_m^0} X \frac{(V^0 + V_3)}{V^0}\right\} \quad \text{...4}$$

Where $T_{L,}$ T^{o}, E°, and V^{o}havethe same significance as in equation (1) above, T_m denotes the total concentration of metal present in solution, V_3 is the volume of metal ions present in solution and β^H is the overall proton ligand stability constant. The metal-ligand stability constants (log K) were determined by employing point wise computational Method (eq. 5 and 6).

$$\text{LogK}_1 = \log\left(\frac{n}{1-n}\right) + \text{pL} \qquad \text{.............}5$$

$$\text{LogK}_2 = \log\left(\frac{1-n}{2-n}\right) + \text{pL}\text{.......................}6$$

Where: Log K is the metal-ligand stability constant, pL is the Free ligand exponent function, **n** is the Average number of ligand attached with metal ion (Janrao*et al.*, 2014).The results obtained were analyzed by an ORIGIN 2016 program using titration data and then the proton-ligand stability constants (pKa) and Metal-ligand stability constant (LogK) calculated (Omar and Ali, 2015).

RESULTS AND DISCUSSION

Fourier transformed infrared (FT-IR) spectra of isolated humic acid from peat soils Figure 2 had distinct clear absorption bands indicating the presence of major humic acid structural elemental groups such as H bonded OH ($3680cm^{-1}$ peak), C=O of carbonyl ($1721cm^{-1}$ peak), functional groups of aliphatic components CH_2 ($2918cm^{-1}$ peak) and C-O stretching of polysaccharide ($1168cm^{-1}$ peak). The positions of the absorption bands of the spectra fell within typical major absorption bands of humic acid which is at frequencies 3680, 2918, 1721, 1168 cm^{-1}. The first peak centred in the vicinity of 3680 cm^{-1} region is attributed to phenol OH group bounded by intermolecular H bonds. The $2918cm^{-1}$ band usually has absorption maximum at 2918 cm^{-1} which is due to C–H stretching of alkane group (CH_2). The next major absorption band is 1721 cm^{-1}. This band has been commonly ascribed to C=O stretching of mainly carboxyl group (COOH) with trace amount of ketones. The last peak was observed at 1168 cm^{-1} due to C–O stretching of polysaccharides and this peak appeared also in the spectra of humic acid from peat soil. The FTIR spectra of the isolated humic acid contained all major characteristic absorption peaks of humic acid. These absorption peaks indicated the presence of the major structural elements of humic acid namely H bonded OH, C=C of aromatic ring, C=O of carbonyl group (both carboxyl and ketonic), CH_2 group. This strongly supports the presence of humic acid.

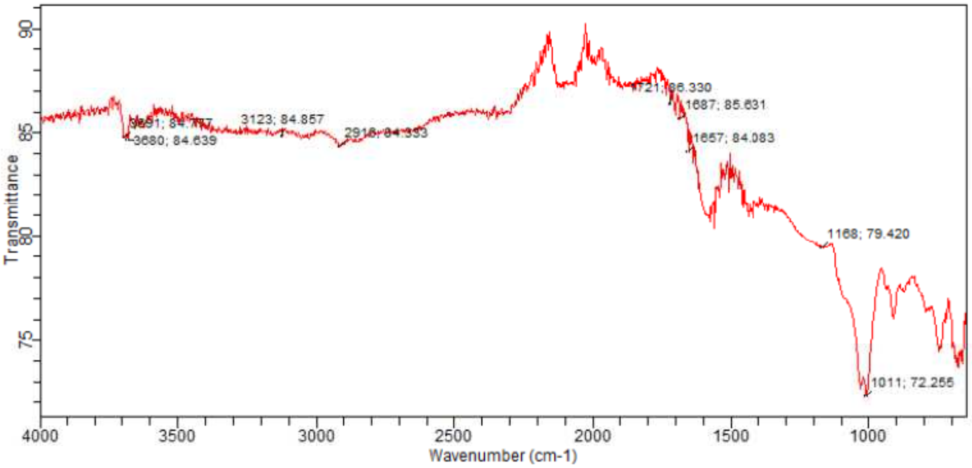


Fig. 2 : FT-IR spectraof peatsoilhumic acid (PSHA)

Evaluation of acid dissociation constant (pka) of acid hydrolysed peat soil humicacid at phenolic group

The value of the dissociation constant of the peat soil humic acid (PSHA) that underwent acidhydrolysis studied was found to be 8.9299 as shown Table 1, which is lower than the literaturevalues reported by Almeida and Szpoganics, (2015), Borges *et al.*, (2005); Badr *et al.*, (2012)and Fernandes *et al*,.(2009) of 9.73, 9.47 and 10.30. The difference between the obtained valuesand the reported values in this study might be probably as a result of acid hydrolysis of humicacid.

Table 1: PKa of (Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	V$_2$-V$_1$	nA	log($\frac{nA}{1-nA}$)	pKa
8.50	5.30	6.29	0.99	0.3594	-0.2510	8.2490
8.72	5.35	6.37	1.02	0.3400	-0.2880	8.4320
9.00	5.40	6.46	1.06	0.3141	-0.3391	8.6609
9.22	5.45	6.55	1.10	0.2882	-0.3927	8.8273
9.51	5.50	6.66	1.16	0.2494	-0.4786	9.0314
9.73	5.55	6.78	1.23	0.2041	-0.5910	9.1390
10.00	5.60	6.90	1.30	0.1589	-0.7238	9.2762
10.23	5.65	7.05	1.40	0.0941	-0.9835	9.2465
10.49	5.70	7.10	1.40	0.0941	-0.9835	9.5065

Average pKa = 8.9299 ± 0.4186

Table 2: PKa of (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	V$_2$-V$_1$	nA	Log($\frac{nA}{1-n}$)	pKa
8.50	5.30	5.81	0.51	0.6619	0.2919	8.7919
8.72	5.35	5.90	0.55	0.6357	0.2418	8.9618
9.00	5.40	6.00	0.60	0.6029	0.1813	9.1813
9.22	5.45	6.10	0.65	0.5701	0.1226	9.3426
9.51	5.50	6.20	0.70	0.5376	0.0654	9.5754
9.73	5.55	6.33	0.78	0.4851	-0.0259	9.7041
10.00	5.60	6.47	0.87	0.4262	-0.1291	9.8709
10.23	5.65	6.62	0.99	0.3609	-0.2481	9.9819
10.49	5.70	6.80	1.10	0.2759	-0.4690	10.0210

Average pKa = 9.4923± 0.4410

Metal-ligand stability constant (Log K)

The stabilityconstants require the accurate values of proton-ligand stability constants (Anil and Maroti, 2008). Metal titration curves crossed over ligand titration curve indicated the formation of complex upon proton release (Santosh, *et al.*, 2011). If the values of n- are within range 0.2-0.8 and 1.2-18 this indicates the formation of 1:1 and 1:2 complexes (Sayyed and Mazahar, 2012).

The metal (II)-humate stepwise stability constants (log k) at phenolic group (Tables 3-18)

Table 3: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	log($\frac{n}{1-n}$)	LogK$_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

LogK$_1$ (Average value) = 2.4788± 0.2203

Table 4: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	Log($\frac{n-1}{2-n}$)	LogK$_2$
9.51	5.50	6.66	6.73	0.07	1.3509	1.70	-0.2671	1.4329
9.73	5.55	6.78	6.85	0.07	1.6383	1.51	0.2467	1.7567
10.00	5.60	6.90	6.98	0.08	2.1783	1.31	-0.2158	1.0942
10.23	5.65	7.05	7.13	0.08	4.1904	1.27		
10.49	5.70	7.10	7.19	0.09	4.6920			

LogK$_2$(Average value) = 1.4280 ± 0.3312

Table 5:Point-wise method,Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	Log($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430

$LogK_1$ **(Average value)** = 2.3059± 0.6153

Table 6:Point-wise method, Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
9.73	5.55	6.33	6.42	0.09	0.9000	1.69		
10.00	5.60	6.47	6.58	0.11	1.2578	1.44	-0.4592	0.9808
10.23	5.65	6.62	6.84	0.12	1.6137	1.26	-0.2010	1.4610
10.49	5.70	6.80	6.92	0.12	2.1052	1.03		

$LogK_2$ **(Average value)** = 1.2209± 0.3398

Table 7:Point-wise method,Pb (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n}{1-n}$)	$LogK_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.60	0.05	0.8333	1.96	0.6989	2.6589

$LogK_1$ (Average value) = 2.5832 ±0.1614

Table 8:Point-wise method,Pb-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n-1}{2-n}$)	$logK_2$
9.51	5.50	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.83	0.05	1.1702	1.44		
10.00	5.60	6.90	6.90	0.05	1.4864	1.22	-0.0237	1.1963
10.23	5.65	7.05	7.10	0.05	2.0190	1.09		
10.49	5.70	7.10	7.17	0.07	3.6492	1.00		

$LogK_2$(Average value) = 1.1963

Table 9:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log ($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.5477	2.3123
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	0.0272	2.2072
9.51	5.50	6.20	6.26	0.07	0.6417	1.89	0.2530	2.1430
9.73	5.55	6.40	6.40	0.07	0.7000	1.67	0.3680	2.0380

$LogK_1$ **(Average value)** = 2.2364 ± 0.1602

Table 10:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
10.00	5.60	6.47	6.55	0.08	1.9503	1.41		
10.23	5.65	6.62	6.72	0.11	1.4792	1.26	-0.0361	1.2239

$LogK_2$ **(Average value)** = 1.2239

Table 11:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n}{n-1}$)	$LogK_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4290	2.2110
8.72	5.35	6.37	6.39	0.02	0.2858	2.42	-0.3978	2.0222
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

$LogK_1$ (Average value)=2.1382**±**0.1046

Table 12:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$\log(\frac{n-1}{2-n})$	$LogK_2$
9.51	5.55	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.84	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.93	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.10		
10.49	5.70	7.10	7.18	0.07	3.6492	0.83		

$LogK_2$(Average value) = 1.5453 **±** 0.3450

Table 13:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$Log(\frac{n}{n-1})$	$Log\ K_1$
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.3477	2.3123
9.00	5.40	6.00	6.04	0.04	0.3236	2.38	-0.3202	2.0598
9.22	5.45	6.10	6.15	0.05	0.4297	2.17	-0.1230	2.0470
9.51	5.50	6.20	6.26	0.06	0.5500	1.89	0.0871	1.9771
9.73	5.55	6.33	6.40	0.07	0.7000	1.67	0.3680	2.0380

$LogK_1$ **(Average value)** = 2.1568 ± 0.2069

Table 14:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$Log(\frac{n-1}{2-n})$	$Log\ K_2$
10.00	5.60	6.47	6.55	0.08	0.9148	1.41		
10.23	5.65	6.62	6.71	0.09	1.2102	1.20	-0.5749	0.6251
10.49	5.70	6.80	6.92	0.09	1.5968	1.03	0.1703	1.2003

$LogK_2$ **(Average value)** = 0.9127± 0.4070

Table15:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$Log(\frac{n}{1-n})$	$LogK_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4210	2.2190
8.72	5.35	6.37	6.40	0.03	0.4286	2.42	-0.1249	2.2951
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.96	0.3010	2.2610
9.51	5.55	6.66	6.70	0.04	0.7720	1.67	0.5297	2.1997

$LogK_1$ (Average value) = 2.2108± 0.0825

Table 16:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$Log(\frac{n-1}{2-n})$	$Log\ K_2$
9.73	5.55	6.78	6.83	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.95	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.09		
10.49	5.70	7.10	7.16	0.06	3.1429	0.89		

$LogK_2$ **(Average value)** = 1.5453± 0.3450

Table 17:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$Log(\frac{n}{n-1})$	$Log\ K_1$
8.50	5.30	5.81	5.86	0.05	0.3717	2.88	-0.2280	2.6520
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.06	0.06	0.4853	2.38	-0.0255	2.3545
9.22	5.45	6.10	6.16	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430
9.73	5.55	6.33	6.41	0.08	0.8000	1.69	0.6020	2.2920

$LogK_1$ **(Average value)** = 2.2516± 0.5380

Table 18:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$\text{Log}(\frac{n-1}{2-n})$	Log K_2
10.00	5.60	6.47	6.57	0.10	1.1434	1.43		
10.23	5.65	6.62	6.72	0.10	1.3448	1.23	-0.2788	0.9512
10.49	5.70	6.80	6.90	0.10	1.7742	1.03	0.5351	1.5651

LogK_2 **(Average value)** = 1.2581± 0.4340

Table 19: Stepwise and overall Stability constants of thehydrolysed and unhydrolysed divalent metal (II) complexes

Chelates	LogK_1	LogK_2	Logβ
[Cu (Hydrolysed PSHA-1)$_2$]	2.4788	1.4280	3.9068
[Pb (Hydrolysed PSHA-1)$_2$]	2.5832	1.1963	3.7795
[Cd (Hydrolysed PSHA-1)$_2$]	2.2108	1.5453	3.7561
[Mg (Hydrolysed PSHA-1)$_2$]	2.1382	1.5453	3.6835
[Cu (Unhydrolysed PSHA-1)$_2$]	2.3059	1.2209	3.5268
[Pb (Unhydrolysed PSHA-1)$_2$]	2.2364	1.2239	3.4603
[Cd (Unhydrolysed PSHA-1)$_2$]	2.2516	1.2581	3.5097
[Mg (Unydrolysed PSHA-1)$_2$]	2.1568	0.9127	3.0695

The results obtained (Table19) shows the stepwise and overall stability constants to be not high indicating low stability of the complexes, because the solubility of most metal ions in the basic pH range is minimal due to metal hydroxide precipitation (Karimi, 2017). In general, the stepwise stability constants (K_1 and K_2) follow the order $K_1 > K_2$ for the copper, lead, magnesium and cadmium complexes respectively. The steady decrease of the values with increasing number of ligands is in agreement with the prediction made by researchers (Na'aliya, 2013). The decrease could be attributed to the fact that as the number of the ligands (Humate ions) that enters the coordination zone increases the aqua molecules available for replacement by the ligands become less. Thus, the metal ions become less electron loving with progressive intake of the ligand and this results in the decrease in the values of the constants (Na'aliya, 2013). Also the stability of the complexes is influenced by the size and number of the chelate rings(Mackay and Mackay,2002).All the complexes form rings in their structure as humate, a bidentate ligand, bond the metal ions in the ratio 1:2 (Boguta and Sokolowska, 2016) forming chelate rings. The values of the overall stability constants (logβ) obtained for humate complexes are not high indicating low stability as the values are not high. LogK values for copper-humates (Table 3 to 6) obtained in this study are lower than those reported for the complexes of humic acids (Pandey *et al*., 2015; Dinu, 2013; Kaschl *et al*., 2010 and Gilbeto and Jorg, 2001). The values of LogK(Table 7 to 10) forlead-humates are lower than those reported for the lead in the literature (Dinu, 2013; Gilbeto and Jorg 2001). Log K values(Table 11 to 14) for magnesium-humates obtained in this study are close to those reported by (Pandey *et al*., 2015). Log K values of cadmium-humates (Table 15 to 18) obtained in this work near to the one reported by (Dinu, 2013 and Pandey *et al*., 2015).The difference between the reported values and the values obtained in this study might be probably as a result of acid hydrolysis of humic acid. The values of the overall stability constants (log β) of the copper humates complexes presented in Table 19 is high than that of other metal humate complexes, show relatively high stability of Cu-HA complexes, show the following order of stability: Cu >Pb> Cd > Mg; which are in close agreement to the findings of (Dinu, 2013 and Pandey *et al*., 2015).The high stability of Cu-humate chelate could be attributed to the existence of coordinate covalent bond between the complexing agents and the Cu^{2+} ions. Since, Cu^{2+} being a metal of the transitional series with $3d^9$ electronic configurations can accept the electrons from the complexing agents. Similarly,the low stabilities of Pb,Cd and Mg - complexes could be explained by that Pb^{2+} with $6s^2$, Cd^{2+} with $4d^{10}$ and Mg^{2+} with $2p^6$ their electronic configuration has a completely filled d,p and s orbitals. Moreover, the stabilities of metal ions with hydrolysed humic acid from peat soil were higher than those with unhydrolysed humic acid from peat soil; which is ascribed to the high content of acidity in hydrolysed humic acid than unhydrolysed humic acid.

CONCLUSION

The values of logK for Cu(II) hydrolysed humic acid complex was higher followed by Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes as compared with metal(II) unhydrolysed humic acid complexes . This indicates acid hydrolysis of humic acid can enhance the complexation behavior of humic acid with metal (II) ions. However, the higher values of logβ for Cu(II), Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes indicates more stable stepwise complexes formed as compared with Cu(II), Pb(II), Cd(II) and Mg(II) unhydrolysed humic acid complexes.

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STABILITY CONSTANTS OF COMPLEXES OF METAL IONS WITH PEATSOIL HUMIC ACIDS UNDER NON-ACID-CONDITIONS

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ABSTRACT

Stability constants of complexes of four divalent metal ions viz. Cu^{2+}, Pb^{2+},Mg^{2+} and Cd^{2+} with humic acids (HA) were determined by potentiometric titration of humic acids with the corresponding salt of the divalent metals in aqueous media under non-acid-condition. The log K (logarithm of the stability constant) ranged from 1.0942 to 2.7471 for metal-humic acid complexes were determined using point-wise computational method. The order of stability constants were obtained as follows: Cu >Pb> Cd > Mg for metal -HA complexes respectively, indicating a higher degree of complexation with Cu metal ion.

Keywords: stability constant, humic acid, potentiometric titration, divalent metals, acid hydrolysis.

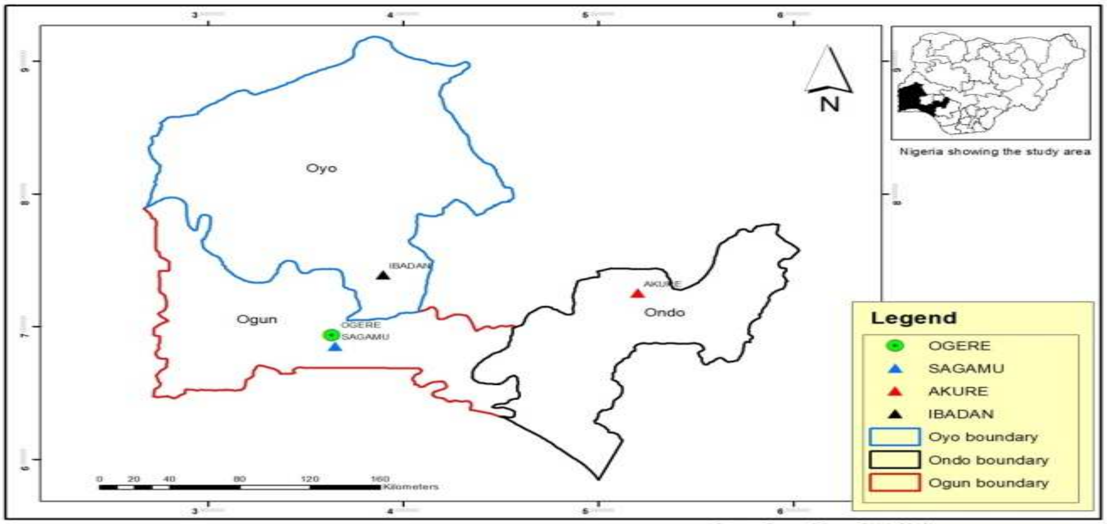
NTRODUCTION

The stability constant of a complex is the numerical expression of its stability and provides a quantitative measure of affinity of the metal ion to the complexing agent. An understanding of the relative stability of metal-complexes helps in predicting the behavior of metal ions in the soil (Ram and Raman, 1982). Extensive researches has been done to determine the stability constants of the complexes formed between humic acid (HA) with a number of metal ions. Ashok *et al*., (2000) reported that humic acid with hydroxyl, phenoxyl and carboxyl reactive groups can form coordination compound with metal ions at pH 3.5. The stability constants(Log K) for different metal-humic acid complexes indicated the following order of the stabilities of complexes formed between humic acid and metal ion, Cu >Fe >Pb> Ni > Co > Ca > Cd > Zn >Mn> Mg. Andelkovic *et al*., (2010) investigated the binding of Cd(II) to soil humic acid at pH 6.5 and in 0.1M KNO_3 ionic medium. The stability constant for binding indicating greater stability in the case when carboxyl groups are involved in complexation reaction. Kostic *et al*.,(2012) investigated the complexation of humic acid with certain heavy metal ions (Co(II), Ni(II),Cu(II), Zn(II), and Pb(II). The experiment was performed at 25°C, at pH 4.0 and ionic strength of 0.01M. Stability constant of complex between Pb(II) ions and humic acid is greater than stability constants of other investigated metal-humate complexes. Bogata and Sokolowska (2016) analyses the interaction between humic acids from different soils and Zn (II) ions at wide concentration ranges and at pH 5. Studies have showed significant impact of Zn concentration, pH and some properties of humic acids with zinc.But all of these studies were limited to acidic pH range. Therefore, the present study was carried out to determine and compare the stability constants of complexes of metal ions with hydrolysed peat soil humic acid and unhydrolysed peat soil humic under non-acid conditions.

MATERIALS AND METHODS

Analytical grade chemicals used includes hydrochloric acid (HCl), nitric acid (HNO_3), sodium hydroxide (NaOH), lead nitrate $Pb(NO_3)_2$, copper nitrate $Cu(NO_3)_2.3H_2O$, cadmium nitrate $Cd(NO_3)_2.4H_2O$, magnesium nitrate $Mg(NO_3)_2.6H_2O$, potassium nitrate (KNO_3), calcium chloride ($CaCl_2$), (sigma-Aldrich). Dowex 50WX8, (20-50 mesh) from Fluka.

Area of study



Source: Dept. of Geog. BUK (2016)

Figure 1: Map showing the sampling point at Sagamu Town, Ogun State.

Description of Sampling Area

Sagamu has geographical coordinates between 6°50′ north; 3° 38′ east is located in south western region of Nigeria. The region has tropical wet and dry climate with a lengthy wet season and relatively constant temperatures throughout the course of the year. Wet season runs from March to October, November to December forms the region dry season. The vegetation type of the region is savannah which is really grassland with small bushes and occasional big trees. Grassland soils have substantially higher organic matter content than forest soils (Novackova, 2011).

Sample Collection

The Peatsoil samples were collected from four different sampling points (0-10cm depth) in Sagamu into polyethylene bag with plastic spoons. Samples were taken to the laboratory, extraneous materials were removed; the samples were air-dried, crushed and ground to a fine powder in a mortar passed through a 0.20mm sieve. The samples were kept for analysis.

Isolation and purification of humic acid from peat soil sample

Peatsoil sample (100g) was mixed with 1000 cm^3 of 0.1M NaOH solution, shaken for 3hours and left to stand overnight. Dark-coloured supernatant was obtained and decanted from solid residue. The dark-coloured supernatant was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 6 hours. Yellowish brown supernatant and dark-brown precipitate were obtained. The yellowish brown supernatant was decanted followed by centrifuge and discarded. The dark-brown precipitate was mixed with 500cm^{3}of 0.1M NaOH solution followed by passing through dowex resin. The dark-brown solution was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 3 hours. The dark-brown precipitate was washed several times with deionized water. The supernatant was treated with $AgNO_3$ solution until no white precipitate observed. The humic acid was transferred to weighed crucible and dried at 60^{o}C in an oven for 12 hours. The humic acid was cooled and dried in the desiccator, weighed and recorded. The obtained humic acid was dried again at 60^{o}C for additional 6 hours cooled and dried in the desiccator, weighed and recorded constant weight was obtained (Baruah *et al*., 2015).

FT-IR analysis

FT-IR spectra of humic acid sample was analysed using Carry 630 FT-IR Agilent Technologies.

Unhydrolysed compost humic acid

The unhydrolysed humic acid was obtained after isolation and purification of compost humic acid and kept for investigation.

Acid hydrolysis of Peatsoil acid

Peatsoil humic acid sample (1g) was refluxed for 12 hours at (160^{o}C) with 50cm^3 of 6M HCl. The mixture was allowed to cool, decanted, and centrifuged after hydrolysis. The insoluble residues were washed with distilled water via centrifugation several times, and the supernatant was treated with $AgNO_3$ solution until no white precipitate was observed. The residue was thoroughly dried over $CaCl_2$ in a desiccator at room temperature (Chefetz *et al*., 2002). Finally, the obtained hydrolysed humic acid was kept for investigation.

Potentiometric Titrations

Potentiometric measurements were carried out using a pH-meter Jenway (model 3510) with combine electrode, the sensitivity of the pH - meter is 0.01 units. The pH meter was switched on half an hour before starting the titration for initial warm up of the instrument. The instrument was calibrated with an aqueous standard buffer solution of pH 4.00 and 10.0 (borate buffer) prepared from a "Qualigens" buffer tablets.

The following sets of solutions were prepared in a 250cm^3 volumetric flask separately for pH metric titrations.

(i) 5 cm^3 0.1 M HCl + 40 cm^3 deionized water
(ii) 5 cm^3 0.1 M HCl + 39 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid
(iii) 5 cm^3 0.1 M HCl + 37 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid + 2 cm^3 0.01 M Cu(II)

The solutions were titrated against standardized 0.110MNaOH separately. The total volume of each mixture was adjusted to 50 cm^3 and the ionic strength of the solutions was maintained constant at by adding appropriate amount of stock solution of 1M KNO$_3$ (Gamal, 2015; Omar and Ali, 2015). A magnetic stirrer was used to achieve thorough mixing of the interacting solutions at 550 rpm. The same set of experimental conditions was applied for potentiometric titration of remaining samples.

Evaluation of pKa of Hydrolysed peat soil Humic Acids

The proton-ligand formation number n$_\mathbf{A}$ were calculated by Irving and Rossotti expression (Omar and Ali, 2015).

$$nA = Y - \frac{(V2-V1)(No-Eo)}{(Vo+V1)TcL} \quad \text{..................................1}$$

Where: Y is number of dissociable proton, (V$_2$-V$_1$) is the measure of displacement of the ligand curve relative to acid curve, N^o and E^o are the resultant concentration of alkali solution, free acid solution, T$_{cL}$^{o} is the total ligand concentration, V^o is the total volume of titration solution,V$_1$ is the volume of alkali added to acid solution,V$_2$ is the volume of alkali added to acid solution + ligand solution, acid dissociation constants (pKa - values) of ligand were calculated by algebraic method point wise calculation (Tables 1). The dissociation constants (pKa) were calculated according to the following relation:

$$pKa = pH + \log\left(\frac{nA}{1-nA}\right) \quad \text{.............................2}$$

Where: pKa is the acid dissociation constant, n$_A$is the Proton-ligand formation number and pH is the pH-values (Omar and Ali, 2015).

Determination of metal-ligand stability constants (log K) of complexes

The potentiometric measurement for the determination of stability constant of a complex in solution is based on the fact that the redox potential of the couple $\frac{M^{+(m-n)}}{M^{+m}}$ is shifted significantly on complexation of the metal ion with the ligand. This method involves change in hydrogen ion concentration [H$^+$] due to the displacement or association of one or more protons taking place during complexation reaction. This change can be found out by titrating the solutions containing free acid, acid with ligand, and acid with ligand and metal ion, individually against a standard alkali solution at a constant ionic strength or temperature. Either ionic strength or temperature may be varied for different sets of solutions. In all the cases, the change in the pH of the solution is measured after each addition of a known amount of alkali to the reaction cell which contains the reaction mixture. The titration curves are then drawn by plotting the measured pH values against the corresponding volume of alkali added and the stability constants of the complexes are determined from the titration curves by employing pH-metric titration technique given by (Irving and Rossoti).

Metal-ligand stability constants (Log K) were determined by using the following relations:

$$\bar{n} = \frac{(V_3 - V_2)(E^0 + N^0)}{(V^0 + V_2)\bar{n}_A T_m^0} \quad \text{...3}$$

and

$$PL = \log_{10}\left\{\frac{1 + \beta_n^H \dfrac{1}{[anti\ \log pH]^n}}{T_L^0 - \bar{n}T_m^0} X \frac{(V^0 + V_3)}{V^0}\right\} \quad \text{..4}$$

Where $T_{L,}$ T^o, E°, and V^ohavethe same significance as in equation (1) above, T_m denotes the total concentration of metal present in solution, V_3 is the volume of metal ions present in solution and β^H is the overall proton ligand stability constant. The metal-ligand stability constants (log K) were determined by employing point wise computational Method (eq. 5 and 6).

$$\mathrm{Log}K_1 = \log\left(\frac{n}{1-n}\right) + pL \qquad \text{.............5}$$

$$\mathrm{Log}K_2 = \log\left(\frac{1-n}{2-n}\right) + pL\text{.......................6}$$

Where: Log K is the metal-ligand stability constant, pL is the Free ligand exponent function, **n** is the Average number of ligand attached with metal ion (Janrao*et al*., 2014).The results obtained were analyzed by an ORIGIN 2016 program using titration data and then the proton-ligand stability constants (pKa) and Metal-ligand stability constant (LogK) calculated (Omar and Ali, 2015).

RESULTS AND DISCUSSION

Fourier transformed infrared (FT-IR) spectra of isolated humic acid from peat soils Figure 2 had distinct clear absorption bands indicating the presence of major humic acid structural elemental groups such as H bonded OH (3680cm^{-1} peak), C=O of carbonyl (1721cm^{-1} peak), functional groups of aliphatic components CH_2 (2918cm^{-1} peak) and C-O stretching of polysaccharide (1168cm^{-1} peak). The positions of the absorption bands of the spectra fell within typical major absorption bands of humic acid which is at frequencies 3680, 2918, 1721, 1168 cm^{-1}. The first peak centred in the vicinity of 3680 cm^{-1} region is attributed to phenol OH group bounded by intermolecular H bonds. The 2918cm^{-1} band usually has absorption maximum at 2918 cm^{-1} which is due to C–H stretching of alkane group (CH_2). The next major absorption band is 1721 cm^{-1}. This band has been commonly ascribed to C=O stretching of mainly carboxyl group (COOH) with trace amount of ketones. The last peak was observed at 1168 cm^{-1} due to C–O stretching of polysaccharides and this peak appeared also in the spectra of humic acid from peat soil. The FTIR spectra of the isolated humic acid contained all major characteristic absorption peaks of humic acid. These absorption peaks indicated the presence of the major structural elements of humic acid namely H bonded OH, C=C of aromatic ring, C=O of carbonyl group (both carboxyl and ketonic), CH_2 group. This strongly supports the presence of humic acid.

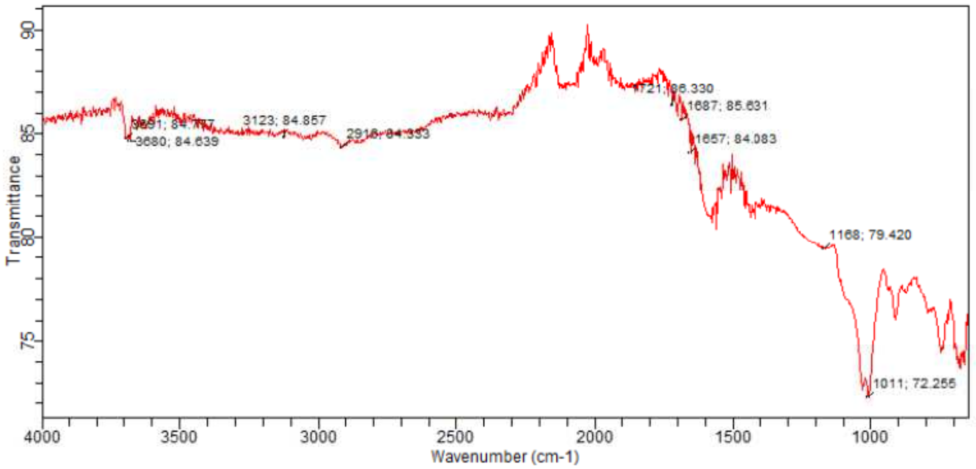


Fig. 2 : FT-IR spectraof peatsoilhumic acid (PSHA)

Evaluation of acid dissociation constant (pka) of acid hydrolysed peat soil humicacid at phenolic group

The value of the dissociation constant of the peat soil humic acid (PSHA) that underwent acidhydrolysis studied was found to be 8.9299 as shown Table 1, which is lower than the literaturevalues reported by Almeida and Szpoganics, (2015), Borges *et al*., (2005); Badr *et al*., (2012)and Fernandes *et al*,.(2009) of 9.73, 9.47 and 10.30. The difference between the obtained valuesand the reported values in this study might be probably as a result of acid hydrolysis of humicacid.

Table 1: PKa of (Hydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	log($\frac{nA}{1-nA}$)	pKa
8.50	5.30	6.29	0.99	0.3594	-0.2510	8.2490
8.72	5.35	6.37	1.02	0.3400	-0.2880	8.4320
9.00	5.40	6.46	1.06	0.3141	-0.3391	8.6609
9.22	5.45	6.55	1.10	0.2882	-0.3927	8.8273
9.51	5.50	6.66	1.16	0.2494	-0.4786	9.0314
9.73	5.55	6.78	1.23	0.2041	-0.5910	9.1390
10.00	5.60	6.90	1.30	0.1589	-0.7238	9.2762
10.23	5.65	7.05	1.40	0.0941	-0.9835	9.2465
10.49	5.70	7.10	1.40	0.0941	-0.9835	9.5065

Average pKa = 8.9299 ± 0.4186

Table 2: PKa of (Unhydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	Log($\frac{nA}{1-n}$)	pKa
8.50	5.30	5.81	0.51	0.6619	0.2919	8.7919
8.72	5.35	5.90	0.55	0.6357	0.2418	8.9618
9.00	5.40	6.00	0.60	0.6029	0.1813	9.1813
9.22	5.45	6.10	0.65	0.5701	0.1226	9.3426
9.51	5.50	6.20	0.70	0.5376	0.0654	9.5754
9.73	5.55	6.33	0.78	0.4851	-0.0259	9.7041
10.00	5.60	6.47	0.87	0.4262	-0.1291	9.8709
10.23	5.65	6.62	0.99	0.3609	-0.2481	9.9819
10.49	5.70	6.80	1.10	0.2759	-0.4690	10.0210

Average pKa = 9.4923± 0.4410

Metal-ligand stability constant (Log K)

The stabilityconstants require the accurate values of proton-ligand stability constants (Anil and Maroti, 2008). Metal titration curves crossed over ligand titration curve indicated the formation of complex upon proton release (Santosh, *et al.*, 2011). If the values of n- are within range 0.2-0.8 and 1.2-18 this indicates the formation of 1:1 and 1:2 complexes (Sayyed and Mazahar, 2012).

The metal (II)-humate stepwise stability constants (log k) at phenolic group (Tables 3-18)

Table 3: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n}{1-n}$)	$LogK_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

$LogK_1$ (Average value) = 2.4788± 0.2203

Table 4: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	Log($\frac{n-1}{2-n}$)	$LogK_2$
9.51	5.50	6.66	6.73	0.07	1.3509	1.70	-0.2671	1.4329
9.73	5.55	6.78	6.85	0.07	1.6383	1.51	0.2467	1.7567
10.00	5.60	6.90	6.98	0.08	2.1783	1.31	-0.2158	1.0942
10.23	5.65	7.05	7.13	0.08	4.1904	1.27		
10.49	5.70	7.10	7.19	0.09	4.6920			

$LogK_2$(Average value) = 1.4280 ± 0.3312

Table 5:Point-wise method,Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	Log($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430

$LogK_1$ **(Average value)** = 2.3059± 0.6153

Table 6:Point-wise method, Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
9.73	5.55	6.33	6.42	0.09	0.9000	1.69		
10.00	5.60	6.47	6.58	0.11	1.2578	1.44	-0.4592	0.9808
10.23	5.65	6.62	6.84	0.12	1.6137	1.26	-0.2010	1.4610
10.49	5.70	6.80	6.92	0.12	2.1052	1.03		

$LogK_2$ **(Average value)** = 1.2209± 0.3398

Table 7:Point-wise method,Pb (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n}{1-n}$)	$LogK_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.60	0.05	0.8333	1.96	0.6989	2.6589

$LogK_1$ (Average value) = 2.5832 ±0.1614

Table 8:Point-wise method,Pb-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n-1}{2-n}$)	$logK_2$
9.51	5.50	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.83	0.05	1.1702	1.44		
10.00	5.60	6.90	6.90	0.05	1.4864	1.22	-0.0237	1.1963
10.23	5.65	7.05	7.10	0.05	2.0190	1.09		
10.49	5.70	7.10	7.17	0.07	3.6492	1.00		

$LogK_2$(Average value) = 1.1963

Table 9:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log ($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.5477	2.3123
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	0.0272	2.2072
9.51	5.50	6.20	6.26	0.07	0.6417	1.89	0.2530	2.1430
9.73	5.55	6.40	6.40	0.07	0.7000	1.67	0.3680	2.0380

$LogK_1$ **(Average value)** = 2.2364 ± 0.1602

Table 10:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
10.00	5.60	6.47	6.55	0.08	1.9503	1.41		
10.23	5.65	6.62	6.72	0.11	1.4792	1.26	-0.0361	1.2239

$LogK_2$ **(Average value)** = 1.2239

Table 11:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n}{n-1}$)	$LogK_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4290	2.2110
8.72	5.35	6.37	6.39	0.02	0.2858	2.42	-0.3978	2.0222
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

$LogK_1$ (Average value)=2.1382±0.1046

Table 12:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n-1}{2-n}$)	$LogK_2$
9.51	5.55	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.84	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.93	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.10		
10.49	5.70	7.10	7.18	0.07	3.6492	0.83		

$LogK_2$(Average value) = 1.5453 **±** 0.3450

Table 13:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.3477	2.3123
9.00	5.40	6.00	6.04	0.04	0.3236	2.38	-0.3202	2.0598
9.22	5.45	6.10	6.15	0.05	0.4297	2.17	-0.1230	2.0470
9.51	5.50	6.20	6.26	0.06	0.5500	1.89	0.0871	1.9771
9.73	5.55	6.33	6.40	0.07	0.7000	1.67	0.3680	2.0380

$LogK_1$ **(Average value)** = 2.1568 ± 0.2069

Table 14:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
10.00	5.60	6.47	6.55	0.08	0.9148	1.41		
10.23	5.65	6.62	6.71	0.09	1.2102	1.20	-0.5749	0.6251
10.49	5.70	6.80	6.92	0.09	1.5968	1.03	0.1703	1.2003

$LogK_2$ **(Average value)** = 0.9127± 0.4070

Table15:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	Log($\frac{n}{1-n}$)	$LogK_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4210	2.2190
8.72	5.35	6.37	6.40	0.03	0.4286	2.42	-0.1249	2.2951
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.96	0.3010	2.2610
9.51	5.55	6.66	6.70	0.04	0.7720	1.67	0.5297	2.1997

$LogK_1$ (Average value) = 2.2108± 0.0825

Table 16:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
9.73	5.55	6.78	6.83	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.95	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.09		
10.49	5.70	7.10	7.16	0.06	3.1429	0.89		

$LogK_2$ **(Average value)** = 1.5453± 0.3450

Table 17:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.86	0.05	0.3717	2.88	-0.2280	2.6520
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.06	0.06	0.4853	2.38	-0.0255	2.3545
9.22	5.45	6.10	6.16	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430
9.73	5.55	6.33	6.41	0.08	0.8000	1.69	0.6020	2.2920

$LogK_1$ **(Average value)** = 2.2516± 0.5380

Table 18:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$\text{Log}(\frac{n-1}{2-n})$	Log K_2
10.00	5.60	6.47	6.57	0.10	1.1434	1.43		
10.23	5.65	6.62	6.72	0.10	1.3448	1.23	-0.2788	0.9512
10.49	5.70	6.80	6.90	0.10	1.7742	1.03	0.5351	1.5651

LogK_2 **(Average value)** = 1.2581± 0.4340

Table 19: Stepwise and overall Stability constants of thehydrolysed and unhydrolysed divalent metal (II) complexes

Chelates	**LogK_1**	**LogK_2**	**Logβ**
[Cu (Hydrolysed PSHA-1)$_2$]	2.4788	1.4280	3.9068
[Pb (Hydrolysed PSHA-1)$_2$]	2.5832	1.1963	3.7795
[Cd (Hydrolysed PSHA-1)$_2$]	2.2108	1.5453	3.7561
[Mg (Hydrolysed PSHA-1)$_2$]	2.1382	1.5453	3.6835
[Cu (Unhydrolysed PSHA-1)$_2$]	2.3059	1.2209	3.5268
[Pb (Unhydrolysed PSHA-1)$_2$]	2.2364	1.2239	3.4603
[Cd (Unhydrolysed PSHA-1)$_2$]	2.2516	1.2581	3.5097
[Mg (Unydrolysed PSHA-1)$_2$]	2.1568	0.9127	3.0695

The results obtained (Table19) shows the stepwise and overall stability constants to be not high indicating low stability of the complexes, because the solubility of most metal ions in the basic pH range is minimal due to metal hydroxide precipitation (Karimi, 2017). In general, the stepwise stability constants (K_1 and K_2) follow the order $K_1 > K_2$ for the copper, lead, magnesium and cadmium complexes respectively. The steady decrease of the values with increasing number of ligands is in agreement with the prediction made by researchers (Na'aliya, 2013). The decrease could be attributed to the fact that as the number of the ligands (Humate ions) that enters the coordination zone increases the aqua molecules available for replacement by the ligands become less. Thus, the metal ions become less electron loving with progressive intake of the ligand and this results in the decrease in the values of the constants (Na'aliya, 2013). Also the stability of the complexes is influenced by the size and number of the chelate rings(Mackay and Mackay,2002).All the complexes form rings in their structure as humate, a bidentate ligand, bond the metal ions in the ratio 1:2 (Boguta and Sokolowska, 2016) forming chelate rings. The values of the overall stability constants (logβ) obtained for humate complexes are not high indicating low stability as the values are not high. LogK values for copper-humates (Table 3 to 6) obtained in this study are lower than those reported for the complexes of humic acids (Pandey *et al.*, 2015; Dinu, 2013; Kaschl *et al.*, 2010 and Gilbeto and Jorg, 2001). The values of LogK(Table 7 to 10) forlead-humates are lower than those reported for the lead in the literature (Dinu, 2013; Gilbeto and Jorg 2001). Log K values(Table 11 to 14) for magnesium-humates obtained in this study are close to those reported by (Pandey *et al.*, 2015). Log K values of cadmium-humates (Table 15 to 18) obtained in this work near to the one reported by (Dinu, 2013 and Pandey *et al.*, 2015).The difference between the reported values and the values obtained in this study might be probably as a result of acid hydrolysis of humic acid. The values of the overall stability constants (log β) of the copper humates complexes presented in Table 19 is high than that of other metal humate complexes, show relatively high stability of Cu-HA complexes, show the following order of stability: Cu >Pb> Cd > Mg; which are in close agreement to the findings of (Dinu, 2013 and Pandey *et al.*, 2015).The high stability of Cu-humate chelate could be attributed to the existence of coordinate covalent bond between the complexing agents and the Cu^{2+} ions. Since, Cu^{2+} being a metal of the transitional series with $3d^9$ electronic configurations can accept the electrons from the complexing agents. Similarly,the low stabilities of Pb,Cd and Mg -complexes could be explained by that Pb^{2+} with $6s^2$, Cd^{2+} with $4d^{10}$ and Mg^{2+} with $2p^6$ their electronic configuration has a completely filled d,p and s orbitals. Moreover, the stabilities of metal ions with hydrolysed humic acid from peat soil were higher than those with unhydrolysed humic acid from peat soil; which is ascribed to the high content of acidity in hydrolysed humic acid than unhydrolysed humic acid.

CONCLUSION

The values of logK for Cu(II) hydrolysed humic acid complex was higher followed by Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes as compared with metal(II) unhydrolysed humic acid complexes . This indicates acid hydrolysis of humic acid can enhance the complexation behavior of humic acid with metal (II) ions. However, the higher values of logβ for Cu(II), Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes indicates more stable stepwise complexes formed as compared with Cu(II), Pb(II), Cd(II) and Mg(II) unhydrolysed humic acid complexes.

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STABILITY CONSTANTS OF COMPLEXES OF METAL IONS WITH PEATSOIL HUMIC ACIDS UNDER NON-ACID-CONDITIONS

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ABSTRACT

Stability constants of complexes of four divalent metal ions viz. Cu^{2+}, Pb^{2+},Mg^{2+} and Cd^{2+} with humic acids (HA) were determined by potentiometric titration of humic acids with the corresponding salt of the divalent metals in aqueous media under non-acid-condition. The log K (logarithm of the stability constant) ranged from 1.0942 to 2.7471 for metal-humic acid complexes were determined using point-wise computational method. The order of stability constants were obtained as follows: Cu >Pb> Cd > Mg for metal -HA complexes respectively, indicating a higher degree of complexation with Cu metal ion.

Keywords: stability constant, humic acid, potentiometric titration, divalent metals, acid hydrolysis.

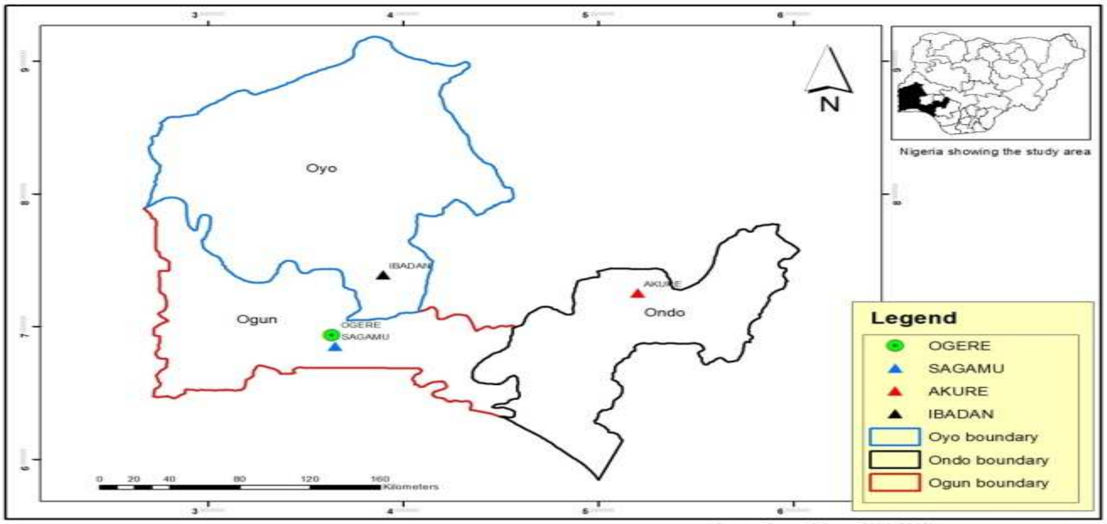
NTRODUCTION

The stability constant of a complex is the numerical expression of its stability and provides a quantitative measure of affinity of the metal ion to the complexing agent. An understanding of the relative stability of metal-complexes helps in predicting the behavior of metal ions in the soil (Ram and Raman, 1982). Extensive researches has been done to determine the stability constants of the complexes formed between humic acid (HA) with a number of metal ions. Ashok *et al.*, (2000) reported that humic acid with hydroxyl, phenoxyl and carboxyl reactive groups can form coordination compound with metal ions at pH 3.5. The stability constants(Log K) for different metal-humic acid complexes indicated the following order of the stabilities of complexes formed between humic acid and metal ion, Cu >Fe >Pb> Ni > Co > Ca > Cd > Zn >Mn> Mg. Andelkovic *et al.*, (2010) investigated the binding of Cd(II) to soil humic acid at pH 6.5 and in 0.1M KNO_3 ionic medium. The stability constant for binding indicating greater stability in the case when carboxyl groups are involved in complexation reaction. Kostic *et al.*,(2012) investigated the complexation of humic acid with certain heavy metal ions (Co(II), Ni(II),Cu(II), Zn(II), and Pb(II). The experiment was performed at 25°C, at pH 4.0 and ionic strength of 0.01M. Stability constant of complex between Pb(II) ions and humic acid is greater than stability constants of other investigated metal-humate complexes. Bogata and Sokolowska (2016) analyses the interaction between humic acids from different soils and Zn (II) ions at wide concentration ranges and at pH 5. Studies have showed significant impact of Zn concentration, pH and some properties of humic acids with zinc.But all of these studies were limited to acidic pH range. Therefore, the present study was carried out to determine and compare the stability constants of complexes of metal ions with hydrolysed peat soil humic acid and unhydrolysed peat soil humic under non-acid conditions.

MATERIALS AND METHODS

Analytical grade chemicals used includes hydrochloric acid (HCl), nitric acid (HNO_3), sodium hydroxide (NaOH), lead nitrate $Pb(NO_3)_2$, copper nitrate $Cu(NO_3)_2.3H_2O$, cadmium nitrate $Cd(NO_3)_2.4H_2O$, magnesium nitrate $Mg(NO_3)_2.6H_2O$, potassium nitrate (KNO_3), calcium chloride ($CaCl_2$), (sigma-Aldrich). Dowex 50WX8, (20-50 mesh) from Fluka.

Area of study



Source: Dept. of Geog. BUK (2016)

Figure 1: Map showing the sampling point at Sagamu Town, Ogun State.

Description of Sampling Area

Sagamu has geographical coordinates between 6°50′ north; 3° 38′ east is located in south western region of Nigeria. The region has tropical wet and dry climate with a lengthy wet season and relatively constant temperatures throughout the course of the year. Wet season runs from March to October, November to December forms the region dry season. The vegetation type of the region is savannah which is really grassland with small bushes and occasional big trees. Grassland soils have substantially higher organic matter content than forest soils (Novackova, 2011).

Sample Collection

The Peatsoil samples were collected from four different sampling points (0-10cm depth) in Sagamu into polyethylene bag with plastic spoons. Samples were taken to the laboratory, extraneous materials were removed; the samples were air-dried, crushed and ground to a fine powder in a mortar passed through a 0.20mm sieve. The samples were kept for analysis.

Isolation and purification of humic acid from peat soil sample

Peatsoil sample (100g) was mixed with 1000 cm^3 of 0.1M NaOH solution, shaken for 3hours and left to stand overnight. Dark-coloured supernatant was obtained and decanted from solid residue. The dark-coloured supernatant was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 6 hours. Yellowish brown supernatant and dark-brown precipitate were obtained. The yellowish brown supernatant was decanted followed by centrifuge and discarded. The dark-brown precipitate was mixed with 500$cm^3$of 0.1M NaOH solution followed by passing through dowex resin. The dark-brown solution was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 3 hours. The dark-brown precipitate was washed several times with deionized water. The supernatant was treated with $AgNO_3$ solution until no white precipitate observed. The humic acid was transferred to weighed crucible and dried at 60°C in an oven for 12 hours. The humic acid was cooled and dried in the desiccator, weighed and recorded. The obtained humic acid was dried again at 60°C for additional 6 hours cooled and dried in the desiccator, weighed and recorded constant weight was obtained (Baruah *et al*., 2015).

FT-IR analysis

FT-IR spectra of humic acid sample was analysed using Carry 630 FT-IR Agilent Technologies.

Unhydrolysed compost humic acid

The unhydrolysed humic acid was obtained after isolation and purification of compost humic acid and kept for investigation.

Acid hydrolysis of Peatsoil acid

Peatsoil humic acid sample (1g) was refluxed for 12 hours at (160°C) with 50cm^3 of 6M HCl. The mixture was allowed to cool, decanted, and centrifuged after hydrolysis. The insoluble residues were washed with distilled water via centrifugation several times, and the supernatant was treated with $AgNO_3$ solution until no white precipitate was observed. The residue was thoroughly dried over $CaCl_2$ in a desiccator at room temperature (Chefetz *et al*., 2002). Finally, the obtained hydrolysed humic acid was kept for investigation.

Potentiometric Titrations

Potentiometric measurements were carried out using a pH-meter Jenway (model 3510) with combine electrode, the sensitivity of the pH - meter is 0.01 units. The pH meter was switched on half an hour before starting the titration for initial warm up of the instrument. The instrument was calibrated with an aqueous standard buffer solution of pH 4.00 and 10.0 (borate buffer) prepared from a "Qualigens" buffer tablets.

The following sets of solutions were prepared in a 250cm^3 volumetric flask separately for pH metric titrations.

(i) 5 cm^3 0.1 M HCl + 40 cm^3 deionized water
(ii) 5 cm^3 0.1 M HCl + 39 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid
(iii) 5 cm^3 0.1 M HCl + 37 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid
+ 2 cm^3 0.01 M Cu(II)

The solutions were titrated against standardized 0.110MNaOH separately. The total volume of each mixture was adjusted to 50 cm^3 and the ionic strength of the solutions was maintained constant at by adding appropriate amount of stock solution of 1M KNO$_3$ (Gamal, 2015; Omar and Ali, 2015). A magnetic stirrer was used to achieve thorough mixing of the interacting solutions at 550 rpm. The same set of experimental conditions was applied for potentiometric titration of remaining samples.

Evaluation of pKa of Hydrolysed peat soil Humic Acids

The proton-ligand formation number n$_{\mathbf{A}}$ were calculated by Irving and Rossotti expression (Omar and Ali, 2015).

$$nA = Y- \frac{(V2-V1)(No-Eo)}{(Vo+V1)TcL} \text{ ....1}$$

Where: Y is number of dissociable proton, (V$_2$-V$_1$) is the measure of displacement of the ligand curve relative to acid curve, N^o and E^o are the resultant concentration of alkali solution, free acid solution, T$_{cL}{}^o$ is the total ligand concentration, V^o is the total volume of titration solution,V$_1$ is the volume of alkali added to acid solution,V$_2$ is the volume of alkali added to acid solution + ligand solution, acid dissociation constants (pKa - values) of ligand were calculated by algebraic method point wise calculation (Tables 1). The dissociation constants (pKa) were calculated according to the following relation:

$$pKa = pH + \log(\frac{nA}{1-nA}) \text{ ....2}$$

Where: pKa is the acid dissociation constant, n$_A$is the Proton-ligand formation number and pH is the pH-values (Omar and Ali, 2015).

Determination of metal-ligand stability constants (log K) of complexes

The potentiometric measurement for the determination of stability constant of a complex in solution is based on the fact that the redox potential of the couple $\frac{M^{+(m-n)}}{M^{+m}}$ is shifted significantly on complexation of the metal ion with the ligand. This method involves change in hydrogen ion concentration [H$^+$] due to the displacement or association of one or more protons taking place during complexation reaction. This change can be found out by titrating the solutions containing free acid, acid with ligand, and acid with ligand and metal ion, individually against a standard alkali solution at a constant ionic strength or temperature. Either ionic strength or temperature may be varied for different sets of solutions. In all the cases, the change in the pH of the solution is measured after each addition of a known amount of alkali to the reaction cell which contains the reaction mixture. The titration curves are then drawn by plotting the measured pH values against the corresponding volume of alkali added and the stability constants of the complexes are determined from the titration curves by employing pH-metric titration technique given by (Irving and Rossoti).

Metal-ligand stability constants (Log K) were determined by using the following relations:

$$\bar{n} = \frac{(V_3 - V_2)(E^0 + N^0)}{(V^0 + V_2)\bar{n}_A T_m^0} \text{ ....3}$$

and

$$PL = \log_{10}\{\frac{1 + \beta_n^H \frac{1}{[anti\ \log pH]^n}}{T_L^0 - \bar{n}T_m^0} X \frac{(V^0 + V_3)}{V^0}\} \text{ ....4}$$

Where $T_{L,}$ T^{o}, E°, and V^{o}havethe same significance as in equation (1) above, T_m denotes the total concentration of metal present in solution, V_3 is the volume of metal ions present in solution and β^H is the overall proton ligand stability constant. The metal-ligand stability constants (log K) were determined by employing point wise computational Method (eq. 5 and 6).

$LogK_1 = \log\left(\frac{n}{1-n}\right) + pL$ 5

$LogK_2 = \log\left(\frac{1-n}{2-n}\right) + pL$.......................6

Where: Log K is the metal-ligand stability constant, pL is the Free ligand exponent function, **n** is the Average number of ligand attached with metal ion (Janrao*et al*., 2014).The results obtained were analyzed by an ORIGIN 2016 program using titration data and then the proton-ligand stability constants (pKa) and Metal-ligand stability constant (LogK) calculated (Omar and Ali, 2015).

RESULTS AND DISCUSSION

Fourier transformed infrared (FT-IR) spectra of isolated humic acid from peat soils Figure 2 had distinct clear absorption bands indicating the presence of major humic acid structural elemental groups such as H bonded OH ($3680cm^{-1}$ peak), C=O of carbonyl ($1721cm^{-1}$ peak), functional groups of aliphatic components CH_2 ($2918cm^{-1}$ peak) and C-O stretching of polysaccharide ($1168cm^{-1}$ peak). The positions of the absorption bands of the spectra fell within typical major absorption bands of humic acid which is at frequencies 3680, 2918, 1721, 1168 cm^{-1}. The first peak centred in the vicinity of 3680 cm^{-1} region is attributed to phenol OH group bounded by intermolecular H bonds. The $2918cm^{-1}$ band usually has absorption maximum at 2918 cm^{-1} which is due to C–H stretching of alkane group (CH_2). The next major absorption band is 1721 cm^{-1}. This band has been commonly ascribed to C=O stretching of mainly carboxyl group (COOH) with trace amount of ketones. The last peak was observed at 1168 cm^{-1} due to C–O stretching of polysaccharides and this peak appeared also in the spectra of humic acid from peat soil. The FTIR spectra of the isolated humic acid contained all major characteristic absorption peaks of humic acid. These absorption peaks indicated the presence of the major structural elements of humic acid namely H bonded OH, C=C of aromatic ring, C=O of carbonyl group (both carboxyl and ketonic), CH_2 group. This strongly supports the presence of humic acid.

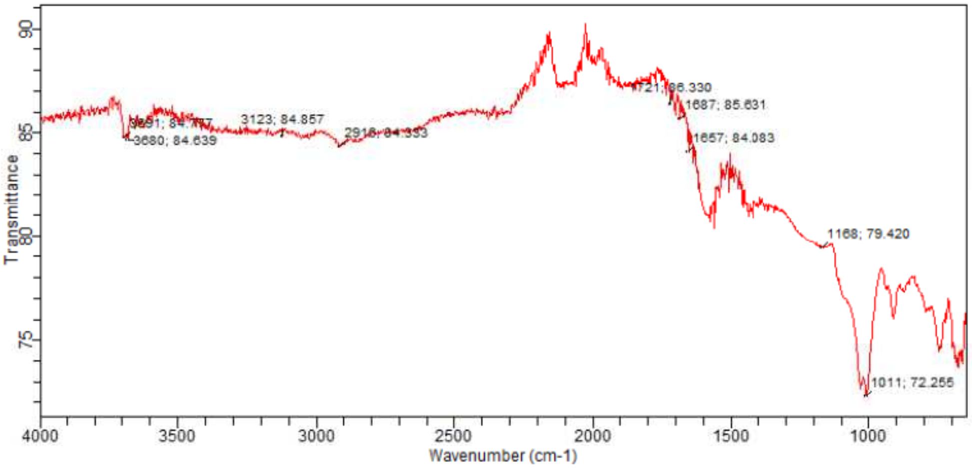


Fig. 2 : FT-IR spectraof peatsoilhumic acid (PSHA)

Evaluation of acid dissociation constant (pka) of acid hydrolysed peat soil humicacid at phenolic group

The value of the dissociation constant of the peat soil humic acid (PSHA) that underwent acidhydrolysis studied was found to be 8.9299 as shown Table 1, which is lower than the literaturevalues reported by Almeida and Szpoganics, (2015), Borges *et al*., (2005); Badr *et al*., (2012)and Fernandes *et al*,.(2009) of 9.73, 9.47 and 10.30. The difference between the obtained valuesand the reported values in this study might be probably as a result of acid hydrolysis of humicacid.

Table 1: PKa of (Hydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	log($\frac{nA}{1-nA}$)	pKa
8.50	5.30	6.29	0.99	0.3594	-0.2510	8.2490
8.72	5.35	6.37	1.02	0.3400	-0.2880	8.4320
9.00	5.40	6.46	1.06	0.3141	-0.3391	8.6609
9.22	5.45	6.55	1.10	0.2882	-0.3927	8.8273
9.51	5.50	6.66	1.16	0.2494	-0.4786	9.0314
9.73	5.55	6.78	1.23	0.2041	-0.5910	9.1390
10.00	5.60	6.90	1.30	0.1589	-0.7238	9.2762
10.23	5.65	7.05	1.40	0.0941	-0.9835	9.2465
10.49	5.70	7.10	1.40	0.0941	-0.9835	9.5065

Average pKa = 8.9299 ± 0.4186

Table 2: PKa of (Unhydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	Log($\frac{nA}{1-n}$)	pKa
8.50	5.30	5.81	0.51	0.6619	0.2919	8.7919
8.72	5.35	5.90	0.55	0.6357	0.2418	8.9618
9.00	5.40	6.00	0.60	0.6029	0.1813	9.1813
9.22	5.45	6.10	0.65	0.5701	0.1226	9.3426
9.51	5.50	6.20	0.70	0.5376	0.0654	9.5754
9.73	5.55	6.33	0.78	0.4851	-0.0259	9.7041
10.00	5.60	6.47	0.87	0.4262	-0.1291	9.8709
10.23	5.65	6.62	0.99	0.3609	-0.2481	9.9819
10.49	5.70	6.80	1.10	0.2759	-0.4690	10.0210

Average pKa = 9.4923± 0.4410

Metal-ligand stability constant (Log K)

The stabilityconstants require the accurate values of proton-ligand stability constants (Anil and Maroti, 2008). Metal titration curves crossed over ligand titration curve indicated the formation of complex upon proton release (Santosh, *et al*., 2011). If the values of n- are within range 0.2-0.8 and 1.2-18 this indicates the formation of 1:1 and 1:2 complexes (Sayyed and Mazahar, 2012).

The metal (II)-humate stepwise stability constants (log k) at phenolic group (Tables 3-18)

Table 3: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n}{1-n}$)	$LogK_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

$LogK_1$ (Average value) = 2.4788± 0.2203

Table 4: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	Log($\frac{n-1}{2-n}$)	$LogK_2$
9.51	5.50	6.66	6.73	0.07	1.3509	1.70	-0.2671	1.4329
9.73	5.55	6.78	6.85	0.07	1.6383	1.51	0.2467	1.7567
10.00	5.60	6.90	6.98	0.08	2.1783	1.31	-0.2158	1.0942
10.23	5.65	7.05	7.13	0.08	4.1904	1.27		
10.49	5.70	7.10	7.19	0.09	4.6920			

$LogK_2$(Average value) = 1.4280 ± 0.3312

Table 5:Point-wise method,Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	Log($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430

LogK_1 **(Average value)** = 2.3059± 0.6153

Table 6:Point-wise method, Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$V_3\text{-}V_2$	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
9.73	5.55	6.33	6.42	0.09	0.9000	1.69		
10.00	5.60	6.47	6.58	0.11	1.2578	1.44	-0.4592	0.9808
10.23	5.65	6.62	6.84	0.12	1.6137	1.26	-0.2010	1.4610
10.49	5.70	6.80	6.92	0.12	2.1052	1.03		

LogK_2 **(Average value)** = 1.2209± 0.3398

Table 7:Point-wise method,Pb (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	log($\frac{n}{1-n}$)	LogK_1
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.60	0.05	0.8333	1.96	0.6989	2.6589

LogK_1 (Average value) = 2.5832 ±0.1614

Table 8:Point-wise method,Pb-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	log($\frac{n-1}{2-n}$)	logK_2
9.51	5.50	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.83	0.05	1.1702	1.44		
10.00	5.60	6.90	6.90	0.05	1.4864	1.22	-0.0237	1.1963
10.23	5.65	7.05	7.10	0.05	2.0190	1.09		
10.49	5.70	7.10	7.17	0.07	3.6492	1.00		

LogK_2(Average value) = 1.1963

Table 9:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$V_3\text{-}V_2$	n	pL	Log ($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.5477	2.3123
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	0.0272	2.2072
9.51	5.50	6.20	6.26	0.07	0.6417	1.89	0.2530	2.1430
9.73	5.55	6.40	6.40	0.07	0.7000	1.67	0.3680	2.0380

LogK_1 **(Average value)** = 2.2364 ± 0.1602

Table 10:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$V_3\text{-}V_2$	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
10.00	5.60	6.47	6.55	0.08	1.9503	1.41		
10.23	5.65	6.62	6.72	0.11	1.4792	1.26	-0.0361	1.2239

LogK_2 **(Average value)** = 1.2239

Table 11:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	log($\frac{n}{n-1}$)	LogK_1
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4290	2.2110
8.72	5.35	6.37	6.39	0.02	0.2858	2.42	-0.3978	2.0222
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

LogK_1 (Average value)=2.1382**±**0.1046

Table 12:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$\log(\frac{n-1}{2-n})$	$LogK_2$
9.51	5.55	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.84	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.93	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.10		
10.49	5.70	7.10	7.18	0.07	3.6492	0.83		

$LogK_2$(Average value) = 1.5453 **±** 0.3450

Table 13:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$Log(\frac{n}{n-1})$	$Log\ K_1$
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.3477	2.3123
9.00	5.40	6.00	6.04	0.04	0.3236	2.38	-0.3202	2.0598
9.22	5.45	6.10	6.15	0.05	0.4297	2.17	-0.1230	2.0470
9.51	5.50	6.20	6.26	0.06	0.5500	1.89	0.0871	1.9771
9.73	5.55	6.33	6.40	0.07	0.7000	1.67	0.3680	2.0380

$LogK_1$ **(Average value)** = 2.1568 ± 0.2069

Table 14:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$Log(\frac{n-1}{2-n})$	$Log\ K_2$
10.00	5.60	6.47	6.55	0.08	0.9148	1.41		
10.23	5.65	6.62	6.71	0.09	1.2102	1.20	-0.5749	0.6251
10.49	5.70	6.80	6.92	0.09	1.5968	1.03	0.1703	1.2003

$LogK_2$ **(Average value)** = 0.9127± 0.4070

Table15:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$Log(\frac{n}{1-n})$	$LogK_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4210	2.2190
8.72	5.35	6.37	6.40	0.03	0.4286	2.42	-0.1249	2.2951
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.96	0.3010	2.2610
9.51	5.55	6.66	6.70	0.04	0.7720	1.67	0.5297	2.1997

$LogK_1$ (Average value) = 2.2108± 0.0825

Table 16:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$Log(\frac{n-1}{2-n})$	$Log\ K_2$
9.73	5.55	6.78	6.83	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.95	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.09		
10.49	5.70	7.10	7.16	0.06	3.1429	0.89		

$LogK_2$ **(Average value)** = 1.5453± 0.3450

Table 17:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$Log(\frac{n}{n-1})$	$Log\ K_1$
8.50	5.30	5.81	5.86	0.05	0.3717	2.88	-0.2280	2.6520
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.06	0.06	0.4853	2.38	-0.0255	2.3545
9.22	5.45	6.10	6.16	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430
9.73	5.55	6.33	6.41	0.08	0.8000	1.69	0.6020	2.2920

$LogK_1$ **(Average value)** = 2.2516± 0.5380

Table 18:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$\mathrm{Log}(\frac{n-1}{2-n})$	Log K_2
10.00	5.60	6.47	6.57	0.10	1.1434	1.43		
10.23	5.65	6.62	6.72	0.10	1.3448	1.23	-0.2788	0.9512
10.49	5.70	6.80	6.90	0.10	1.7742	1.03	0.5351	1.5651

LogK_2 **(Average value)** = 1.2581± 0.4340

Table 19: Stepwise and overall Stability constants of thehydrolysed and unhydrolysed divalent metal (II) complexes

Chelates	**LogK_1**	**LogK_2**	**Logβ**
[Cu (Hydrolysed PSHA-1)$_2$]	2.4788	1.4280	3.9068
[Pb (Hydrolysed PSHA-1)$_2$]	2.5832	1.1963	3.7795
[Cd (Hydrolysed PSHA-1)$_2$]	2.2108	1.5453	3.7561
[Mg (Hydrolysed PSHA-1)$_2$]	2.1382	1.5453	3.6835
[Cu (Unhydrolysed PSHA-1)$_2$]	2.3059	1.2209	3.5268
[Pb (Unhydrolysed PSHA-1)$_2$]	2.2364	1.2239	3.4603
[Cd (Unhydrolysed PSHA-1)$_2$]	2.2516	1.2581	3.5097
[Mg (Unydrolysed PSHA-1)$_2$]	2.1568	0.9127	3.0695

The results obtained (Table19) shows the stepwise and overall stability constants to be not high indicating low stability of the complexes, because the solubility of most metal ions in the basic pH range is minimal due to metal hydroxide precipitation (Karimi, 2017). In general, the stepwise stability constants (K_1 and K_2) follow the order $K_1 > K_2$ for the copper, lead, magnesium and cadmium complexes respectively. The steady decrease of the values with increasing number of ligands is in agreement with the prediction made by researchers (Na'aliya, 2013). The decrease could be attributed to the fact that as the number of the ligands (Humate ions) that enters the coordination zone increases the aqua molecules available for replacement by the ligands become less. Thus, the metal ions become less electron loving with progressive intake of the ligand and this results in the decrease in the values of the constants (Na'aliya, 2013). Also the stability of the complexes is influenced by the size and number of the chelate rings(Mackay and Mackay,2002).All the complexes form rings in their structure as humate, a bidentate ligand, bond the metal ions in the ratio 1:2 (Boguta and Sokolowska, 2016) forming chelate rings. The values of the overall stability constants (logβ) obtained for humate complexes are not high indicating low stability as the values are not high. LogK values for copper-humates (Table 3 to 6) obtained in this study are lower than those reported for the complexes of humic acids (Pandey *et al*., 2015; Dinu, 2013; Kaschl *et al*., 2010 and Gilbeto and Jorg, 2001). The values of LogK(Table 7 to 10) forlead-humates are lower than those reported for the lead in the literature (Dinu, 2013; Gilbeto and Jorg 2001). Log K values(Table 11 to 14) for magnesium-humates obtained in this study are close to those reported by (Pandey *et al*., 2015). Log K values of cadmium-humates (Table 15 to 18) obtained in this work near to the one reported by (Dinu, 2013 and Pandey *et al*., 2015).The difference between the reported values and the values obtained in this study might be probably as a result of acid hydrolysis of humic acid. The values of the overall stability constants (log β) of the copper humates complexes presented in Table 19 is high than that of other metal humate complexes, show relatively high stability of Cu-HA complexes, show the following order of stability: Cu >Pb> Cd > Mg; which are in close agreement to the findings of (Dinu, 2013 and Pandey *et al*., 2015).The high stability of Cu-humate chelate could be attributed to the existence of coordinate covalent bond between the complexing agents and the Cu^{2+} ions. Since, Cu^{2+} being a metal of the transitional series with $3d^9$ electronic configurations can accept the electrons from the complexing agents. Similarly,the low stabilities of Pb,Cd and Mg -complexes could be explained by that Pb^{2+} with $6s^2$, Cd^{2+} with $4d^{10}$ and Mg^{2+} with $2p^6$ their electronic configuration has a completely filled d,p and s orbitals. Moreover, the stabilities of metal ions with hydrolysed humic acid from peat soil were higher than those with unhydrolysed humic acid from peat soil; which is ascribed to the high content of acidity in hydrolysed humic acid than unhydrolysed humic acid.

CONCLUSION

The values of logK for Cu(II) hydrolysed humic acid complex was higher followed by Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes as compared with metal(II) unhydrolysed humic acid complexes . This indicates acid hydrolysis of humic acid can enhance the complexation behavior of humic acid with metal (II) ions. However, the higher values of logβ for Cu(II), Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes indicates more stable stepwise complexes formed as compared with Cu(II), Pb(II), Cd(II) and Mg(II) unhydrolysed humic acid complexes.

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STABILITY CONSTANTS OF COMPLEXES OF METAL IONS WITH PEATSOIL HUMIC ACIDS UNDER NON-ACID-CONDITIONS

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ABSTRACT

Stability constants of complexes of four divalent metal ions viz. Cu^{2+}, Pb^{2+},Mg^{2+} and Cd^{2+} with humic acids (HA) were determined by potentiometric titration of humic acids with the corresponding salt of the divalent metals in aqueous media under non-acid-condition. The log K (logarithm of the stability constant) ranged from 1.0942 to 2.7471 for metal-humic acid complexes were determined using point-wise computational method. The order of stability constants were obtained as follows: Cu >Pb> Cd > Mg for metal -HA complexes respectively, indicating a higher degree of complexation with Cu metal ion.

Keywords: stability constant, humic acid, potentiometric titration, divalent metals, acid hydrolysis.

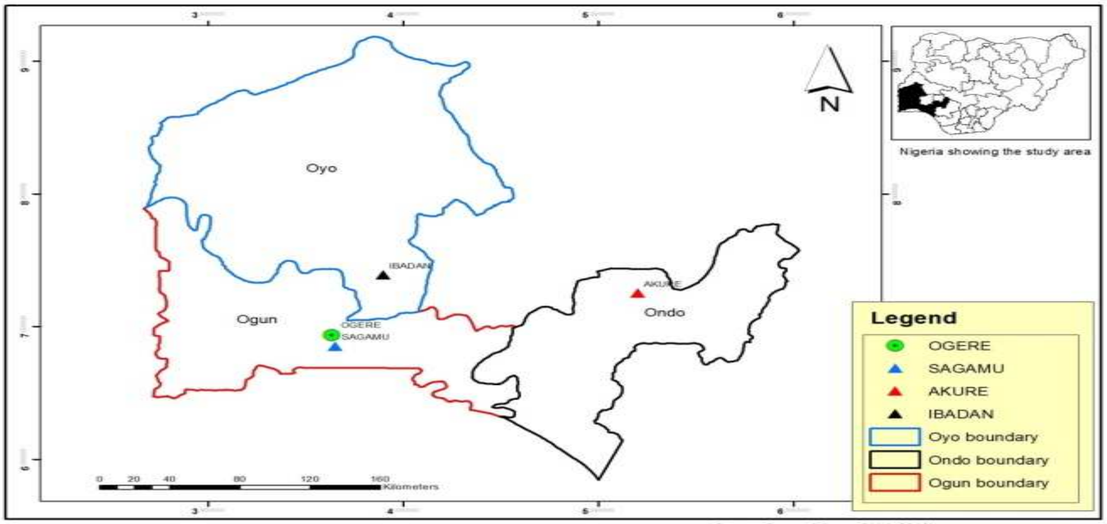
NTRODUCTION

The stability constant of a complex is the numerical expression of its stability and provides a quantitative measure of affinity of the metal ion to the complexing agent. An understanding of the relative stability of metal-complexes helps in predicting the behavior of metal ions in the soil (Ram and Raman, 1982). Extensive researches has been done to determine the stability constants of the complexes formed between humic acid (HA) with a number of metal ions. Ashok *et al*., (2000) reported that humic acid with hydroxyl, phenoxyl and carboxyl reactive groups can form coordination compound with metal ions at pH 3.5. The stability constants(Log K) for different metal-humic acid complexes indicated the following order of the stabilities of complexes formed between humic acid and metal ion, Cu >Fe >Pb> Ni > Co > Ca > Cd > Zn >Mn> Mg. Andelkovic *et al*., (2010) investigated the binding of Cd(II) to soil humic acid at pH 6.5 and in 0.1M KNO_3 ionic medium. The stability constant for binding indicating greater stability in the case when carboxyl groups are involved in complexation reaction. Kostic *et al*.,(2012) investigated the complexation of humic acid with certain heavy metal ions (Co(II), Ni(II),Cu(II), Zn(II), and Pb(II). The experiment was performed at 25°C, at pH 4.0 and ionic strength of 0.01M. Stability constant of complex between Pb(II) ions and humic acid is greater than stability constants of other investigated metal-humate complexes. Bogata and Sokolowska (2016) analyses the interaction between humic acids from different soils and Zn (II) ions at wide concentration ranges and at pH 5. Studies have showed significant impact of Zn concentration, pH and some properties of humic acids with zinc.But all of these studies were limited to acidic pH range. Therefore, the present study was carried out to determine and compare the stability constants of complexes of metal ions with hydrolysed peat soil humic acid and unhydrolysed peat soil humic under non-acid conditions.

MATERIALS AND METHODS

Analytical grade chemicals used includes hydrochloric acid (HCl), nitric acid (HNO_3), sodium hydroxide (NaOH), lead nitrate $Pb(NO_3)_2$, copper nitrate $Cu(NO_3)_2.3H_2O$, cadmium nitrate $Cd(NO_3)_2.4H_2O$, magnesium nitrate $Mg(NO_3)_2.6H_2O$, potassium nitrate (KNO_3), calcium chloride ($CaCl_2$), (sigma-Aldrich). Dowex 50WX8, (20-50 mesh) from Fluka.

Area of study



Source: Dept. of Geog. BUK (2016)

Figure 1: Map showing the sampling point at Sagamu Town, Ogun State.

Description of Sampling Area

Sagamu has geographical coordinates between 6°50′ north; 3° 38′ east is located in south western region of Nigeria. The region has tropical wet and dry climate with a lengthy wet season and relatively constant temperatures throughout the course of the year. Wet season runs from March to October, November to December forms the region dry season. The vegetation type of the region is savannah which is really grassland with small bushes and occasional big trees. Grassland soils have substantially higher organic matter content than forest soils (Novackova, 2011).

Sample Collection

The Peatsoil samples were collected from four different sampling points (0-10cm depth) in Sagamu into polyethylene bag with plastic spoons. Samples were taken to the laboratory, extraneous materials were removed; the samples were air-dried, crushed and ground to a fine powder in a mortar passed through a 0.20mm sieve. The samples were kept for analysis.

Isolation and purification of humic acid from peat soil sample

Peatsoil sample (100g) was mixed with 1000 cm^3 of 0.1M NaOH solution, shaken for 3hours and left to stand overnight. Dark-coloured supernatant was obtained and decanted from solid residue. The dark-coloured supernatant was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 6 hours. Yellowish brown supernatant and dark-brown precipitate were obtained. The yellowish brown supernatant was decanted followed by centrifuge and discarded. The dark-brown precipitate was mixed with $500cm^3$of 0.1M NaOH solution followed by passing through dowex resin. The dark-brown solution was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 3 hours. The dark-brown precipitate was washed several times with deionized water. The supernatant was treated with $AgNO_3$ solution until no white precipitate observed. The humic acid was transferred to weighed crucible and dried at 60°C in an oven for 12 hours. The humic acid was cooled and dried in the desiccator, weighed and recorded. The obtained humic acid was dried again at 60°C for additional 6 hours cooled and dried in the desiccator, weighed and recorded constant weight was obtained (Baruah *et al*., 2015).

FT-IR analysis

FT-IR spectra of humic acid sample was analysed using Carry 630 FT-IR Agilent Technologies.

Unhydrolysed compost humic acid

The unhydrolysed humic acid was obtained after isolation and purification of compost humic acid and kept for investigation.

Acid hydrolysis of Peatsoil acid

Peatsoil humic acid sample (1g) was refluxed for 12 hours at (160°C) with $50cm^3$ of 6M HCl. The mixture was allowed to cool, decanted, and centrifuged after hydrolysis. The insoluble residues were washed with distilled water via centrifugation several times, and the supernatant was treated with $AgNO_3$ solution until no white precipitate was observed. The residue was thoroughly dried over $CaCl_2$ in a desiccator at room temperature (Chefetz *et al*., 2002). Finally, the obtained hydrolysed humic acid was kept for investigation.

Potentiometric Titrations

Potentiometric measurements were carried out using a pH-meter Jenway (model 3510) with combine electrode, the sensitivity of the pH - meter is 0.01 units. The pH meter was switched on half an hour before starting the titration for initial warm up of the instrument. The instrument was calibrated with an aqueous standard buffer solution of pH 4.00 and 10.0 (borate buffer) prepared from a "Qualigens" buffer tablets.

The following sets of solutions were prepared in a 250cm^3 volumetric flask separately for pH metric titrations.

(i) 5 cm^3 0.1 M HCl + 40 cm^3 deionized water
(ii) 5 cm^3 0.1 M HCl + 39 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid
(iii) 5 cm^3 0.1 M HCl + 37 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid + 2 cm^3 0.01 M Cu(II)

The solutions were titrated against standardized 0.110MNaOH separately. The total volume of each mixture was adjusted to 50 cm^3 and the ionic strength of the solutions was maintained constant at by adding appropriate amount of stock solution of 1M KNO$_3$ (Gamal, 2015; Omar and Ali, 2015). A magnetic stirrer was used to achieve thorough mixing of the interacting solutions at 550 rpm. The same set of experimental conditions was applied for potentiometric titration of remaining samples.

Evaluation of pKa of Hydrolysed peat soil Humic Acids

The proton-ligand formation number n$_{\mathbf{A}}$ were calculated by Irving and Rossotti expression (Omar and Ali, 2015).

$$nA = Y - \frac{(V2-V1)(No-Eo)}{(Vo+V1)TcL} \quad \text{..................................1}$$

Where: Y is number of dissociable proton, (V$_2$-V$_1$) is the measure of displacement of the ligand curve relative to acid curve, N^o and E^o are the resultant concentration of alkali solution, free acid solution, T$_{cL}$^{o} is the total ligand concentration, V^o is the total volume of titration solution,V$_1$ is the volume of alkali added to acid solution,V$_2$ is the volume of alkali added to acid solution + ligand solution, acid dissociation constants (pKa - values) of ligand were calculated by algebraic method point wise calculation (Tables 1). The dissociation constants (pKa) were calculated according to the following relation:

$$pKa = pH + \log\left(\frac{nA}{1-nA}\right) \quad \text{.............................2}$$

Where: pKa is the acid dissociation constant, n$_A$is the Proton-ligand formation number and pH is the pH-values (Omar and Ali, 2015).

Determination of metal-ligand stability constants (log K) of complexes

The potentiometric measurement for the determination of stability constant of a complex in solution is based on the fact that the redox potential of the couple $\frac{M^{+(m-n)}}{M^{+m}}$ is shifted significantly on complexation of the metal ion with the ligand. This method involves change in hydrogen ion concentration [H$^+$] due to the displacement or association of one or more protons taking place during complexation reaction. This change can be found out by titrating the solutions containing free acid, acid with ligand, and acid with ligand and metal ion, individually against a standard alkali solution at a constant ionic strength or temperature. Either ionic strength or temperature may be varied for different sets of solutions. In all the cases, the change in the pH of the solution is measured after each addition of a known amount of alkali to the reaction cell which contains the reaction mixture. The titration curves are then drawn by plotting the measured pH values against the corresponding volume of alkali added and the stability constants of the complexes are determined from the titration curves by employing pH-metric titration technique given by (Irving and Rossoti).

Metal-ligand stability constants (Log K) were determined by using the following relations:

$$\bar{n} = \frac{(V_3 - V_2)(E^0 + N^0)}{(V^0 + V_2)\bar{n}_A T_m^0} \quad \text{...3}$$

and

$$PL = \log_{10}\left\{\frac{1+\beta_n^H \dfrac{1}{[anti\ \log pH]^n}}{T_L^0 - \bar{n}T_m^0} X \frac{(V^0+V_3)}{V^0}\right\} \quad \text{...4}$$

Where $T_{L,}$ T^{o}, E°, and V^{o}havethe same significance as in equation (1) above, T_m denotes the total concentration of metal present in solution, V_3 is the volume of metal ions present in solution and β^{H} is the overall proton ligand stability constant. The metal-ligand stability constants (log K) were determined by employing point wise computational Method (eq. 5 and 6).

$\text{Log}K_1 = \log\left(\frac{n}{1-n}\right) + pL$ 5

$\text{Log}K_2 = \log\left(\frac{1-n}{2-n}\right) + pL$........................6

Where: Log K is the metal-ligand stability constant, pL is the Free ligand exponent function, **n** is the Average number of ligand attached with metal ion (Janrao*et al.*, 2014).The results obtained were analyzed by an ORIGIN 2016 program using titration data and then the proton-ligand stability constants (pKa) and Metal-ligand stability constant (LogK) calculated (Omar and Ali, 2015).

RESULTS AND DISCUSSION

Fourier transformed infrared (FT-IR) spectra of isolated humic acid from peat soils Figure 2 had distinct clear absorption bands indicating the presence of major humic acid structural elemental groups such as H bonded OH ($3680cm^{-1}$ peak), C=O of carbonyl ($1721cm^{-1}$ peak), functional groups of aliphatic components CH_2 ($2918cm^{-1}$ peak) and C-O stretching of polysaccharide ($1168cm^{-1}$ peak). The positions of the absorption bands of the spectra fell within typical major absorption bands of humic acid which is at frequencies 3680, 2918, 1721, 1168 cm^{-1}. The first peak centred in the vicinity of 3680 cm^{-1} region is attributed to phenol OH group bounded by intermolecular H bonds. The $2918cm^{-1}$ band usually has absorption maximum at 2918 cm^{-1} which is due to C–H stretching of alkane group (CH_2). The next major absorption band is 1721 cm^{-1}. This band has been commonly ascribed to C=O stretching of mainly carboxyl group (COOH) with trace amount of ketones. The last peak was observed at 1168 cm^{-1} due to C–O stretching of polysaccharides and this peak appeared also in the spectra of humic acid from peat soil. The FTIR spectra of the isolated humic acid contained all major characteristic absorption peaks of humic acid. These absorption peaks indicated the presence of the major structural elements of humic acid namely H bonded OH, C=C of aromatic ring, C=O of carbonyl group (both carboxyl and ketonic), CH_2 group. This strongly supports the presence of humic acid.

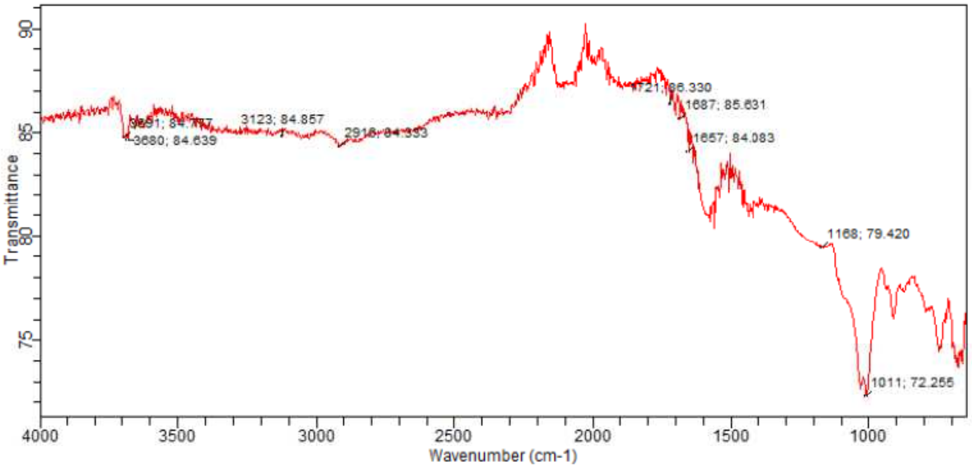


Fig. 2 : FT-IR spectraof peatsoilhumic acid (PSHA)

Evaluation of acid dissociation constant (pka) of acid hydrolysed peat soil humicacid at phenolic group

The value of the dissociation constant of the peat soil humic acid (PSHA) that underwent acidhydrolysis studied was found to be 8.9299 as shown Table 1, which is lower than the literaturevalues reported by Almeida and Szpoganics, (2015), Borges *et al.*, (2005); Badr *et al.*, (2012)and Fernandes *et al*,.(2009) of 9.73, 9.47 and 10.30. The difference between the obtained valuesand the reported values in this study might be probably as a result of acid hydrolysis of humicacid.

Table 1: PKa of (Hydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	$\log(\frac{nA}{1-nA})$	pKa
8.50	5.30	6.29	0.99	0.3594	-0.2510	8.2490
8.72	5.35	6.37	1.02	0.3400	-0.2880	8.4320
9.00	5.40	6.46	1.06	0.3141	-0.3391	8.6609
9.22	5.45	6.55	1.10	0.2882	-0.3927	8.8273
9.51	5.50	6.66	1.16	0.2494	-0.4786	9.0314
9.73	5.55	6.78	1.23	0.2041	-0.5910	9.1390
10.00	5.60	6.90	1.30	0.1589	-0.7238	9.2762
10.23	5.65	7.05	1.40	0.0941	-0.9835	9.2465
10.49	5.70	7.10	1.40	0.0941	-0.9835	9.5065

Average pKa = 8.9299 ± 0.4186

Table 2: PKa of (Unhydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	$\text{Log}(\frac{nA}{1-n})$	pKa
8.50	5.30	5.81	0.51	0.6619	0.2919	8.7919
8.72	5.35	5.90	0.55	0.6357	0.2418	8.9618
9.00	5.40	6.00	0.60	0.6029	0.1813	9.1813
9.22	5.45	6.10	0.65	0.5701	0.1226	9.3426
9.51	5.50	6.20	0.70	0.5376	0.0654	9.5754
9.73	5.55	6.33	0.78	0.4851	-0.0259	9.7041
10.00	5.60	6.47	0.87	0.4262	-0.1291	9.8709
10.23	5.65	6.62	0.99	0.3609	-0.2481	9.9819
10.49	5.70	6.80	1.10	0.2759	-0.4690	10.0210

Average pKa = 9.4923± 0.4410

Metal-ligand stability constant (Log K)

The stabilityconstants require the accurate values of proton-ligand stability constants (Anil and Maroti, 2008). Metal titration curves crossed over ligand titration curve indicated the formation of complex upon proton release (Santosh, *et al*., 2011). If the values of n- are within range 0.2-0.8 and 1.2-18 this indicates the formation of 1:1 and 1:2 complexes (Sayyed and Mazahar, 2012).

The metal (II)-humate stepwise stability constants (log k) at phenolic group (Tables 3-18)

Table 3: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3$-$V_2)$	n	pL	$\log(\frac{n}{1-n})$	LogK_1
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

LogK_1 (Average value) = 2.4788± 0.2203

Table 4: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3$-$V_2)$	n	pL	$\text{Log}(\frac{n-1}{2-n})$	LogK_2
9.51	5.50	6.66	6.73	0.07	1.3509	1.70	-0.2671	1.4329
9.73	5.55	6.78	6.85	0.07	1.6383	1.51	0.2467	1.7567
10.00	5.60	6.90	6.98	0.08	2.1783	1.31	-0.2158	1.0942
10.23	5.65	7.05	7.13	0.08	4.1904	1.27		
10.49	5.70	7.10	7.19	0.09	4.6920			

LogK_2(Average value) = 1.4280 ± 0.3312

Table 5:Point-wise method,Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3$-$V_2)$	n	pL	$\text{Log}(\frac{n}{n-1})$	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430

$\text{Log}K_1$ **(Average value)** = 2.3059± 0.6153

Table 6:Point-wise method, Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$\text{Log}(\frac{n-1}{2-n})$	Log K_2
9.73	5.55	6.33	6.42	0.09	0.9000	1.69		
10.00	5.60	6.47	6.58	0.11	1.2578	1.44	-0.4592	0.9808
10.23	5.65	6.62	6.84	0.12	1.6137	1.26	-0.2010	1.4610
10.49	5.70	6.80	6.92	0.12	2.1052	1.03		

$\text{Log}K_2$ **(Average value)** = 1.2209± 0.3398

Table 7:Point-wise method,Pb (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3$-$V_2)$	n	pL	$\log(\frac{n}{1-n})$	$\text{Log}K_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.60	0.05	0.8333	1.96	0.6989	2.6589

$\text{Log}K_1$ (Average value) = 2.5832 ±0.1614

Table 8:Point-wise method,Pb-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3$-$V_2)$	n	pL	$\log(\frac{n-1}{2-n})$	$\log K_2$
9.51	5.50	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.83	0.05	1.1702	1.44		
10.00	5.60	6.90	6.90	0.05	1.4864	1.22	-0.0237	1.1963
10.23	5.65	7.05	7.10	0.05	2.0190	1.09		
10.49	5.70	7.10	7.17	0.07	3.6492	1.00		

$\text{Log}K_2$(Average value) = 1.1963

Table 9:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log $(\frac{n}{n-1})$	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.5477	2.3123
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	0.0272	2.2072
9.51	5.50	6.20	6.26	0.07	0.6417	1.89	0.2530	2.1430
9.73	5.55	6.40	6.40	0.07	0.7000	1.67	0.3680	2.0380

$\text{Log}K_1$ **(Average value)** = 2.2364 ± 0.1602

Table 10:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$\text{Log}(\frac{n-1}{2-n})$	Log K_2
10.00	5.60	6.47	6.55	0.08	1.9503	1.41		
10.23	5.65	6.62	6.72	0.11	1.4792	1.26	-0.0361	1.2239

$\text{Log}K_2$ **(Average value)** = 1.2239

Table 11:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3$-$V_2)$	n	pL	$\log(\frac{n}{n-1})$	$\text{Log}K_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4290	2.2110
8.72	5.35	6.37	6.39	0.02	0.2858	2.42	-0.3978	2.0222
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

$\text{Log}K_1$ (Average value)=2.1382**±**0.1046

Table 12:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$\log(\frac{n-1}{2-n})$	$LogK_2$
9.51	5.55	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.84	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.93	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.10		
10.49	5.70	7.10	7.18	0.07	3.6492	0.83		

$LogK_2$(Average value) = 1.5453 **±** 0.3450

Table 13:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$Log(\frac{n}{n-1})$	$Log K_1$
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.3477	2.3123
9.00	5.40	6.00	6.04	0.04	0.3236	2.38	-0.3202	2.0598
9.22	5.45	6.10	6.15	0.05	0.4297	2.17	-0.1230	2.0470
9.51	5.50	6.20	6.26	0.06	0.5500	1.89	0.0871	1.9771
9.73	5.55	6.33	6.40	0.07	0.7000	1.67	0.3680	2.0380

$LogK_1$ **(Average value)** = 2.1568 ± 0.2069

Table 14:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$Log(\frac{n-1}{2-n})$	$Log K_2$
10.00	5.60	6.47	6.55	0.08	0.9148	1.41		
10.23	5.65	6.62	6.71	0.09	1.2102	1.20	-0.5749	0.6251
10.49	5.70	6.80	6.92	0.09	1.5968	1.03	0.1703	1.2003

$LogK_2$ **(Average value)** = 0.9127± 0.4070

Table15:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$Log(\frac{n}{1-n})$	$LogK_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4210	2.2190
8.72	5.35	6.37	6.40	0.03	0.4286	2.42	-0.1249	2.2951
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.96	0.3010	2.2610
9.51	5.55	6.66	6.70	0.04	0.7720	1.67	0.5297	2.1997

$LogK_1$ (Average value) = 2.2108± 0.0825

Table 16:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$Log(\frac{n-1}{2-n})$	$Log K_2$
9.73	5.55	6.78	6.83	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.95	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.09		
10.49	5.70	7.10	7.16	0.06	3.1429	0.89		

$LogK_2$ **(Average value)** = 1.5453± 0.3450

Table 17:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$Log(\frac{n}{n-1})$	$Log K_1$
8.50	5.30	5.81	5.86	0.05	0.3717	2.88	-0.2280	2.6520
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.06	0.06	0.4853	2.38	-0.0255	2.3545
9.22	5.45	6.10	6.16	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430
9.73	5.55	6.33	6.41	0.08	0.8000	1.69	0.6020	2.2920

$LogK_1$ **(Average value)** = 2.2516± 0.5380

Table 18:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$\text{Log}(\frac{n-1}{2-n})$	Log K_2
10.00	5.60	6.47	6.57	0.10	1.1434	1.43		
10.23	5.65	6.62	6.72	0.10	1.3448	1.23	-0.2788	0.9512
10.49	5.70	6.80	6.90	0.10	1.7742	1.03	0.5351	1.5651

LogK_2 **(Average value)** = 1.2581± 0.4340

Table 19: Stepwise and overall Stability constants of thehydrolysed and unhydrolysed divalent metal (II) complexes

Chelates	**LogK_1**	**LogK_2**	**Logβ**
[Cu (Hydrolysed PSHA-1)$_2$]	2.4788	1.4280	3.9068
[Pb (Hydrolysed PSHA-1)$_2$]	2.5832	1.1963	3.7795
[Cd (Hydrolysed PSHA-1)$_2$]	2.2108	1.5453	3.7561
[Mg (Hydrolysed PSHA-1)$_2$]	2.1382	1.5453	3.6835
[Cu (Unhydrolysed PSHA-1)$_2$]	2.3059	1.2209	3.5268
[Pb (Unhydrolysed PSHA-1)$_2$]	2.2364	1.2239	3.4603
[Cd (Unhydrolysed PSHA-1)$_2$]	2.2516	1.2581	3.5097
[Mg (Unydrolysed PSHA-1)$_2$]	2.1568	0.9127	3.0695

The results obtained (Table19) shows the stepwise and overall stability constants to be not high indicating low stability of the complexes, because the solubility of most metal ions in the basic pH range is minimal due to metal hydroxide precipitation (Karimi, 2017). In general, the stepwise stability constants (K_1 and K_2) follow the order $K_1 > K_2$ for the copper, lead, magnesium and cadmium complexes respectively. The steady decrease of the values with increasing number of ligands is in agreement with the prediction made by researchers (Na'aliya, 2013). The decrease could be attributed to the fact that as the number of the ligands (Humate ions) that enters the coordination zone increases the aqua molecules available for replacement by the ligands become less. Thus, the metal ions become less electron loving with progressive intake of the ligand and this results in the decrease in the values of the constants (Na'aliya, 2013). Also the stability of the complexes is influenced by the size and number of the chelate rings(Mackay and Mackay,2002).All the complexes form rings in their structure as humate, a bidentate ligand, bond the metal ions in the ratio 1:2 (Boguta and Sokolowska, 2016) forming chelate rings. The values of the overall stability constants (logβ) obtained for humate complexes are not high indicating low stability as the values are not high. LogK values for copper-humates (Table 3 to 6) obtained in this study are lower than those reported for the complexes of humic acids (Pandey *et al*., 2015; Dinu, 2013; Kaschl *et al*., 2010 and Gilbeto and Jorg, 2001). The values of LogK(Table 7 to 10) forlead-humates are lower than those reported for the lead in the literature (Dinu, 2013; Gilbeto and Jorg 2001). Log K values(Table 11 to 14) for magnesium-humates obtained in this study are close to those reported by (Pandey *et al*., 2015). Log K values of cadmium-humates (Table 15 to 18) obtained in this work near to the one reported by (Dinu, 2013 and Pandey *et al*., 2015).The difference between the reported values and the values obtained in this study might be probably as a result of acid hydrolysis of humic acid. The values of the overall stability constants (log β) of the copper humates complexes presented in Table 19 is high than that of other metal humate complexes, show relatively high stability of Cu-HA complexes, show the following order of stability: Cu >Pb> Cd > Mg; which are in close agreement to the findings of (Dinu, 2013 and Pandey *et al*., 2015).The high stability of Cu-humate chelate could be attributed to the existence of coordinate covalent bond between the complexing agents and the Cu^{2+} ions. Since, Cu^{2+} being a metal of the transitional series with $3d^9$ electronic configurations can accept the electrons from the complexing agents. Similarly,the low stabilities of Pb,Cd and Mg -complexes could be explained by that Pb^{2+} with $6s^2$, Cd^{2+} with $4d^{10}$ and Mg^{2+} with $2p^6$ their electronic configuration has a completely filled d,p and s orbitals. Moreover, the stabilities of metal ions with hydrolysed humic acid from peat soil were higher than those with unhydrolysed humic acid from peat soil; which is ascribed to the high content of acidity in hydrolysed humic acid than unhydrolysed humic acid.

CONCLUSION

The values of logK for Cu(II) hydrolysed humic acid complex was higher followed by Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes as compared with metal(II) unhydrolysed humic acid complexes . This indicates acid hydrolysis of humic acid can enhance the complexation behavior of humic acid with metal (II) ions. However, the higher values of logβ for Cu(II), Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes indicates more stable stepwise complexes formed as compared with Cu(II), Pb(II), Cd(II) and Mg(II) unhydrolysed humic acid complexes.

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STABILITY CONSTANTS OF COMPLEXES OF METAL IONS WITH PEATSOIL HUMIC ACIDS UNDER NON-ACID-CONDITIONS

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ABSTRACT

Stability constants of complexes of four divalent metal ions viz. Cu^{2+}, Pb^{2+},Mg^{2+} and Cd^{2+} with humic acids (HA) were determined by potentiometric titration of humic acids with the corresponding salt of the divalent metals in aqueous media under non-acid-condition. The log K (logarithm of the stability constant) ranged from 1.0942 to 2.7471 for metal-humic acid complexes were determined using point-wise computational method. The order of stability constants were obtained as follows: Cu >Pb> Cd > Mg for metal -HA complexes respectively, indicating a higher degree of complexation with Cu metal ion.

Keywords: stability constant, humic acid, potentiometric titration, divalent metals, acid hydrolysis.

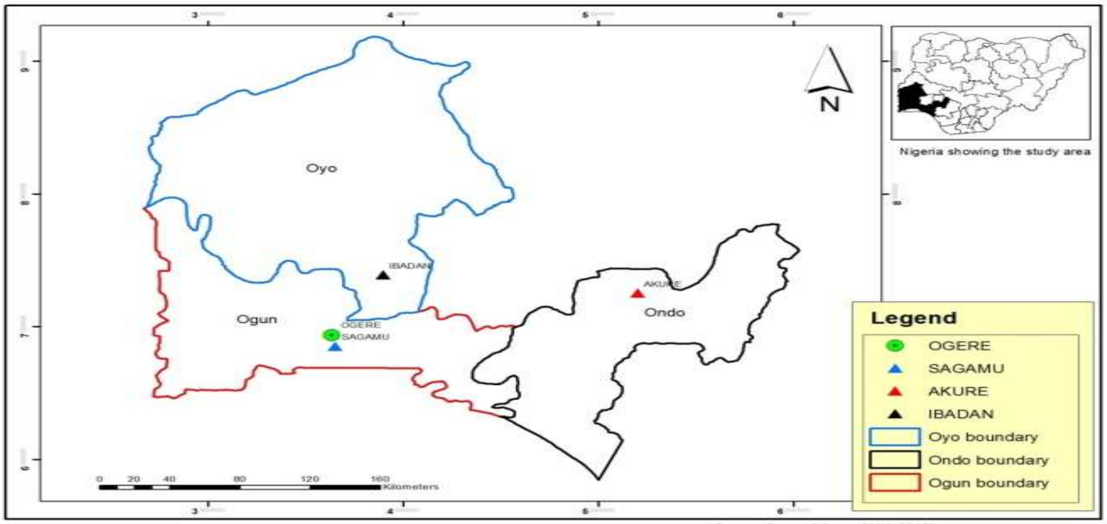
NTRODUCTION

The stability constant of a complex is the numerical expression of its stability and provides a quantitative measure of affinity of the metal ion to the complexing agent. An understanding of the relative stability of metal-complexes helps in predicting the behavior of metal ions in the soil (Ram and Raman, 1982). Extensive researches has been done to determine the stability constants of the complexes formed between humic acid (HA) with a number of metal ions. Ashok *et al*., (2000) reported that humic acid with hydroxyl, phenoxyl and carboxyl reactive groups can form coordination compound with metal ions at pH 3.5. The stability constants(Log K) for different metal-humic acid complexes indicated the following order of the stabilities of complexes formed between humic acid and metal ion, Cu >Fe >Pb> Ni > Co > Ca > Cd > Zn >Mn> Mg. Andelkovic *et al*., (2010) investigated the binding of Cd(II) to soil humic acid at pH 6.5 and in 0.1M KNO_3 ionic medium. The stability constant for binding indicating greater stability in the case when carboxyl groups are involved in complexation reaction. Kostic *et al*.,(2012) investigated the complexation of humic acid with certain heavy metal ions (Co(II), Ni(II),Cu(II), Zn(II), and Pb(II). The experiment was performed at 25°C, at pH 4.0 and ionic strength of 0.01M. Stability constant of complex between Pb(II) ions and humic acid is greater than stability constants of other investigated metal-humate complexes. Bogata and Sokolowska (2016) analyses the interaction between humic acids from different soils and Zn (II) ions at wide concentration ranges and at pH 5. Studies have showed significant impact of Zn concentration, pH and some properties of humic acids with zinc.But all of these studies were limited to acidic pH range. Therefore, the present study was carried out to determine and compare the stability constants of complexes of metal ions with hydrolysed peat soil humic acid and unhydrolysed peat soil humic under non-acid conditions.

MATERIALS AND METHODS

Analytical grade chemicals used includes hydrochloric acid (HCl), nitric acid (HNO_3), sodium hydroxide (NaOH), lead nitrate $Pb(NO_3)_2$, copper nitrate $Cu(NO_3)_2.3H_2O$, cadmium nitrate $Cd(NO_3)_2.4H_2O$, magnesium nitrate $Mg(NO_3)_2.6H_2O$, potassium nitrate (KNO_3), calcium chloride ($CaCl_2$), (sigma-Aldrich). Dowex 50WX8, (20-50 mesh) from Fluka.

Area of study



Source: Dept. of Geog. BUK (2016)

Figure 1: Map showing the sampling point at Sagamu Town, Ogun State.

Description of Sampling Area

Sagamu has geographical coordinates between 6°50′ north; 3° 38′ east is located in south western region of Nigeria. The region has tropical wet and dry climate with a lengthy wet season and relatively constant temperatures throughout the course of the year. Wet season runs from March to October, November to December forms the region dry season. The vegetation type of the region is savannah which is really grassland with small bushes and occasional big trees. Grassland soils have substantially higher organic matter content than forest soils (Novackova, 2011).

Sample Collection

The Peatsoil samples were collected from four different sampling points (0-10cm depth) in Sagamu into polyethylene bag with plastic spoons. Samples were taken to the laboratory, extraneous materials were removed; the samples were air-dried, crushed and ground to a fine powder in a mortar passed through a 0.20mm sieve. The samples were kept for analysis.

Isolation and purification of humic acid from peat soil sample

Peatsoil sample (100g) was mixed with 1000 cm^3 of 0.1M NaOH solution, shaken for 3hours and left to stand overnight. Dark-coloured supernatant was obtained and decanted from solid residue. The dark-coloured supernatant was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 6 hours. Yellowish brown supernatant and dark-brown precipitate were obtained. The yellowish brown supernatant was decanted followed by centrifuge and discarded. The dark-brown precipitate was mixed with $500cm^3$of 0.1M NaOH solution followed by passing through dowex resin. The dark-brown solution was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 3 hours. The dark-brown precipitate was washed several times with deionized water. The supernatant was treated with $AgNO_3$ solution until no white precipitate observed. The humic acid was transferred to weighed crucible and dried at 60°C in an oven for 12 hours. The humic acid was cooled and dried in the desiccator, weighed and recorded. The obtained humic acid was dried again at 60°C for additional 6 hours cooled and dried in the desiccator, weighed and recorded constant weight was obtained (Baruah *et al*., 2015).

FT-IR analysis

FT-IR spectra of humic acid sample was analysed using Carry 630 FT-IR Agilent Technologies.

Unhydrolysed compost humic acid

The unhydrolysed humic acid was obtained after isolation and purification of compost humic acid and kept for investigation.

Acid hydrolysis of Peatsoil acid

Peatsoil humic acid sample (1g) was refluxed for 12 hours at (160°C) with $50cm^3$ of 6M HCl. The mixture was allowed to cool, decanted, and centrifuged after hydrolysis. The insoluble residues were washed with distilled water via centrifugation several times, and the supernatant was treated with $AgNO_3$ solution until no white precipitate was observed. The residue was thoroughly dried over $CaCl_2$ in a desiccator at room temperature (Chefetz *et al.*, 2002). Finally, the obtained hydrolysed humic acid was kept for investigation.

Potentiometric Titrations

Potentiometric measurements were carried out using a pH-meter Jenway (model 3510) with combine electrode, the sensitivity of the pH - meter is 0.01 units. The pH meter was switched on half an hour before starting the titration for initial warm up of the instrument. The instrument was calibrated with an aqueous standard buffer solution of pH 4.00 and 10.0 (borate buffer) prepared from a "Qualigens" buffer tablets.

The following sets of solutions were prepared in a 250cm^3 volumetric flask separately for pH metric titrations.

(i) 5 cm^3 0.1 M HCl + 40 cm^3 deionized water
(ii) 5 cm^3 0.1 M HCl + 39 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid
(iii) 5 cm^3 0.1 M HCl + 37 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid + 2 cm^3 0.01 M Cu(II)

The solutions were titrated against standardized 0.110MNaOH separately. The total volume of each mixture was adjusted to 50 cm^3 and the ionic strength of the solutions was maintained constant at by adding appropriate amount of stock solution of 1M KNO$_3$ (Gamal, 2015; Omar and Ali, 2015). A magnetic stirrer was used to achieve thorough mixing of the interacting solutions at 550 rpm. The same set of experimental conditions was applied for potentiometric titration of remaining samples.

Evaluation of pKa of Hydrolysed peat soil Humic Acids

The proton-ligand formation number n$_{\mathbf{A}}$ were calculated by Irving and Rossotti expression (Omar and Ali, 2015).

$$nA = Y - \frac{(V2-V1)(No-Eo)}{(Vo+V1)TcL} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 1$$

Where: Y is number of dissociable proton, (V$_2$-V$_1$) is the measure of displacement of the ligand curve relative to acid curve, N^o and E^o are the resultant concentration of alkali solution, free acid solution, T$_{cL}$^{o} is the total ligand concentration, V^o is the total volume of titration solution,V$_1$ is the volume of alkali added to acid solution,V$_2$ is the volume of alkali added to acid solution + ligand solution, acid dissociation constants (pKa - values) of ligand were calculated by algebraic method point wise calculation (Tables 1). The dissociation constants (pKa) were calculated according to the following relation:

$$pKa = pH + \log\left(\frac{nA}{1-nA}\right) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 2$$

Where: pKa is the acid dissociation constant, n$_A$is the Proton-ligand formation number and pH is the pH-values (Omar and Ali, 2015).

Determination of metal-ligand stability constants (log K) of complexes

The potentiometric measurement for the determination of stability constant of a complex in solution is based on the fact that the redox potential of the couple $\frac{M^{+(m-n)}}{M^{+m}}$ is shifted significantly on complexation of the metal ion with the ligand. This method involves change in hydrogen ion concentration [H$^+$] due to the displacement or association of one or more protons taking place during complexation reaction. This change can be found out by titrating the solutions containing free acid, acid with ligand, and acid with ligand and metal ion, individually against a standard alkali solution at a constant ionic strength or temperature. Either ionic strength or temperature may be varied for different sets of solutions. In all the cases, the change in the pH of the solution is measured after each addition of a known amount of alkali to the reaction cell which contains the reaction mixture. The titration curves are then drawn by plotting the measured pH values against the corresponding volume of alkali added and the stability constants of the complexes are determined from the titration curves by employing pH-metric titration technique given by (Irving and Rossoti).

Metal-ligand stability constants (Log K) were determined by using the following relations:

$$\bar{n} = \frac{(V_3 - V_2)(E^0 + N^0)}{(V^0 + V_2)\bar{n}_A T_m^0} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 3$$

and

$$PL = \log_{10}\left\{\frac{1+\beta_n^H \dfrac{1}{[anti\ \log pH]^n}}{T_L^0 - \bar{n}T_m^0} X \frac{(V^0 + V_3)}{V^0}\right\} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 4$$

Where $T_{L,}$ T^{o}, E°, and V^{o}havethe same significance as in equation (1) above, T_m denotes the total concentration of metal present in solution, V_3 is the volume of metal ions present in solution and β^{H} is the overall proton ligand stability constant. The metal-ligand stability constants (log K) were determined by employing point wise computational Method (eq. 5 and 6).

$$\mathrm{Log}K_1 = \log\left(\frac{n}{1-n}\right) + pL \qquad ....5$$

$$\mathrm{Log}K_2 = \log\left(\frac{1-n}{2-n}\right) + pL.......................6$$

Where: Log K is the metal-ligand stability constant, pL is the Free ligand exponent function, **n** is the Average number of ligand attached with metal ion (Janrao*et al.*, 2014).The results obtained were analyzed by an ORIGIN 2016 program using titration data and then the proton-ligand stability constants (pKa) and Metal-ligand stability constant (LogK) calculated (Omar and Ali, 2015).

RESULTS AND DISCUSSION

Fourier transformed infrared (FT-IR) spectra of isolated humic acid from peat soils Figure 2 had distinct clear absorption bands indicating the presence of major humic acid structural elemental groups such as H bonded OH ($3680cm^{-1}$ peak), C=O of carbonyl ($1721cm^{-1}$ peak), functional groups of aliphatic components CH_2 ($2918cm^{-1}$ peak) and C-O stretching of polysaccharide ($1168cm^{-1}$ peak). The positions of the absorption bands of the spectra fell within typical major absorption bands of humic acid which is at frequencies 3680, 2918, 1721, 1168 cm^{-1}. The first peak centred in the vicinity of 3680 cm^{-1} region is attributed to phenol OH group bounded by intermolecular H bonds. The $2918cm^{-1}$ band usually has absorption maximum at 2918 cm^{-1} which is due to C–H stretching of alkane group (CH_2). The next major absorption band is 1721 cm^{-1}. This band has been commonly ascribed to C=O stretching of mainly carboxyl group (COOH) with trace amount of ketones. The last peak was observed at 1168 cm^{-1} due to C–O stretching of polysaccharides and this peak appeared also in the spectra of humic acid from peat soil. The FTIR spectra of the isolated humic acid contained all major characteristic absorption peaks of humic acid. These absorption peaks indicated the presence of the major structural elements of humic acid namely H bonded OH, C=C of aromatic ring, C=O of carbonyl group (both carboxyl and ketonic), CH_2 group. This strongly supports the presence of humic acid.

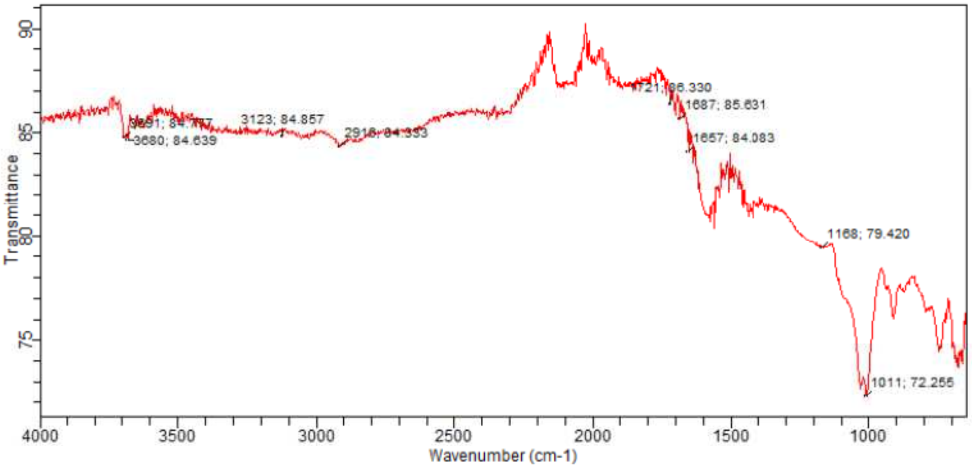


Fig. 2 : FT-IR spectraof peatsoilhumic acid (PSHA)

Evaluation of acid dissociation constant (pka) of acid hydrolysed peat soil humicacid at phenolic group

The value of the dissociation constant of the peat soil humic acid (PSHA) that underwent acidhydrolysis studied was found to be 8.9299 as shown Table 1, which is lower than the literaturevalues reported by Almeida and Szpoganics, (2015), Borges *et al.*, (2005); Badr *et al.*, (2012)and Fernandes *et al*,.(2009) of 9.73, 9.47 and 10.30. The difference between the obtained valuesand the reported values in this study might be probably as a result of acid hydrolysis of humicacid.

Table 1: PKa of (Hydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	$\log(\frac{nA}{1-nA})$	pKa
8.50	5.30	6.29	0.99	0.3594	-0.2510	8.2490
8.72	5.35	6.37	1.02	0.3400	-0.2880	8.4320
9.00	5.40	6.46	1.06	0.3141	-0.3391	8.6609
9.22	5.45	6.55	1.10	0.2882	-0.3927	8.8273
9.51	5.50	6.66	1.16	0.2494	-0.4786	9.0314
9.73	5.55	6.78	1.23	0.2041	-0.5910	9.1390
10.00	5.60	6.90	1.30	0.1589	-0.7238	9.2762
10.23	5.65	7.05	1.40	0.0941	-0.9835	9.2465
10.49	5.70	7.10	1.40	0.0941	-0.9835	9.5065

Average pKa = 8.9299 ± 0.4186

Table 2: PKa of (Unhydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	$\text{Log}(\frac{nA}{1-n})$	pKa
8.50	5.30	5.81	0.51	0.6619	0.2919	8.7919
8.72	5.35	5.90	0.55	0.6357	0.2418	8.9618
9.00	5.40	6.00	0.60	0.6029	0.1813	9.1813
9.22	5.45	6.10	0.65	0.5701	0.1226	9.3426
9.51	5.50	6.20	0.70	0.5376	0.0654	9.5754
9.73	5.55	6.33	0.78	0.4851	-0.0259	9.7041
10.00	5.60	6.47	0.87	0.4262	-0.1291	9.8709
10.23	5.65	6.62	0.99	0.3609	-0.2481	9.9819
10.49	5.70	6.80	1.10	0.2759	-0.4690	10.0210

Average pKa = 9.4923± 0.4410

Metal-ligand stability constant (Log K)

The stabilityconstants require the accurate values of proton-ligand stability constants (Anil and Maroti, 2008). Metal titration curves crossed over ligand titration curve indicated the formation of complex upon proton release (Santosh, *et al.*, 2011). If the values of n- are within range 0.2-0.8 and 1.2-18 this indicates the formation of 1:1 and 1:2 complexes (Sayyed and Mazahar, 2012).

The metal (II)-humate stepwise stability constants (log k) at phenolic group (Tables 3-18)

Table 3: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$\log(\frac{n}{1-n})$	LogK_1
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

LogK_1 (Average value) = 2.4788± 0.2203

Table 4: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$\text{Log}(\frac{n-1}{2-n})$	LogK_2
9.51	5.50	6.66	6.73	0.07	1.3509	1.70	-0.2671	1.4329
9.73	5.55	6.78	6.85	0.07	1.6383	1.51	0.2467	1.7567
10.00	5.60	6.90	6.98	0.08	2.1783	1.31	-0.2158	1.0942
10.23	5.65	7.05	7.13	0.08	4.1904	1.27		
10.49	5.70	7.10	7.19	0.09	4.6920			

LogK_2(Average value) = 1.4280 ± 0.3312

Table 5:Point-wise method,Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$\mathrm{Log}(\frac{n}{n-1})$	$\mathrm{Log}\ K_1$
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430

$\mathrm{LogK_1}$ **(Average value)** = 2.3059± 0.6153

Table 6:Point-wise method, Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$\mathrm{Log}(\frac{n-1}{2-n})$	$\mathrm{Log}\ K_2$
9.73	5.55	6.33	6.42	0.09	0.9000	1.69		
10.00	5.60	6.47	6.58	0.11	1.2578	1.44	-0.4592	0.9808
10.23	5.65	6.62	6.84	0.12	1.6137	1.26	-0.2010	1.4610
10.49	5.70	6.80	6.92	0.12	2.1052	1.03		

$\mathrm{LogK_2}$ **(Average value)** = 1.2209± 0.3398

Table 7:Point-wise method,Pb (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$\log(\frac{n}{1-n})$	$\mathrm{LogK_1}$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.60	0.05	0.8333	1.96	0.6989	2.6589

$\mathbf{LogK_1}$ **(Average value)** = 2.5832 ±0.1614

Table 8:Point-wise method,Pb-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$\log(\frac{n-1}{2-n})$	$\mathrm{logK_2}$
9.51	5.50	6.66	6.71	0.05	0.9650	1.67	-0.0237	1.1963
9.73	5.55	6.78	6.83	0.05	1.1702	1.44		
10.00	5.60	6.90	6.90	0.05	1.4864	1.22		
10.23	5.65	7.05	7.10	0.05	2.0190	1.09		
10.49	5.70	7.10	7.17	0.07	3.6492	1.00		

$\mathbf{LogK_2}$**(Average value)** = 1.1963

Table 9:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$\mathrm{Log}\ (\frac{n}{n-1})$	$\mathrm{Log}\ K_1$
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.5477	2.3123
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	0.0272	2.2072
9.51	5.50	6.20	6.26	0.07	0.6417	1.89	0.2530	2.1430
9.73	5.55	6.40	6.40	0.07	0.7000	1.67	0.3680	2.0380

$\mathrm{LogK_1}$ **(Average value)** = 2.2364 ± 0.1602

Table 10:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$\mathrm{Log}(\frac{n-1}{2-n})$	$\mathrm{Log}\ K_2$
10.00	5.60	6.47	6.55	0.08	1.9503	1.41		
10.23	5.65	6.62	6.72	0.11	1.4792	1.26	-0.0361	1.2239

$\mathrm{LogK_2}$ **(Average value)** = 1.2239

Table 11:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$\log(\frac{n}{n-1})$	$\mathrm{LogK_1}$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4290	2.2110
8.72	5.35	6.37	6.39	0.02	0.2858	2.42	-0.3978	2.0222
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

$\mathbf{LogK_1}$ **(Average value)=**2.1382**±**0.1046

Table 12:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	log$(\frac{n-1}{2-n})$	LogK$_2$
9.51	5.55	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.84	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.93	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.10		
10.49	5.70	7.10	7.18	0.07	3.6492	0.83		

LogK$_2$(Average value) = 1.5453 **±** 0.3450

Table 13:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	V$_3$-V$_2$	n	pL	Log$(\frac{n}{n-1})$	Log K$_1$
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.3477	2.3123
9.00	5.40	6.00	6.04	0.04	0.3236	2.38	-0.3202	2.0598
9.22	5.45	6.10	6.15	0.05	0.4297	2.17	-0.1230	2.0470
9.51	5.50	6.20	6.26	0.06	0.5500	1.89	0.0871	1.9771
9.73	5.55	6.33	6.40	0.07	0.7000	1.67	0.3680	2.0380

LogK$_1$ **(Average value)** = 2.1568 ± 0.2069

Table 14:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	V$_3$-V$_2$	n	pL	Log$(\frac{n-1}{2-n})$	Log K$_2$
10.00	5.60	6.47	6.55	0.08	0.9148	1.41		
10.23	5.65	6.62	6.71	0.09	1.2102	1.20	-0.5749	0.6251
10.49	5.70	6.80	6.92	0.09	1.5968	1.03	0.1703	1.2003

LogK$_2$ **(Average value)** = 0.9127± 0.4070

Table15:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	Log$(\frac{n}{1-n})$	LogK$_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4210	2.2190
8.72	5.35	6.37	6.40	0.03	0.4286	2.42	-0.1249	2.2951
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.96	0.3010	2.2610
9.51	5.55	6.66	6.70	0.04	0.7720	1.67	0.5297	2.1997

LogK$_1$ (Average value) = 2.2108± 0.0825

Table 16:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	Log$(\frac{n-1}{2-n})$	Log K$_2$
9.73	5.55	6.78	6.83	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.95	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.09		
10.49	5.70	7.10	7.16	0.06	3.1429	0.89		

LogK$_2$ **(Average value)** = 1.5453± 0.3450

Table 17:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	V$_3$-V$_2$	n	pL	Log$(\frac{n}{n-1})$	Log K$_1$
8.50	5.30	5.81	5.86	0.05	0.3717	2.88	-0.2280	2.6520
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.06	0.06	0.4853	2.38	-0.0255	2.3545
9.22	5.45	6.10	6.16	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430
9.73	5.55	6.33	6.41	0.08	0.8000	1.69	0.6020	2.2920

LogK$_1$ **(Average value)** = 2.2516± 0.5380

Table 18:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$\mathrm{Log}(\frac{n-1}{2-n})$	Log K_2
10.00	5.60	6.47	6.57	0.10	1.1434	1.43		
10.23	5.65	6.62	6.72	0.10	1.3448	1.23	-0.2788	0.9512
10.49	5.70	6.80	6.90	0.10	1.7742	1.03	0.5351	1.5651

LogK_2 **(Average value)** = 1.2581± 0.4340

Table 19: Stepwise and overall Stability constants of thehydrolysed and unhydrolysed divalent metal (II) complexes

Chelates	**LogK_1**	**LogK_2**	**Logβ**
[Cu (Hydrolysed PSHA-1)$_2$]	2.4788	1.4280	3.9068
[Pb (Hydrolysed PSHA-1)$_2$]	2.5832	1.1963	3.7795
[Cd (Hydrolysed PSHA-1)$_2$]	2.2108	1.5453	3.7561
[Mg (Hydrolysed PSHA-1)$_2$]	2.1382	1.5453	3.6835
[Cu (Unhydrolysed PSHA-1)$_2$]	2.3059	1.2209	3.5268
[Pb (Unhydrolysed PSHA-1)$_2$]	2.2364	1.2239	3.4603
[Cd (Unhydrolysed PSHA-1)$_2$]	2.2516	1.2581	3.5097
[Mg (Unydrolysed PSHA-1)$_2$]	2.1568	0.9127	3.0695

The results obtained (Table19) shows the stepwise and overall stability constants to be not high indicating low stability of the complexes, because the solubility of most metal ions in the basic pH range is minimal due to metal hydroxide precipitation (Karimi, 2017). In general, the stepwise stability constants (K_1 and K_2) follow the order $K_1 > K_2$ for the copper, lead, magnesium and cadmium complexes respectively. The steady decrease of the values with increasing number of ligands is in agreement with the prediction made by researchers (Na'aliya, 2013). The decrease could be attributed to the fact that as the number of the ligands (Humate ions) that enters the coordination zone increases the aqua molecules available for replacement by the ligands become less. Thus, the metal ions become less electron loving with progressive intake of the ligand and this results in the decrease in the values of the constants (Na'aliya, 2013). Also the stability of the complexes is influenced by the size and number of the chelate rings(Mackay and Mackay,2002).All the complexes form rings in their structure as humate, a bidentate ligand, bond the metal ions in the ratio 1:2 (Boguta and Sokolowska, 2016) forming chelate rings. The values of the overall stability constants (logβ) obtained for humate complexes are not high indicating low stability as the values are not high. LogK values for copper-humates (Table 3 to 6) obtained in this study are lower than those reported for the complexes of humic acids (Pandey *et al*., 2015; Dinu, 2013; Kaschl *et al*., 2010 and Gilbeto and Jorg, 2001). The values of LogK(Table 7 to 10) forlead-humates are lower than those reported for the lead in the literature (Dinu, 2013; Gilbeto and Jorg 2001). Log K values(Table 11 to 14) for magnesium-humates obtained in this study are close to those reported by (Pandey *et al*., 2015). Log K values of cadmium-humates (Table 15 to 18) obtained in this work near to the one reported by (Dinu, 2013 and Pandey *et al*., 2015).The difference between the reported values and the values obtained in this study might be probably as a result of acid hydrolysis of humic acid. The values of the overall stability constants (log β) of the copper humates complexes presented in Table 19 is high than that of other metal humate complexes, show relatively high stability of Cu-HA complexes, show the following order of stability: Cu >Pb> Cd > Mg; which are in close agreement to the findings of (Dinu, 2013 and Pandey *et al*., 2015).The high stability of Cu-humate chelate could be attributed to the existence of coordinate covalent bond between the complexing agents and the Cu^{2+} ions. Since, Cu^{2+} being a metal of the transitional series with $3d^9$ electronic configurations can accept the electrons from the complexing agents. Similarly,the low stabilities of Pb,Cd and Mg -complexes could be explained by that Pb^{2+} with $6s^2$, Cd^{2+} with $4d^{10}$ and Mg^{2+} with $2p^6$ their electronic configuration has a completely filled d,p and s orbitals. Moreover, the stabilities of metal ions with hydrolysed humic acid from peat soil were higher than those with unhydrolysed humic acid from peat soil; which is ascribed to the high content of acidity in hydrolysed humic acid than unhydrolysed humic acid.

CONCLUSION

The values of logK for Cu(II) hydrolysed humic acid complex was higher followed by Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes as compared with metal(II) unhydrolysed humic acid complexes . This indicates acid hydrolysis of humic acid can enhance the complexation behavior of humic acid with metal (II) ions. However, the higher values of logβ for Cu(II), Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes indicates more stable stepwise complexes formed as compared with Cu(II), Pb(II), Cd(II) and Mg(II) unhydrolysed humic acid complexes.

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STABILITY CONSTANTS OF COMPLEXES OF METAL IONS WITH PEATSOIL HUMIC ACIDS UNDER NON-ACID-CONDITIONS

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ABSTRACT

Stability constants of complexes of four divalent metal ions viz. Cu^{2+}, Pb^{2+},Mg^{2+} and Cd^{2+} with humic acids (HA) were determined by potentiometric titration of humic acids with the corresponding salt of the divalent metals in aqueous media under non-acid-condition. The log K (logarithm of the stability constant) ranged from 1.0942 to 2.7471 for metal-humic acid complexes were determined using point-wise computational method. The order of stability constants were obtained as follows: Cu >Pb> Cd > Mg for metal -HA complexes respectively, indicating a higher degree of complexation with Cu metal ion.

Keywords: stability constant, humic acid, potentiometric titration, divalent metals, acid hydrolysis.

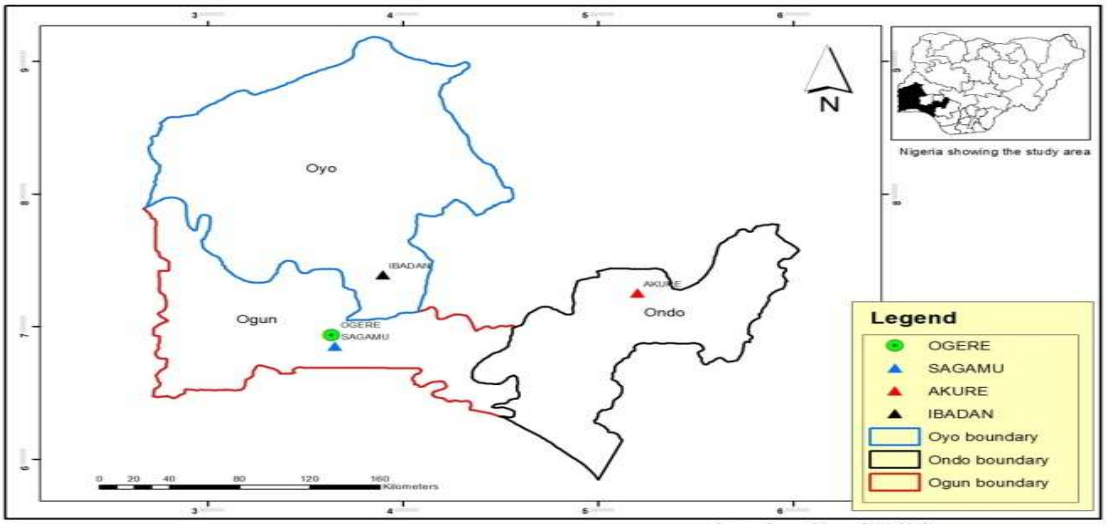
NTRODUCTION

The stability constant of a complex is the numerical expression of its stability and provides a quantitative measure of affinity of the metal ion to the complexing agent. An understanding of the relative stability of metal-complexes helps in predicting the behavior of metal ions in the soil (Ram and Raman, 1982). Extensive researches has been done to determine the stability constants of the complexes formed between humic acid (HA) with a number of metal ions. Ashok *et al*., (2000) reported that humic acid with hydroxyl, phenoxyl and carboxyl reactive groups can form coordination compound with metal ions at pH 3.5. The stability constants(Log K) for different metal-humic acid complexes indicated the following order of the stabilities of complexes formed between humic acid and metal ion, Cu >Fe >Pb> Ni > Co > Ca > Cd > Zn >Mn> Mg. Andelkovic *et al*., (2010) investigated the binding of Cd(II) to soil humic acid at pH 6.5 and in 0.1M KNO_3 ionic medium. The stability constant for binding indicating greater stability in the case when carboxyl groups are involved in complexation reaction. Kostic *et al*.,(2012) investigated the complexation of humic acid with certain heavy metal ions (Co(II), Ni(II),Cu(II), Zn(II), and Pb(II). The experiment was performed at 25°C, at pH 4.0 and ionic strength of 0.01M. Stability constant of complex between Pb(II) ions and humic acid is greater than stability constants of other investigated metal-humate complexes. Bogata and Sokolowska (2016) analyses the interaction between humic acids from different soils and Zn (II) ions at wide concentration ranges and at pH 5. Studies have showed significant impact of Zn concentration, pH and some properties of humic acids with zinc.But all of these studies were limited to acidic pH range. Therefore, the present study was carried out to determine and compare the stability constants of complexes of metal ions with hydrolysed peat soil humic acid and unhydrolysed peat soil humic under non-acid conditions.

MATERIALS AND METHODS

Analytical grade chemicals used includes hydrochloric acid (HCl), nitric acid (HNO_3), sodium hydroxide (NaOH), lead nitrate $Pb(NO_3)_2$, copper nitrate $Cu(NO_3)_2.3H_2O$, cadmium nitrate $Cd(NO_3)_2.4H_2O$, magnesium nitrate $Mg(NO_3)_2.6H_2O$, potassium nitrate (KNO_3), calcium chloride ($CaCl_2$), (sigma-Aldrich). Dowex 50WX8, (20-50 mesh) from Fluka.

Area of study



Source: Dept. of Geog. BUK (2016)

Figure 1: Map showing the sampling point at Sagamu Town, Ogun State.

Description of Sampling Area

Sagamu has geographical coordinates between 6°50′ north; 3° 38′ east is located in south western region of Nigeria. The region has tropical wet and dry climate with a lengthy wet season and relatively constant temperatures throughout the course of the year. Wet season runs from March to October, November to December forms the region dry season. The vegetation type of the region is savannah which is really grassland with small bushes and occasional big trees. Grassland soils have substantially higher organic matter content than forest soils (Novackova, 2011).

Sample Collection

The Peatsoil samples were collected from four different sampling points (0-10cm depth) in Sagamu into polyethylene bag with plastic spoons. Samples were taken to the laboratory, extraneous materials were removed; the samples were air-dried, crushed and ground to a fine powder in a mortar passed through a 0.20mm sieve. The samples were kept for analysis.

Isolation and purification of humic acid from peat soil sample

Peatsoil sample (100g) was mixed with 1000 cm^3 of 0.1M NaOH solution, shaken for 3hours and left to stand overnight. Dark-coloured supernatant was obtained and decanted from solid residue. The dark-coloured supernatant was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 6 hours. Yellowish brown supernatant and dark-brown precipitate were obtained. The yellowish brown supernatant was decanted followed by centrifuge and discarded. The dark-brown precipitate was mixed with 500$cm^3$of 0.1M NaOH solution followed by passing through dowex resin. The dark-brown solution was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 3 hours. The dark-brown precipitate was washed several times with deionized water. The supernatant was treated with $AgNO_3$ solution until no white precipitate observed. The humic acid was transferred to weighed crucible and dried at 60°C in an oven for 12 hours. The humic acid was cooled and dried in the desiccator, weighed and recorded. The obtained humic acid was dried again at 60°C for additional 6 hours cooled and dried in the desiccator, weighed and recorded constant weight was obtained (Baruah *et al*., 2015).

FT-IR analysis

FT-IR spectra of humic acid sample was analysed using Carry 630 FT-IR Agilent Technologies.

Unhydrolysed compost humic acid

The unhydrolysed humic acid was obtained after isolation and purification of compost humic acid and kept for investigation.

Acid hydrolysis of Peatsoil acid

Peatsoil humic acid sample (1g) was refluxed for 12 hours at (160°C) with 50cm^3 of 6M HCl. The mixture was allowed to cool, decanted, and centrifuged after hydrolysis. The insoluble residues were washed with distilled water via centrifugation several times, and the supernatant was treated with $AgNO_3$ solution until no white precipitate was observed. The residue was thoroughly dried over $CaCl_2$ in a desiccator at room temperature (Chefetz *et al*., 2002). Finally, the obtained hydrolysed humic acid was kept for investigation.

Potentiometric Titrations

Potentiometric measurements were carried out using a pH-meter Jenway (model 3510) with combine electrode, the sensitivity of the pH - meter is 0.01 units. The pH meter was switched on half an hour before starting the titration for initial warm up of the instrument. The instrument was calibrated with an aqueous standard buffer solution of pH 4.00 and 10.0 (borate buffer) prepared from a "Qualigens" buffer tablets.

The following sets of solutions were prepared in a 250cm^3 volumetric flask separately for pH metric titrations.

(i) 5 cm^3 0.1 M HCl + 40 cm^3 deionized water
(ii) 5 cm^3 0.1 M HCl + 39 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid
(iii) 5 cm^3 0.1 M HCl + 37 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid + 2 cm^3 0.01 M Cu(II)

The solutions were titrated against standardized 0.110MNaOH separately. The total volume of each mixture was adjusted to 50 cm^3 and the ionic strength of the solutions was maintained constant at by adding appropriate amount of stock solution of 1M KNO$_3$ (Gamal, 2015; Omar and Ali, 2015). A magnetic stirrer was used to achieve thorough mixing of the interacting solutions at 550 rpm. The same set of experimental conditions was applied for potentiometric titration of remaining samples.

Evaluation of pKa of Hydrolysed peat soil Humic Acids

The proton-ligand formation number n$_{\mathbf{A}}$ were calculated by Irving and Rossotti expression (Omar and Ali, 2015).

$$nA = Y - \frac{(V2-V1)(No-Eo)}{(Vo+V1)TcL} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 1$$

Where: Y is number of dissociable proton, (V$_2$-V$_1$) is the measure of displacement of the ligand curve relative to acid curve, N^o and E^o are the resultant concentration of alkali solution, free acid solution, T$_{cL}$^{o} is the total ligand concentration, V^o is the total volume of titration solution,V$_1$ is the volume of alkali added to acid solution,V$_2$ is the volume of alkali added to acid solution + ligand solution, acid dissociation constants (pKa - values) of ligand were calculated by algebraic method point wise calculation (Tables 1). The dissociation constants (pKa) were calculated according to the following relation:

$$pKa = pH + \log\left(\frac{nA}{1-nA}\right) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 2$$

Where: pKa is the acid dissociation constant, n$_A$is the Proton-ligand formation number and pH is the pH-values (Omar and Ali, 2015).

Determination of metal-ligand stability constants (log K) of complexes

The potentiometric measurement for the determination of stability constant of a complex in solution is based on the fact that the redox potential of the couple $\frac{M^{+(m-n)}}{M^{+m}}$ is shifted significantly on complexation of the metal ion with the ligand. This method involves change in hydrogen ion concentration [H$^+$] due to the displacement or association of one or more protons taking place during complexation reaction. This change can be found out by titrating the solutions containing free acid, acid with ligand, and acid with ligand and metal ion, individually against a standard alkali solution at a constant ionic strength or temperature. Either ionic strength or temperature may be varied for different sets of solutions. In all the cases, the change in the pH of the solution is measured after each addition of a known amount of alkali to the reaction cell which contains the reaction mixture. The titration curves are then drawn by plotting the measured pH values against the corresponding volume of alkali added and the stability constants of the complexes are determined from the titration curves by employing pH-metric titration technique given by (Irving and Rossoti).

Metal-ligand stability constants (Log K) were determined by using the following relations:

$$\bar{n} = \frac{(V_3 - V_2)(E^0 + N^0)}{(V^0 + V_2)\bar{n}_A T_m^0} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 3$$

and

$$PL = \log_{10}\{\frac{1 + \beta_n^H \dfrac{1}{[anti\ \log \mathrm{pH}]^n}}{T_L^0 - \bar{n}T_m^0} \mathrm{X} \frac{(V^0 + V_3)}{V^0}\} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 4$$

Where $T_{L,}$ T^o, $E°$, and V^ohavethe same significance as in equation (1) above, T_m denotes the total concentration of metal present in solution, V_3 is the volume of metal ions present in solution and β^H is the overall proton ligand stability constant. The metal-ligand stability constants (log K) were determined by employing point wise computational Method (eq. 5 and 6).

$\mathrm{Log}K_1 = \log\left(\frac{n}{1-n}\right) + pL$ …………..5

$\mathrm{Log}K_2 = \log\left(\frac{1-n}{2-n}\right) + pL$……………………6

Where: Log K is the metal-ligand stability constant, pL is the Free ligand exponent function, **n** is the Average number of ligand attached with metal ion (Janrao*et al.*, 2014).The results obtained were analyzed by an ORIGIN 2016 program using titration data and then the proton-ligand stability constants (pKa) and Metal-ligand stability constant (LogK) calculated (Omar and Ali, 2015).

RESULTS AND DISCUSSION

Fourier transformed infrared (FT-IR) spectra of isolated humic acid from peat soils Figure 2 had distinct clear absorption bands indicating the presence of major humic acid structural elemental groups such as H bonded OH ($3680cm^{-1}$ peak), C=O of carbonyl ($1721cm^{-1}$ peak), functional groups of aliphatic components CH_2 ($2918cm^{-1}$ peak) and C-O stretching of polysaccharide ($1168cm^{-1}$ peak). The positions of the absorption bands of the spectra fell within typical major absorption bands of humic acid which is at frequencies 3680, 2918, 1721, 1168 cm^{-1}. The first peak centred in the vicinity of 3680 cm^{-1} region is attributed to phenol OH group bounded by intermolecular H bonds. The $2918cm^{-1}$ band usually has absorption maximum at 2918 cm^{-1} which is due to C–H stretching of alkane group (CH_2). The next major absorption band is 1721 cm^{-1}. This band has been commonly ascribed to C=O stretching of mainly carboxyl group (COOH) with trace amount of ketones. The last peak was observed at 1168 cm^{-1} due to C–O stretching of polysaccharides and this peak appeared also in the spectra of humic acid from peat soil. The FTIR spectra of the isolated humic acid contained all major characteristic absorption peaks of humic acid. These absorption peaks indicated the presence of the major structural elements of humic acid namely H bonded OH, C=C of aromatic ring, C=O of carbonyl group (both carboxyl and ketonic), CH_2 group. This strongly supports the presence of humic acid.

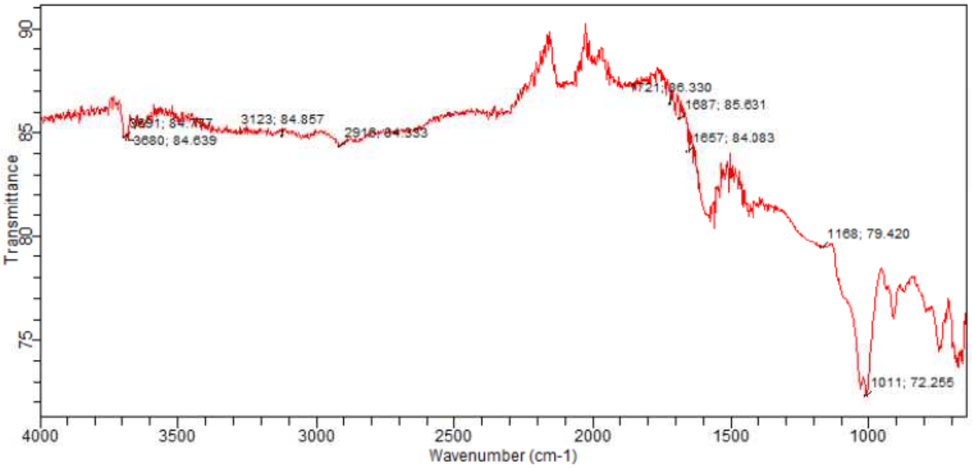


Fig. 2 : FT-IR spectraof peatsoilhumic acid (PSHA)

Evaluation of acid dissociation constant (pka) of acid hydrolysed peat soil humicacid at phenolic group

The value of the dissociation constant of the peat soil humic acid (PSHA) that underwent acidhydrolysis studied was found to be 8.9299 as shown Table 1, which is lower than the literaturevalues reported by Almeida and Szpoganics, (2015), Borges *et al.*, (2005); Badr *et al.*, (2012)and Fernandes *et al*,.(2009) of 9.73, 9.47 and 10.30. The difference between the obtained valuesand the reported values in this study might be probably as a result of acid hydrolysis of humicacid.

Table 1: PKa of (Hydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	$\log(\frac{nA}{1-nA})$	pKa
8.50	5.30	6.29	0.99	0.3594	-0.2510	8.2490
8.72	5.35	6.37	1.02	0.3400	-0.2880	8.4320
9.00	5.40	6.46	1.06	0.3141	-0.3391	8.6609
9.22	5.45	6.55	1.10	0.2882	-0.3927	8.8273
9.51	5.50	6.66	1.16	0.2494	-0.4786	9.0314
9.73	5.55	6.78	1.23	0.2041	-0.5910	9.1390
10.00	5.60	6.90	1.30	0.1589	-0.7238	9.2762
10.23	5.65	7.05	1.40	0.0941	-0.9835	9.2465
10.49	5.70	7.10	1.40	0.0941	-0.9835	9.5065

Average pKa = 8.9299 ± 0.4186

Table 2: PKa of (Unhydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	$\mathrm{Log}(\frac{nA}{1-n})$	pKa
8.50	5.30	5.81	0.51	0.6619	0.2919	8.7919
8.72	5.35	5.90	0.55	0.6357	0.2418	8.9618
9.00	5.40	6.00	0.60	0.6029	0.1813	9.1813
9.22	5.45	6.10	0.65	0.5701	0.1226	9.3426
9.51	5.50	6.20	0.70	0.5376	0.0654	9.5754
9.73	5.55	6.33	0.78	0.4851	-0.0259	9.7041
10.00	5.60	6.47	0.87	0.4262	-0.1291	9.8709
10.23	5.65	6.62	0.99	0.3609	-0.2481	9.9819
10.49	5.70	6.80	1.10	0.2759	-0.4690	10.0210

Average pKa = 9.4923± 0.4410

Metal-ligand stability constant (Log K)

The stabilityconstants require the accurate values of proton-ligand stability constants (Anil and Maroti, 2008). Metal titration curves crossed over ligand titration curve indicated the formation of complex upon proton release (Santosh, *et al.*, 2011). If the values of n- are within range 0.2-0.8 and 1.2-18 this indicates the formation of 1:1 and 1:2 complexes (Sayyed and Mazahar, 2012).

The metal (II)-humate stepwise stability constants (log k) at phenolic group (Tables 3-18)

Table 3: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$\log(\frac{n}{1-n})$	$\mathrm{Log}K_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

$\mathrm{LogK_1}$ (Average value) = 2.4788± 0.2203

Table 4: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$\mathrm{Log}(\frac{n-1}{2-n})$	$\mathrm{Log}K_2$
9.51	5.50	6.66	6.73	0.07	1.3509	1.70	-0.2671	1.4329
9.73	5.55	6.78	6.85	0.07	1.6383	1.51	0.2467	1.7567
10.00	5.60	6.90	6.98	0.08	2.1783	1.31	-0.2158	1.0942
10.23	5.65	7.05	7.13	0.08	4.1904	1.27		
10.49	5.70	7.10	7.19	0.09	4.6920			

$\mathrm{LogK_2}$(Average value) = 1.4280 ± 0.3312

Table 5:Point-wise method,Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	Log$(\frac{n}{n-1})$	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430

$LogK_1$ **(Average value)** = 2.3059± 0.6153

Table 6:Point-wise method, Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log$(\frac{n-1}{2-n})$	Log K_2
9.73	5.55	6.33	6.42	0.09	0.9000	1.69		
10.00	5.60	6.47	6.58	0.11	1.2578	1.44	-0.4592	0.9808
10.23	5.65	6.62	6.84	0.12	1.6137	1.26	-0.2010	1.4610
10.49	5.70	6.80	6.92	0.12	2.1052	1.03		

$LogK_2$ **(Average value)** = 1.2209± 0.3398

Table 7:Point-wise method,Pb (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log$(\frac{n}{1-n})$	$LogK_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.60	0.05	0.8333	1.96	0.6989	2.6589

$LogK_1$ (Average value) = 2.5832 ±0.1614

Table 8:Point-wise method,Pb-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log$(\frac{n-1}{2-n})$	$logK_2$
9.51	5.50	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.83	0.05	1.1702	1.44		
10.00	5.60	6.90	6.90	0.05	1.4864	1.22	-0.0237	1.1963
10.23	5.65	7.05	7.10	0.05	2.0190	1.09		
10.49	5.70	7.10	7.17	0.07	3.6492	1.00		

$LogK_2$(Average value) = 1.1963

Table 9:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log $(\frac{n}{n-1})$	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.5477	2.3123
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	0.0272	2.2072
9.51	5.50	6.20	6.26	0.07	0.6417	1.89	0.2530	2.1430
9.73	5.55	6.40	6.40	0.07	0.7000	1.67	0.3680	2.0380

$LogK_1$ **(Average value)** = 2.2364 ± 0.1602

Table 10:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log$(\frac{n-1}{2-n})$	Log K_2
10.00	5.60	6.47	6.55	0.08	1.9503	1.41		
10.23	5.65	6.62	6.72	0.11	1.4792	1.26	-0.0361	1.2239

$LogK_2$ **(Average value)** = 1.2239

Table 11:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log$(\frac{n}{n-1})$	$LogK_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4290	2.2110
8.72	5.35	6.37	6.39	0.02	0.2858	2.42	-0.3978	2.0222
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

$LogK_1$ (Average value)=2.1382**±**0.1046

Table 12:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n-1}{2-n}$)	$LogK_2$
9.51	5.55	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.84	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.93	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.10		
10.49	5.70	7.10	7.18	0.07	3.6492	0.83		

$LogK_2$(Average value) = 1.5453 **±** 0.3450

Table 13:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.3477	2.3123
9.00	5.40	6.00	6.04	0.04	0.3236	2.38	-0.3202	2.0598
9.22	5.45	6.10	6.15	0.05	0.4297	2.17	-0.1230	2.0470
9.51	5.50	6.20	6.26	0.06	0.5500	1.89	0.0871	1.9771
9.73	5.55	6.33	6.40	0.07	0.7000	1.67	0.3680	2.0380

$LogK_1$ **(Average value)** = 2.1568 ± 0.2069

Table 14:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
10.00	5.60	6.47	6.55	0.08	0.9148	1.41		
10.23	5.65	6.62	6.71	0.09	1.2102	1.20	-0.5749	0.6251
10.49	5.70	6.80	6.92	0.09	1.5968	1.03	0.1703	1.2003

$LogK_2$ **(Average value)** = 0.9127± 0.4070

Table15:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	Log($\frac{n}{1-n}$)	$LogK_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4210	2.2190
8.72	5.35	6.37	6.40	0.03	0.4286	2.42	-0.1249	2.2951
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.96	0.3010	2.2610
9.51	5.55	6.66	6.70	0.04	0.7720	1.67	0.5297	2.1997

$LogK_1$ (Average value) = 2.2108± 0.0825

Table 16:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
9.73	5.55	6.78	6.83	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.95	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.09		
10.49	5.70	7.10	7.16	0.06	3.1429	0.89		

$LogK_2$ **(Average value)** = 1.5453± 0.3450

Table 17:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.86	0.05	0.3717	2.88	-0.2280	2.6520
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.06	0.06	0.4853	2.38	-0.0255	2.3545
9.22	5.45	6.10	6.16	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430
9.73	5.55	6.33	6.41	0.08	0.8000	1.69	0.6020	2.2920

$LogK_1$ **(Average value)** = 2.2516± 0.5380

Table 18:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$\text{Log}(\frac{n-1}{2-n})$	Log K_2
10.00	5.60	6.47	6.57	0.10	1.1434	1.43		
10.23	5.65	6.62	6.72	0.10	1.3448	1.23	-0.2788	0.9512
10.49	5.70	6.80	6.90	0.10	1.7742	1.03	0.5351	1.5651

$\text{Log}K_2$ **(Average value)** = 1.2581± 0.4340

Table 19: Stepwise and overall Stability constants of thehydrolysed and unhydrolysed divalent metal (II) complexes

Chelates	**$\text{Log}K_1$**	**$\text{Log}K_2$**	**$\text{Log}\beta$**
[Cu (Hydrolysed PSHA-1)$_2$]	2.4788	1.4280	3.9068
[Pb (Hydrolysed PSHA-1)$_2$]	2.5832	1.1963	3.7795
[Cd (Hydrolysed PSHA-1)$_2$]	2.2108	1.5453	3.7561
[Mg (Hydrolysed PSHA-1)$_2$]	2.1382	1.5453	3.6835
[Cu (Unhydrolysed PSHA-1)$_2$]	2.3059	1.2209	3.5268
[Pb (Unhydrolysed PSHA-1)$_2$]	2.2364	1.2239	3.4603
[Cd (Unhydrolysed PSHA-1)$_2$]	2.2516	1.2581	3.5097
[Mg (Unydrolysed PSHA-1)$_2$]	2.1568	0.9127	3.0695

The results obtained (Table19) shows the stepwise and overall stability constants to be not high indicating low stability of the complexes, because the solubility of most metal ions in the basic pH range is minimal due to metal hydroxide precipitation (Karimi, 2017). In general, the stepwise stability constants (K_1 and K_2) follow the order $K_1 > K_2$ for the copper, lead, magnesium and cadmium complexes respectively. The steady decrease of the values with increasing number of ligands is in agreement with the prediction made by researchers (Na'aliya, 2013). The decrease could be attributed to the fact that as the number of the ligands (Humate ions) that enters the coordination zone increases the aqua molecules available for replacement by the ligands become less. Thus, the metal ions become less electron loving with progressive intake of the ligand and this results in the decrease in the values of the constants (Na'aliya, 2013). Also the stability of the complexes is influenced by the size and number of the chelate rings(Mackay and Mackay,2002).All the complexes form rings in their structure as humate, a bidentate ligand, bond the metal ions in the ratio 1:2 (Boguta and Sokolowska, 2016) forming chelate rings. The values of the overall stability constants (logβ) obtained for humate complexes are not high indicating low stability as the values are not high. LogK values for copper-humates (Table 3 to 6) obtained in this study are lower than those reported for the complexes of humic acids (Pandey *et al*., 2015; Dinu, 2013; Kaschl *et al*., 2010 and Gilbeto and Jorg, 2001). The values of LogK(Table 7 to 10) forlead-humates are lower than those reported for the lead in the literature (Dinu, 2013; Gilbeto and Jorg 2001). Log K values(Table 11 to 14) for magnesium-humates obtained in this study are close to those reported by (Pandey *et al*., 2015). Log K values of cadmium-humates (Table 15 to 18) obtained in this work near to the one reported by (Dinu, 2013 and Pandey *et al*., 2015).The difference between the reported values and the values obtained in this study might be probably as a result of acid hydrolysis of humic acid. The values of the overall stability constants (log β) of the copper humates complexes presented in Table 19 is high than that of other metal humate complexes, show relatively high stability of Cu-HA complexes, show the following order of stability: Cu >Pb> Cd > Mg; which are in close agreement to the findings of (Dinu, 2013 and Pandey *et al*., 2015).The high stability of Cu-humate chelate could be attributed to the existence of coordinate covalent bond between the complexing agents and the Cu^{2+} ions. Since, Cu^{2+} being a metal of the transitional series with $3d^9$ electronic configurations can accept the electrons from the complexing agents. Similarly,the low stabilities of Pb,Cd and Mg -complexes could be explained by that Pb^{2+} with $6s^2$, Cd^{2+} with $4d^{10}$ and Mg^{2+} with $2p^6$ their electronic configuration has a completely filled d,p and s orbitals. Moreover, the stabilities of metal ions with hydrolysed humic acid from peat soil were higher than those with unhydrolysed humic acid from peat soil; which is ascribed to the high content of acidity in hydrolysed humic acid than unhydrolysed humic acid.

CONCLUSION

The values of logK for Cu(II) hydrolysed humic acid complex was higher followed by Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes as compared with metal(II) unhydrolysed humic acid complexes . This indicates acid hydrolysis of humic acid can enhance the complexation behavior of humic acid with metal (II) ions. However, the higher values of logβ for Cu(II), Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes indicates more stable stepwise complexes formed as compared with Cu(II), Pb(II), Cd(II) and Mg(II) unhydrolysed humic acid complexes.

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STABILITY CONSTANTS OF COMPLEXES OF METAL IONS WITH PEATSOIL HUMIC ACIDS UNDER NON-ACID-CONDITIONS

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ABSTRACT

Stability constants of complexes of four divalent metal ions viz. Cu^{2+}, Pb^{2+},Mg^{2+} and Cd^{2+} with humic acids (HA) were determined by potentiometric titration of humic acids with the corresponding salt of the divalent metals in aqueous media under non-acid-condition. The log K (logarithm of the stability constant) ranged from 1.0942 to 2.7471 for metal-humic acid complexes were determined using point-wise computational method. The order of stability constants were obtained as follows: Cu >Pb> Cd > Mg for metal -HA complexes respectively, indicating a higher degree of complexation with Cu metal ion.

Keywords: stability constant, humic acid, potentiometric titration, divalent metals, acid hydrolysis.

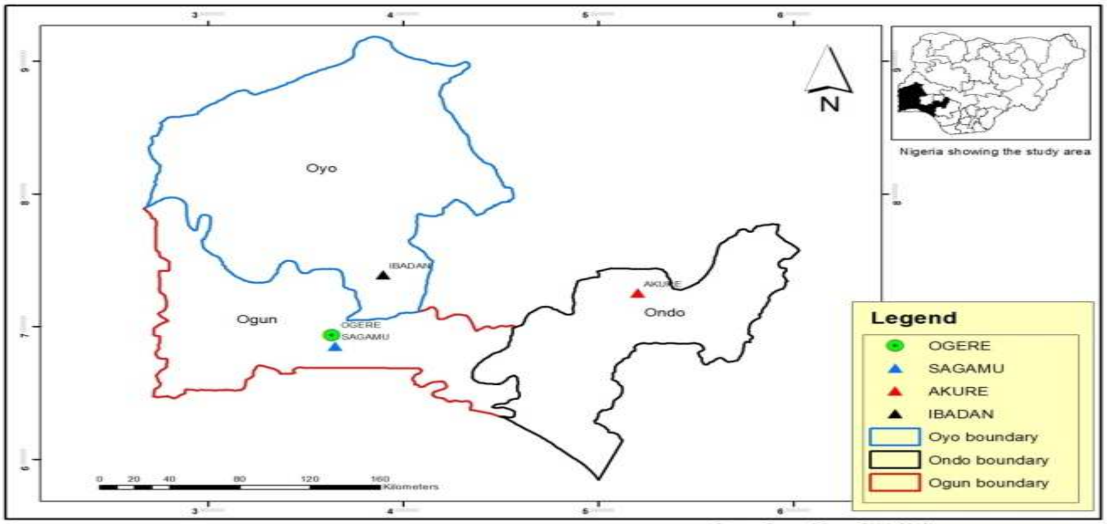
NTRODUCTION

The stability constant of a complex is the numerical expression of its stability and provides a quantitative measure of affinity of the metal ion to the complexing agent. An understanding of the relative stability of metal-complexes helps in predicting the behavior of metal ions in the soil (Ram and Raman, 1982). Extensive researches has been done to determine the stability constants of the complexes formed between humic acid (HA) with a number of metal ions. Ashok *et al.*, (2000) reported that humic acid with hydroxyl, phenoxyl and carboxyl reactive groups can form coordination compound with metal ions at pH 3.5. The stability constants(Log K) for different metal-humic acid complexes indicated the following order of the stabilities of complexes formed between humic acid and metal ion, Cu >Fe >Pb> Ni > Co > Ca > Cd > Zn >Mn> Mg. Andelkovic *et al.*, (2010) investigated the binding of Cd(II) to soil humic acid at pH 6.5 and in 0.1M KNO_3 ionic medium. The stability constant for binding indicating greater stability in the case when carboxyl groups are involved in complexation reaction. Kostic *et al.*,(2012) investigated the complexation of humic acid with certain heavy metal ions (Co(II), Ni(II),Cu(II), Zn(II), and Pb(II). The experiment was performed at 25°C, at pH 4.0 and ionic strength of 0.01M. Stability constant of complex between Pb(II) ions and humic acid is greater than stability constants of other investigated metal-humate complexes. Bogata and Sokolowska (2016) analyses the interaction between humic acids from different soils and Zn (II) ions at wide concentration ranges and at pH 5. Studies have showed significant impact of Zn concentration, pH and some properties of humic acids with zinc.But all of these studies were limited to acidic pH range. Therefore, the present study was carried out to determine and compare the stability constants of complexes of metal ions with hydrolysed peat soil humic acid and unhydrolysed peat soil humic under non-acid conditions.

MATERIALS AND METHODS

Analytical grade chemicals used includes hydrochloric acid (HCl), nitric acid (HNO_3), sodium hydroxide (NaOH), lead nitrate $Pb(NO_3)_2$, copper nitrate $Cu(NO_3)_2.3H_2O$, cadmium nitrate $Cd(NO_3)_2.4H_2O$, magnesium nitrate $Mg(NO_3)_2.6H_2O$, potassium nitrate (KNO_3), calcium chloride ($CaCl_2$), (sigma-Aldrich). Dowex 50WX8, (20-50 mesh) from Fluka.

Area of study



Source: Dept. of Geog. BUK (2016)

Figure 1: Map showing the sampling point at Sagamu Town, Ogun State.

Description of Sampling Area

Sagamu has geographical coordinates between 6°50′ north; 3° 38′ east is located in south western region of Nigeria. The region has tropical wet and dry climate with a lengthy wet season and relatively constant temperatures throughout the course of the year. Wet season runs from March to October, November to December forms the region dry season. The vegetation type of the region is savannah which is really grassland with small bushes and occasional big trees. Grassland soils have substantially higher organic matter content than forest soils (Novackova, 2011).

Sample Collection

The Peatsoil samples were collected from four different sampling points (0-10cm depth) in Sagamu into polyethylene bag with plastic spoons. Samples were taken to the laboratory, extraneous materials were removed; the samples were air-dried, crushed and ground to a fine powder in a mortar passed through a 0.20mm sieve. The samples were kept for analysis.

Isolation and purification of humic acid from peat soil sample

Peatsoil sample (100g) was mixed with 1000 cm^3 of 0.1M NaOH solution, shaken for 3hours and left to stand overnight. Dark-coloured supernatant was obtained and decanted from solid residue. The dark-coloured supernatant was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 6 hours. Yellowish brown supernatant and dark-brown precipitate were obtained. The yellowish brown supernatant was decanted followed by centrifuge and discarded. The dark-brown precipitate was mixed with 500cm^{3}of 0.1M NaOH solution followed by passing through dowex resin. The dark-brown solution was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 3 hours. The dark-brown precipitate was washed several times with deionized water. The supernatant was treated with AgNO$_3$ solution until no white precipitate observed. The humic acid was transferred to weighed crucible and dried at 60^{o}C in an oven for 12 hours. The humic acid was cooled and dried in the desiccator, weighed and recorded. The obtained humic acid was dried again at 60^{o}C for additional 6 hours cooled and dried in the desiccator, weighed and recorded constant weight was obtained (Baruah *et al*., 2015).

FT-IR analysis

FT-IR spectra of humic acid sample was analysed using Carry 630 FT-IR Agilent Technologies.

Unhydrolysed compost humic acid

The unhydrolysed humic acid was obtained after isolation and purification of compost humic acid and kept for investigation.

Acid hydrolysis of Peatsoil acid

Peatsoil humic acid sample (1g) was refluxed for 12 hours at (160^{o}C) with 50cm^3 of 6M HCl. The mixture was allowed to cool, decanted, and centrifuged after hydrolysis. The insoluble residues were washed with distilled water via centrifugation several times, and the supernatant was treated with AgNO$_3$ solution until no white precipitate was observed. The residue was thoroughly dried over CaCl$_2$ in a desiccator at room temperature (Chefetz *et al*., 2002). Finally, the obtained hydrolysed humic acid was kept for investigation.

Potentiometric Titrations

Potentiometric measurements were carried out using a pH-meter Jenway (model 3510) with combine electrode, the sensitivity of the pH - meter is 0.01 units. The pH meter was switched on half an hour before starting the titration for initial warm up of the instrument. The instrument was calibrated with an aqueous standard buffer solution of pH 4.00 and 10.0 (borate buffer) prepared from a "Qualigens" buffer tablets.

The following sets of solutions were prepared in a 250cm^3 volumetric flask separately for pH metric titrations.

(i) 5 cm^3 0.1 M HCl + 40 cm^3 deionized water

(ii) 5 cm^3 0.1 M HCl + 39 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid

(iii) 5 cm^3 0.1 M HCl + 37 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid + 2 cm^3 0.01 M Cu(II)

The solutions were titrated against standardized 0.110MNaOH separately. The total volume of each mixture was adjusted to 50 cm^3 and the ionic strength of the solutions was maintained constant at by adding appropriate amount of stock solution of 1M KNO$_3$ (Gamal, 2015; Omar and Ali, 2015). A magnetic stirrer was used to achieve thorough mixing of the interacting solutions at 550 rpm. The same set of experimental conditions was applied for potentiometric titration of remaining samples.

Evaluation of pKa of Hydrolysed peat soil Humic Acids

The proton-ligand formation number n$_{\mathbf{A}}$ were calculated by Irving and Rossotti expression (Omar and Ali, 2015).

$$nA = Y - \frac{(V2-V1)(No-Eo)}{(Vo+V1)TcL} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 1$$

Where: Y is number of dissociable proton, (V$_2$-V$_1$) is the measure of displacement of the ligand curve relative to acid curve, N^o and E^o are the resultant concentration of alkali solution, free acid solution, T$_{cL}$^{o} is the total ligand concentration, V^o is the total volume of titration solution,V$_1$ is the volume of alkali added to acid solution,V$_2$ is the volume of alkali added to acid solution + ligand solution, acid dissociation constants (pKa - values) of ligand were calculated by algebraic method point wise calculation (Tables 1). The dissociation constants (pKa) were calculated according to the following relation:

$$pKa = pH + \log(\frac{nA}{1-nA}) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 2$$

Where: pKa is the acid dissociation constant, n$_A$is the Proton-ligand formation number and pH is the pH-values (Omar and Ali, 2015).

Determination of metal-ligand stability constants (log K) of complexes

The potentiometric measurement for the determination of stability constant of a complex in solution is based on the fact that the redox potential of the couple $\frac{M^{+(m-n)}}{M^{+m}}$ is shifted significantly on complexation of the metal ion with the ligand. This method involves change in hydrogen ion concentration [H$^+$] due to the displacement or association of one or more protons taking place during complexation reaction. This change can be found out by titrating the solutions containing free acid, acid with ligand, and acid with ligand and metal ion, individually against a standard alkali solution at a constant ionic strength or temperature. Either ionic strength or temperature may be varied for different sets of solutions. In all the cases, the change in the pH of the solution is measured after each addition of a known amount of alkali to the reaction cell which contains the reaction mixture. The titration curves are then drawn by plotting the measured pH values against the corresponding volume of alkali added and the stability constants of the complexes are determined from the titration curves by employing pH-metric titration technique given by (Irving and Rossoti).

Metal-ligand stability constants (Log K) were determined by using the following relations:

$$\bar{n} = \frac{(V_3 - V_2)(E^0 + N^0)}{(V^0 + V_2)\bar{n}_A T_m^0} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 3$$

and

$$PL = \log_{10}\{\frac{1 + \beta_n^H \frac{1}{[anti\ \log \mathrm{pH}]^n}}{\mathrm{T}_L^0 - \bar{n}T_m^0} \mathrm{X} \frac{(V^0 + V_3)}{V^0}\} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 4$$

Where $T_{L,}$ T^{o}, E°, and V^{o}havethe same significance as in equation (1) above, T_m denotes the total concentration of metal present in solution, V_3 is the volume of metal ions present in solution and β^H is the overall proton ligand stability constant. The metal-ligand stability constants (log K) were determined by employing point wise computational Method (eq. 5 and 6).

$$\mathrm{Log}K_1 = \log\left(\frac{n}{1-n}\right) + pL \qquad \text{.............}5$$

$$\mathrm{Log}K_2 = \log\left(\frac{1-n}{2-n}\right) + pL\text{.......................}6$$

Where: Log K is the metal-ligand stability constant, pL is the Free ligand exponent function, **n** is the Average number of ligand attached with metal ion (Janrao*et al*., 2014).The results obtained were analyzed by an ORIGIN 2016 program using titration data and then the proton-ligand stability constants (pKa) and Metal-ligand stability constant (LogK) calculated (Omar and Ali, 2015).

RESULTS AND DISCUSSION

Fourier transformed infrared (FT-IR) spectra of isolated humic acid from peat soils Figure 2 had distinct clear absorption bands indicating the presence of major humic acid structural elemental groups such as H bonded OH ($3680cm^{-1}$ peak), C=O of carbonyl ($1721cm^{-1}$ peak), functional groups of aliphatic components CH_2 ($2918cm^{-1}$ peak) and C-O stretching of polysaccharide ($1168cm^{-1}$ peak). The positions of the absorption bands of the spectra fell within typical major absorption bands of humic acid which is at frequencies 3680, 2918, 1721, 1168 cm^{-1}. The first peak centred in the vicinity of 3680 cm^{-1} region is attributed to phenol OH group bounded by intermolecular H bonds. The $2918cm^{-1}$ band usually has absorption maximum at 2918 cm^{-1} which is due to C–H stretching of alkane group (CH_2). The next major absorption band is 1721 cm^{-1}. This band has been commonly ascribed to C=O stretching of mainly carboxyl group (COOH) with trace amount of ketones. The last peak was observed at 1168 cm^{-1} due to C–O stretching of polysaccharides and this peak appeared also in the spectra of humic acid from peat soil. The FTIR spectra of the isolated humic acid contained all major characteristic absorption peaks of humic acid. These absorption peaks indicated the presence of the major structural elements of humic acid namely H bonded OH, C=C of aromatic ring, C=O of carbonyl group (both carboxyl and ketonic), CH_2 group. This strongly supports the presence of humic acid.

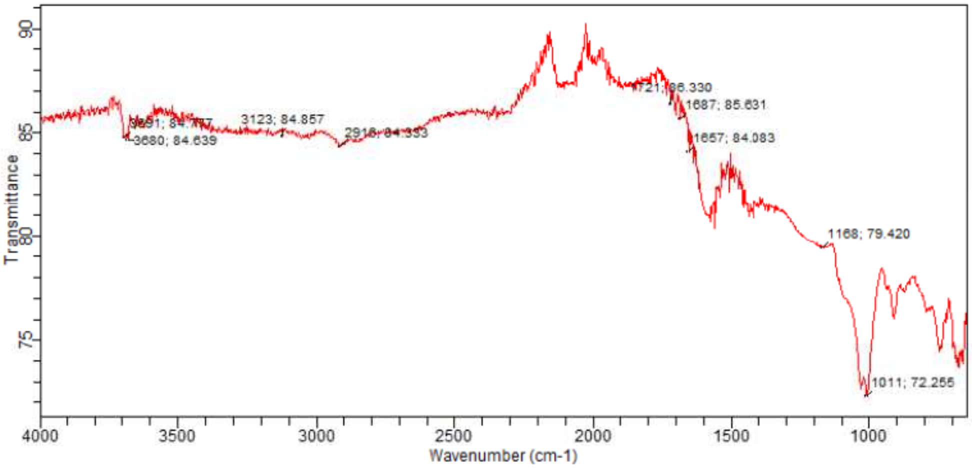


Fig. 2 : FT-IR spectraof peatsoilhumic acid (PSHA)

Evaluation of acid dissociation constant (pka) of acid hydrolysed peat soil humicacid at phenolic group

The value of the dissociation constant of the peat soil humic acid (PSHA) that underwent acidhydrolysis studied was found to be 8.9299 as shown Table 1, which is lower than the literaturevalues reported by Almeida and Szpoganics, (2015), Borges *et al*., (2005); Badr *et al*., (2012)and Fernandes *et al*,.(2009) of 9.73, 9.47 and 10.30. The difference between the obtained valuesand the reported values in this study might be probably as a result of acid hydrolysis of humicacid.

Table 1: PKa of (Hydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	$\log(\frac{nA}{1-nA})$	pKa
8.50	5.30	6.29	0.99	0.3594	-0.2510	8.2490
8.72	5.35	6.37	1.02	0.3400	-0.2880	8.4320
9.00	5.40	6.46	1.06	0.3141	-0.3391	8.6609
9.22	5.45	6.55	1.10	0.2882	-0.3927	8.8273
9.51	5.50	6.66	1.16	0.2494	-0.4786	9.0314
9.73	5.55	6.78	1.23	0.2041	-0.5910	9.1390
10.00	5.60	6.90	1.30	0.1589	-0.7238	9.2762
10.23	5.65	7.05	1.40	0.0941	-0.9835	9.2465
10.49	5.70	7.10	1.40	0.0941	-0.9835	9.5065

Average pKa = 8.9299 ± 0.4186

Table 2: PKa of (Unhydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	$\text{Log}(\frac{nA}{1-n})$	pKa
8.50	5.30	5.81	0.51	0.6619	0.2919	8.7919
8.72	5.35	5.90	0.55	0.6357	0.2418	8.9618
9.00	5.40	6.00	0.60	0.6029	0.1813	9.1813
9.22	5.45	6.10	0.65	0.5701	0.1226	9.3426
9.51	5.50	6.20	0.70	0.5376	0.0654	9.5754
9.73	5.55	6.33	0.78	0.4851	-0.0259	9.7041
10.00	5.60	6.47	0.87	0.4262	-0.1291	9.8709
10.23	5.65	6.62	0.99	0.3609	-0.2481	9.9819
10.49	5.70	6.80	1.10	0.2759	-0.4690	10.0210

Average pKa = 9.4923± 0.4410

Metal-ligand stability constant (Log K)

The stabilityconstants require the accurate values of proton-ligand stability constants (Anil and Maroti, 2008). Metal titration curves crossed over ligand titration curve indicated the formation of complex upon proton release (Santosh, *et al.*, 2011). If the values of n- are within range 0.2-0.8 and 1.2-18 this indicates the formation of 1:1 and 1:2 complexes (Sayyed and Mazahar, 2012).

The metal (II)-humate stepwise stability constants (log k) at phenolic group (Tables 3-18)

Table 3: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$\log(\frac{n}{1-n})$	$\text{Log}K_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

LogK_1 (Average value) = 2.4788± 0.2203

Table 4: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$\text{Log}(\frac{n-1}{2-n})$	$\text{Log}K_2$
9.51	5.50	6.66	6.73	0.07	1.3509	1.70	-0.2671	1.4329
9.73	5.55	6.78	6.85	0.07	1.6383	1.51	0.2467	1.7567
10.00	5.60	6.90	6.98	0.08	2.1783	1.31	-0.2158	1.0942
10.23	5.65	7.05	7.13	0.08	4.1904	1.27		
10.49	5.70	7.10	7.19	0.09	4.6920			

LogK_2(Average value) = 1.4280 ± 0.3312

Table 5:Point-wise method,Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	Log($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430

$LogK_1$ **(Average value)** = 2.3059± 0.6153

Table 6:Point-wise method, Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
9.73	5.55	6.33	6.42	0.09	0.9000	1.69		
10.00	5.60	6.47	6.58	0.11	1.2578	1.44	-0.4592	0.9808
10.23	5.65	6.62	6.84	0.12	1.6137	1.26	-0.2010	1.4610
10.49	5.70	6.80	6.92	0.12	2.1052	1.03		

$LogK_2$ **(Average value)** = 1.2209± 0.3398

Table 7:Point-wise method,Pb (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n}{1-n}$)	$LogK_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.60	0.05	0.8333	1.96	0.6989	2.6589

$LogK_1$ (Average value) = 2.5832 ±0.1614

Table 8:Point-wise method,Pb-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n-1}{2-n}$)	$logK_2$
9.51	5.50	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.83	0.05	1.1702	1.44		
10.00	5.60	6.90	6.90	0.05	1.4864	1.22	-0.0237	1.1963
10.23	5.65	7.05	7.10	0.05	2.0190	1.09		
10.49	5.70	7.10	7.17	0.07	3.6492	1.00		

$LogK_2$(Average value) = 1.1963

Table 9:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log ($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.5477	2.3123
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	0.0272	2.2072
9.51	5.50	6.20	6.26	0.07	0.6417	1.89	0.2530	2.1430
9.73	5.55	6.40	6.40	0.07	0.7000	1.67	0.3680	2.0380

$LogK_1$ **(Average value)** = 2.2364 ± 0.1602

Table 10:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
10.00	5.60	6.47	6.55	0.08	1.9503	1.41		
10.23	5.65	6.62	6.72	0.11	1.4792	1.26	-0.0361	1.2239

$LogK_2$ **(Average value)** = 1.2239

Table 11:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n}{n-1}$)	$LogK_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4290	2.2110
8.72	5.35	6.37	6.39	0.02	0.2858	2.42	-0.3978	2.0222
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

$LogK_1$ (Average value)=2.1382±0.1046

Table 12:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	log$(\frac{n-1}{2-n})$	LogK$_2$
9.51	5.55	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.84	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.93	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.10		
10.49	5.70	7.10	7.18	0.07	3.6492	0.83		

LogK$_2$(Average value) = 1.5453 **±** 0.3450

Table 13:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	V$_3$-V$_2$	n	pL	Log$(\frac{n}{n-1})$	Log K$_1$
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.3477	2.3123
9.00	5.40	6.00	6.04	0.04	0.3236	2.38	-0.3202	2.0598
9.22	5.45	6.10	6.15	0.05	0.4297	2.17	-0.1230	2.0470
9.51	5.50	6.20	6.26	0.06	0.5500	1.89	0.0871	1.9771
9.73	5.55	6.33	6.40	0.07	0.7000	1.67	0.3680	2.0380

LogK$_1$ **(Average value)** = 2.1568 ± 0.2069

Table 14:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	V$_3$-V$_2$	n	pL	Log$(\frac{n-1}{2-n})$	Log K$_2$
10.00	5.60	6.47	6.55	0.08	0.9148	1.41		
10.23	5.65	6.62	6.71	0.09	1.2102	1.20	-0.5749	0.6251
10.49	5.70	6.80	6.92	0.09	1.5968	1.03	0.1703	1.2003

LogK$_2$ **(Average value)** = 0.9127± 0.4070

Table15:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	Log$(\frac{n}{1-n})$	LogK$_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4210	2.2190
8.72	5.35	6.37	6.40	0.03	0.4286	2.42	-0.1249	2.2951
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.96	0.3010	2.2610
9.51	5.55	6.66	6.70	0.04	0.7720	1.67	0.5297	2.1997

LogK$_1$ (Average value) = 2.2108± 0.0825

Table 16:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	Log$(\frac{n-1}{2-n})$	Log K$_2$
9.73	5.55	6.78	6.83	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.95	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.09		
10.49	5.70	7.10	7.16	0.06	3.1429	0.89		

LogK$_2$ **(Average value)** = 1.5453± 0.3450

Table 17:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	V$_3$-V$_2$	n	pL	Log$(\frac{n}{n-1})$	Log K$_1$
8.50	5.30	5.81	5.86	0.05	0.3717	2.88	-0.2280	2.6520
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.06	0.06	0.4853	2.38	-0.0255	2.3545
9.22	5.45	6.10	6.16	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430
9.73	5.55	6.33	6.41	0.08	0.8000	1.69	0.6020	2.2920

LogK$_1$ **(Average value)** = 2.2516± 0.5380

Table 18:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$\text{Log}(\frac{n-1}{2-n})$	Log K_2
10.00	5.60	6.47	6.57	0.10	1.1434	1.43		
10.23	5.65	6.62	6.72	0.10	1.3448	1.23	-0.2788	0.9512
10.49	5.70	6.80	6.90	0.10	1.7742	1.03	0.5351	1.5651

LogK_2 **(Average value)** = 1.2581± 0.4340

Table 19: Stepwise and overall Stability constants of thehydrolysed and unhydrolysed divalent metal (II) complexes

Chelates	**LogK_1**	**LogK_2**	**Logβ**
[Cu (Hydrolysed PSHA-1)$_2$]	2.4788	1.4280	3.9068
[Pb (Hydrolysed PSHA-1)$_2$]	2.5832	1.1963	3.7795
[Cd (Hydrolysed PSHA-1)$_2$]	2.2108	1.5453	3.7561
[Mg (Hydrolysed PSHA-1)$_2$]	2.1382	1.5453	3.6835
[Cu (Unhydrolysed PSHA-1)$_2$]	2.3059	1.2209	3.5268
[Pb (Unhydrolysed PSHA-1)$_2$]	2.2364	1.2239	3.4603
[Cd (Unhydrolysed PSHA-1)$_2$]	2.2516	1.2581	3.5097
[Mg (Unydrolysed PSHA-1)$_2$]	2.1568	0.9127	3.0695

The results obtained (Table19) shows the stepwise and overall stability constants to be not high indicating low stability of the complexes, because the solubility of most metal ions in the basic pH range is minimal due to metal hydroxide precipitation (Karimi, 2017). In general, the stepwise stability constants (K_1 and K_2) follow the order $K_1 > K_2$ for the copper, lead, magnesium and cadmium complexes respectively. The steady decrease of the values with increasing number of ligands is in agreement with the prediction made by researchers (Na'aliya, 2013). The decrease could be attributed to the fact that as the number of the ligands (Humate ions) that enters the coordination zone increases the aqua molecules available for replacement by the ligands become less. Thus, the metal ions become less electron loving with progressive intake of the ligand and this results in the decrease in the values of the constants (Na'aliya, 2013). Also the stability of the complexes is influenced by the size and number of the chelate rings(Mackay and Mackay,2002).All the complexes form rings in their structure as humate, a bidentate ligand, bond the metal ions in the ratio 1:2 (Boguta and Sokolowska, 2016) forming chelate rings. The values of the overall stability constants (logβ) obtained for humate complexes are not high indicating low stability as the values are not high. LogK values for copper-humates (Table 3 to 6) obtained in this study are lower than those reported for the complexes of humic acids (Pandey *et al.*, 2015; Dinu, 2013; Kaschl *et al.*, 2010 and Gilbeto and Jorg, 2001). The values of LogK(Table 7 to 10) forlead-humates are lower than those reported for the lead in the literature (Dinu, 2013; Gilbeto and Jorg 2001). Log K values(Table 11 to 14) for magnesium-humates obtained in this study are close to those reported by (Pandey *et al.*, 2015). Log K values of cadmium-humates (Table 15 to 18) obtained in this work near to the one reported by (Dinu, 2013 and Pandey *et al.*, 2015).The difference between the reported values and the values obtained in this study might be probably as a result of acid hydrolysis of humic acid. The values of the overall stability constants (log β) of the copper humates complexes presented in Table 19 is high than that of other metal humate complexes, show relatively high stability of Cu-HA complexes, show the following order of stability: Cu >Pb> Cd > Mg; which are in close agreement to the findings of (Dinu, 2013 and Pandey *et al.*, 2015).The high stability of Cu-humate chelate could be attributed to the existence of coordinate covalent bond between the complexing agents and the Cu^{2+} ions. Since, Cu^{2+} being a metal of the transitional series with $3d^9$ electronic configurations can accept the electrons from the complexing agents. Similarly,the low stabilities of Pb,Cd and Mg - complexes could be explained by that Pb^{2+} with $6s^2$, Cd^{2+} with $4d^{10}$ and Mg^{2+} with $2p^6$ their electronic configuration has a completely filled d,p and s orbitals. Moreover, the stabilities of metal ions with hydrolysed humic acid from peat soil were higher than those with unhydrolysed humic acid from peat soil; which is ascribed to the high content of acidity in hydrolysed humic acid than unhydrolysed humic acid.

CONCLUSION

The values of logK for Cu(II) hydrolysed humic acid complex was higher followed by Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes as compared with metal(II) unhydrolysed humic acid complexes . This indicates acid hydrolysis of humic acid can enhance the complexation behavior of humic acid with metal (II) ions. However, the higher values of logβ for Cu(II), Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes indicates more stable stepwise complexes formed as compared with Cu(II), Pb(II), Cd(II) and Mg(II) unhydrolysed humic acid complexes.

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STABILITY CONSTANTS OF COMPLEXES OF METAL IONS WITH PEATSOIL HUMIC ACIDS UNDER NON-ACID-CONDITIONS

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ABSTRACT
Stability constants of complexes of four divalent metal ions viz. Cu^{2+}, Pb^{2+},Mg^{2+} and Cd^{2+} with humic acids (HA) were determined by potentiometric titration of humic acids with the corresponding salt of the divalent metals in aqueous media under non-acid-condition. The log K (logarithm of the stability constant) ranged from 1.0942 to 2.7471 for metal-humic acid complexes were determined using point-wise computational method. The order of stability constants were obtained as follows: Cu >Pb> Cd > Mg for metal -HA complexes respectively, indicating a higher degree of complexation with Cu metal ion.
Keywords: stability constant, humic acid, potentiometric titration, divalent metals, acid hydrolysis.

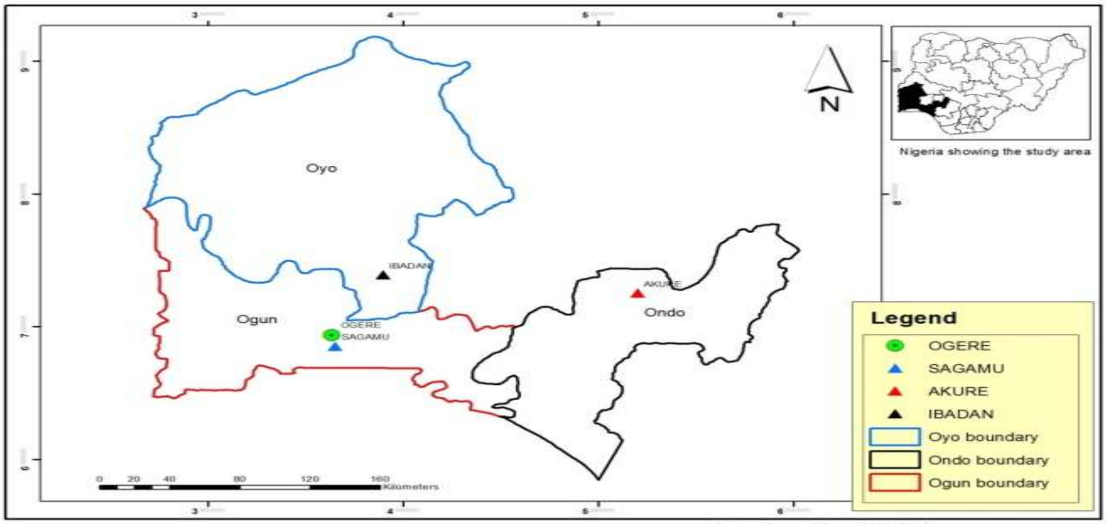
NTRODUCTION

The stability constant of a complex is the numerical expression of its stability and provides a quantitative measure of affinity of the metal ion to the complexing agent. An understanding of the relative stability of metal-complexes helps in predicting the behavior of metal ions in the soil (Ram and Raman, 1982). Extensive researches has been done to determine the stability constants of the complexes formed between humic acid (HA) with a number of metal ions. Ashok *et al*., (2000) reported that humic acid with hydroxyl, phenoxyl and carboxyl reactive groups can form coordination compound with metal ions at pH 3.5. The stability constants(Log K) for different metal-humic acid complexes indicated the following order of the stabilities of complexes formed between humic acid and metal ion, Cu >Fe >Pb> Ni > Co > Ca > Cd > Zn >Mn> Mg. Andelkovic *et al*., (2010) investigated the binding of Cd(II) to soil humic acid at pH 6.5 and in 0.1M KNO_3 ionic medium. The stability constant for binding indicating greater stability in the case when carboxyl groups are involved in complexation reaction. Kostic *et al*.,(2012) investigated the complexation of humic acid with certain heavy metal ions (Co(II), Ni(II),Cu(II), Zn(II), and Pb(II). The experiment was performed at 25°C, at pH 4.0 and ionic strength of 0.01M. Stability constant of complex between Pb(II) ions and humic acid is greater than stability constants of other investigated metal-humate complexes. Bogata and Sokolowska (2016) analyses the interaction between humic acids from different soils and Zn (II) ions at wide concentration ranges and at pH 5. Studies have showed significant impact of Zn concentration, pH and some properties of humic acids with zinc.But all of these studies were limited to acidic pH range. Therefore, the present study was carried out to determine and compare the stability constants of complexes of metal ions with hydrolysed peat soil humic acid and unhydrolysed peat soil humic under non-acid conditions.

MATERIALS AND METHODS

Analytical grade chemicals used includes hydrochloric acid (HCl), nitric acid (HNO_3), sodium hydroxide (NaOH), lead nitrate $Pb(NO_3)_2$, copper nitrate $Cu(NO_3)_2.3H_2O$, cadmium nitrate $Cd(NO_3)_2.4H_2O$, magnesium nitrate $Mg(NO_3)_2.6H_2O$, potassium nitrate (KNO_3), calcium chloride ($CaCl_2$), (sigma-Aldrich). Dowex 50WX8, (20-50 mesh) from Fluka.

Area of study



Source: Dept. of Geog. BUK (2016)

Figure 1: Map showing the sampling point at Sagamu Town, Ogun State.

Description of Sampling Area

Sagamu has geographical coordinates between 6°50′ north; 3° 38′ east is located in south western region of Nigeria. The region has tropical wet and dry climate with a lengthy wet season and relatively constant temperatures throughout the course of the year. Wet season runs from March to October, November to December forms the region dry season. The vegetation type of the region is savannah which is really grassland with small bushes and occasional big trees. Grassland soils have substantially higher organic matter content than forest soils (Novackova, 2011).

Sample Collection

The Peatsoil samples were collected from four different sampling points (0-10cm depth) in Sagamu into polyethylene bag with plastic spoons. Samples were taken to the laboratory, extraneous materials were removed; the samples were air-dried, crushed and ground to a fine powder in a mortar passed through a 0.20mm sieve. The samples were kept for analysis.

Isolation and purification of humic acid from peat soil sample

Peatsoil sample (100g) was mixed with 1000 cm^3 of 0.1M NaOH solution, shaken for 3hours and left to stand overnight. Dark-coloured supernatant was obtained and decanted from solid residue. The dark-coloured supernatant was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 6 hours. Yellowish brown supernatant and dark-brown precipitate were obtained. The yellowish brown supernatant was decanted followed by centrifuge and discarded. The dark-brown precipitate was mixed with $500cm^3$of 0.1M NaOH solution followed by passing through dowex resin. The dark-brown solution was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 3 hours. The dark-brown precipitate was washed several times with deionized water. The supernatant was treated with $AgNO_3$ solution until no white precipitate observed. The humic acid was transferred to weighed crucible and dried at 60°C in an oven for 12 hours. The humic acid was cooled and dried in the desiccator, weighed and recorded. The obtained humic acid was dried again at 60°C for additional 6 hours cooled and dried in the desiccator, weighed and recorded constant weight was obtained (Baruah *et al*., 2015).

FT-IR analysis

FT-IR spectra of humic acid sample was analysed using Carry 630 FT-IR Agilent Technologies.

Unhydrolysed compost humic acid

The unhydrolysed humic acid was obtained after isolation and purification of compost humic acid and kept for investigation.

Acid hydrolysis of Peatsoil acid

Peatsoil humic acid sample (1g) was refluxed for 12 hours at (160°C) with $50cm^3$ of 6M HCl. The mixture was allowed to cool, decanted, and centrifuged after hydrolysis. The insoluble residues were washed with distilled water via centrifugation several times, and the supernatant was treated with $AgNO_3$ solution until no white precipitate was observed. The residue was thoroughly dried over $CaCl_2$ in a desiccator at room temperature (Chefetz *et al*., 2002). Finally, the obtained hydrolysed humic acid was kept for investigation.

Potentiometric Titrations

Potentiometric measurements were carried out using a pH-meter Jenway (model 3510) with combine electrode, the sensitivity of the pH - meter is 0.01 units. The pH meter was switched on half an hour before starting the titration for initial warm up of the instrument. The instrument was calibrated with an aqueous standard buffer solution of pH 4.00 and 10.0 (borate buffer) prepared from a "Qualigens" buffer tablets.

The following sets of solutions were prepared in a 250cm^3 volumetric flask separately for pH metric titrations.

(i) 5 cm^3 0.1 M HCl + 40 cm^3 deionized water

(ii) 5 cm^3 0.1 M HCl + 39 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid

(iii) 5 cm^3 0.1 M HCl + 37 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid + 2 cm^3 0.01 M Cu(II)

The solutions were titrated against standardized 0.110MNaOH separately. The total volume of each mixture was adjusted to 50 cm^3 and the ionic strength of the solutions was maintained constant at by adding appropriate amount of stock solution of 1M KNO_3 (Gamal, 2015; Omar and Ali, 2015). A magnetic stirrer was used to achieve thorough mixing of the interacting solutions at 550 rpm. The same set of experimental conditions was applied for potentiometric titration of remaining samples.

Evaluation of pKa of Hydrolysed peat soil Humic Acids

The proton-ligand formation number $n_{\mathbf{A}}$ were calculated by Irving and Rossotti expression (Omar and Ali, 2015).

$$nA = Y- \frac{(V2-V1)(No-Eo)}{(Vo+V1)TcL} \text{ ....1}$$

Where: Y is number of dissociable proton, (V_2-V_1) is the measure of displacement of the ligand curve relative to acid curve, N^o and E^o are the resultant concentration of alkali solution, free acid solution, $T_{cL}{}^o$ is the total ligand concentration, V^o is the total volume of titration solution,V_1 is the volume of alkali added to acid solution,V_2 is the volume of alkali added to acid solution + ligand solution, acid dissociation constants (pKa - values) of ligand were calculated by algebraic method point wise calculation (Tables 1). The dissociation constants (pKa) were calculated according to the following relation:

$$pKa = pH + \log(\frac{nA}{1-nA}) \text{ ....2}$$

Where: pKa is the acid dissociation constant, $n_A$is the Proton-ligand formation number and pH is the pH-values (Omar and Ali, 2015).

Determination of metal-ligand stability constants (log K) of complexes

The potentiometric measurement for the determination of stability constant of a complex in solution is based on the fact that the redox potential of the couple $\frac{M^{+(m-n)}}{M^{+m}}$ is shifted significantly on complexation of the metal ion with the ligand. This method involves change in hydrogen ion concentration [H$^+$] due to the displacement or association of one or more protons taking place during complexation reaction. This change can be found out by titrating the solutions containing free acid, acid with ligand, and acid with ligand and metal ion, individually against a standard alkali solution at a constant ionic strength or temperature. Either ionic strength or temperature may be varied for different sets of solutions. In all the cases, the change in the pH of the solution is measured after each addition of a known amount of alkali to the reaction cell which contains the reaction mixture. The titration curves are then drawn by plotting the measured pH values against the corresponding volume of alkali added and the stability constants of the complexes are determined from the titration curves by employing pH-metric titration technique given by (Irving and Rossoti).

Metal-ligand stability constants (Log K) were determined by using the following relations:

$$\bar{n} = \frac{(V_3 - V_2)(E^0 + N^0)}{(V^0 + V_2)\bar{n}_A T_m^0} \text{ ....3}$$

and

$$PL = \log_{10}\{\frac{1+\beta_n^H \frac{1}{[anti \ \log pH]^n}}{T_L^0 - \bar{n}T_m^0} X \frac{(V^0 + V_3)}{V^0}\} \text{ ....4}$$

Where $T_{L,}$ T^{o}, E°, and V^{o}havethe same significance as in equation (1) above, T_m denotes the total concentration of metal present in solution, V_3 is the volume of metal ions present in solution and β^H is the overall proton ligand stability constant. The metal-ligand stability constants (log K) were determined by employing point wise computational Method (eq. 5 and 6).

$$\text{LogK}_1 = \log\left(\frac{n}{1-n}\right) + \text{pL} \qquad \text{.............5}$$

$$\text{LogK}_2 = \log\left(\frac{1-n}{2-n}\right) + \text{pL} \text{.......................6}$$

Where: Log K is the metal-ligand stability constant, pL is the Free ligand exponent function, **n** is the Average number of ligand attached with metal ion (Janrao*et al*., 2014).The results obtained were analyzed by an ORIGIN 2016 program using titration data and then the proton-ligand stability constants (pKa) and Metal-ligand stability constant (LogK) calculated (Omar and Ali, 2015).

RESULTS AND DISCUSSION

Fourier transformed infrared (FT-IR) spectra of isolated humic acid from peat soils Figure 2 had distinct clear absorption bands indicating the presence of major humic acid structural elemental groups such as H bonded OH (3680cm^{-1} peak), C=O of carbonyl (1721cm^{-1} peak), functional groups of aliphatic components CH_2 (2918cm^{-1} peak) and C-O stretching of polysaccharide (1168cm^{-1} peak). The positions of the absorption bands of the spectra fell within typical major absorption bands of humic acid which is at frequencies 3680, 2918, 1721, 1168 cm^{-1}. The first peak centred in the vicinity of 3680 cm^{-1} region is attributed to phenol OH group bounded by intermolecular H bonds. The 2918cm^{-1} band usually has absorption maximum at 2918 cm^{-1} which is due to C–H stretching of alkane group (CH_2). The next major absorption band is 1721 cm^{-1}. This band has been commonly ascribed to C=O stretching of mainly carboxyl group (COOH) with trace amount of ketones. The last peak was observed at 1168 cm^{-1} due to C–O stretching of polysaccharides and this peak appeared also in the spectra of humic acid from peat soil. The FTIR spectra of the isolated humic acid contained all major characteristic absorption peaks of humic acid. These absorption peaks indicated the presence of the major structural elements of humic acid namely H bonded OH, C=C of aromatic ring, C=O of carbonyl group (both carboxyl and ketonic), CH_2 group. This strongly supports the presence of humic acid.

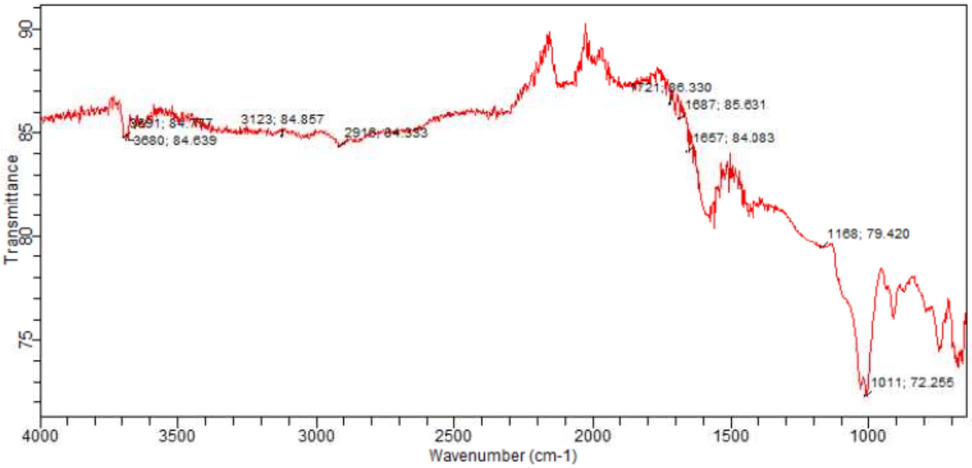


Fig. 2 : FT-IR spectraof peatsoilhumic acid (PSHA)

Evaluation of acid dissociation constant (pka) of acid hydrolysed peat soil humicacid at phenolic group

The value of the dissociation constant of the peat soil humic acid (PSHA) that underwent acidhydrolysis studied was found to be 8.9299 as shown Table 1, which is lower than the literaturevalues reported by Almeida and Szpoganics, (2015), Borges *et al*., (2005); Badr *et al*., (2012)and Fernandes *et al*,.(2009) of 9.73, 9.47 and 10.30. The difference between the obtained valuesand the reported values in this study might be probably as a result of acid hydrolysis of humicacid.

Table 1: PKa of (Hydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	log($\frac{nA}{1-nA}$)	pKa
8.50	5.30	6.29	0.99	0.3594	-0.2510	8.2490
8.72	5.35	6.37	1.02	0.3400	-0.2880	8.4320
9.00	5.40	6.46	1.06	0.3141	-0.3391	8.6609
9.22	5.45	6.55	1.10	0.2882	-0.3927	8.8273
9.51	5.50	6.66	1.16	0.2494	-0.4786	9.0314
9.73	5.55	6.78	1.23	0.2041	-0.5910	9.1390
10.00	5.60	6.90	1.30	0.1589	-0.7238	9.2762
10.23	5.65	7.05	1.40	0.0941	-0.9835	9.2465
10.49	5.70	7.10	1.40	0.0941	-0.9835	9.5065

Average pKa = 8.9299 ± 0.4186

Table 2: PKa of (Unhydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	Log($\frac{nA}{1-n}$)	pKa
8.50	5.30	5.81	0.51	0.6619	0.2919	8.7919
8.72	5.35	5.90	0.55	0.6357	0.2418	8.9618
9.00	5.40	6.00	0.60	0.6029	0.1813	9.1813
9.22	5.45	6.10	0.65	0.5701	0.1226	9.3426
9.51	5.50	6.20	0.70	0.5376	0.0654	9.5754
9.73	5.55	6.33	0.78	0.4851	-0.0259	9.7041
10.00	5.60	6.47	0.87	0.4262	-0.1291	9.8709
10.23	5.65	6.62	0.99	0.3609	-0.2481	9.9819
10.49	5.70	6.80	1.10	0.2759	-0.4690	10.0210

Average pKa = 9.4923± 0.4410

Metal-ligand stability constant (Log K)

The stabilityconstants require the accurate values of proton-ligand stability constants (Anil and Maroti, 2008). Metal titration curves crossed over ligand titration curve indicated the formation of complex upon proton release (Santosh, *et al.*, 2011). If the values of n- are within range 0.2-0.8 and 1.2-18 this indicates the formation of 1:1 and 1:2 complexes (Sayyed and Mazahar, 2012).

The metal (II)-humate stepwise stability constants (log k) at phenolic group (Tables 3-18)

Table 3: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n}{1-n}$)	$LogK_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

$LogK_1$ (Average value) = 2.4788± 0.2203

Table 4: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	Log($\frac{n-1}{2-n}$)	$LogK_2$
9.51	5.50	6.66	6.73	0.07	1.3509	1.70	-0.2671	1.4329
9.73	5.55	6.78	6.85	0.07	1.6383	1.51	0.2467	1.7567
10.00	5.60	6.90	6.98	0.08	2.1783	1.31	-0.2158	1.0942
10.23	5.65	7.05	7.13	0.08	4.1904	1.27		
10.49	5.70	7.10	7.19	0.09	4.6920			

$LogK_2$(Average value) = 1.4280 ± 0.3312

Table 5:Point-wise method,Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	Log($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430

$LogK_1$ **(Average value)** = 2.3059± 0.6153

Table 6:Point-wise method, Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$V_3\text{-}V_2$	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
9.73	5.55	6.33	6.42	0.09	0.9000	1.69		
10.00	5.60	6.47	6.58	0.11	1.2578	1.44	-0.4592	0.9808
10.23	5.65	6.62	6.84	0.12	1.6137	1.26	-0.2010	1.4610
10.49	5.70	6.80	6.92	0.12	2.1052	1.03		

$LogK_2$ **(Average value)** = 1.2209± 0.3398

Table 7:Point-wise method,Pb (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	log($\frac{n}{1-n}$)	$LogK_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.60	0.05	0.8333	1.96	0.6989	2.6589

$\mathbf{LogK_1}$ **(Average value)** = 2.5832 ±0.1614

Table 8:Point-wise method,Pb-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	log($\frac{n-1}{2-n}$)	$logK_2$
9.51	5.50	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.83	0.05	1.1702	1.44		
10.00	5.60	6.90	6.90	0.05	1.4864	1.22	-0.0237	1.1963
10.23	5.65	7.05	7.10	0.05	2.0190	1.09		
10.49	5.70	7.10	7.17	0.07	3.6492	1.00		

$\mathbf{LogK_2}$**(Average value)** = 1.1963

Table 9:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$V_3\text{-}V_2$	n	pL	Log ($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.5477	2.3123
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	0.0272	2.2072
9.51	5.50	6.20	6.26	0.07	0.6417	1.89	0.2530	2.1430
9.73	5.55	6.40	6.40	0.07	0.7000	1.67	0.3680	2.0380

$LogK_1$ **(Average value)** = 2.2364 ± 0.1602

Table 10:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$V_3\text{-}V_2$	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
10.00	5.60	6.47	6.55	0.08	1.9503	1.41		
10.23	5.65	6.62	6.72	0.11	1.4792	1.26	-0.0361	1.2239

$LogK_2$ **(Average value)** = 1.2239

Table 11:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	log($\frac{n}{n-1}$)	$LogK_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4290	2.2110
8.72	5.35	6.37	6.39	0.02	0.2858	2.42	-0.3978	2.0222
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

$\mathbf{LogK_1}$ **(Average value)=**2.1382**±**0.1046

Table 12:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	log($\frac{n-1}{2-n}$)	LogK$_2$
9.51	5.55	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.84	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.93	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.10		
10.49	5.70	7.10	7.18	0.07	3.6492	0.83		

LogK$_2$(Average value) = 1.5453 **±** 0.3450

Table 13:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	V$_3$-V$_2$	n	pL	Log($\frac{n}{n-1}$)	Log K$_1$
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.3477	2.3123
9.00	5.40	6.00	6.04	0.04	0.3236	2.38	-0.3202	2.0598
9.22	5.45	6.10	6.15	0.05	0.4297	2.17	-0.1230	2.0470
9.51	5.50	6.20	6.26	0.06	0.5500	1.89	0.0871	1.9771
9.73	5.55	6.33	6.40	0.07	0.7000	1.67	0.3680	2.0380

LogK$_1$ **(Average value)** = 2.1568 ± 0.2069

Table 14:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	V$_3$-V$_2$	n	pL	Log($\frac{n-1}{2-n}$)	Log K$_2$
10.00	5.60	6.47	6.55	0.08	0.9148	1.41		
10.23	5.65	6.62	6.71	0.09	1.2102	1.20	-0.5749	0.6251
10.49	5.70	6.80	6.92	0.09	1.5968	1.03	0.1703	1.2003

LogK$_2$ **(Average value)** = 0.9127± 0.4070

Table15:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	Log($\frac{n}{1-n}$)	LogK$_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4210	2.2190
8.72	5.35	6.37	6.40	0.03	0.4286	2.42	-0.1249	2.2951
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.96	0.3010	2.2610
9.51	5.55	6.66	6.70	0.04	0.7720	1.67	0.5297	2.1997

LogK$_1$ (Average value) = 2.2108± 0.0825

Table 16:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	Log($\frac{n-1}{2-n}$)	Log K$_2$
9.73	5.55	6.78	6.83	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.95	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.09		
10.49	5.70	7.10	7.16	0.06	3.1429	0.89		

LogK$_2$ **(Average value)** = 1.5453± 0.3450

Table 17:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	V$_3$-V$_2$	n	pL	Log($\frac{n}{n-1}$)	Log K$_1$
8.50	5.30	5.81	5.86	0.05	0.3717	2.88	-0.2280	2.6520
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.06	0.06	0.4853	2.38	-0.0255	2.3545
9.22	5.45	6.10	6.16	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430
9.73	5.55	6.33	6.41	0.08	0.8000	1.69	0.6020	2.2920

LogK$_1$ **(Average value)** = 2.2516± 0.5380

Table 18:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	V$_3$-V$_2$	n	pL	Log($\frac{n-1}{2-n}$)	Log K$_2$
10.00	5.60	6.47	6.57	0.10	1.1434	1.43		
10.23	5.65	6.62	6.72	0.10	1.3448	1.23	-0.2788	0.9512
10.49	5.70	6.80	6.90	0.10	1.7742	1.03	0.5351	1.5651

LogK$_2$ **(Average value)** = 1.2581± 0.4340

Table 19: Stepwise and overall Stability constants of thehydrolysed and unhydrolysed divalent metal (II) complexes

Chelates	**LogK$_1$**	**LogK$_2$**	**Logβ**
[Cu (Hydrolysed PSHA-1)$_2$]	2.4788	1.4280	3.9068
[Pb (Hydrolysed PSHA-1)$_2$]	2.5832	1.1963	3.7795
[Cd (Hydrolysed PSHA-1)$_2$]	2.2108	1.5453	3.7561
[Mg (Hydrolysed PSHA-1)$_2$]	2.1382	1.5453	3.6835
[Cu (Unhydrolysed PSHA-1)$_2$]	2.3059	1.2209	3.5268
[Pb (Unhydrolysed PSHA-1)$_2$]	2.2364	1.2239	3.4603
[Cd (Unhydrolysed PSHA-1)$_2$]	2.2516	1.2581	3.5097
[Mg (Unydrolysed PSHA-1)$_2$]	2.1568	0.9127	3.0695

The results obtained (Table19) shows the stepwise and overall stability constants to be not high indicating low stability of the complexes, because the solubility of most metal ions in the basic pH range is minimal due to metal hydroxide precipitation (Karimi, 2017). In general, the stepwise stability constants (K$_1$ and K$_2$) follow the order K$_1$> K$_2$ for the copper, lead, magnesium and cadmium complexes respectively. The steady decrease of the values with increasing number of ligands is in agreement with the prediction made by researchers (Na'aliya, 2013). The decrease could be attributed to the fact that as the number of the ligands (Humate ions) that enters the coordination zone increases the aqua molecules available for replacement by the ligands become less. Thus, the metal ions become less electron loving with progressive intake of the ligand and this results in the decrease in the values of the constants (Na'aliya, 2013). Also the stability of the complexes is influenced by the size and number of the chelate rings(Mackay and Mackay,2002).All the complexes form rings in their structure as humate, a bidentate ligand, bond the metal ions in the ratio 1:2 (Boguta and Sokolowska, 2016) forming chelate rings. The values of the overall stability constants (logβ) obtained for humate complexes are not high indicating low stability as the values are not high. LogK values for copper-humates (Table 3 to 6) obtained in this study are lower than those reported for the complexes of humic acids (Pandey *et al*., 2015; Dinu, 2013; Kaschl *et al*., 2010 and Gilbeto and Jorg, 2001). The values of LogK(Table 7 to 10) forlead-humates are lower than those reported for the lead in the literature (Dinu, 2013; Gilbeto and Jorg 2001). Log K values(Table 11 to 14) for magnesium-humates obtained in this study are close to those reported by (Pandey *et al*., 2015). Log K values of cadmium-humates (Table 15 to 18) obtained in this work near to the one reported by (Dinu, 2013 and Pandey *et al*., 2015).The difference between the reported values and the values obtained in this study might be probably as a result of acid hydrolysis of humic acid. The values of the overall stability constants (log β) of the copper humates complexes presented in Table 19 is high than that of other metal humate complexes, show relatively high stability of Cu-HA complexes, show the following order of stability: Cu >Pb> Cd > Mg; which are in close agreement to the findings of (Dinu, 2013 and Pandey *et al*., 2015).The high stability of Cu-humate chelate could be attributed to the existence of coordinate covalent bond between the complexing agents and the Cu^{2+} ions. Since, Cu^{2+} being a metal of the transitional series with $3d^9$ electronic configurations can accept the electrons from the complexing agents. Similarly,the low stabilities of Pb,Cd and Mg -complexes could be explained by that Pb^{2+} with $6s^2$, Cd^{2+} with $4d^{10}$ and Mg^{2+} with $2p^6$ their electronic configuration has a completely filled d,p and s orbitals. Moreover, the stabilities of metal ions with hydrolysed humic acid from peat soil were higher than those with unhydrolysed humic acid from peat soil; which is ascribed to the high content of acidity in hydrolysed humic acid than unhydrolysed humic acid.

CONCLUSION

The values of logK for Cu(II) hydrolysed humic acid complex was higher followed by Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes as compared with metal(II) unhydrolysed humic acid complexes . This indicates acid hydrolysis of humic acid can enhance the complexation behavior of humic acid with metal (II) ions. However, the higher values of logβ for Cu(II), Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes indicates more stable stepwise complexes formed as compared with Cu(II), Pb(II), Cd(II) and Mg(II) unhydrolysed humic acid complexes.

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STABILITY CONSTANTS OF COMPLEXES OF METAL IONS WITH PEATSOIL HUMIC ACIDS UNDER NON-ACID-CONDITIONS

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ABSTRACT

Stability constants of complexes of four divalent metal ions viz. Cu^{2+}, Pb^{2+},Mg^{2+} and Cd^{2+} with humic acids (HA) were determined by potentiometric titration of humic acids with the corresponding salt of the divalent metals in aqueous media under non-acid-condition. The log K (logarithm of the stability constant) ranged from 1.0942 to 2.7471 for metal-humic acid complexes were determined using point-wise computational method. The order of stability constants were obtained as follows: Cu >Pb> Cd > Mg for metal -HA complexes respectively, indicating a higher degree of complexation with Cu metal ion.

Keywords: stability constant, humic acid, potentiometric titration, divalent metals, acid hydrolysis.

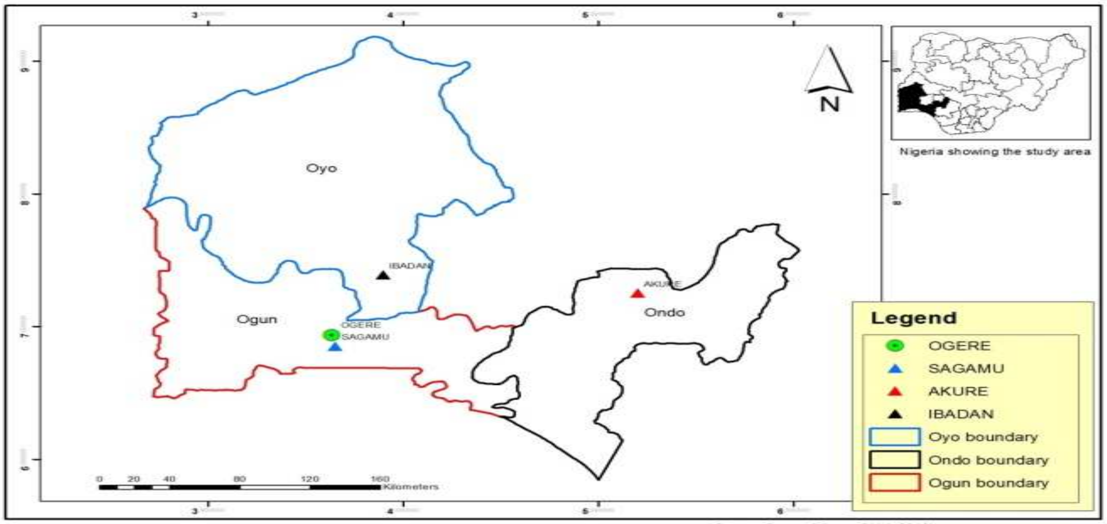
NTRODUCTION

The stability constant of a complex is the numerical expression of its stability and provides a quantitative measure of affinity of the metal ion to the complexing agent. An understanding of the relative stability of metal-complexes helps in predicting the behavior of metal ions in the soil (Ram and Raman, 1982). Extensive researches has been done to determine the stability constants of the complexes formed between humic acid (HA) with a number of metal ions. Ashok *et al*., (2000) reported that humic acid with hydroxyl, phenoxyl and carboxyl reactive groups can form coordination compound with metal ions at pH 3.5. The stability constants(Log K) for different metal-humic acid complexes indicated the following order of the stabilities of complexes formed between humic acid and metal ion, Cu >Fe >Pb> Ni > Co > Ca > Cd > Zn >Mn> Mg. Andelkovic *et al*., (2010) investigated the binding of Cd(II) to soil humic acid at pH 6.5 and in 0.1M KNO_3 ionic medium. The stability constant for binding indicating greater stability in the case when carboxyl groups are involved in complexation reaction. Kostic *et al*.,(2012) investigated the complexation of humic acid with certain heavy metal ions (Co(II), Ni(II),Cu(II), Zn(II), and Pb(II). The experiment was performed at 25°C, at pH 4.0 and ionic strength of 0.01M. Stability constant of complex between Pb(II) ions and humic acid is greater than stability constants of other investigated metal-humate complexes. Bogata and Sokolowska (2016) analyses the interaction between humic acids from different soils and Zn (II) ions at wide concentration ranges and at pH 5. Studies have showed significant impact of Zn concentration, pH and some properties of humic acids with zinc.But all of these studies were limited to acidic pH range. Therefore, the present study was carried out to determine and compare the stability constants of complexes of metal ions with hydrolysed peat soil humic acid and unhydrolysed peat soil humic under non-acid conditions.

MATERIALS AND METHODS

Analytical grade chemicals used includes hydrochloric acid (HCl), nitric acid (HNO_3), sodium hydroxide (NaOH), lead nitrate $Pb(NO_3)_2$, copper nitrate $Cu(NO_3)_2.3H_2O$, cadmium nitrate $Cd(NO_3)_2.4H_2O$, magnesium nitrate $Mg(NO_3)_2.6H_2O$, potassium nitrate (KNO_3), calcium chloride ($CaCl_2$), (sigma-Aldrich). Dowex 50WX8, (20-50 mesh) from Fluka.

Area of study



Source: Dept. of Geog. BUK (2016)

Figure 1: Map showing the sampling point at Sagamu Town, Ogun State.

Description of Sampling Area

Sagamu has geographical coordinates between 6°50′ north; 3° 38′ east is located in south western region of Nigeria. The region has tropical wet and dry climate with a lengthy wet season and relatively constant temperatures throughout the course of the year. Wet season runs from March to October, November to December forms the region dry season. The vegetation type of the region is savannah which is really grassland with small bushes and occasional big trees. Grassland soils have substantially higher organic matter content than forest soils (Novackova, 2011).

Sample Collection

The Peatsoil samples were collected from four different sampling points (0-10cm depth) in Sagamu into polyethylene bag with plastic spoons. Samples were taken to the laboratory, extraneous materials were removed; the samples were air-dried, crushed and ground to a fine powder in a mortar passed through a 0.20mm sieve. The samples were kept for analysis.

Isolation and purification of humic acid from peat soil sample

Peatsoil sample (100g) was mixed with 1000 cm^3 of 0.1M NaOH solution, shaken for 3hours and left to stand overnight. Dark-coloured supernatant was obtained and decanted from solid residue. The dark-coloured supernatant was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 6 hours. Yellowish brown supernatant and dark-brown precipitate were obtained. The yellowish brown supernatant was decanted followed by centrifuge and discarded. The dark-brown precipitate was mixed with $500cm^3$of 0.1M NaOH solution followed by passing through dowex resin. The dark-brown solution was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 3 hours. The dark-brown precipitate was washed several times with deionized water. The supernatant was treated with $AgNO_3$ solution until no white precipitate observed. The humic acid was transferred to weighed crucible and dried at 60°C in an oven for 12 hours. The humic acid was cooled and dried in the desiccator, weighed and recorded. The obtained humic acid was dried again at 60°C for additional 6 hours cooled and dried in the desiccator, weighed and recorded constant weight was obtained (Baruah *et al.*, 2015).

FT-IR analysis

FT-IR spectra of humic acid sample was analysed using Carry 630 FT-IR Agilent Technologies.

Unhydrolysed compost humic acid

The unhydrolysed humic acid was obtained after isolation and purification of compost humic acid and kept for investigation.

Acid hydrolysis of Peatsoil acid

Peatsoil humic acid sample (1g) was refluxed for 12 hours at (160°C) with $50cm^3$ of 6M HCl. The mixture was allowed to cool, decanted, and centrifuged after hydrolysis. The insoluble residues were washed with distilled water via centrifugation several times, and the supernatant was treated with $AgNO_3$ solution until no white precipitate was observed. The residue was thoroughly dried over $CaCl_2$ in a desiccator at room temperature (Chefetz *et al.*, 2002). Finally, the obtained hydrolysed humic acid was kept for investigation.

Potentiometric Titrations

Potentiometric measurements were carried out using a pH-meter Jenway (model 3510) with combine electrode, the sensitivity of the pH - meter is 0.01 units. The pH meter was switched on half an hour before starting the titration for initial warm up of the instrument. The instrument was calibrated with an aqueous standard buffer solution of pH 4.00 and 10.0 (borate buffer) prepared from a "Qualigens" buffer tablets.

The following sets of solutions were prepared in a 250cm^3 volumetric flask separately for pH metric titrations.

(i) 5 cm^3 0.1 M HCl + 40 cm^3 deionized water

(ii) 5 cm^3 0.1 M HCl + 39 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid

(iii) 5 cm^3 0.1 M HCl + 37 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid + 2 cm^3 0.01 M Cu(II)

The solutions were titrated against standardized 0.110MNaOH separately. The total volume of each mixture was adjusted to 50 cm^3 and the ionic strength of the solutions was maintained constant at by adding appropriate amount of stock solution of 1M KNO$_3$ (Gamal, 2015; Omar and Ali, 2015). A magnetic stirrer was used to achieve thorough mixing of the interacting solutions at 550 rpm. The same set of experimental conditions was applied for potentiometric titration of remaining samples.

Evaluation of pKa of Hydrolysed peat soil Humic Acids

The proton-ligand formation number n$_{\mathbf{A}}$ were calculated by Irving and Rossotti expression (Omar and Ali, 2015).

$$nA = Y - \frac{(V2-V1)(No-Eo)}{(Vo+V1)TcL} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 1$$

Where: Y is number of dissociable proton, (V_2-V_1) is the measure of displacement of the ligand curve relative to acid curve, N^o and E^o are the resultant concentration of alkali solution, free acid solution, $T_{cL}{}^o$ is the total ligand concentration, V^o is the total volume of titration solution,V$_1$ is the volume of alkali added to acid solution,V$_2$ is the volume of alkali added to acid solution + ligand solution, acid dissociation constants (pKa - values) of ligand were calculated by algebraic method point wise calculation (Tables 1). The dissociation constants (pKa) were calculated according to the following relation:

$$pKa = pH + \log\left(\frac{nA}{1-nA}\right) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 2$$

Where: pKa is the acid dissociation constant, n$_A$is the Proton-ligand formation number and pH is the pH-values (Omar and Ali, 2015).

Determination of metal-ligand stability constants (log K) of complexes

The potentiometric measurement for the determination of stability constant of a complex in solution is based on the fact that the redox potential of the couple $\frac{M^{+(m-n)}}{M^{+m}}$ is shifted significantly on complexation of the metal ion with the ligand. This method involves change in hydrogen ion concentration [H$^+$] due to the displacement or association of one or more protons taking place during complexation reaction. This change can be found out by titrating the solutions containing free acid, acid with ligand, and acid with ligand and metal ion, individually against a standard alkali solution at a constant ionic strength or temperature. Either ionic strength or temperature may be varied for different sets of solutions. In all the cases, the change in the pH of the solution is measured after each addition of a known amount of alkali to the reaction cell which contains the reaction mixture. The titration curves are then drawn by plotting the measured pH values against the corresponding volume of alkali added and the stability constants of the complexes are determined from the titration curves by employing pH-metric titration technique given by (Irving and Rossoti).

Metal-ligand stability constants (Log K) were determined by using the following relations:

$$\bar{n} = \frac{(V_3 - V_2)(E^0 + N^0)}{(V^0 + V_2)\bar{n}_A T_m^0} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 3$$

and

$$PL = \log_{10}\left\{\frac{1 + \beta_n^H \dfrac{1}{[anti\ \log pH]^n}}{T_L^0 - \bar{n}T_m^0} X \frac{(V^0 + V_3)}{V^0}\right\} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 4$$

Where $T_{L,}$ T^{o}, E°, and V^{o}havethe same significance as in equation (1) above, T_m denotes the total concentration of metal present in solution, V_3 is the volume of metal ions present in solution and β^H is the overall proton ligand stability constant. The metal-ligand stability constants (log K) were determined by employing point wise computational Method (eq. 5 and 6).

$$\mathrm{Log}K_1 = \log\left(\frac{n}{1-n}\right) + pL \quad \ldots\ldots\ldots\ldots.5$$

$$\mathrm{Log}K_2 = \log\left(\frac{1-n}{2-n}\right) + pL\ldots\ldots\ldots\ldots\ldots\ldots\ldots.6$$

Where: Log K is the metal-ligand stability constant, pL is the Free ligand exponent function, **n** is the Average number of ligand attached with metal ion (Janrao*et al.*, 2014).The results obtained were analyzed by an ORIGIN 2016 program using titration data and then the proton-ligand stability constants (pKa) and Metal-ligand stability constant (LogK) calculated (Omar and Ali, 2015).

RESULTS AND DISCUSSION

Fourier transformed infrared (FT-IR) spectra of isolated humic acid from peat soils Figure 2 had distinct clear absorption bands indicating the presence of major humic acid structural elemental groups such as H bonded OH ($3680cm^{-1}$ peak), C=O of carbonyl ($1721cm^{-1}$ peak), functional groups of aliphatic components CH_2 ($2918cm^{-1}$ peak) and C-O stretching of polysaccharide ($1168cm^{-1}$ peak). The positions of the absorption bands of the spectra fell within typical major absorption bands of humic acid which is at frequencies 3680, 2918, 1721, 1168 cm^{-1}. The first peak centred in the vicinity of 3680 cm^{-1} region is attributed to phenol OH group bounded by intermolecular H bonds. The $2918cm^{-1}$ band usually has absorption maximum at 2918 cm^{-1} which is due to C–H stretching of alkane group (CH_2). The next major absorption band is 1721 cm^{-1}. This band has been commonly ascribed to C=O stretching of mainly carboxyl group (COOH) with trace amount of ketones. The last peak was observed at 1168 cm^{-1} due to C–O stretching of polysaccharides and this peak appeared also in the spectra of humic acid from peat soil. The FTIR spectra of the isolated humic acid contained all major characteristic absorption peaks of humic acid. These absorption peaks indicated the presence of the major structural elements of humic acid namely H bonded OH, C=C of aromatic ring, C=O of carbonyl group (both carboxyl and ketonic), CH_2 group. This strongly supports the presence of humic acid.

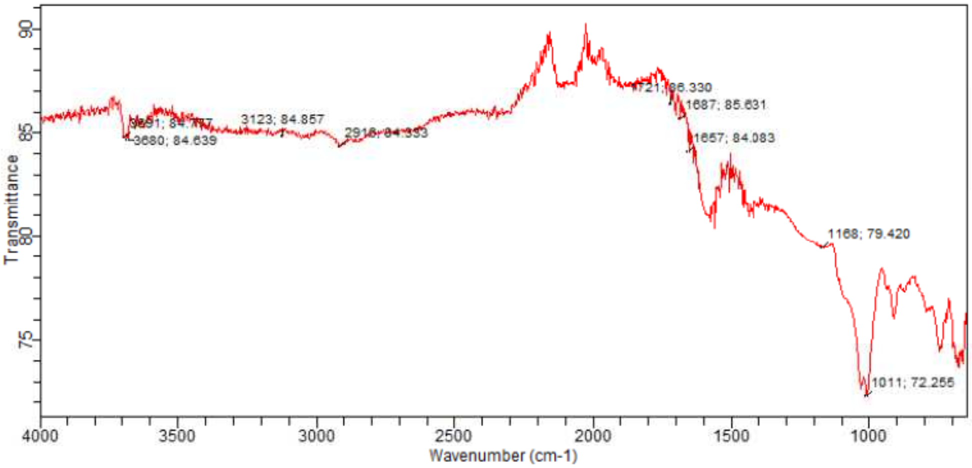


Fig. 2 : FT-IR spectraof peatsoilhumic acid (PSHA)

Evaluation of acid dissociation constant (pka) of acid hydrolysed peat soil humicacid at phenolic group

The value of the dissociation constant of the peat soil humic acid (PSHA) that underwent acidhydrolysis studied was found to be 8.9299 as shown Table 1, which is lower than the literaturevalues reported by Almeida and Szpoganics, (2015), Borges *et al.*, (2005); Badr *et al.*, (2012)and Fernandes *et al*,.(2009) of 9.73, 9.47 and 10.30. The difference between the obtained valuesand the reported values in this study might be probably as a result of acid hydrolysis of humicacid.

Table 1: PKa of (Hydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	$\log(\frac{nA}{1-nA})$	pKa
8.50	5.30	6.29	0.99	0.3594	-0.2510	8.2490
8.72	5.35	6.37	1.02	0.3400	-0.2880	8.4320
9.00	5.40	6.46	1.06	0.3141	-0.3391	8.6609
9.22	5.45	6.55	1.10	0.2882	-0.3927	8.8273
9.51	5.50	6.66	1.16	0.2494	-0.4786	9.0314
9.73	5.55	6.78	1.23	0.2041	-0.5910	9.1390
10.00	5.60	6.90	1.30	0.1589	-0.7238	9.2762
10.23	5.65	7.05	1.40	0.0941	-0.9835	9.2465
10.49	5.70	7.10	1.40	0.0941	-0.9835	9.5065

Average pKa = 8.9299 ± 0.4186

Table 2: PKa of (Unhydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	$\text{Log}(\frac{nA}{1-n})$	pKa
8.50	5.30	5.81	0.51	0.6619	0.2919	8.7919
8.72	5.35	5.90	0.55	0.6357	0.2418	8.9618
9.00	5.40	6.00	0.60	0.6029	0.1813	9.1813
9.22	5.45	6.10	0.65	0.5701	0.1226	9.3426
9.51	5.50	6.20	0.70	0.5376	0.0654	9.5754
9.73	5.55	6.33	0.78	0.4851	-0.0259	9.7041
10.00	5.60	6.47	0.87	0.4262	-0.1291	9.8709
10.23	5.65	6.62	0.99	0.3609	-0.2481	9.9819
10.49	5.70	6.80	1.10	0.2759	-0.4690	10.0210

Average pKa = 9.4923± 0.4410

Metal-ligand stability constant (Log K)

The stabilityconstants require the accurate values of proton-ligand stability constants (Anil and Maroti, 2008). Metal titration curves crossed over ligand titration curve indicated the formation of complex upon proton release (Santosh, *et al.*, 2011). If the values of n- are within range 0.2-0.8 and 1.2-18 this indicates the formation of 1:1 and 1:2 complexes (Sayyed and Mazahar, 2012).

The metal (II)-humate stepwise stability constants (log k) at phenolic group (Tables 3-18)

Table 3: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$\log(\frac{n}{1-n})$	LogK_1
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

LogK_1 (Average value) = 2.4788± 0.2203

Table 4: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$\text{Log}(\frac{n-1}{2-n})$	LogK_2
9.51	5.50	6.66	6.73	0.07	1.3509	1.70	-0.2671	1.4329
9.73	5.55	6.78	6.85	0.07	1.6383	1.51	0.2467	1.7567
10.00	5.60	6.90	6.98	0.08	2.1783	1.31	-0.2158	1.0942
10.23	5.65	7.05	7.13	0.08	4.1904	1.27		
10.49	5.70	7.10	7.19	0.09	4.6920			

LogK_2(Average value) = 1.4280 ± 0.3312

Table 5:Point-wise method,Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	Log($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430

$LogK_1$ **(Average value)** = 2.3059± 0.6153

Table 6:Point-wise method, Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$V_3\text{-}V_2$	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
9.73	5.55	6.33	6.42	0.09	0.9000	1.69		
10.00	5.60	6.47	6.58	0.11	1.2578	1.44	-0.4592	0.9808
10.23	5.65	6.62	6.84	0.12	1.6137	1.26	-0.2010	1.4610
10.49	5.70	6.80	6.92	0.12	2.1052	1.03		

$LogK_2$ **(Average value)** = 1.2209± 0.3398

Table 7:Point-wise method,Pb (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	log($\frac{n}{1-n}$)	$LogK_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.60	0.05	0.8333	1.96	0.6989	2.6589

$LogK_1$ (Average value) = 2.5832 ±0.1614

Table 8:Point-wise method,Pb-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	log($\frac{n-1}{2-n}$)	$logK_2$
9.51	5.50	6.66	6.71	0.05	0.9650	1.67	-0.0237	1.1963
9.73	5.55	6.78	6.83	0.05	1.1702	1.44		
10.00	5.60	6.90	6.90	0.05	1.4864	1.22		
10.23	5.65	7.05	7.10	0.05	2.0190	1.09		
10.49	5.70	7.10	7.17	0.07	3.6492	1.00		

$LogK_2$(Average value) = 1.1963

Table 9:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$V_3\text{-}V_2$	n	pL	Log ($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.5477	2.3123
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	0.0272	2.2072
9.51	5.50	6.20	6.26	0.07	0.6417	1.89	0.2530	2.1430
9.73	5.55	6.40	6.40	0.07	0.7000	1.67	0.3680	2.0380

$LogK_1$ **(Average value)** = 2.2364 ± 0.1602

Table 10:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$V_3\text{-}V_2$	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
10.00	5.60	6.47	6.55	0.08	1.9503	1.41		
10.23	5.65	6.62	6.72	0.11	1.4792	1.26	-0.0361	1.2239

$LogK_2$ **(Average value)** = 1.2239

Table 11:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	log($\frac{n}{n-1}$)	$LogK_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4290	2.2110
8.72	5.35	6.37	6.39	0.02	0.2858	2.42	-0.3978	2.0222
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

$LogK_1$ (Average value)=2.1382±0.1046

Table 12:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n-1}{2-n}$)	$LogK_2$
9.51	5.55	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.84	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.93	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.10		
10.49	5.70	7.10	7.18	0.07	3.6492	0.83		

$LogK_2$(Average value) = 1.5453 **±** 0.3450

Table 13:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.3477	2.3123
9.00	5.40	6.00	6.04	0.04	0.3236	2.38	-0.3202	2.0598
9.22	5.45	6.10	6.15	0.05	0.4297	2.17	-0.1230	2.0470
9.51	5.50	6.20	6.26	0.06	0.5500	1.89	0.0871	1.9771
9.73	5.55	6.33	6.40	0.07	0.7000	1.67	0.3680	2.0380

$LogK_1$ **(Average value)** = 2.1568 ± 0.2069

Table 14:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
10.00	5.60	6.47	6.55	0.08	0.9148	1.41		
10.23	5.65	6.62	6.71	0.09	1.2102	1.20	-0.5749	0.6251
10.49	5.70	6.80	6.92	0.09	1.5968	1.03	0.1703	1.2003

$LogK_2$ **(Average value)** = 0.9127± 0.4070

Table15:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	Log($\frac{n}{1-n}$)	$LogK_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4210	2.2190
8.72	5.35	6.37	6.40	0.03	0.4286	2.42	-0.1249	2.2951
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.96	0.3010	2.2610
9.51	5.55	6.66	6.70	0.04	0.7720	1.67	0.5297	2.1997

$LogK_1$ (Average value) = 2.2108± 0.0825

Table 16:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
9.73	5.55	6.78	6.83	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.95	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.09		
10.49	5.70	7.10	7.16	0.06	3.1429	0.89		

$LogK_2$ **(Average value)** = 1.5453± 0.3450

Table 17:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.86	0.05	0.3717	2.88	-0.2280	2.6520
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.06	0.06	0.4853	2.38	-0.0255	2.3545
9.22	5.45	6.10	6.16	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430
9.73	5.55	6.33	6.41	0.08	0.8000	1.69	0.6020	2.2920

$LogK_1$ **(Average value)** = 2.2516± 0.5380

Table 18:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$\mathrm{Log}(\frac{n-1}{2-n})$	Log K_2
10.00	5.60	6.47	6.57	0.10	1.1434	1.43		
10.23	5.65	6.62	6.72	0.10	1.3448	1.23	-0.2788	0.9512
10.49	5.70	6.80	6.90	0.10	1.7742	1.03	0.5351	1.5651

LogK_2 **(Average value)** = 1.2581± 0.4340

Table 19: Stepwise and overall Stability constants of thehydrolysed and unhydrolysed divalent metal (II) complexes

Chelates	**LogK_1**	**LogK_2**	**Logβ**
[Cu (Hydrolysed PSHA-1)$_2$]	2.4788	1.4280	3.9068
[Pb (Hydrolysed PSHA-1)$_2$]	2.5832	1.1963	3.7795
[Cd (Hydrolysed PSHA-1)$_2$]	2.2108	1.5453	3.7561
[Mg (Hydrolysed PSHA-1)$_2$]	2.1382	1.5453	3.6835
[Cu (Unhydrolysed PSHA-1)$_2$]	2.3059	1.2209	3.5268
[Pb (Unhydrolysed PSHA-1)$_2$]	2.2364	1.2239	3.4603
[Cd (Unhydrolysed PSHA-1)$_2$]	2.2516	1.2581	3.5097
[Mg (Unydrolysed PSHA-1)$_2$]	2.1568	0.9127	3.0695

The results obtained (Table19) shows the stepwise and overall stability constants to be not high indicating low stability of the complexes, because the solubility of most metal ions in the basic pH range is minimal due to metal hydroxide precipitation (Karimi, 2017). In general, the stepwise stability constants (K_1 and K_2) follow the order $K_1 > K_2$ for the copper, lead, magnesium and cadmium complexes respectively. The steady decrease of the values with increasing number of ligands is in agreement with the prediction made by researchers (Na'aliya, 2013). The decrease could be attributed to the fact that as the number of the ligands (Humate ions) that enters the coordination zone increases the aqua molecules available for replacement by the ligands become less. Thus, the metal ions become less electron loving with progressive intake of the ligand and this results in the decrease in the values of the constants (Na'aliya, 2013). Also the stability of the complexes is influenced by the size and number of the chelate rings(Mackay and Mackay,2002).All the complexes form rings in their structure as humate, a bidentate ligand, bond the metal ions in the ratio 1:2 (Boguta and Sokolowska, 2016) forming chelate rings. The values of the overall stability constants (logβ) obtained for humate complexes are not high indicating low stability as the values are not high. LogK values for copper-humates (Table 3 to 6) obtained in this study are lower than those reported for the complexes of humic acids (Pandey *et al.*, 2015; Dinu, 2013; Kaschl *et al.*, 2010 and Gilbeto and Jorg, 2001). The values of LogK(Table 7 to 10) forlead-humates are lower than those reported for the lead in the literature (Dinu, 2013; Gilbeto and Jorg 2001). Log K values(Table 11 to 14) for magnesium-humates obtained in this study are close to those reported by (Pandey *et al.*, 2015). Log K values of cadmium-humates (Table 15 to 18) obtained in this work near to the one reported by (Dinu, 2013 and Pandey *et al.*, 2015).The difference between the reported values and the values obtained in this study might be probably as a result of acid hydrolysis of humic acid. The values of the overall stability constants (log β) of the copper humates complexes presented in Table 19 is high than that of other metal humate complexes, show relatively high stability of Cu-HA complexes, show the following order of stability: Cu >Pb> Cd > Mg; which are in close agreement to the findings of (Dinu, 2013 and Pandey *et al.*, 2015).The high stability of Cu-humate chelate could be attributed to the existence of coordinate covalent bond between the complexing agents and the Cu^{2+} ions. Since, Cu^{2+} being a metal of the transitional series with $3d^9$ electronic configurations can accept the electrons from the complexing agents. Similarly,the low stabilities of Pb,Cd and Mg -complexes could be explained by that Pb^{2+} with $6s^2$, Cd^{2+} with $4d^{10}$ and Mg^{2+} with $2p^6$ their electronic configuration has a completely filled d,p and s orbitals. Moreover, the stabilities of metal ions with hydrolysed humic acid from peat soil were higher than those with unhydrolysed humic acid from peat soil; which is ascribed to the high content of acidity in hydrolysed humic acid than unhydrolysed humic acid.

CONCLUSION

The values of logK for Cu(II) hydrolysed humic acid complex was higher followed by Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes as compared with metal(II) unhydrolysed humic acid complexes . This indicates acid hydrolysis of humic acid can enhance the complexation behavior of humic acid with metal (II) ions. However, the higher values of logβ for Cu(II), Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes indicates more stable stepwise complexes formed as compared with Cu(II), Pb(II), Cd(II) and Mg(II) unhydrolysed humic acid complexes.

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STABILITY CONSTANTS OF COMPLEXES OF METAL IONS WITH PEATSOIL HUMIC ACIDS UNDER NON-ACID-CONDITIONS

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ABSTRACT

Stability constants of complexes of four divalent metal ions viz. Cu^{2+}, Pb^{2+},Mg^{2+} and Cd^{2+} with humic acids (HA) were determined by potentiometric titration of humic acids with the corresponding salt of the divalent metals in aqueous media under non-acid-condition. The log K (logarithm of the stability constant) ranged from 1.0942 to 2.7471 for metal-humic acid complexes were determined using point-wise computational method. The order of stability constants were obtained as follows: Cu >Pb> Cd > Mg for metal -HA complexes respectively, indicating a higher degree of complexation with Cu metal ion.

Keywords: stability constant, humic acid, potentiometric titration, divalent metals, acid hydrolysis.

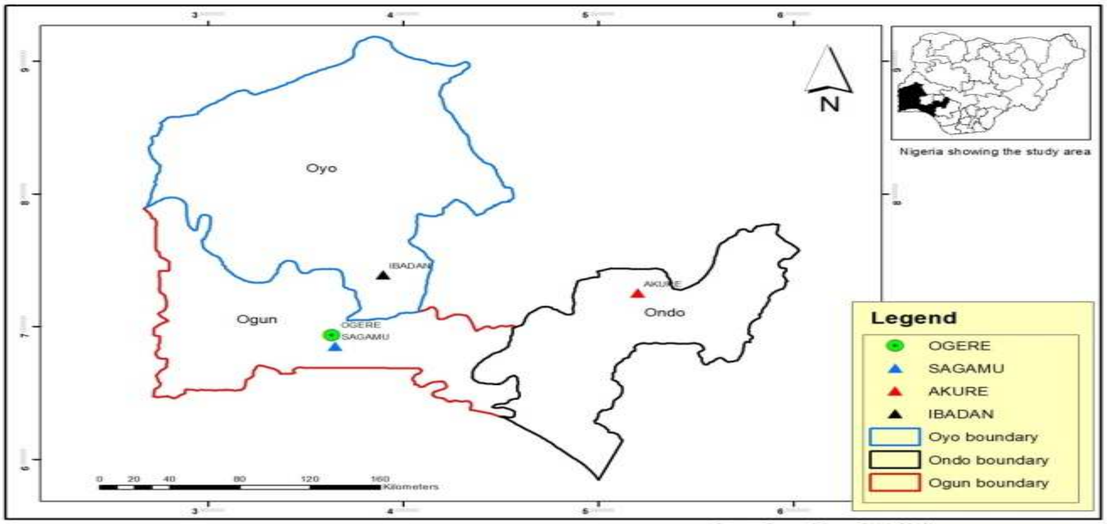
NTRODUCTION

The stability constant of a complex is the numerical expression of its stability and provides a quantitative measure of affinity of the metal ion to the complexing agent. An understanding of the relative stability of metal-complexes helps in predicting the behavior of metal ions in the soil (Ram and Raman, 1982). Extensive researches has been done to determine the stability constants of the complexes formed between humic acid (HA) with a number of metal ions. Ashok *et al.*, (2000) reported that humic acid with hydroxyl, phenoxyl and carboxyl reactive groups can form coordination compound with metal ions at pH 3.5. The stability constants(Log K) for different metal-humic acid complexes indicated the following order of the stabilities of complexes formed between humic acid and metal ion, Cu >Fe >Pb> Ni > Co > Ca > Cd > Zn >Mn> Mg. Andelkovic *et al.*, (2010) investigated the binding of Cd(II) to soil humic acid at pH 6.5 and in 0.1M KNO_3 ionic medium. The stability constant for binding indicating greater stability in the case when carboxyl groups are involved in complexation reaction. Kostic *et al.*,(2012) investigated the complexation of humic acid with certain heavy metal ions (Co(II), Ni(II),Cu(II), Zn(II), and Pb(II). The experiment was performed at 25°C, at pH 4.0 and ionic strength of 0.01M. Stability constant of complex between Pb(II) ions and humic acid is greater than stability constants of other investigated metal-humate complexes. Bogata and Sokolowska (2016) analyses the interaction between humic acids from different soils and Zn (II) ions at wide concentration ranges and at pH 5. Studies have showed significant impact of Zn concentration, pH and some properties of humic acids with zinc.But all of these studies were limited to acidic pH range. Therefore, the present study was carried out to determine and compare the stability constants of complexes of metal ions with hydrolysed peat soil humic acid and unhydrolysed peat soil humic under non-acid conditions.

MATERIALS AND METHODS

Analytical grade chemicals used includes hydrochloric acid (HCl), nitric acid (HNO_3), sodium hydroxide (NaOH), lead nitrate $Pb(NO_3)_2$, copper nitrate $Cu(NO_3)_2.3H_2O$, cadmium nitrate $Cd(NO_3)_2.4H_2O$, magnesium nitrate $Mg(NO_3)_2.6H_2O$, potassium nitrate (KNO_3), calcium chloride ($CaCl_2$), (sigma-Aldrich). Dowex 50WX8, (20-50 mesh) from Fluka.

Area of study



Source: Dept. of Geog. BUK (2016)

Figure 1: Map showing the sampling point at Sagamu Town, Ogun State.

Description of Sampling Area

Sagamu has geographical coordinates between 6°50′ north; 3° 38′ east is located in south western region of Nigeria. The region has tropical wet and dry climate with a lengthy wet season and relatively constant temperatures throughout the course of the year. Wet season runs from March to October, November to December forms the region dry season. The vegetation type of the region is savannah which is really grassland with small bushes and occasional big trees. Grassland soils have substantially higher organic matter content than forest soils (Novackova, 2011).

Sample Collection

The Peatsoil samples were collected from four different sampling points (0-10cm depth) in Sagamu into polyethylene bag with plastic spoons. Samples were taken to the laboratory, extraneous materials were removed; the samples were air-dried, crushed and ground to a fine powder in a mortar passed through a 0.20mm sieve. The samples were kept for analysis.

Isolation and purification of humic acid from peat soil sample

Peatsoil sample (100g) was mixed with 1000 cm^3 of 0.1M NaOH solution, shaken for 3hours and left to stand overnight. Dark-coloured supernatant was obtained and decanted from solid residue. The dark-coloured supernatant was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 6 hours. Yellowish brown supernatant and dark-brown precipitate were obtained. The yellowish brown supernatant was decanted followed by centrifuge and discarded. The dark-brown precipitate was mixed with $500cm^3$of 0.1M NaOH solution followed by passing through dowex resin. The dark-brown solution was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 3 hours. The dark-brown precipitate was washed several times with deionized water. The supernatant was treated with $AgNO_3$ solution until no white precipitate observed. The humic acid was transferred to weighed crucible and dried at 60°C in an oven for 12 hours. The humic acid was cooled and dried in the desiccator, weighed and recorded. The obtained humic acid was dried again at 60°C for additional 6 hours cooled and dried in the desiccator, weighed and recorded constant weight was obtained (Baruah *et al*., 2015).

FT-IR analysis

FT-IR spectra of humic acid sample was analysed using Carry 630 FT-IR Agilent Technologies.

Unhydrolysed compost humic acid

The unhydrolysed humic acid was obtained after isolation and purification of compost humic acid and kept for investigation.

Acid hydrolysis of Peatsoil acid

Peatsoil humic acid sample (1g) was refluxed for 12 hours at (160°C) with $50cm^3$ of 6M HCl. The mixture was allowed to cool, decanted, and centrifuged after hydrolysis. The insoluble residues were washed with distilled water via centrifugation several times, and the supernatant was treated with $AgNO_3$ solution until no white precipitate was observed. The residue was thoroughly dried over $CaCl_2$ in a desiccator at room temperature (Chefetz *et al.*, 2002). Finally, the obtained hydrolysed humic acid was kept for investigation.

Potentiometric Titrations

Potentiometric measurements were carried out using a pH-meter Jenway (model 3510) with combine electrode, the sensitivity of the pH - meter is 0.01 units. The pH meter was switched on half an hour before starting the titration for initial warm up of the instrument. The instrument was calibrated with an aqueous standard buffer solution of pH 4.00 and 10.0 (borate buffer) prepared from a "Qualigens" buffer tablets.

The following sets of solutions were prepared in a 250cm^3 volumetric flask separately for pH metric titrations.

(i) 5 cm^3 0.1 M HCl + 40 cm^3 deionized water
(ii) 5 cm^3 0.1 M HCl + 39 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid
(iii) 5 cm^3 0.1 M HCl + 37 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid + 2 cm^3 0.01 M Cu(II)

The solutions were titrated against standardized 0.110MNaOH separately. The total volume of each mixture was adjusted to 50 cm^3 and the ionic strength of the solutions was maintained constant at by adding appropriate amount of stock solution of 1M KNO_3 (Gamal, 2015; Omar and Ali, 2015). A magnetic stirrer was used to achieve thorough mixing of the interacting solutions at 550 rpm. The same set of experimental conditions was applied for potentiometric titration of remaining samples.

Evaluation of pKa of Hydrolysed peat soil Humic Acids

The proton-ligand formation number $n_{\mathbf{A}}$ were calculated by Irving and Rossotti expression (Omar and Ali, 2015).

nA = Y- $\frac{(V2-V1)(No-Eo)}{(Vo+V1)TcL}$ 1

Where: Y is number of dissociable proton, (V_2-V_1) is the measure of displacement of the ligand curve relative to acid curve, N^o and E^o are the resultant concentration of alkali solution, free acid solution, $T_{cL}{}^o$ is the total ligand concentration, V^o is the total volume of titration solution,V_1 is the volume of alkali added to acid solution,V_2 is the volume of alkali added to acid solution + ligand solution, acid dissociation constants (pKa - values) of ligand were calculated by algebraic method point wise calculation (Tables 1). The dissociation constants (pKa) were calculated according to the following relation:

pKa = pH + log($\frac{nA}{1-nA}$) 2

Where: pKa is the acid dissociation constant, $n_A$is the Proton-ligand formation number and pH is the pH-values (Omar and Ali, 2015).

Determination of metal-ligand stability constants (log K) of complexes

The potentiometric measurement for the determination of stability constant of a complex in solution is based on the fact that the redox potential of the couple $\frac{M^{+(m-n)}}{M^{+m}}$ is shifted significantly on complexation of the metal ion with the ligand. This method involves change in hydrogen ion concentration [H$^+$] due to the displacement or association of one or more protons taking place during complexation reaction. This change can be found out by titrating the solutions containing free acid, acid with ligand, and acid with ligand and metal ion, individually against a standard alkali solution at a constant ionic strength or temperature. Either ionic strength or temperature may be varied for different sets of solutions. In all the cases, the change in the pH of the solution is measured after each addition of a known amount of alkali to the reaction cell which contains the reaction mixture. The titration curves are then drawn by plotting the measured pH values against the corresponding volume of alkali added and the stability constants of the complexes are determined from the titration curves by employing pH-metric titration technique given by (Irving and Rossoti).

Metal-ligand stability constants (Log K) were determined by using the following relations:

$$\bar{n} = \frac{(V_3 - V_2)(E^0 + N^0)}{(V^0 + V_2)\bar{n}_A T_m^0} \qquad \text{...3}$$

and

$$PL = \log_{10}\{\frac{1+\beta_n^H \frac{1}{[anti \ \log pH]^n}}{T_L^0 - \bar{n} T_m^0} X \frac{(V^0 + V_3)}{V^0}\} \qquad \text{..4}$$

Where $T_{L,}$ T^{o}, E°, and V^{o}havethe same significance as in equation (1) above, T_m denotes the total concentration of metal present in solution, V_3 is the volume of metal ions present in solution and β^H is the overall proton ligand stability constant. The metal-ligand stability constants (log K) were determined by employing point wise computational Method (eq. 5 and 6).

$$\mathrm{Log}K_1 = \log\left(\frac{n}{1-n}\right) + pL \qquad \ldots\ldots\ldots\ldots.5$$

$$\mathrm{Log}K_2 = \log\left(\frac{1-n}{2-n}\right) + pL\ldots\ldots\ldots\ldots\ldots\ldots\ldots.6$$

Where: Log K is the metal-ligand stability constant, pL is the Free ligand exponent function, **n** is the Average number of ligand attached with metal ion (Janrao*et al.*, 2014).The results obtained were analyzed by an ORIGIN 2016 program using titration data and then the proton-ligand stability constants (pKa) and Metal-ligand stability constant (LogK) calculated (Omar and Ali, 2015).

RESULTS AND DISCUSSION

Fourier transformed infrared (FT-IR) spectra of isolated humic acid from peat soils Figure 2 had distinct clear absorption bands indicating the presence of major humic acid structural elemental groups such as H bonded OH ($3680cm^{-1}$ peak), C=O of carbonyl ($1721cm^{-1}$ peak), functional groups of aliphatic components CH_2 ($2918cm^{-1}$ peak) and C-O stretching of polysaccharide ($1168cm^{-1}$ peak). The positions of the absorption bands of the spectra fell within typical major absorption bands of humic acid which is at frequencies 3680, 2918, 1721, 1168 cm^{-1}. The first peak centred in the vicinity of 3680 cm^{-1} region is attributed to phenol OH group bounded by intermolecular H bonds. The $2918cm^{-1}$ band usually has absorption maximum at 2918 cm^{-1} which is due to C–H stretching of alkane group (CH_2). The next major absorption band is 1721 cm^{-1}. This band has been commonly ascribed to C=O stretching of mainly carboxyl group (COOH) with trace amount of ketones. The last peak was observed at 1168 cm^{-1} due to C–O stretching of polysaccharides and this peak appeared also in the spectra of humic acid from peat soil. The FTIR spectra of the isolated humic acid contained all major characteristic absorption peaks of humic acid. These absorption peaks indicated the presence of the major structural elements of humic acid namely H bonded OH, C=C of aromatic ring, C=O of carbonyl group (both carboxyl and ketonic), CH_2 group. This strongly supports the presence of humic acid.

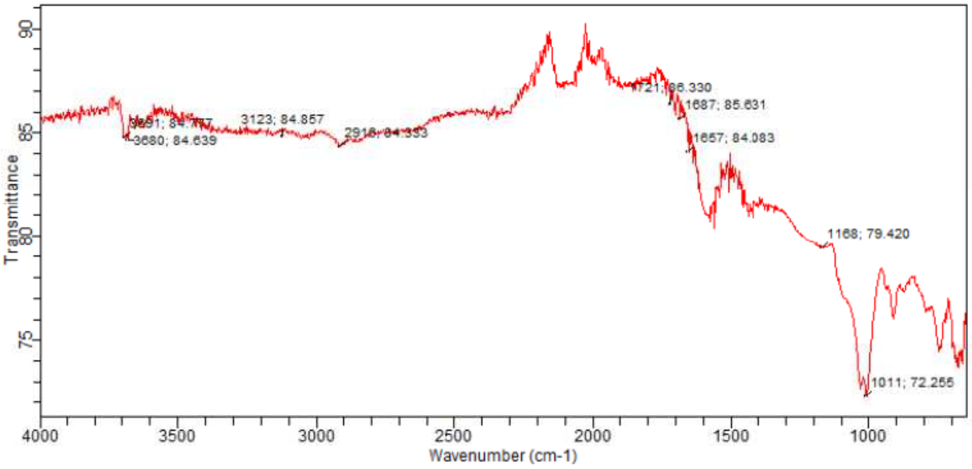


Fig. 2 : FT-IR spectraof peatsoilhumic acid (PSHA)

Evaluation of acid dissociation constant (pka) of acid hydrolysed peat soil humicacid at phenolic group

The value of the dissociation constant of the peat soil humic acid (PSHA) that underwent acidhydrolysis studied was found to be 8.9299 as shown Table 1, which is lower than the literaturevalues reported by Almeida and Szpoganics, (2015), Borges *et al.*, (2005); Badr *et al.*, (2012)and Fernandes *et al*,.(2009) of 9.73, 9.47 and 10.30. The difference between the obtained valuesand the reported values in this study might be probably as a result of acid hydrolysis of humicacid.

Table 1: PKa of (Hydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	$\log(\frac{nA}{1-nA})$	pKa
8.50	5.30	6.29	0.99	0.3594	-0.2510	8.2490
8.72	5.35	6.37	1.02	0.3400	-0.2880	8.4320
9.00	5.40	6.46	1.06	0.3141	-0.3391	8.6609
9.22	5.45	6.55	1.10	0.2882	-0.3927	8.8273
9.51	5.50	6.66	1.16	0.2494	-0.4786	9.0314
9.73	5.55	6.78	1.23	0.2041	-0.5910	9.1390
10.00	5.60	6.90	1.30	0.1589	-0.7238	9.2762
10.23	5.65	7.05	1.40	0.0941	-0.9835	9.2465
10.49	5.70	7.10	1.40	0.0941	-0.9835	9.5065

Average pKa = 8.9299 ± 0.4186

Table 2: PKa of (Unhydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	$\mathrm{Log}(\frac{nA}{1-n})$	pKa
8.50	5.30	5.81	0.51	0.6619	0.2919	8.7919
8.72	5.35	5.90	0.55	0.6357	0.2418	8.9618
9.00	5.40	6.00	0.60	0.6029	0.1813	9.1813
9.22	5.45	6.10	0.65	0.5701	0.1226	9.3426
9.51	5.50	6.20	0.70	0.5376	0.0654	9.5754
9.73	5.55	6.33	0.78	0.4851	-0.0259	9.7041
10.00	5.60	6.47	0.87	0.4262	-0.1291	9.8709
10.23	5.65	6.62	0.99	0.3609	-0.2481	9.9819
10.49	5.70	6.80	1.10	0.2759	-0.4690	10.0210

Average pKa = 9.4923± 0.4410

Metal-ligand stability constant (Log K)

The stabilityconstants require the accurate values of proton-ligand stability constants (Anil and Maroti, 2008). Metal titration curves crossed over ligand titration curve indicated the formation of complex upon proton release (Santosh, *et al.*, 2011). If the values of n- are within range 0.2-0.8 and 1.2-18 this indicates the formation of 1:1 and 1:2 complexes (Sayyed and Mazahar, 2012).

The metal (II)-humate stepwise stability constants (log k) at phenolic group (Tables 3-18)

Table 3: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3$-$V_2)$	n	pL	$\log(\frac{n}{1-n})$	LogK_1
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

LogK_1 (Average value) = 2.4788± 0.2203

Table 4: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3$-$V_2)$	n	pL	$\mathrm{Log}(\frac{n-1}{2-n})$	LogK_2
9.51	5.50	6.66	6.73	0.07	1.3509	1.70	-0.2671	1.4329
9.73	5.55	6.78	6.85	0.07	1.6383	1.51	0.2467	1.7567
10.00	5.60	6.90	6.98	0.08	2.1783	1.31	-0.2158	1.0942
10.23	5.65	7.05	7.13	0.08	4.1904	1.27		
10.49	5.70	7.10	7.19	0.09	4.6920			

LogK_2(Average value) = 1.4280 ± 0.3312

Table 5:Point-wise method,Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	Log($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430

$LogK_1$ **(Average value)** = 2.3059± 0.6153

Table 6:Point-wise method, Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$V_3\text{-}V_2$	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
9.73	5.55	6.33	6.42	0.09	0.9000	1.69		
10.00	5.60	6.47	6.58	0.11	1.2578	1.44	-0.4592	0.9808
10.23	5.65	6.62	6.84	0.12	1.6137	1.26	-0.2010	1.4610
10.49	5.70	6.80	6.92	0.12	2.1052	1.03		

$LogK_2$ **(Average value)** = 1.2209± 0.3398

Table 7:Point-wise method,Pb (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	log($\frac{n}{1-n}$)	$LogK_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.60	0.05	0.8333	1.96	0.6989	2.6589

$LogK_1$ (Average value) = 2.5832 ±0.1614

Table 8:Point-wise method,Pb-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	log($\frac{n-1}{2-n}$)	$logK_2$
9.51	5.50	6.66	6.71	0.05	0.9650	1.67	-0.0237	1.1963
9.73	5.55	6.78	6.83	0.05	1.1702	1.44		
10.00	5.60	6.90	6.90	0.05	1.4864	1.22		
10.23	5.65	7.05	7.10	0.05	2.0190	1.09		
10.49	5.70	7.10	7.17	0.07	3.6492	1.00		

$LogK_2$(Average value) = 1.1963

Table 9:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$V_3\text{-}V_2$	n	pL	Log ($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.5477	2.3123
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	0.0272	2.2072
9.51	5.50	6.20	6.26	0.07	0.6417	1.89	0.2530	2.1430
9.73	5.55	6.40	6.40	0.07	0.7000	1.67	0.3680	2.0380

$LogK_1$ **(Average value)** = 2.2364 ± 0.1602

Table 10:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$V_3\text{-}V_2$	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
10.00	5.60	6.47	6.55	0.08	1.9503	1.41		
10.23	5.65	6.62	6.72	0.11	1.4792	1.26	-0.0361	1.2239

$LogK_2$ **(Average value)** = 1.2239

Table 11:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	log($\frac{n}{n-1}$)	$LogK_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4290	2.2110
8.72	5.35	6.37	6.39	0.02	0.2858	2.42	-0.3978	2.0222
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

$LogK_1$ (Average value)=2.1382**±**0.1046

Table 12:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$\log(\frac{n-1}{2-n})$	$LogK_2$
9.51	5.55	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.84	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.93	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.10		
10.49	5.70	7.10	7.18	0.07	3.6492	0.83		

$LogK_2$(Average value) = 1.5453 **±** 0.3450

Table 13:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$Log(\frac{n}{n-1})$	$Log\ K_1$
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.3477	2.3123
9.00	5.40	6.00	6.04	0.04	0.3236	2.38	-0.3202	2.0598
9.22	5.45	6.10	6.15	0.05	0.4297	2.17	-0.1230	2.0470
9.51	5.50	6.20	6.26	0.06	0.5500	1.89	0.0871	1.9771
9.73	5.55	6.33	6.40	0.07	0.7000	1.67	0.3680	2.0380

$LogK_1$ **(Average value)** = 2.1568 ± 0.2069

Table 14:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$Log(\frac{n-1}{2-n})$	$Log\ K_2$
10.00	5.60	6.47	6.55	0.08	0.9148	1.41		
10.23	5.65	6.62	6.71	0.09	1.2102	1.20	-0.5749	0.6251
10.49	5.70	6.80	6.92	0.09	1.5968	1.03	0.1703	1.2003

$LogK_2$ **(Average value)** = 0.9127± 0.4070

Table15:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$Log(\frac{n}{1-n})$	$LogK_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4210	2.2190
8.72	5.35	6.37	6.40	0.03	0.4286	2.42	-0.1249	2.2951
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.96	0.3010	2.2610
9.51	5.55	6.66	6.70	0.04	0.7720	1.67	0.5297	2.1997

$LogK_1$ (Average value) = 2.2108± 0.0825

Table 16:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$Log(\frac{n-1}{2-n})$	$Log\ K_2$
9.73	5.55	6.78	6.83	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.95	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.09		
10.49	5.70	7.10	7.16	0.06	3.1429	0.89		

$LogK_2$ **(Average value)** = 1.5453± 0.3450

Table 17:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$Log(\frac{n}{n-1})$	$Log\ K_1$
8.50	5.30	5.81	5.86	0.05	0.3717	2.88	-0.2280	2.6520
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.06	0.06	0.4853	2.38	-0.0255	2.3545
9.22	5.45	6.10	6.16	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430
9.73	5.55	6.33	6.41	0.08	0.8000	1.69	0.6020	2.2920

$LogK_1$ **(Average value)** = 2.2516± 0.5380

Table 18:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$\text{Log}(\frac{n-1}{2-n})$	Log K_2
10.00	5.60	6.47	6.57	0.10	1.1434	1.43		
10.23	5.65	6.62	6.72	0.10	1.3448	1.23	-0.2788	0.9512
10.49	5.70	6.80	6.90	0.10	1.7742	1.03	0.5351	1.5651

LogK_2 **(Average value)** = 1.2581± 0.4340

Table 19: Stepwise and overall Stability constants of thehydrolysed and unhydrolysed divalent metal (II) complexes

Chelates	**LogK_1**	**LogK_2**	**Logβ**
[Cu (Hydrolysed PSHA-1)$_2$]	2.4788	1.4280	3.9068
[Pb (Hydrolysed PSHA-1)$_2$]	2.5832	1.1963	3.7795
[Cd (Hydrolysed PSHA-1)$_2$]	2.2108	1.5453	3.7561
[Mg (Hydrolysed PSHA-1)$_2$]	2.1382	1.5453	3.6835
[Cu (Unhydrolysed PSHA-1)$_2$]	2.3059	1.2209	3.5268
[Pb (Unhydrolysed PSHA-1)$_2$]	2.2364	1.2239	3.4603
[Cd (Unhydrolysed PSHA-1)$_2$]	2.2516	1.2581	3.5097
[Mg (Unydrolysed PSHA-1)$_2$]	2.1568	0.9127	3.0695

The results obtained (Table19) shows the stepwise and overall stability constants to be not high indicating low stability of the complexes, because the solubility of most metal ions in the basic pH range is minimal due to metal hydroxide precipitation (Karimi, 2017). In general, the stepwise stability constants (K_1 and K_2) follow the order $K_1 > K_2$ for the copper, lead, magnesium and cadmium complexes respectively. The steady decrease of the values with increasing number of ligands is in agreement with the prediction made by researchers (Na'aliya, 2013). The decrease could be attributed to the fact that as the number of the ligands (Humate ions) that enters the coordination zone increases the aqua molecules available for replacement by the ligands become less. Thus, the metal ions become less electron loving with progressive intake of the ligand and this results in the decrease in the values of the constants (Na'aliya, 2013). Also the stability of the complexes is influenced by the size and number of the chelate rings(Mackay and Mackay,2002).All the complexes form rings in their structure as humate, a bidentate ligand, bond the metal ions in the ratio 1:2 (Boguta and Sokolowska, 2016) forming chelate rings. The values of the overall stability constants (logβ) obtained for humate complexes are not high indicating low stability as the values are not high. LogK values for copper-humates (Table 3 to 6) obtained in this study are lower than those reported for the complexes of humic acids (Pandey *et al*., 2015; Dinu, 2013; Kaschl *et al*., 2010 and Gilbeto and Jorg, 2001). The values of LogK(Table 7 to 10) forlead-humates are lower than those reported for the lead in the literature (Dinu, 2013; Gilbeto and Jorg 2001). Log K values(Table 11 to 14) for magnesium-humates obtained in this study are close to those reported by (Pandey *et al*., 2015). Log K values of cadmium-humates (Table 15 to 18) obtained in this work near to the one reported by (Dinu, 2013 and Pandey *et al*., 2015).The difference between the reported values and the values obtained in this study might be probably as a result of acid hydrolysis of humic acid. The values of the overall stability constants (log β) of the copper humates complexes presented in Table 19 is high than that of other metal humate complexes, show relatively high stability of Cu-HA complexes, show the following order of stability: Cu >Pb> Cd > Mg; which are in close agreement to the findings of (Dinu, 2013 and Pandey *et al*., 2015).The high stability of Cu-humate chelate could be attributed to the existence of coordinate covalent bond between the complexing agents and the Cu^{2+} ions. Since, Cu^{2+} being a metal of the transitional series with $3d^9$ electronic configurations can accept the electrons from the complexing agents. Similarly,the low stabilities of Pb,Cd and Mg - complexes could be explained by that Pb^{2+} with $6s^2$, Cd^{2+} with $4d^{10}$ and Mg^{2+} with $2p^6$ their electronic configuration has a completely filled d,p and s orbitals. Moreover, the stabilities of metal ions with hydrolysed humic acid from peat soil were higher than those with unhydrolysed humic acid from peat soil; which is ascribed to the high content of acidity in hydrolysed humic acid than unhydrolysed humic acid.

CONCLUSION

The values of logK for Cu(II) hydrolysed humic acid complex was higher followed by Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes as compared with metal(II) unhydrolysed humic acid complexes . This indicates acid hydrolysis of humic acid can enhance the complexation behavior of humic acid with metal (II) ions. However, the higher values of logβ for Cu(II), Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes indicates more stable stepwise complexes formed as compared with Cu(II), Pb(II), Cd(II) and Mg(II) unhydrolysed humic acid complexes.

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STABILITY CONSTANTS OF COMPLEXES OF METAL IONS WITH PEATSOIL HUMIC ACIDS UNDER NON-ACID-CONDITIONS

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ABSTRACT

Stability constants of complexes of four divalent metal ions viz. Cu^{2+}, Pb^{2+},Mg^{2+} and Cd^{2+} with humic acids (HA) were determined by potentiometric titration of humic acids with the corresponding salt of the divalent metals in aqueous media under non-acid-condition. The log K (logarithm of the stability constant) ranged from 1.0942 to 2.7471 for metal-humic acid complexes were determined using point-wise computational method. The order of stability constants were obtained as follows: Cu >Pb> Cd > Mg for metal -HA complexes respectively, indicating a higher degree of complexation with Cu metal ion.

Keywords: stability constant, humic acid, potentiometric titration, divalent metals, acid hydrolysis.

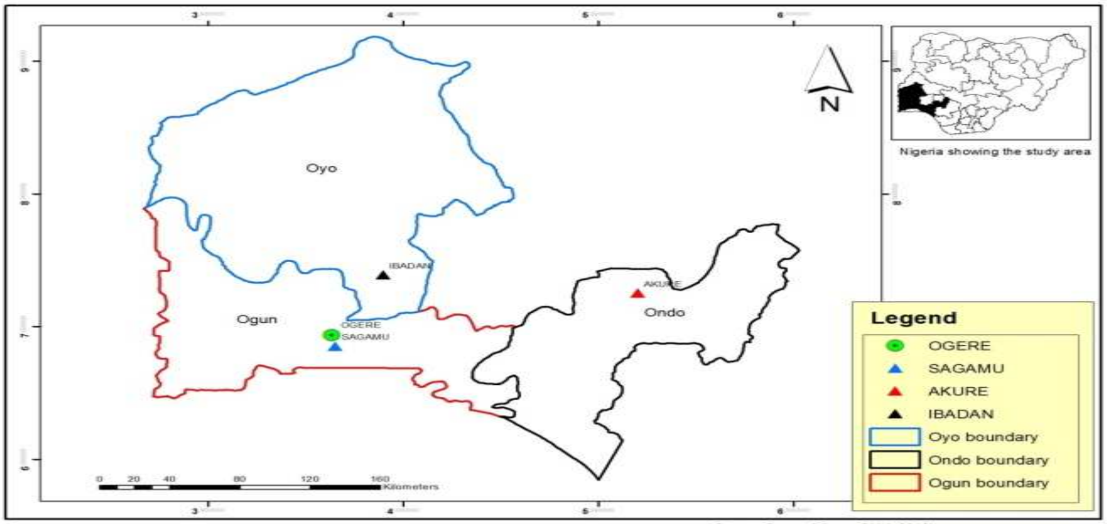
NTRODUCTION

The stability constant of a complex is the numerical expression of its stability and provides a quantitative measure of affinity of the metal ion to the complexing agent. An understanding of the relative stability of metal-complexes helps in predicting the behavior of metal ions in the soil (Ram and Raman, 1982). Extensive researches has been done to determine the stability constants of the complexes formed between humic acid (HA) with a number of metal ions. Ashok *et al.*, (2000) reported that humic acid with hydroxyl, phenoxyl and carboxyl reactive groups can form coordination compound with metal ions at pH 3.5. The stability constants(Log K) for different metal-humic acid complexes indicated the following order of the stabilities of complexes formed between humic acid and metal ion, Cu >Fe >Pb> Ni > Co > Ca > Cd > Zn >Mn> Mg. Andelkovic *et al.*, (2010) investigated the binding of Cd(II) to soil humic acid at pH 6.5 and in 0.1M KNO_3 ionic medium. The stability constant for binding indicating greater stability in the case when carboxyl groups are involved in complexation reaction. Kostic *et al.*,(2012) investigated the complexation of humic acid with certain heavy metal ions (Co(II), Ni(II),Cu(II), Zn(II), and Pb(II). The experiment was performed at 25°C, at pH 4.0 and ionic strength of 0.01M. Stability constant of complex between Pb(II) ions and humic acid is greater than stability constants of other investigated metal-humate complexes. Bogata and Sokolowska (2016) analyses the interaction between humic acids from different soils and Zn (II) ions at wide concentration ranges and at pH 5. Studies have showed significant impact of Zn concentration, pH and some properties of humic acids with zinc.But all of these studies were limited to acidic pH range. Therefore, the present study was carried out to determine and compare the stability constants of complexes of metal ions with hydrolysed peat soil humic acid and unhydrolysed peat soil humic under non-acid conditions.

MATERIALS AND METHODS

Analytical grade chemicals used includes hydrochloric acid (HCl), nitric acid (HNO_3), sodium hydroxide (NaOH), lead nitrate $Pb(NO_3)_2$, copper nitrate $Cu(NO_3)_2.3H_2O$, cadmium nitrate $Cd(NO_3)_2.4H_2O$, magnesium nitrate $Mg(NO_3)_2.6H_2O$, potassium nitrate (KNO_3), calcium chloride ($CaCl_2$), (sigma-Aldrich). Dowex 50WX8, (20-50 mesh) from Fluka.

Area of study



Source: Dept. of Geog. BUK (2016)

Figure 1: Map showing the sampling point at Sagamu Town, Ogun State.

Description of Sampling Area

Sagamu has geographical coordinates between 6°50′ north; 3° 38′ east is located in south western region of Nigeria. The region has tropical wet and dry climate with a lengthy wet season and relatively constant temperatures throughout the course of the year. Wet season runs from March to October, November to December forms the region dry season. The vegetation type of the region is savannah which is really grassland with small bushes and occasional big trees. Grassland soils have substantially higher organic matter content than forest soils (Novackova, 2011).

Sample Collection

The Peatsoil samples were collected from four different sampling points (0-10cm depth) in Sagamu into polyethylene bag with plastic spoons. Samples were taken to the laboratory, extraneous materials were removed; the samples were air-dried, crushed and ground to a fine powder in a mortar passed through a 0.20mm sieve. The samples were kept for analysis.

Isolation and purification of humic acid from peat soil sample

Peatsoil sample (100g) was mixed with 1000 cm^3 of 0.1M NaOH solution, shaken for 3hours and left to stand overnight. Dark-coloured supernatant was obtained and decanted from solid residue. The dark-coloured supernatant was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 6 hours. Yellowish brown supernatant and dark-brown precipitate were obtained. The yellowish brown supernatant was decanted followed by centrifuge and discarded. The dark-brown precipitate was mixed with $500cm^3$of 0.1M NaOH solution followed by passing through dowex resin. The dark-brown solution was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 3 hours. The dark-brown precipitate was washed several times with deionized water. The supernatant was treated with $AgNO_3$ solution until no white precipitate observed. The humic acid was transferred to weighed crucible and dried at 60°C in an oven for 12 hours. The humic acid was cooled and dried in the desiccator, weighed and recorded. The obtained humic acid was dried again at 60°C for additional 6 hours cooled and dried in the desiccator, weighed and recorded constant weight was obtained (Baruah *et al.*, 2015).

FT-IR analysis

FT-IR spectra of humic acid sample was analysed using Carry 630 FT-IR Agilent Technologies.

Unhydrolysed compost humic acid

The unhydrolysed humic acid was obtained after isolation and purification of compost humic acid and kept for investigation.

Acid hydrolysis of Peatsoil acid

Peatsoil humic acid sample (1g) was refluxed for 12 hours at (160°C) with $50cm^3$ of 6M HCl. The mixture was allowed to cool, decanted, and centrifuged after hydrolysis. The insoluble residues were washed with distilled water via centrifugation several times, and the supernatant was treated with $AgNO_3$ solution until no white precipitate was observed. The residue was thoroughly dried over $CaCl_2$ in a desiccator at room temperature (Chefetz *et al.*, 2002). Finally, the obtained hydrolysed humic acid was kept for investigation.

Potentiometric Titrations

Potentiometric measurements were carried out using a pH-meter Jenway (model 3510) with combine electrode, the sensitivity of the pH -meter is 0.01 units. The pH meter was switched on half an hour before starting the titration for initial warm up of the instrument. The instrument was calibrated with an aqueous standard buffer solution of pH 4.00 and 10.0 (borate buffer) prepared from a "Qualigens" buffer tablets.

The following sets of solutions were prepared in a 250cm^3 volumetric flask separately for pH metric titrations.

(i) 5 cm^3 0.1 M HCl + 40 cm^3 deionized water
(ii) 5 cm^3 0.1 M HCl + 39 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid
(iii) 5 cm^3 0.1 M HCl + 37 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid + 2 cm^3 0.01 M Cu(II)

The solutions were titrated against standardized 0.110MNaOH separately. The total volume of each mixture was adjusted to 50 cm^3 and the ionic strength of the solutions was maintained constant at by adding appropriate amount of stock solution of 1M KNO_3 (Gamal, 2015; Omar and Ali, 2015). A magnetic stirrer was used to achieve thorough mixing of the interacting solutions at 550 rpm. The same set of experimental conditions was applied for potentiometric titration of remaining samples.

Evaluation of pKa of Hydrolysed peat soil Humic Acids

The proton-ligand formation number $n_{\mathbf{A}}$ were calculated by Irving and Rossotti expression (Omar and Ali, 2015).

$$nA = Y- \frac{(V2-V1)(No-Eo)}{(Vo+V1)TcL} \quad \text{……………………………1}$$

Where: Y is number of dissociable proton, (V_2-V_1) is the measure of displacement of the ligand curve relative to acid curve, N^o and E^o are the resultant concentration of alkali solution, free acid solution, $T_{cL}{}^o$ is the total ligand concentration, V^o is the total volume of titration solution,V_1 is the volume of alkali added to acid solution,V_2 is the volume of alkali added to acid solution + ligand solution, acid dissociation constants (pKa - values) of ligand were calculated by algebraic method point wise calculation (Tables 1). The dissociation constants (pKa) were calculated according to the following relation:

$$\text{pKa} = \text{pH} + \log(\frac{nA}{1-nA}) \quad \text{………………………..2}$$

Where: pKa is the acid dissociation constant, $n_A$is the Proton-ligand formation number and pH is the pH-values (Omar and Ali, 2015).

Determination of metal-ligand stability constants (log K) of complexes

The potentiometric measurement for the determination of stability constant of a complex in solution is based on the fact that the redox potential of the couple $\frac{M^{+(m-n)}}{M^{+m}}$ is shifted significantly on complexation of the metal ion with the ligand. This method involves change in hydrogen ion concentration [H$^+$] due to the displacement or association of one or more protons taking place during complexation reaction. This change can be found out by titrating the solutions containing free acid, acid with ligand, and acid with ligand and metal ion, individually against a standard alkali solution at a constant ionic strength or temperature. Either ionic strength or temperature may be varied for different sets of solutions. In all the cases, the change in the pH of the solution is measured after each addition of a known amount of alkali to the reaction cell which contains the reaction mixture. The titration curves are then drawn by plotting the measured pH values against the corresponding volume of alkali added and the stability constants of the complexes are determined from the titration curves by employing pH-metric titration technique given by (Irving and Rossoti).

Metal-ligand stability constants (Log K) were determined by using the following relations:

$$\bar{n} = \frac{(V_3 - V_2)(E^0 + N^0)}{(V^0 + V_2)\bar{n}_A T_m^0} \quad \text{……………………………………………………………………..3}$$

and

$$PL = \log_{10}\{\frac{1 + \beta_n^H \frac{1}{[anti\ \log \text{pH}]^n}}{\text{T}_\text{L}^0 - \bar{n}T_m^0} \text{X} \frac{(V^0 + V_3)}{V^0}\} \quad \text{……………………………………………………..4}$$

Where $T_{L,}$ T^o, E°, and V^ohavethe same significance as in equation (1) above, T_m denotes the total concentration of metal present in solution, V_3 is the volume of metal ions present in solution and β^H is the overall proton ligand stability constant. The metal-ligand stability constants (log K) were determined by employing point wise computational Method (eq. 5 and 6).

$$\text{LogK}_1 = \log\left(\frac{n}{1-n}\right) + \text{pL} \qquad \ldots\ldots\ldots\ldots.5$$

$$\text{LogK}_2 = \log\left(\frac{1-n}{2-n}\right) + \text{pL}\ldots\ldots\ldots\ldots\ldots\ldots\ldots.6$$

Where: Log K is the metal-ligand stability constant, pL is the Free ligand exponent function, **n** is the Average number of ligand attached with metal ion (Janrao*et al*., 2014).The results obtained were analyzed by an ORIGIN 2016 program using titration data and then the proton-ligand stability constants (pKa) and Metal-ligand stability constant (LogK) calculated (Omar and Ali, 2015).

RESULTS AND DISCUSSION

Fourier transformed infrared (FT-IR) spectra of isolated humic acid from peat soils Figure 2 had distinct clear absorption bands indicating the presence of major humic acid structural elemental groups such as H bonded OH ($3680cm^{-1}$ peak), C=O of carbonyl ($1721cm^{-1}$ peak), functional groups of aliphatic components CH_2 ($2918cm^{-1}$ peak) and C-O stretching of polysaccharide ($1168cm^{-1}$ peak). The positions of the absorption bands of the spectra fell within typical major absorption bands of humic acid which is at frequencies 3680, 2918, 1721, 1168 cm^{-1}. The first peak centred in the vicinity of 3680 cm^{-1} region is attributed to phenol OH group bounded by intermolecular H bonds. The $2918cm^{-1}$ band usually has absorption maximum at 2918 cm^{-1} which is due to C–H stretching of alkane group (CH_2). The next major absorption band is 1721 cm^{-1}. This band has been commonly ascribed to C=O stretching of mainly carboxyl group (COOH) with trace amount of ketones. The last peak was observed at 1168 cm^{-1} due to C–O stretching of polysaccharides and this peak appeared also in the spectra of humic acid from peat soil. The FTIR spectra of the isolated humic acid contained all major characteristic absorption peaks of humic acid. These absorption peaks indicated the presence of the major structural elements of humic acid namely H bonded OH, C=C of aromatic ring, C=O of carbonyl group (both carboxyl and ketonic), CH_2 group. This strongly supports the presence of humic acid.

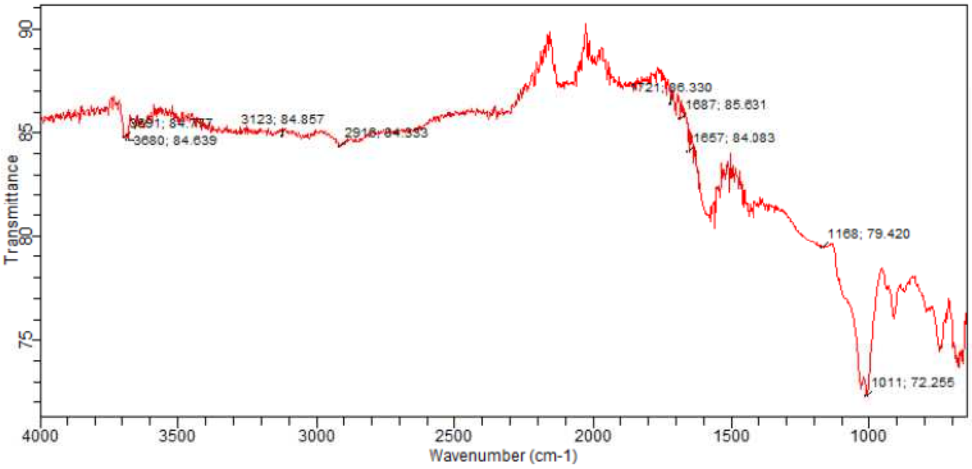


Fig. 2 : FT-IR spectraof peatsoilhumic acid (PSHA)

Evaluation of acid dissociation constant (pka) of acid hydrolysed peat soil humicacid at phenolic group

The value of the dissociation constant of the peat soil humic acid (PSHA) that underwent acidhydrolysis studied was found to be 8.9299 as shown Table 1, which is lower than the literaturevalues reported by Almeida and Szpoganics, (2015), Borges *et al*., (2005); Badr *et al*., (2012)and Fernandes *et al*,.(2009) of 9.73, 9.47 and 10.30. The difference between the obtained valuesand the reported values in this study might be probably as a result of acid hydrolysis of humicacid.

Table 1: PKa of (Hydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	$\log(\frac{nA}{1-nA})$	pKa
8.50	5.30	6.29	0.99	0.3594	-0.2510	8.2490
8.72	5.35	6.37	1.02	0.3400	-0.2880	8.4320
9.00	5.40	6.46	1.06	0.3141	-0.3391	8.6609
9.22	5.45	6.55	1.10	0.2882	-0.3927	8.8273
9.51	5.50	6.66	1.16	0.2494	-0.4786	9.0314
9.73	5.55	6.78	1.23	0.2041	-0.5910	9.1390
10.00	5.60	6.90	1.30	0.1589	-0.7238	9.2762
10.23	5.65	7.05	1.40	0.0941	-0.9835	9.2465
10.49	5.70	7.10	1.40	0.0941	-0.9835	9.5065

Average pKa = 8.9299 ± 0.4186

Table 2: PKa of (Unhydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	$\log(\frac{nA}{1-n})$	pKa
8.50	5.30	5.81	0.51	0.6619	0.2919	8.7919
8.72	5.35	5.90	0.55	0.6357	0.2418	8.9618
9.00	5.40	6.00	0.60	0.6029	0.1813	9.1813
9.22	5.45	6.10	0.65	0.5701	0.1226	9.3426
9.51	5.50	6.20	0.70	0.5376	0.0654	9.5754
9.73	5.55	6.33	0.78	0.4851	-0.0259	9.7041
10.00	5.60	6.47	0.87	0.4262	-0.1291	9.8709
10.23	5.65	6.62	0.99	0.3609	-0.2481	9.9819
10.49	5.70	6.80	1.10	0.2759	-0.4690	10.0210

Average pKa = 9.4923± 0.4410

Metal-ligand stability constant (Log K)

The stabilityconstants require the accurate values of proton-ligand stability constants (Anil and Maroti, 2008). Metal titration curves crossed over ligand titration curve indicated the formation of complex upon proton release (Santosh, *et al.*, 2011). If the values of n- are within range 0.2-0.8 and 1.2-18 this indicates the formation of 1:1 and 1:2 complexes (Sayyed and Mazahar, 2012).

The metal (II)-humate stepwise stability constants (log k) at phenolic group (Tables 3-18)

Table 3: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$\log(\frac{n}{1-n})$	$\log K_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

$\log K_1$ (Average value) = 2.4788± 0.2203

Table 4: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$\log(\frac{n-1}{2-n})$	$\log K_2$
9.51	5.50	6.66	6.73	0.07	1.3509	1.70	-0.2671	1.4329
9.73	5.55	6.78	6.85	0.07	1.6383	1.51	0.2467	1.7567
10.00	5.60	6.90	6.98	0.08	2.1783	1.31	-0.2158	1.0942
10.23	5.65	7.05	7.13	0.08	4.1904	1.27		
10.49	5.70	7.10	7.19	0.09	4.6920			

$\log K_2$(Average value) = 1.4280 ± 0.3312

Table 5:Point-wise method,Cu (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	Log$(\frac{n}{n-1})$	Log K$_1$
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430

LogK$_1$ **(Average value)** = 2.3059± 0.6153

Table 6:Point-wise method, Cu (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	V$_3$-V$_2$	n	pL	Log$(\frac{n-1}{2-n})$	Log K$_2$
9.73	5.55	6.33	6.42	0.09	0.9000	1.69		
10.00	5.60	6.47	6.58	0.11	1.2578	1.44	-0.4592	0.9808
10.23	5.65	6.62	6.84	0.12	1.6137	1.26	-0.2010	1.4610
10.49	5.70	6.80	6.92	0.12	2.1052	1.03		

LogK$_2$ **(Average value)** = 1.2209± 0.3398

Table 7:Point-wise method,Pb (Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	log$(\frac{n}{1-n})$	LogK$_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.60	0.05	0.8333	1.96	0.6989	2.6589

LogK$_1$ (Average value) = 2.5832 ±0.1614

Table 8:Point-wise method,Pb-(Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	log$(\frac{n-1}{2-n})$	logK$_2$
9.51	5.50	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.83	0.05	1.1702	1.44		
10.00	5.60	6.90	6.90	0.05	1.4864	1.22	-0.0237	1.1963
10.23	5.65	7.05	7.10	0.05	2.0190	1.09		
10.49	5.70	7.10	7.17	0.07	3.6492	1.00		

LogK$_2$(Average value) = 1.1963

Table 9:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	V$_3$-V$_2$	n	pL	Log $(\frac{n}{n-1})$	Log K$_1$
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.5477	2.3123
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	0.0272	2.2072
9.51	5.50	6.20	6.26	0.07	0.6417	1.89	0.2530	2.1430
9.73	5.55	6.40	6.40	0.07	0.7000	1.67	0.3680	2.0380

LogK$_1$ **(Average value)** = 2.2364 ± 0.1602

Table 10:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	V$_3$-V$_2$	n	pL	Log$(\frac{n-1}{2-n})$	Log K$_2$
10.00	5.60	6.47	6.55	0.08	1.9503	1.41		
10.23	5.65	6.62	6.72	0.11	1.4792	1.26	-0.0361	1.2239

LogK$_2$ **(Average value)** = 1.2239

Table 11:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	log$(\frac{n}{n-1})$	LogK$_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4290	2.2110
8.72	5.35	6.37	6.39	0.02	0.2858	2.42	-0.3978	2.0222
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

LogK$_1$ (Average value)=2.1382**±**0.1046

Table 12:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	$\log(\frac{n-1}{2-n})$	$LogK_2$
9.51	5.55	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.84	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.93	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.10		
10.49	5.70	7.10	7.18	0.07	3.6492	0.83		

$LogK_2$(Average value) = 1.5453 **±** 0.3450

Table 13:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$V_3\text{-}V_2$	n	pL	$Log(\frac{n}{n-1})$	$Log\ K_1$
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.3477	2.3123
9.00	5.40	6.00	6.04	0.04	0.3236	2.38	-0.3202	2.0598
9.22	5.45	6.10	6.15	0.05	0.4297	2.17	-0.1230	2.0470
9.51	5.50	6.20	6.26	0.06	0.5500	1.89	0.0871	1.9771
9.73	5.55	6.33	6.40	0.07	0.7000	1.67	0.3680	2.0380

$LogK_1$ **(Average value)** = 2.1568 ± 0.2069

Table 14:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$V_3\text{-}V_2$	n	pL	$Log(\frac{n-1}{2-n})$	$Log\ K_2$
10.00	5.60	6.47	6.55	0.08	0.9148	1.41		
10.23	5.65	6.62	6.71	0.09	1.2102	1.20	-0.5749	0.6251
10.49	5.70	6.80	6.92	0.09	1.5968	1.03	0.1703	1.2003

$LogK_2$ **(Average value)** = 0.9127± 0.4070

Table15:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	$Log(\frac{n}{1-n})$	$LogK_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4210	2.2190
8.72	5.35	6.37	6.40	0.03	0.4286	2.42	-0.1249	2.2951
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.96	0.3010	2.2610
9.51	5.55	6.66	6.70	0.04	0.7720	1.67	0.5297	2.1997

$LogK_1$ (Average value) = 2.2108± 0.0825

Table 16:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	$Log(\frac{n-1}{2-n})$	$Log\ K_2$
9.73	5.55	6.78	6.83	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.95	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.09		
10.49	5.70	7.10	7.16	0.06	3.1429	0.89		

$LogK_2$ **(Average value)** = 1.5453± 0.3450

Table 17:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$V_3\text{-}V_2$	n	pL	$Log(\frac{n}{n-1})$	$Log\ K_1$
8.50	5.30	5.81	5.86	0.05	0.3717	2.88	-0.2280	2.6520
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.06	0.06	0.4853	2.38	-0.0255	2.3545
9.22	5.45	6.10	6.16	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430
9.73	5.55	6.33	6.41	0.08	0.8000	1.69	0.6020	2.2920

$LogK_1$ **(Average value)** = 2.2516± 0.5380

Table 18:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$\text{Log}(\frac{n-1}{2-n})$	Log K_2
10.00	5.60	6.47	6.57	0.10	1.1434	1.43		
10.23	5.65	6.62	6.72	0.10	1.3448	1.23	-0.2788	0.9512
10.49	5.70	6.80	6.90	0.10	1.7742	1.03	0.5351	1.5651

LogK_2 **(Average value)** = 1.2581± 0.4340

Table 19: Stepwise and overall Stability constants of thehydrolysed and unhydrolysed divalent metal (II) complexes

Chelates	**LogK_1**	**LogK_2**	**Logβ**
[Cu (Hydrolysed PSHA-1)$_2$]	2.4788	1.4280	3.9068
[Pb (Hydrolysed PSHA-1)$_2$]	2.5832	1.1963	3.7795
[Cd (Hydrolysed PSHA-1)$_2$]	2.2108	1.5453	3.7561
[Mg (Hydrolysed PSHA-1)$_2$]	2.1382	1.5453	3.6835
[Cu (Unhydrolysed PSHA-1)$_2$]	2.3059	1.2209	3.5268
[Pb (Unhydrolysed PSHA-1)$_2$]	2.2364	1.2239	3.4603
[Cd (Unhydrolysed PSHA-1)$_2$]	2.2516	1.2581	3.5097
[Mg (Unydrolysed PSHA-1)$_2$]	2.1568	0.9127	3.0695

The results obtained (Table19) shows the stepwise and overall stability constants to be not high indicating low stability of the complexes, because the solubility of most metal ions in the basic pH range is minimal due to metal hydroxide precipitation (Karimi, 2017). In general, the stepwise stability constants (K_1 and K_2) follow the order $K_1 > K_2$ for the copper, lead, magnesium and cadmium complexes respectively. The steady decrease of the values with increasing number of ligands is in agreement with the prediction made by researchers (Na'aliya, 2013). The decrease could be attributed to the fact that as the number of the ligands (Humate ions) that enters the coordination zone increases the aqua molecules available for replacement by the ligands become less. Thus, the metal ions become less electron loving with progressive intake of the ligand and this results in the decrease in the values of the constants (Na'aliya, 2013). Also the stability of the complexes is influenced by the size and number of the chelate rings(Mackay and Mackay,2002).All the complexes form rings in their structure as humate, a bidentate ligand, bond the metal ions in the ratio 1:2 (Boguta and Sokolowska, 2016) forming chelate rings. The values of the overall stability constants (logβ) obtained for humate complexes are not high indicating low stability as the values are not high. LogK values for copper-humates (Table 3 to 6) obtained in this study are lower than those reported for the complexes of humic acids (Pandey *et al*., 2015; Dinu, 2013; Kaschl *et al*., 2010 and Gilbeto and Jorg, 2001). The values of LogK(Table 7 to 10) forlead-humates are lower than those reported for the lead in the literature (Dinu, 2013; Gilbeto and Jorg 2001). Log K values(Table 11 to 14) for magnesium-humates obtained in this study are close to those reported by (Pandey *et al*., 2015). Log K values of cadmium-humates (Table 15 to 18) obtained in this work near to the one reported by (Dinu, 2013 and Pandey *et al*., 2015).The difference between the reported values and the values obtained in this study might be probably as a result of acid hydrolysis of humic acid. The values of the overall stability constants (log β) of the copper humates complexes presented in Table 19 is high than that of other metal humate complexes, show relatively high stability of Cu-HA complexes, show the following order of stability: Cu >Pb> Cd > Mg; which are in close agreement to the findings of (Dinu, 2013 and Pandey *et al*., 2015).The high stability of Cu-humate chelate could be attributed to the existence of coordinate covalent bond between the complexing agents and the Cu^{2+} ions. Since, Cu^{2+} being a metal of the transitional series with $3d^9$ electronic configurations can accept the electrons from the complexing agents. Similarly,the low stabilities of Pb,Cd and Mg -complexes could be explained by that Pb^{2+} with $6s^2$, Cd^{2+} with $4d^{10}$ and Mg^{2+} with $2p^6$ their electronic configuration has a completely filled d,p and s orbitals. Moreover, the stabilities of metal ions with hydrolysed humic acid from peat soil were higher than those with unhydrolysed humic acid from peat soil; which is ascribed to the high content of acidity in hydrolysed humic acid than unhydrolysed humic acid.

CONCLUSION

The values of logK for Cu(II) hydrolysed humic acid complex was higher followed by Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes as compared with metal(II) unhydrolysed humic acid complexes . This indicates acid hydrolysis of humic acid can enhance the complexation behavior of humic acid with metal (II) ions. However, the higher values of logβ for Cu(II), Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes indicates more stable stepwise complexes formed as compared with Cu(II), Pb(II), Cd(II) and Mg(II) unhydrolysed humic acid complexes.

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STABILITY CONSTANTS OF COMPLEXES OF METAL IONS WITH PEATSOIL HUMIC ACIDS UNDER NON-ACID-CONDITIONS

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ABSTRACT

Stability constants of complexes of four divalent metal ions viz. Cu^{2+}, Pb^{2+},Mg^{2+} and Cd^{2+} with humic acids (HA) were determined by potentiometric titration of humic acids with the corresponding salt of the divalent metals in aqueous media under non-acid-condition. The log K (logarithm of the stability constant) ranged from 1.0942 to 2.7471 for metal-humic acid complexes were determined using point-wise computational method. The order of stability constants were obtained as follows: Cu >Pb> Cd > Mg for metal -HA complexes respectively, indicating a higher degree of complexation with Cu metal ion.

Keywords: stability constant, humic acid, potentiometric titration, divalent metals, acid hydrolysis.

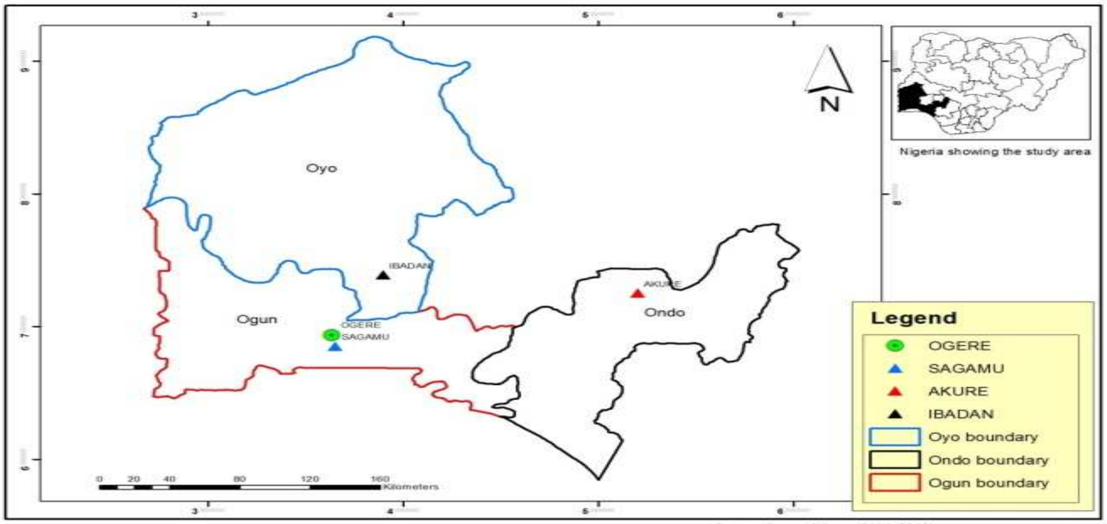
NTRODUCTION

The stability constant of a complex is the numerical expression of its stability and provides a quantitative measure of affinity of the metal ion to the complexing agent. An understanding of the relative stability of metal-complexes helps in predicting the behavior of metal ions in the soil (Ram and Raman, 1982). Extensive researches has been done to determine the stability constants of the complexes formed between humic acid (HA) with a number of metal ions. Ashok *et al.*, (2000) reported that humic acid with hydroxyl, phenoxyl and carboxyl reactive groups can form coordination compound with metal ions at pH 3.5. The stability constants(Log K) for different metal-humic acid complexes indicated the following order of the stabilities of complexes formed between humic acid and metal ion, Cu >Fe >Pb> Ni > Co > Ca > Cd > Zn >Mn> Mg. Andelkovic *et al.*, (2010) investigated the binding of Cd(II) to soil humic acid at pH 6.5 and in 0.1M KNO_3 ionic medium. The stability constant for binding indicating greater stability in the case when carboxyl groups are involved in complexation reaction. Kostic *et al.*,(2012) investigated the complexation of humic acid with certain heavy metal ions (Co(II), Ni(II),Cu(II), Zn(II), and Pb(II). The experiment was performed at 25°C, at pH 4.0 and ionic strength of 0.01M. Stability constant of complex between Pb(II) ions and humic acid is greater than stability constants of other investigated metal-humate complexes. Bogata and Sokolowska (2016) analyses the interaction between humic acids from different soils and Zn (II) ions at wide concentration ranges and at pH 5. Studies have showed significant impact of Zn concentration, pH and some properties of humic acids with zinc.But all of these studies were limited to acidic pH range. Therefore, the present study was carried out to determine and compare the stability constants of complexes of metal ions with hydrolysed peat soil humic acid and unhydrolysed peat soil humic under non-acid conditions.

MATERIALS AND METHODS

Analytical grade chemicals used includes hydrochloric acid (HCl), nitric acid (HNO_3), sodium hydroxide (NaOH), lead nitrate $Pb(NO_3)_2$, copper nitrate $Cu(NO_3)_2.3H_2O$, cadmium nitrate $Cd(NO_3)_2.4H_2O$, magnesium nitrate $Mg(NO_3)_2.6H_2O$, potassium nitrate (KNO_3), calcium chloride ($CaCl_2$), (sigma-Aldrich). Dowex 50WX8, (20-50 mesh) from Fluka.

Area of study



Source: Dept. of Geog. BUK (2016)

Figure 1: Map showing the sampling point at Sagamu Town, Ogun State.

Description of Sampling Area

Sagamu has geographical coordinates between 6°50′ north; 3° 38′ east is located in south western region of Nigeria. The region has tropical wet and dry climate with a lengthy wet season and relatively constant temperatures throughout the course of the year. Wet season runs from March to October, November to December forms the region dry season. The vegetation type of the region is savannah which is really grassland with small bushes and occasional big trees. Grassland soils have substantially higher organic matter content than forest soils (Novackova, 2011).

Sample Collection

The Peatsoil samples were collected from four different sampling points (0-10cm depth) in Sagamu into polyethylene bag with plastic spoons. Samples were taken to the laboratory, extraneous materials were removed; the samples were air-dried, crushed and ground to a fine powder in a mortar passed through a 0.20mm sieve. The samples were kept for analysis.

Isolation and purification of humic acid from peat soil sample

Peatsoil sample (100g) was mixed with 1000 cm^3 of 0.1M NaOH solution, shaken for 3hours and left to stand overnight. Dark-coloured supernatant was obtained and decanted from solid residue. The dark-coloured supernatant was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 6 hours. Yellowish brown supernatant and dark-brown precipitate were obtained. The yellowish brown supernatant was decanted followed by centrifuge and discarded. The dark-brown precipitate was mixed with $500cm^3$of 0.1M NaOH solution followed by passing through dowex resin. The dark-brown solution was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 3 hours. The dark-brown precipitate was washed several times with deionized water. The supernatant was treated with $AgNO_3$ solution until no white precipitate observed. The humic acid was transferred to weighed crucible and dried at 60°C in an oven for 12 hours. The humic acid was cooled and dried in the desiccator, weighed and recorded. The obtained humic acid was dried again at 60°C for additional 6 hours cooled and dried in the desiccator, weighed and recorded constant weight was obtained (Baruah *et al.*, 2015).

FT-IR analysis

FT-IR spectra of humic acid sample was analysed using Carry 630 FT-IR Agilent Technologies.

Unhydrolysed compost humic acid

The unhydrolysed humic acid was obtained after isolation and purification of compost humic acid and kept for investigation.

Acid hydrolysis of Peatsoil acid

Peatsoil humic acid sample (1g) was refluxed for 12 hours at (160°C) with $50cm^3$ of 6M HCl. The mixture was allowed to cool, decanted, and centrifuged after hydrolysis. The insoluble residues were washed with distilled water via centrifugation several times, and the supernatant was treated with $AgNO_3$ solution until no white precipitate was observed. The residue was thoroughly dried over $CaCl_2$ in a desiccator at room temperature (Chefetz *et al.*, 2002). Finally, the obtained hydrolysed humic acid was kept for investigation.

Potentiometric Titrations

Potentiometric measurements were carried out using a pH-meter Jenway (model 3510) with combine electrode, the sensitivity of the pH - meter is 0.01 units. The pH meter was switched on half an hour before starting the titration for initial warm up of the instrument. The instrument was calibrated with an aqueous standard buffer solution of pH 4.00 and 10.0 (borate buffer) prepared from a "Qualigens" buffer tablets.

The following sets of solutions were prepared in a 250cm^3 volumetric flask separately for pH metric titrations.

(i) 5 cm^3 0.1 M HCl + 40 cm^3 deionized water

(ii) 5 cm^3 0.1 M HCl + 39 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid

(iii) 5 cm^3 0.1 M HCl + 37 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid + 2 cm^3 0.01 M Cu(II)

The solutions were titrated against standardized 0.110MNaOH separately. The total volume of each mixture was adjusted to 50 cm^3 and the ionic strength of the solutions was maintained constant at by adding appropriate amount of stock solution of 1M KNO$_3$ (Gamal, 2015; Omar and Ali, 2015). A magnetic stirrer was used to achieve thorough mixing of the interacting solutions at 550 rpm. The same set of experimental conditions was applied for potentiometric titration of remaining samples.

Evaluation of pKa of Hydrolysed peat soil Humic Acids

The proton-ligand formation number n$_{\mathbf{A}}$ were calculated by Irving and Rossotti expression (Omar and Ali, 2015).

$$nA = Y- \frac{(V2-V1)(No-Eo)}{(Vo+V1)TcL} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 1$$

Where: Y is number of dissociable proton, (V$_2$-V$_1$) is the measure of displacement of the ligand curve relative to acid curve, N^o and E^o are the resultant concentration of alkali solution, free acid solution, T$_{cL}$^{o} is the total ligand concentration, V^o is the total volume of titration solution,V$_1$ is the volume of alkali added to acid solution,V$_2$ is the volume of alkali added to acid solution + ligand solution, acid dissociation constants (pKa - values) of ligand were calculated by algebraic method point wise calculation (Tables 1). The dissociation constants (pKa) were calculated according to the following relation:

$$pKa = pH + \log\left(\frac{nA}{1-nA}\right) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 2$$

Where: pKa is the acid dissociation constant, n$_A$is the Proton-ligand formation number and pH is the pH-values (Omar and Ali, 2015).

Determination of metal-ligand stability constants (log K) of complexes

The potentiometric measurement for the determination of stability constant of a complex in solution is based on the fact that the redox potential of the couple $\frac{M^{+(m-n)}}{M^{+m}}$ is shifted significantly on complexation of the metal ion with the ligand. This method involves change in hydrogen ion concentration [H$^+$] due to the displacement or association of one or more protons taking place during complexation reaction. This change can be found out by titrating the solutions containing free acid, acid with ligand, and acid with ligand and metal ion, individually against a standard alkali solution at a constant ionic strength or temperature. Either ionic strength or temperature may be varied for different sets of solutions. In all the cases, the change in the pH of the solution is measured after each addition of a known amount of alkali to the reaction cell which contains the reaction mixture. The titration curves are then drawn by plotting the measured pH values against the corresponding volume of alkali added and the stability constants of the complexes are determined from the titration curves by employing pH-metric titration technique given by (Irving and Rossoti).

Metal-ligand stability constants (Log K) were determined by using the following relations:

$$\bar{n} = \frac{(V_3 - V_2)(E^0 + N^0)}{(V^0 + V_2)\bar{n}_A T_m^0} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 3$$

and

$$PL = \log_{10}\left\{\frac{1 + \beta_n^H \frac{1}{[anti\ \log \mathrm{pH}]^n}}{\mathrm{T}_{\mathrm{L}}^0 - \bar{n} T_m^0} \mathrm{X} \frac{(V^0 + V_3)}{V^0}\right\} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 4$$

Where $T_{L,}$ T^{o}, E°, and V^{o}havethe same significance as in equation (1) above, T_m denotes the total concentration of metal present in solution, V_3 is the volume of metal ions present in solution and β^H is the overall proton ligand stability constant. The metal-ligand stability constants (log K) were determined by employing point wise computational Method (eq. 5 and 6).

$$\text{Log}K_1 = \log\left(\frac{n}{1-n}\right) + pL \quad \text{.............}5$$

$$\text{Log}K_2 = \log\left(\frac{1-n}{2-n}\right) + pL\text{.......................}6$$

Where: Log K is the metal-ligand stability constant, pL is the Free ligand exponent function, **n** is the Average number of ligand attached with metal ion (Janrao*et al*., 2014).The results obtained were analyzed by an ORIGIN 2016 program using titration data and then the proton-ligand stability constants (pKa) and Metal-ligand stability constant (LogK) calculated (Omar and Ali, 2015).

RESULTS AND DISCUSSION

Fourier transformed infrared (FT-IR) spectra of isolated humic acid from peat soils Figure 2 had distinct clear absorption bands indicating the presence of major humic acid structural elemental groups such as H bonded OH ($3680cm^{-1}$ peak), C=O of carbonyl ($1721cm^{-1}$ peak), functional groups of aliphatic components CH_2 ($2918cm^{-1}$ peak) and C-O stretching of polysaccharide ($1168cm^{-1}$ peak). The positions of the absorption bands of the spectra fell within typical major absorption bands of humic acid which is at frequencies 3680, 2918, 1721, 1168 cm^{-1}. The first peak centred in the vicinity of 3680 cm^{-1} region is attributed to phenol OH group bounded by intermolecular H bonds. The $2918cm^{-1}$ band usually has absorption maximum at 2918 cm^{-1} which is due to C–H stretching of alkane group (CH_2). The next major absorption band is 1721 cm^{-1}. This band has been commonly ascribed to C=O stretching of mainly carboxyl group (COOH) with trace amount of ketones. The last peak was observed at 1168 cm^{-1} due to C–O stretching of polysaccharides and this peak appeared also in the spectra of humic acid from peat soil. The FTIR spectra of the isolated humic acid contained all major characteristic absorption peaks of humic acid. These absorption peaks indicated the presence of the major structural elements of humic acid namely H bonded OH, C=C of aromatic ring, C=O of carbonyl group (both carboxyl and ketonic), CH_2 group. This strongly supports the presence of humic acid.

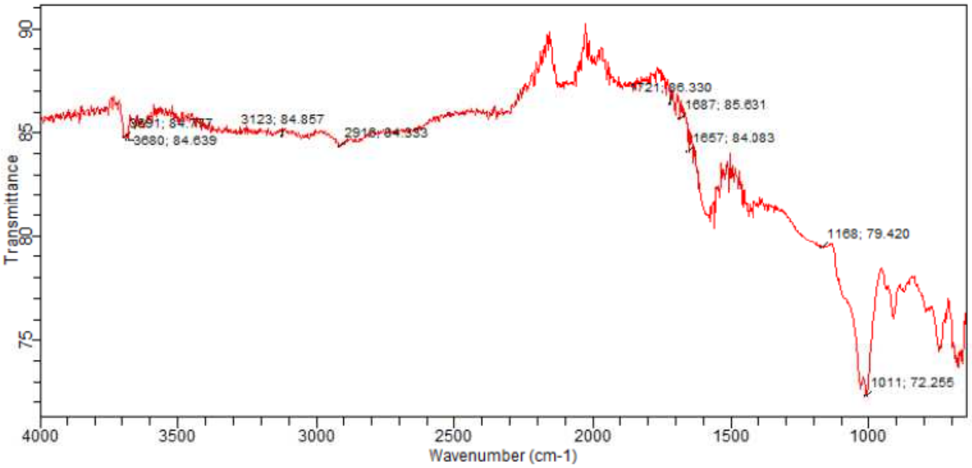


Fig. 2 : FT-IR spectraof peatsoilhumic acid (PSHA)

Evaluation of acid dissociation constant (pka) of acid hydrolysed peat soil humicacid at phenolic group

The value of the dissociation constant of the peat soil humic acid (PSHA) that underwent acidhydrolysis studied was found to be 8.9299 as shown Table 1, which is lower than the literaturevalues reported by Almeida and Szpoganics, (2015), Borges *et al*., (2005); Badr *et al*., (2012)and Fernandes *et al*,.(2009) of 9.73, 9.47 and 10.30. The difference between the obtained valuesand the reported values in this study might be probably as a result of acid hydrolysis of humicacid.

Table 1: PKa of (Hydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	$\log(\frac{nA}{1-nA})$	pKa
8.50	5.30	6.29	0.99	0.3594	-0.2510	8.2490
8.72	5.35	6.37	1.02	0.3400	-0.2880	8.4320
9.00	5.40	6.46	1.06	0.3141	-0.3391	8.6609
9.22	5.45	6.55	1.10	0.2882	-0.3927	8.8273
9.51	5.50	6.66	1.16	0.2494	-0.4786	9.0314
9.73	5.55	6.78	1.23	0.2041	-0.5910	9.1390
10.00	5.60	6.90	1.30	0.1589	-0.7238	9.2762
10.23	5.65	7.05	1.40	0.0941	-0.9835	9.2465
10.49	5.70	7.10	1.40	0.0941	-0.9835	9.5065

Average pKa = 8.9299 ± 0.4186

Table 2: PKa of (Unhydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	$\mathrm{Log}(\frac{nA}{1-n})$	pKa
8.50	5.30	5.81	0.51	0.6619	0.2919	8.7919
8.72	5.35	5.90	0.55	0.6357	0.2418	8.9618
9.00	5.40	6.00	0.60	0.6029	0.1813	9.1813
9.22	5.45	6.10	0.65	0.5701	0.1226	9.3426
9.51	5.50	6.20	0.70	0.5376	0.0654	9.5754
9.73	5.55	6.33	0.78	0.4851	-0.0259	9.7041
10.00	5.60	6.47	0.87	0.4262	-0.1291	9.8709
10.23	5.65	6.62	0.99	0.3609	-0.2481	9.9819
10.49	5.70	6.80	1.10	0.2759	-0.4690	10.0210

Average pKa = 9.4923± 0.4410

Metal-ligand stability constant (Log K)

The stabilityconstants require the accurate values of proton-ligand stability constants (Anil and Maroti, 2008). Metal titration curves crossed over ligand titration curve indicated the formation of complex upon proton release (Santosh, *et al.*, 2011). If the values of n- are within range 0.2-0.8 and 1.2-18 this indicates the formation of 1:1 and 1:2 complexes (Sayyed and Mazahar, 2012).

The metal (II)-humate stepwise stability constants (log k) at phenolic group (Tables 3-18)

Table 3: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$\log(\frac{n}{1-n})$	$\mathrm{Log}K_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

$\mathrm{LogK_1}$ (Average value) = 2.4788± 0.2203

Table 4: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$\mathrm{Log}(\frac{n-1}{2-n})$	$\mathrm{Log}K_2$
9.51	5.50	6.66	6.73	0.07	1.3509	1.70	-0.2671	1.4329
9.73	5.55	6.78	6.85	0.07	1.6383	1.51	0.2467	1.7567
10.00	5.60	6.90	6.98	0.08	2.1783	1.31	-0.2158	1.0942
10.23	5.65	7.05	7.13	0.08	4.1904	1.27		
10.49	5.70	7.10	7.19	0.09	4.6920			

$\mathrm{LogK_2}$(Average value) = 1.4280 ± 0.3312

Table 5:Point-wise method,Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	Log($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430

$LogK_1$ **(Average value)** = 2.3059± 0.6153

Table 6:Point-wise method, Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
9.73	5.55	6.33	6.42	0.09	0.9000	1.69		
10.00	5.60	6.47	6.58	0.11	1.2578	1.44	-0.4592	0.9808
10.23	5.65	6.62	6.84	0.12	1.6137	1.26	-0.2010	1.4610
10.49	5.70	6.80	6.92	0.12	2.1052	1.03		

$LogK_2$ **(Average value)** = 1.2209± 0.3398

Table 7:Point-wise method,Pb (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n}{1-n}$)	$LogK_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.60	0.05	0.8333	1.96	0.6989	2.6589

$LogK_1$ (Average value) = 2.5832 ±0.1614

Table 8:Point-wise method,Pb-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n-1}{2-n}$)	$logK_2$
9.51	5.50	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.83	0.05	1.1702	1.44		
10.00	5.60	6.90	6.90	0.05	1.4864	1.22	-0.0237	1.1963
10.23	5.65	7.05	7.10	0.05	2.0190	1.09		
10.49	5.70	7.10	7.17	0.07	3.6492	1.00		

$LogK_2$(Average value) = 1.1963

Table 9:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log ($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.5477	2.3123
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	0.0272	2.2072
9.51	5.50	6.20	6.26	0.07	0.6417	1.89	0.2530	2.1430
9.73	5.55	6.40	6.40	0.07	0.7000	1.67	0.3680	2.0380

$LogK_1$ **(Average value)** = 2.2364 ± 0.1602

Table 10:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
10.00	5.60	6.47	6.55	0.08	1.9503	1.41		
10.23	5.65	6.62	6.72	0.11	1.4792	1.26	-0.0361	1.2239

$LogK_2$ **(Average value)** = 1.2239

Table 11:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n}{n-1}$)	$LogK_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4290	2.2110
8.72	5.35	6.37	6.39	0.02	0.2858	2.42	-0.3978	2.0222
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

$LogK_1$ (Average value)=2.1382±0.1046

Table 12:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n-1}{2-n}$)	$LogK_2$
9.51	5.55	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.84	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.93	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.10		
10.49	5.70	7.10	7.18	0.07	3.6492	0.83		

$LogK_2$(Average value) = 1.5453 **±** 0.3450

Table 13:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.3477	2.3123
9.00	5.40	6.00	6.04	0.04	0.3236	2.38	-0.3202	2.0598
9.22	5.45	6.10	6.15	0.05	0.4297	2.17	-0.1230	2.0470
9.51	5.50	6.20	6.26	0.06	0.5500	1.89	0.0871	1.9771
9.73	5.55	6.33	6.40	0.07	0.7000	1.67	0.3680	2.0380

$LogK_1$ **(Average value)** = 2.1568 ± 0.2069

Table 14:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
10.00	5.60	6.47	6.55	0.08	0.9148	1.41		
10.23	5.65	6.62	6.71	0.09	1.2102	1.20	-0.5749	0.6251
10.49	5.70	6.80	6.92	0.09	1.5968	1.03	0.1703	1.2003

$LogK_2$ **(Average value)** = 0.9127± 0.4070

Table15:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	Log($\frac{n}{1-n}$)	$LogK_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4210	2.2190
8.72	5.35	6.37	6.40	0.03	0.4286	2.42	-0.1249	2.2951
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.96	0.3010	2.2610
9.51	5.55	6.66	6.70	0.04	0.7720	1.67	0.5297	2.1997

$LogK_1$ (Average value) = 2.2108± 0.0825

Table 16:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
9.73	5.55	6.78	6.83	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.95	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.09		
10.49	5.70	7.10	7.16	0.06	3.1429	0.89		

$LogK_2$ **(Average value)** = 1.5453± 0.3450

Table 17:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.86	0.05	0.3717	2.88	-0.2280	2.6520
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.06	0.06	0.4853	2.38	-0.0255	2.3545
9.22	5.45	6.10	6.16	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430
9.73	5.55	6.33	6.41	0.08	0.8000	1.69	0.6020	2.2920

$LogK_1$ **(Average value)** = 2.2516± 0.5380

Table 18:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
10.00	5.60	6.47	6.57	0.10	1.1434	1.43		
10.23	5.65	6.62	6.72	0.10	1.3448	1.23	-0.2788	0.9512
10.49	5.70	6.80	6.90	0.10	1.7742	1.03	0.5351	1.5651

LogK_2 **(Average value)** = 1.2581± 0.4340

Table 19: Stepwise and overall Stability constants of thehydrolysed and unhydrolysed divalent metal (II) complexes

Chelates	**LogK_1**	**LogK_2**	**Logβ**
[Cu (Hydrolysed PSHA-1)$_2$]	2.4788	1.4280	3.9068
[Pb (Hydrolysed PSHA-1)$_2$]	2.5832	1.1963	3.7795
[Cd (Hydrolysed PSHA-1)$_2$]	2.2108	1.5453	3.7561
[Mg (Hydrolysed PSHA-1)$_2$]	2.1382	1.5453	3.6835
[Cu (Unhydrolysed PSHA-1)$_2$]	2.3059	1.2209	3.5268
[Pb (Unhydrolysed PSHA-1)$_2$]	2.2364	1.2239	3.4603
[Cd (Unhydrolysed PSHA-1)$_2$]	2.2516	1.2581	3.5097
[Mg (Unydrolysed PSHA-1)$_2$]	2.1568	0.9127	3.0695

The results obtained (Table19) shows the stepwise and overall stability constants to be not high indicating low stability of the complexes, because the solubility of most metal ions in the basic pH range is minimal due to metal hydroxide precipitation (Karimi, 2017). In general, the stepwise stability constants (K_1 and K_2) follow the order $K_1 > K_2$ for the copper, lead, magnesium and cadmium complexes respectively. The steady decrease of the values with increasing number of ligands is in agreement with the prediction made by researchers (Na'aliya, 2013). The decrease could be attributed to the fact that as the number of the ligands (Humate ions) that enters the coordination zone increases the aqua molecules available for replacement by the ligands become less. Thus, the metal ions become less electron loving with progressive intake of the ligand and this results in the decrease in the values of the constants (Na'aliya, 2013). Also the stability of the complexes is influenced by the size and number of the chelate rings(Mackay and Mackay,2002).All the complexes form rings in their structure as humate, a bidentate ligand, bond the metal ions in the ratio 1:2 (Boguta and Sokolowska, 2016) forming chelate rings. The values of the overall stability constants (logβ) obtained for humate complexes are not high indicating low stability as the values are not high. LogK values for copper-humates (Table 3 to 6) obtained in this study are lower than those reported for the complexes of humic acids (Pandey *et al*., 2015; Dinu, 2013; Kaschl *et al*., 2010 and Gilbeto and Jorg, 2001). The values of LogK(Table 7 to 10) forlead-humates are lower than those reported for the lead in the literature (Dinu, 2013; Gilbeto and Jorg 2001). Log K values(Table 11 to 14) for magnesium-humates obtained in this study are close to those reported by (Pandey *et al*., 2015). Log K values of cadmium-humates (Table 15 to 18) obtained in this work near to the one reported by (Dinu, 2013 and Pandey *et al*., 2015).The difference between the reported values and the values obtained in this study might be probably as a result of acid hydrolysis of humic acid. The values of the overall stability constants (log β) of the copper humates complexes presented in Table 19 is high than that of other metal humate complexes, show relatively high stability of Cu-HA complexes, show the following order of stability: Cu >Pb> Cd > Mg; which are in close agreement to the findings of (Dinu, 2013 and Pandey *et al*., 2015).The high stability of Cu-humate chelate could be attributed to the existence of coordinate covalent bond between the complexing agents and the Cu^{2+} ions. Since, Cu^{2+} being a metal of the transitional series with $3d^9$ electronic configurations can accept the electrons from the complexing agents. Similarly,the low stabilities of Pb,Cd and Mg - complexes could be explained by that Pb^{2+} with $6s^2$, Cd^{2+} with $4d^{10}$ and Mg^{2+} with $2p^6$ their electronic configuration has a completely filled d,p and s orbitals. Moreover, the stabilities of metal ions with hydrolysed humic acid from peat soil were higher than those with unhydrolysed humic acid from peat soil; which is ascribed to the high content of acidity in hydrolysed humic acid than unhydrolysed humic acid.

CONCLUSION

The values of logK for Cu(II) hydrolysed humic acid complex was higher followed by Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes as compared with metal(II) unhydrolysed humic acid complexes . This indicates acid hydrolysis of humic acid can enhance the complexation behavior of humic acid with metal (II) ions. However, the higher values of logβ for Cu(II), Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes indicates more stable stepwise complexes formed as compared with Cu(II), Pb(II), Cd(II) and Mg(II) unhydrolysed humic acid complexes.

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STABILITY CONSTANTS OF COMPLEXES OF METAL IONS WITH PEATSOIL HUMIC ACIDS UNDER NON-ACID-CONDITIONS

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ABSTRACT

Stability constants of complexes of four divalent metal ions viz. Cu^{2+}, Pb^{2+},Mg^{2+} and Cd^{2+} with humic acids (HA) were determined by potentiometric titration of humic acids with the corresponding salt of the divalent metals in aqueous media under non-acid-condition. The log K (logarithm of the stability constant) ranged from 1.0942 to 2.7471 for metal-humic acid complexes were determined using point-wise computational method. The order of stability constants were obtained as follows: Cu >Pb> Cd > Mg for metal -HA complexes respectively, indicating a higher degree of complexation with Cu metal ion.

Keywords: stability constant, humic acid, potentiometric titration, divalent metals, acid hydrolysis.

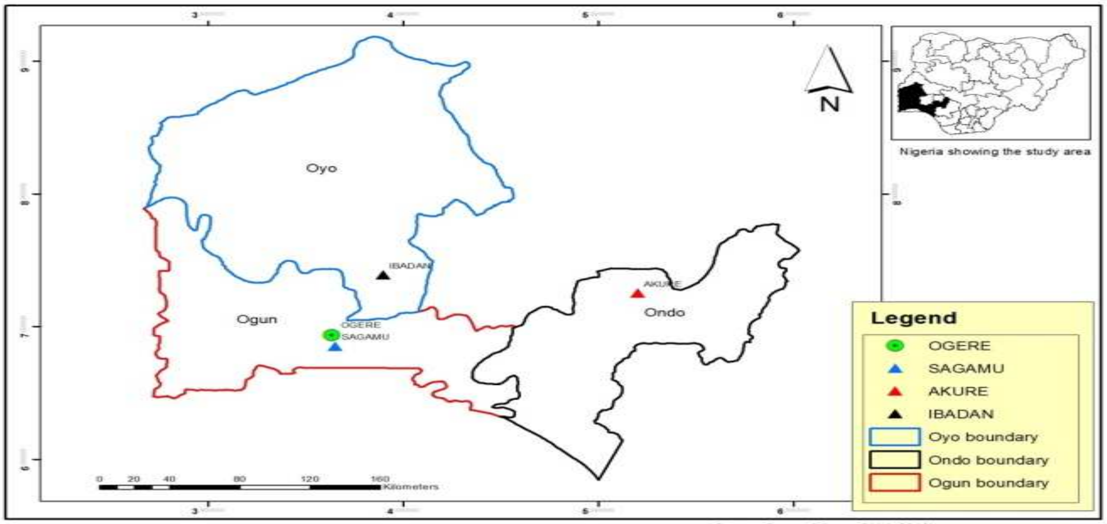
NTRODUCTION

The stability constant of a complex is the numerical expression of its stability and provides a quantitative measure of affinity of the metal ion to the complexing agent. An understanding of the relative stability of metal-complexes helps in predicting the behavior of metal ions in the soil (Ram and Raman, 1982). Extensive researches has been done to determine the stability constants of the complexes formed between humic acid (HA) with a number of metal ions. Ashok *et al.*, (2000) reported that humic acid with hydroxyl, phenoxyl and carboxyl reactive groups can form coordination compound with metal ions at pH 3.5. The stability constants(Log K) for different metal-humic acid complexes indicated the following order of the stabilities of complexes formed between humic acid and metal ion, Cu >Fe >Pb> Ni > Co > Ca > Cd > Zn >Mn> Mg. Andelkovic *et al.*, (2010) investigated the binding of Cd(II) to soil humic acid at pH 6.5 and in 0.1M KNO_3 ionic medium. The stability constant for binding indicating greater stability in the case when carboxyl groups are involved in complexation reaction. Kostic *et al.*,(2012) investigated the complexation of humic acid with certain heavy metal ions (Co(II), Ni(II),Cu(II), Zn(II), and Pb(II). The experiment was performed at 25°C, at pH 4.0 and ionic strength of 0.01M. Stability constant of complex between Pb(II) ions and humic acid is greater than stability constants of other investigated metal-humate complexes. Bogata and Sokolowska (2016) analyses the interaction between humic acids from different soils and Zn (II) ions at wide concentration ranges and at pH 5. Studies have showed significant impact of Zn concentration, pH and some properties of humic acids with zinc.But all of these studies were limited to acidic pH range. Therefore, the present study was carried out to determine and compare the stability constants of complexes of metal ions with hydrolysed peat soil humic acid and unhydrolysed peat soil humic under non-acid conditions.

MATERIALS AND METHODS

Analytical grade chemicals used includes hydrochloric acid (HCl), nitric acid (HNO_3), sodium hydroxide (NaOH), lead nitrate $Pb(NO_3)_2$, copper nitrate $Cu(NO_3)_2.3H_2O$, cadmium nitrate $Cd(NO_3)_2.4H_2O$, magnesium nitrate $Mg(NO_3)_2.6H_2O$, potassium nitrate (KNO_3), calcium chloride ($CaCl_2$), (sigma-Aldrich). Dowex 50WX8, (20-50 mesh) from Fluka.

Area of study



Source: Dept. of Geog. BUK (2016)

Figure 1: Map showing the sampling point at Sagamu Town, Ogun State.

Description of Sampling Area

Sagamu has geographical coordinates between 6°50′ north; 3° 38′ east is located in south western region of Nigeria. The region has tropical wet and dry climate with a lengthy wet season and relatively constant temperatures throughout the course of the year. Wet season runs from March to October, November to December forms the region dry season. The vegetation type of the region is savannah which is really grassland with small bushes and occasional big trees. Grassland soils have substantially higher organic matter content than forest soils (Novackova, 2011).

Sample Collection

The Peatsoil samples were collected from four different sampling points (0-10cm depth) in Sagamu into polyethylene bag with plastic spoons. Samples were taken to the laboratory, extraneous materials were removed; the samples were air-dried, crushed and ground to a fine powder in a mortar passed through a 0.20mm sieve. The samples were kept for analysis.

Isolation and purification of humic acid from peat soil sample

Peatsoil sample (100g) was mixed with 1000 cm^3 of 0.1M NaOH solution, shaken for 3hours and left to stand overnight. Dark-coloured supernatant was obtained and decanted from solid residue. The dark-coloured supernatant was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 6 hours. Yellowish brown supernatant and dark-brown precipitate were obtained. The yellowish brown supernatant was decanted followed by centrifuge and discarded. The dark-brown precipitate was mixed with $500cm^3$of 0.1M NaOH solution followed by passing through dowex resin. The dark-brown solution was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 3 hours. The dark-brown precipitate was washed several times with deionized water. The supernatant was treated with $AgNO_3$ solution until no white precipitate observed. The humic acid was transferred to weighed crucible and dried at 60°C in an oven for 12 hours. The humic acid was cooled and dried in the desiccator, weighed and recorded. The obtained humic acid was dried again at 60°C for additional 6 hours cooled and dried in the desiccator, weighed and recorded constant weight was obtained (Baruah *et al*., 2015).

FT-IR analysis

FT-IR spectra of humic acid sample was analysed using Carry 630 FT-IR Agilent Technologies.

Unhydrolysed compost humic acid

The unhydrolysed humic acid was obtained after isolation and purification of compost humic acid and kept for investigation.

Acid hydrolysis of Peatsoil acid

Peatsoil humic acid sample (1g) was refluxed for 12 hours at (160°C) with $50cm^3$ of 6M HCl. The mixture was allowed to cool, decanted, and centrifuged after hydrolysis. The insoluble residues were washed with distilled water via centrifugation several times, and the supernatant was treated with $AgNO_3$ solution until no white precipitate was observed. The residue was thoroughly dried over $CaCl_2$ in a desiccator at room temperature (Chefetz *et al*., 2002). Finally, the obtained hydrolysed humic acid was kept for investigation.

Potentiometric Titrations

Potentiometric measurements were carried out using a pH-meter Jenway (model 3510) with combine electrode, the sensitivity of the pH -meter is 0.01 units. The pH meter was switched on half an hour before starting the titration for initial warm up of the instrument. The instrument was calibrated with an aqueous standard buffer solution of pH 4.00 and 10.0 (borate buffer) prepared from a "Qualigens" buffer tablets.

The following sets of solutions were prepared in a 250cm^3 volumetric flask separately for pH metric titrations.

(i) 5 cm^3 0.1 M HCl + 40 cm^3 deionized water
(ii) 5 cm^3 0.1 M HCl + 39 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid
(iii) 5 cm^3 0.1 M HCl + 37 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid + 2 cm^3 0.01 M Cu(II)

The solutions were titrated against standardized 0.110MNaOH separately. The total volume of each mixture was adjusted to 50 cm^3 and the ionic strength of the solutions was maintained constant at by adding appropriate amount of stock solution of 1M KNO_3 (Gamal, 2015; Omar and Ali, 2015). A magnetic stirrer was used to achieve thorough mixing of the interacting solutions at 550 rpm. The same set of experimental conditions was applied for potentiometric titration of remaining samples.

Evaluation of pKa of Hydrolysed peat soil Humic Acids

The proton-ligand formation number n**A** were calculated by Irving and Rossotti expression (Omar and Ali, 2015).

$$nA = Y- \frac{(V2-V1)(No-Eo)}{(Vo+V1)TcL} \quad \text{.....................................1}$$

Where: Y is number of dissociable proton, (V_2-V_1) is the measure of displacement of the ligand curve relative to acid curve, N^o and E^o are the resultant concentration of alkali solution, free acid solution, $T_{cL}{}^o$ is the total ligand concentration, V^o is the total volume of titration solution,V_1 is the volume of alkali added to acid solution,V_2 is the volume of alkali added to acid solution + ligand solution, acid dissociation constants (pKa - values) of ligand were calculated by algebraic method point wise calculation (Tables 1). The dissociation constants (pKa) were calculated according to the following relation:

$$pKa = pH + \log(\frac{nA}{1-nA}) \quad \text{..............................2}$$

Where: pKa is the acid dissociation constant, $n_A$is the Proton-ligand formation number and pH is the pH-values (Omar and Ali, 2015).

Determination of metal-ligand stability constants (log K) of complexes

The potentiometric measurement for the determination of stability constant of a complex in solution is based on the fact that the redox potential of the couple $\frac{M^{+(m-n)}}{M^{+m}}$ is shifted significantly on complexation of the metal ion with the ligand. This method involves change in hydrogen ion concentration [H$^+$] due to the displacement or association of one or more protons taking place during complexation reaction. This change can be found out by titrating the solutions containing free acid, acid with ligand, and acid with ligand and metal ion, individually against a standard alkali solution at a constant ionic strength or temperature. Either ionic strength or temperature may be varied for different sets of solutions. In all the cases, the change in the pH of the solution is measured after each addition of a known amount of alkali to the reaction cell which contains the reaction mixture. The titration curves are then drawn by plotting the measured pH values against the corresponding volume of alkali added and the stability constants of the complexes are determined from the titration curves by employing pH-metric titration technique given by (Irving and Rossoti).

Metal-ligand stability constants (Log K) were determined by using the following relations:

$$\bar{n} = \frac{(V_3 - V_2)(E^0 + N^0)}{(V^0 + V_2)\bar{n}_A T_m^0} \quad \text{..3}$$

and

$$PL = \log_{10}\{\frac{1 + \beta_n^H \frac{1}{[anti\ \log pH]^n}}{T_L^0 - \bar{n}T_m^0} X \frac{(V^0 + V_3)}{V^0}\} \quad \text{...4}$$

Where $T_{L,}$ T^o, E°, and V^ohavethe same significance as in equation (1) above, T_m denotes the total concentration of metal present in solution, V_3 is the volume of metal ions present in solution and β^H is the overall proton ligand stability constant. The metal-ligand stability constants (log K) were determined by employing point wise computational Method (eq. 5 and 6).

$$\mathrm{Log}K_1 = \log\left(\frac{n}{1-n}\right) + pL \quad \ldots\ldots\ldots\ldots.5$$

$$\mathrm{Log}K_2 = \log\left(\frac{1-n}{2-n}\right) + pL\ldots\ldots\ldots\ldots\ldots\ldots\ldots.6$$

Where: Log K is the metal-ligand stability constant, pL is the Free ligand exponent function, **n** is the Average number of ligand attached with metal ion (Janrao*et al*., 2014).The results obtained were analyzed by an ORIGIN 2016 program using titration data and then the proton-ligand stability constants (pKa) and Metal-ligand stability constant (LogK) calculated (Omar and Ali, 2015).

RESULTS AND DISCUSSION

Fourier transformed infrared (FT-IR) spectra of isolated humic acid from peat soils Figure 2 had distinct clear absorption bands indicating the presence of major humic acid structural elemental groups such as H bonded OH ($3680cm^{-1}$ peak), C=O of carbonyl ($1721cm^{-1}$ peak), functional groups of aliphatic components CH_2 ($2918cm^{-1}$ peak) and C-O stretching of polysaccharide ($1168cm^{-1}$ peak). The positions of the absorption bands of the spectra fell within typical major absorption bands of humic acid which is at frequencies 3680, 2918, 1721, 1168 cm^{-1}. The first peak centred in the vicinity of 3680 cm^{-1} region is attributed to phenol OH group bounded by intermolecular H bonds. The $2918cm^{-1}$ band usually has absorption maximum at 2918 cm^{-1} which is due to C–H stretching of alkane group (CH_2). The next major absorption band is 1721 cm^{-1}. This band has been commonly ascribed to C=O stretching of mainly carboxyl group (COOH) with trace amount of ketones. The last peak was observed at 1168 cm^{-1} due to C–O stretching of polysaccharides and this peak appeared also in the spectra of humic acid from peat soil. The FTIR spectra of the isolated humic acid contained all major characteristic absorption peaks of humic acid. These absorption peaks indicated the presence of the major structural elements of humic acid namely H bonded OH, C=C of aromatic ring, C=O of carbonyl group (both carboxyl and ketonic), CH_2 group. This strongly supports the presence of humic acid.

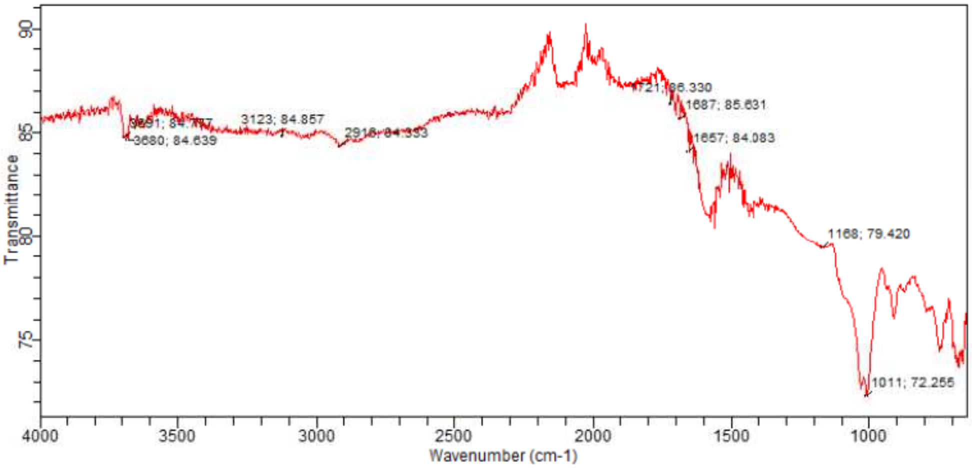


Fig. 2 : FT-IR spectraof peatsoilhumic acid (PSHA)

Evaluation of acid dissociation constant (pka) of acid hydrolysed peat soil humicacid at phenolic group

The value of the dissociation constant of the peat soil humic acid (PSHA) that underwent acidhydrolysis studied was found to be 8.9299 as shown Table 1, which is lower than the literaturevalues reported by Almeida and Szpoganics, (2015), Borges *et al*., (2005); Badr *et al*., (2012)and Fernandes *et al*,.(2009) of 9.73, 9.47 and 10.30. The difference between the obtained valuesand the reported values in this study might be probably as a result of acid hydrolysis of humicacid.

Table 1: PKa of (Hydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	$\log(\frac{nA}{1-nA})$	pKa
8.50	5.30	6.29	0.99	0.3594	-0.2510	8.2490
8.72	5.35	6.37	1.02	0.3400	-0.2880	8.4320
9.00	5.40	6.46	1.06	0.3141	-0.3391	8.6609
9.22	5.45	6.55	1.10	0.2882	-0.3927	8.8273
9.51	5.50	6.66	1.16	0.2494	-0.4786	9.0314
9.73	5.55	6.78	1.23	0.2041	-0.5910	9.1390
10.00	5.60	6.90	1.30	0.1589	-0.7238	9.2762
10.23	5.65	7.05	1.40	0.0941	-0.9835	9.2465
10.49	5.70	7.10	1.40	0.0941	-0.9835	9.5065

Average pKa = 8.9299 ± 0.4186

Table 2: PKa of (Unhydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	$\mathrm{Log}(\frac{nA}{1-n})$	pKa
8.50	5.30	5.81	0.51	0.6619	0.2919	8.7919
8.72	5.35	5.90	0.55	0.6357	0.2418	8.9618
9.00	5.40	6.00	0.60	0.6029	0.1813	9.1813
9.22	5.45	6.10	0.65	0.5701	0.1226	9.3426
9.51	5.50	6.20	0.70	0.5376	0.0654	9.5754
9.73	5.55	6.33	0.78	0.4851	-0.0259	9.7041
10.00	5.60	6.47	0.87	0.4262	-0.1291	9.8709
10.23	5.65	6.62	0.99	0.3609	-0.2481	9.9819
10.49	5.70	6.80	1.10	0.2759	-0.4690	10.0210

Average pKa = 9.4923± 0.4410

Metal-ligand stability constant (Log K)

The stabilityconstants require the accurate values of proton-ligand stability constants (Anil and Maroti, 2008). Metal titration curves crossed over ligand titration curve indicated the formation of complex upon proton release (Santosh, *et al.*, 2011). If the values of n- are within range 0.2-0.8 and 1.2-18 this indicates the formation of 1:1 and 1:2 complexes (Sayyed and Mazahar, 2012).

The metal (II)-humate stepwise stability constants (log k) at phenolic group (Tables 3-18)

Table 3: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$\log(\frac{n}{1-n})$	LogK_1
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

LogK_1 (Average value) = 2.4788± 0.2203

Table 4: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$\mathrm{Log}(\frac{n-1}{2-n})$	LogK_2
9.51	5.50	6.66	6.73	0.07	1.3509	1.70	-0.2671	1.4329
9.73	5.55	6.78	6.85	0.07	1.6383	1.51	0.2467	1.7567
10.00	5.60	6.90	6.98	0.08	2.1783	1.31	-0.2158	1.0942
10.23	5.65	7.05	7.13	0.08	4.1904	1.27		
10.49	5.70	7.10	7.19	0.09	4.6920			

LogK_2(Average value) = 1.4280 ± 0.3312

Table 5:Point-wise method,Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	Log($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430

$LogK_1$ **(Average value)** = 2.3059± 0.6153

Table 6:Point-wise method, Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
9.73	5.55	6.33	6.42	0.09	0.9000	1.69		
10.00	5.60	6.47	6.58	0.11	1.2578	1.44	-0.4592	0.9808
10.23	5.65	6.62	6.84	0.12	1.6137	1.26	-0.2010	1.4610
10.49	5.70	6.80	6.92	0.12	2.1052	1.03		

$LogK_2$ **(Average value)** = 1.2209± 0.3398

Table 7:Point-wise method,Pb (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n}{1-n}$)	$LogK_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.60	0.05	0.8333	1.96	0.6989	2.6589

$LogK_1$ (Average value) = 2.5832 ±0.1614

Table 8:Point-wise method,Pb-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n-1}{2-n}$)	$logK_2$
9.51	5.50	6.66	6.71	0.05	0.9650	1.67	-0.0237	1.1963
9.73	5.55	6.78	6.83	0.05	1.1702	1.44		
10.00	5.60	6.90	6.90	0.05	1.4864	1.22		
10.23	5.65	7.05	7.10	0.05	2.0190	1.09		
10.49	5.70	7.10	7.17	0.07	3.6492	1.00		

$LogK_2$(Average value) = 1.1963

Table 9:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log ($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.5477	2.3123
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	0.0272	2.2072
9.51	5.50	6.20	6.26	0.07	0.6417	1.89	0.2530	2.1430
9.73	5.55	6.40	6.40	0.07	0.7000	1.67	0.3680	2.0380

$LogK_1$ **(Average value)** = 2.2364 ± 0.1602

Table 10:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
10.00	5.60	6.47	6.55	0.08	1.9503	1.41		
10.23	5.65	6.62	6.72	0.11	1.4792	1.26	-0.0361	1.2239

$LogK_2$ **(Average value)** = 1.2239

Table 11:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n}{n-1}$)	$LogK_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4290	2.2110
8.72	5.35	6.37	6.39	0.02	0.2858	2.42	-0.3978	2.0222
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

$LogK_1$ (Average value)=2.1382**±**0.1046

Table 12:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n-1}{2-n}$)	LogK_2
9.51	5.55	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.84	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.93	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.10		
10.49	5.70	7.10	7.18	0.07	3.6492	0.83		

LogK_2(Average value) = 1.5453 **±** 0.3450

Table 13:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.3477	2.3123
9.00	5.40	6.00	6.04	0.04	0.3236	2.38	-0.3202	2.0598
9.22	5.45	6.10	6.15	0.05	0.4297	2.17	-0.1230	2.0470
9.51	5.50	6.20	6.26	0.06	0.5500	1.89	0.0871	1.9771
9.73	5.55	6.33	6.40	0.07	0.7000	1.67	0.3680	2.0380

LogK_1 **(Average value)** = 2.1568 ± 0.2069

Table 14:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
10.00	5.60	6.47	6.55	0.08	0.9148	1.41		
10.23	5.65	6.62	6.71	0.09	1.2102	1.20	-0.5749	0.6251
10.49	5.70	6.80	6.92	0.09	1.5968	1.03	0.1703	1.2003

LogK_2 **(Average value)** = 0.9127± 0.4070

Table15:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	Log($\frac{n}{1-n}$)	LogK_1
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4210	2.2190
8.72	5.35	6.37	6.40	0.03	0.4286	2.42	-0.1249	2.2951
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.96	0.3010	2.2610
9.51	5.55	6.66	6.70	0.04	0.7720	1.67	0.5297	2.1997

LogK_1 (Average value) = 2.2108± 0.0825

Table 16:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
9.73	5.55	6.78	6.83	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.95	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.09		
10.49	5.70	7.10	7.16	0.06	3.1429	0.89		

LogK_2 **(Average value)** = 1.5453± 0.3450

Table 17:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.86	0.05	0.3717	2.88	-0.2280	2.6520
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.06	0.06	0.4853	2.38	-0.0255	2.3545
9.22	5.45	6.10	6.16	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430
9.73	5.55	6.33	6.41	0.08	0.8000	1.69	0.6020	2.2920

LogK_1 **(Average value)** = 2.2516± 0.5380

Table 18:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$\text{Log}(\frac{n-1}{2-n})$	Log K_2
10.00	5.60	6.47	6.57	0.10	1.1434	1.43		
10.23	5.65	6.62	6.72	0.10	1.3448	1.23	-0.2788	0.9512
10.49	5.70	6.80	6.90	0.10	1.7742	1.03	0.5351	1.5651

LogK_2 **(Average value)** = 1.2581± 0.4340

Table 19: Stepwise and overall Stability constants of thehydrolysed and unhydrolysed divalent metal (II) complexes

Chelates	**LogK_1**	**LogK_2**	**Logβ**
[Cu (Hydrolysed PSHA-1)$_2$]	2.4788	1.4280	3.9068
[Pb (Hydrolysed PSHA-1)$_2$]	2.5832	1.1963	3.7795
[Cd (Hydrolysed PSHA-1)$_2$]	2.2108	1.5453	3.7561
[Mg (Hydrolysed PSHA-1)$_2$]	2.1382	1.5453	3.6835
[Cu (Unhydrolysed PSHA-1)$_2$]	2.3059	1.2209	3.5268
[Pb (Unhydrolysed PSHA-1)$_2$]	2.2364	1.2239	3.4603
[Cd (Unhydrolysed PSHA-1)$_2$]	2.2516	1.2581	3.5097
[Mg (Unydrolysed PSHA-1)$_2$]	2.1568	0.9127	3.0695

The results obtained (Table19) shows the stepwise and overall stability constants to be not high indicating low stability of the complexes, because the solubility of most metal ions in the basic pH range is minimal due to metal hydroxide precipitation (Karimi, 2017). In general, the stepwise stability constants (K_1 and K_2) follow the order $K_1 > K_2$ for the copper, lead, magnesium and cadmium complexes respectively. The steady decrease of the values with increasing number of ligands is in agreement with the prediction made by researchers (Na'aliya, 2013). The decrease could be attributed to the fact that as the number of the ligands (Humate ions) that enters the coordination zone increases the aqua molecules available for replacement by the ligands become less. Thus, the metal ions become less electron loving with progressive intake of the ligand and this results in the decrease in the values of the constants (Na'aliya, 2013). Also the stability of the complexes is influenced by the size and number of the chelate rings(Mackay and Mackay,2002).All the complexes form rings in their structure as humate, a bidentate ligand, bond the metal ions in the ratio 1:2 (Boguta and Sokolowska, 2016) forming chelate rings. The values of the overall stability constants (logβ) obtained for humate complexes are not high indicating low stability as the values are not high. LogK values for copper-humates (Table 3 to 6) obtained in this study are lower than those reported for the complexes of humic acids (Pandey *et al.*, 2015; Dinu, 2013; Kaschl *et al.*, 2010 and Gilbeto and Jorg, 2001). The values of LogK(Table 7 to 10) forlead-humates are lower than those reported for the lead in the literature (Dinu, 2013; Gilbeto and Jorg 2001). Log K values(Table 11 to 14) for magnesium-humates obtained in this study are close to those reported by (Pandey *et al.*, 2015). Log K values of cadmium-humates (Table 15 to 18) obtained in this work near to the one reported by (Dinu, 2013 and Pandey *et al.*, 2015).The difference between the reported values and the values obtained in this study might be probably as a result of acid hydrolysis of humic acid. The values of the overall stability constants (log β) of the copper humates complexes presented in Table 19 is high than that of other metal humate complexes, show relatively high stability of Cu-HA complexes, show the following order of stability: Cu >Pb> Cd > Mg; which are in close agreement to the findings of (Dinu, 2013 and Pandey *et al.*, 2015).The high stability of Cu-humate chelate could be attributed to the existence of coordinate covalent bond between the complexing agents and the Cu^{2+} ions. Since, Cu^{2+} being a metal of the transitional series with $3d^9$ electronic configurations can accept the electrons from the complexing agents. Similarly,the low stabilities of Pb,Cd and Mg -complexes could be explained by that Pb^{2+} with $6s^2$, Cd^{2+} with $4d^{10}$ and Mg^{2+} with $2p^6$ their electronic configuration has a completely filled d,p and s orbitals. Moreover, the stabilities of metal ions with hydrolysed humic acid from peat soil were higher than those with unhydrolysed humic acid from peat soil; which is ascribed to the high content of acidity in hydrolysed humic acid than unhydrolysed humic acid.

CONCLUSION

The values of logK for Cu(II) hydrolysed humic acid complex was higher followed by Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes as compared with metal(II) unhydrolysed humic acid complexes . This indicates acid hydrolysis of humic acid can enhance the complexation behavior of humic acid with metal (II) ions. However, the higher values of logβ for Cu(II), Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes indicates more stable stepwise complexes formed as compared with Cu(II), Pb(II), Cd(II) and Mg(II) unhydrolysed humic acid complexes.

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STABILITY CONSTANTS OF COMPLEXES OF METAL IONS WITH PEATSOIL HUMIC ACIDS UNDER NON-ACID-CONDITIONS

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ABSTRACT

Stability constants of complexes of four divalent metal ions viz. Cu^{2+}, Pb^{2+},Mg^{2+} and Cd^{2+} with humic acids (HA) were determined by potentiometric titration of humic acids with the corresponding salt of the divalent metals in aqueous media under non-acid-condition. The log K (logarithm of the stability constant) ranged from 1.0942 to 2.7471 for metal-humic acid complexes were determined using point-wise computational method. The order of stability constants were obtained as follows: Cu >Pb> Cd > Mg for metal -HA complexes respectively, indicating a higher degree of complexation with Cu metal ion.

Keywords: stability constant, humic acid, potentiometric titration, divalent metals, acid hydrolysis.

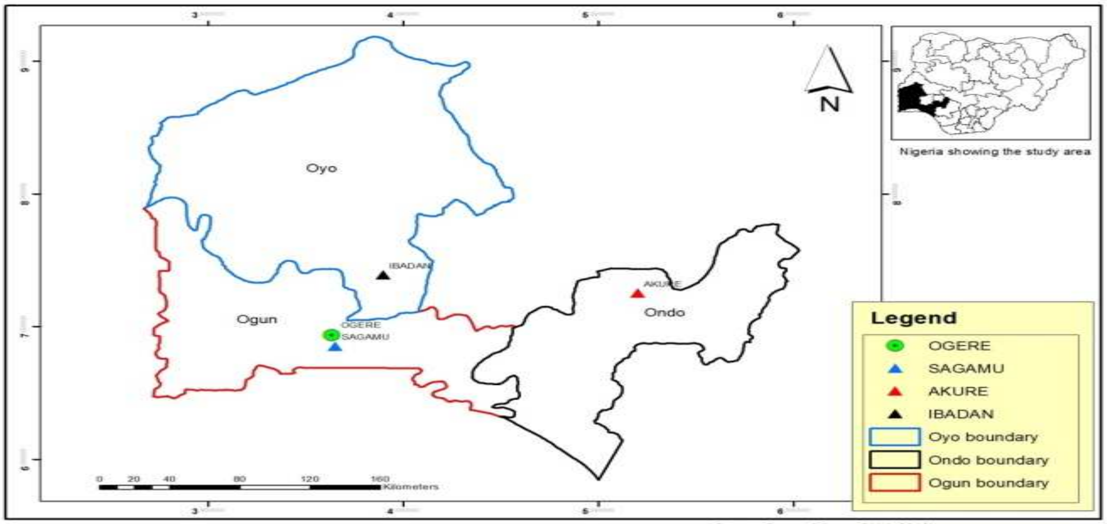
NTRODUCTION

The stability constant of a complex is the numerical expression of its stability and provides a quantitative measure of affinity of the metal ion to the complexing agent. An understanding of the relative stability of metal-complexes helps in predicting the behavior of metal ions in the soil (Ram and Raman, 1982). Extensive researches has been done to determine the stability constants of the complexes formed between humic acid (HA) with a number of metal ions. Ashok *et al*., (2000) reported that humic acid with hydroxyl, phenoxyl and carboxyl reactive groups can form coordination compound with metal ions at pH 3.5. The stability constants(Log K) for different metal-humic acid complexes indicated the following order of the stabilities of complexes formed between humic acid and metal ion, Cu >Fe >Pb> Ni > Co > Ca > Cd > Zn >Mn> Mg. Andelkovic *et al*., (2010) investigated the binding of Cd(II) to soil humic acid at pH 6.5 and in 0.1M KNO_3 ionic medium. The stability constant for binding indicating greater stability in the case when carboxyl groups are involved in complexation reaction. Kostic *et al*.,(2012) investigated the complexation of humic acid with certain heavy metal ions (Co(II), Ni(II),Cu(II), Zn(II), and Pb(II). The experiment was performed at 25°C, at pH 4.0 and ionic strength of 0.01M. Stability constant of complex between Pb(II) ions and humic acid is greater than stability constants of other investigated metal-humate complexes. Bogata and Sokolowska (2016) analyses the interaction between humic acids from different soils and Zn (II) ions at wide concentration ranges and at pH 5. Studies have showed significant impact of Zn concentration, pH and some properties of humic acids with zinc.But all of these studies were limited to acidic pH range. Therefore, the present study was carried out to determine and compare the stability constants of complexes of metal ions with hydrolysed peat soil humic acid and unhydrolysed peat soil humic under non-acid conditions.

MATERIALS AND METHODS

Analytical grade chemicals used includes hydrochloric acid (HCl), nitric acid (HNO_3), sodium hydroxide (NaOH), lead nitrate $Pb(NO_3)_2$, copper nitrate $Cu(NO_3)_2.3H_2O$, cadmium nitrate $Cd(NO_3)_2.4H_2O$, magnesium nitrate $Mg(NO_3)_2.6H_2O$, potassium nitrate (KNO_3), calcium chloride ($CaCl_2$), (sigma-Aldrich). Dowex 50WX8, (20-50 mesh) from Fluka.

Area of study



Source: Dept. of Geog. BUK (2016)

Figure 1: Map showing the sampling point at Sagamu Town, Ogun State.

Description of Sampling Area

Sagamu has geographical coordinates between 6°50′ north; 3° 38′ east is located in south western region of Nigeria. The region has tropical wet and dry climate with a lengthy wet season and relatively constant temperatures throughout the course of the year. Wet season runs from March to October, November to December forms the region dry season. The vegetation type of the region is savannah which is really grassland with small bushes and occasional big trees. Grassland soils have substantially higher organic matter content than forest soils (Novackova, 2011).

Sample Collection

The Peatsoil samples were collected from four different sampling points (0-10cm depth) in Sagamu into polyethylene bag with plastic spoons. Samples were taken to the laboratory, extraneous materials were removed; the samples were air-dried, crushed and ground to a fine powder in a mortar passed through a 0.20mm sieve. The samples were kept for analysis.

Isolation and purification of humic acid from peat soil sample

Peatsoil sample (100g) was mixed with 1000 cm^3 of 0.1M NaOH solution, shaken for 3hours and left to stand overnight. Dark-coloured supernatant was obtained and decanted from solid residue. The dark-coloured supernatant was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 6 hours. Yellowish brown supernatant and dark-brown precipitate were obtained. The yellowish brown supernatant was decanted followed by centrifuge and discarded. The dark-brown precipitate was mixed with 500$cm^3$of 0.1M NaOH solution followed by passing through dowex resin. The dark-brown solution was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 3 hours. The dark-brown precipitate was washed several times with deionized water. The supernatant was treated with $AgNO_3$ solution until no white precipitate observed. The humic acid was transferred to weighed crucible and dried at 60°C in an oven for 12 hours. The humic acid was cooled and dried in the desiccator, weighed and recorded. The obtained humic acid was dried again at 60°C for additional 6 hours cooled and dried in the desiccator, weighed and recorded constant weight was obtained (Baruah *et al*., 2015).

FT-IR analysis

FT-IR spectra of humic acid sample was analysed using Carry 630 FT-IR Agilent Technologies.

Unhydrolysed compost humic acid

The unhydrolysed humic acid was obtained after isolation and purification of compost humic acid and kept for investigation.

Acid hydrolysis of Peatsoil acid

Peatsoil humic acid sample (1g) was refluxed for 12 hours at (160°C) with 50cm^3 of 6M HCl. The mixture was allowed to cool, decanted, and centrifuged after hydrolysis. The insoluble residues were washed with distilled water via centrifugation several times, and the supernatant was treated with $AgNO_3$ solution until no white precipitate was observed. The residue was thoroughly dried over $CaCl_2$ in a desiccator at room temperature (Chefetz *et al*., 2002). Finally, the obtained hydrolysed humic acid was kept for investigation.

Potentiometric Titrations

Potentiometric measurements were carried out using a pH-meter Jenway (model 3510) with combine electrode, the sensitivity of the pH - meter is 0.01 units. The pH meter was switched on half an hour before starting the titration for initial warm up of the instrument. The instrument was calibrated with an aqueous standard buffer solution of pH 4.00 and 10.0 (borate buffer) prepared from a "Qualigens" buffer tablets.

The following sets of solutions were prepared in a 250cm^3 volumetric flask separately for pH metric titrations.

(i) 5 cm^3 0.1 M HCl + 40 cm^3 deionized water
(ii) 5 cm^3 0.1 M HCl + 39 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid
(iii) 5 cm^3 0.1 M HCl + 37 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid + 2 cm^3 0.01 M Cu(II)

The solutions were titrated against standardized 0.110MNaOH separately. The total volume of each mixture was adjusted to 50 cm^3 and the ionic strength of the solutions was maintained constant at by adding appropriate amount of stock solution of 1M KNO$_3$ (Gamal, 2015; Omar and Ali, 2015). A magnetic stirrer was used to achieve thorough mixing of the interacting solutions at 550 rpm. The same set of experimental conditions was applied for potentiometric titration of remaining samples.

Evaluation of pKa of Hydrolysed peat soil Humic Acids

The proton-ligand formation number n$_{\mathbf{A}}$ were calculated by Irving and Rossotti expression (Omar and Ali, 2015).

$$nA = Y- \frac{(V2-V1)(No-Eo)}{(Vo+V1)TcL} \quad \text{...................................1}$$

Where: Y is number of dissociable proton, (V$_2$-V$_1$) is the measure of displacement of the ligand curve relative to acid curve, N^o and E^o are the resultant concentration of alkali solution, free acid solution, T$_{cL}{}^o$ is the total ligand concentration, V^o is the total volume of titration solution,V$_1$ is the volume of alkali added to acid solution,V$_2$ is the volume of alkali added to acid solution + ligand solution, acid dissociation constants (pKa - values) of ligand were calculated by algebraic method point wise calculation (Tables 1). The dissociation constants (pKa) were calculated according to the following relation:

$$pKa = pH + \log(\frac{nA}{1-nA}) \quad \text{..............................2}$$

Where: pKa is the acid dissociation constant, n$_A$is the Proton-ligand formation number and pH is the pH-values (Omar and Ali, 2015).

Determination of metal-ligand stability constants (log K) of complexes

The potentiometric measurement for the determination of stability constant of a complex in solution is based on the fact that the redox potential of the couple $\frac{M^{+(m-n)}}{M^{+m}}$ is shifted significantly on complexation of the metal ion with the ligand. This method involves change in hydrogen ion concentration [H$^+$] due to the displacement or association of one or more protons taking place during complexation reaction. This change can be found out by titrating the solutions containing free acid, acid with ligand, and acid with ligand and metal ion, individually against a standard alkali solution at a constant ionic strength or temperature. Either ionic strength or temperature may be varied for different sets of solutions. In all the cases, the change in the pH of the solution is measured after each addition of a known amount of alkali to the reaction cell which contains the reaction mixture. The titration curves are then drawn by plotting the measured pH values against the corresponding volume of alkali added and the stability constants of the complexes are determined from the titration curves by employing pH-metric titration technique given by (Irving and Rossoti).

Metal-ligand stability constants (Log K) were determined by using the following relations:

$$\bar{n} = \frac{(V_3 - V_2)(E^0 + N^0)}{(V^0 + V_2)\bar{n}_A T_m^0} \quad \text{...3}$$

and

$$PL = \log_{10}\{\frac{1 + \beta_n^H \frac{1}{[anti\ \log pH]^n}}{T_L^0 - \bar{n} T_m^0} X \frac{(V^0 + V_3)}{V^0}\} \quad \text{..4}$$

Where $T_{L,}$ T^o, E°, and V^ohavethe same significance as in equation (1) above, T_m denotes the total concentration of metal present in solution, V_3 is the volume of metal ions present in solution and β^H is the overall proton ligand stability constant. The metal-ligand stability constants (log K) were determined by employing point wise computational Method (eq. 5 and 6).

$$\text{LogK}_1 = \log\left(\frac{n}{1-n}\right) + \text{pL} \qquad \ldots\ldots\ldots\ldots.5$$

$$\text{LogK}_2 = \log\left(\frac{1-n}{2-n}\right) + \text{pL}\ldots\ldots\ldots\ldots\ldots\ldots.6$$

Where: Log K is the metal-ligand stability constant, pL is the Free ligand exponent function, **n** is the Average number of ligand attached with metal ion (Janrao*et al.*, 2014).The results obtained were analyzed by an ORIGIN 2016 program using titration data and then the proton-ligand stability constants (pKa) and Metal-ligand stability constant (LogK) calculated (Omar and Ali, 2015).

RESULTS AND DISCUSSION

Fourier transformed infrared (FT-IR) spectra of isolated humic acid from peat soils Figure 2 had distinct clear absorption bands indicating the presence of major humic acid structural elemental groups such as H bonded OH (3680cm^{-1} peak), C=O of carbonyl (1721cm^{-1} peak), functional groups of aliphatic components CH_2 (2918cm^{-1} peak) and C-O stretching of polysaccharide (1168cm^{-1} peak). The positions of the absorption bands of the spectra fell within typical major absorption bands of humic acid which is at frequencies 3680, 2918, 1721, 1168 cm^{-1}. The first peak centred in the vicinity of 3680 cm^{-1} region is attributed to phenol OH group bounded by intermolecular H bonds. The 2918cm^{-1} band usually has absorption maximum at 2918 cm^{-1} which is due to C–H stretching of alkane group (CH_2). The next major absorption band is 1721 cm^{-1}. This band has been commonly ascribed to C=O stretching of mainly carboxyl group (COOH) with trace amount of ketones. The last peak was observed at 1168 cm^{-1} due to C–O stretching of polysaccharides and this peak appeared also in the spectra of humic acid from peat soil. The FTIR spectra of the isolated humic acid contained all major characteristic absorption peaks of humic acid. These absorption peaks indicated the presence of the major structural elements of humic acid namely H bonded OH, C=C of aromatic ring, C=O of carbonyl group (both carboxyl and ketonic), CH_2 group. This strongly supports the presence of humic acid.

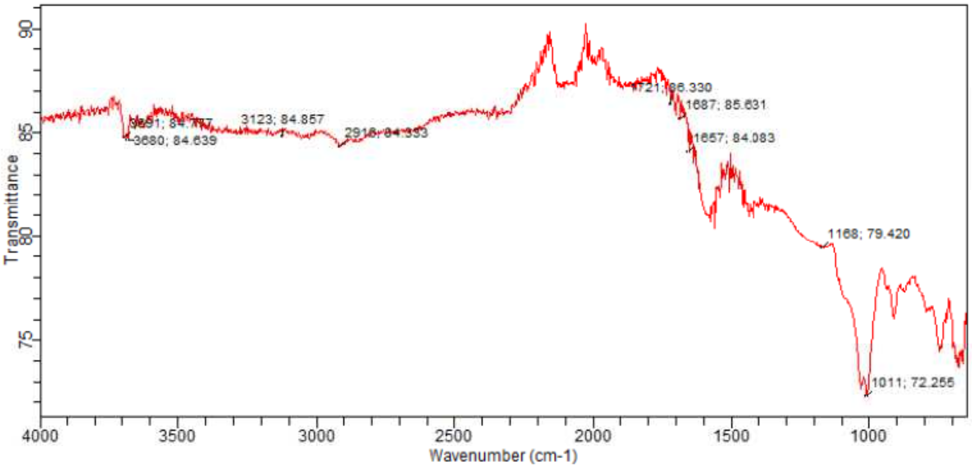


Fig. 2 : FT-IR spectraof peatsoilhumic acid (PSHA)

Evaluation of acid dissociation constant (pka) of acid hydrolysed peat soil humicacid at phenolic group

The value of the dissociation constant of the peat soil humic acid (PSHA) that underwent acidhydrolysis studied was found to be 8.9299 as shown Table 1, which is lower than the literaturevalues reported by Almeida and Szpoganics, (2015), Borges *et al.*, (2005); Badr *et al.*, (2012)and Fernandes *et al*,.(2009) of 9.73, 9.47 and 10.30. The difference between the obtained valuesand the reported values in this study might be probably as a result of acid hydrolysis of humicacid.

Table 1: PKa of (Hydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	$\log(\frac{nA}{1-nA})$	pKa
8.50	5.30	6.29	0.99	0.3594	-0.2510	8.2490
8.72	5.35	6.37	1.02	0.3400	-0.2880	8.4320
9.00	5.40	6.46	1.06	0.3141	-0.3391	8.6609
9.22	5.45	6.55	1.10	0.2882	-0.3927	8.8273
9.51	5.50	6.66	1.16	0.2494	-0.4786	9.0314
9.73	5.55	6.78	1.23	0.2041	-0.5910	9.1390
10.00	5.60	6.90	1.30	0.1589	-0.7238	9.2762
10.23	5.65	7.05	1.40	0.0941	-0.9835	9.2465
10.49	5.70	7.10	1.40	0.0941	-0.9835	9.5065

Average pKa = 8.9299 ± 0.4186

Table 2: PKa of (Unhydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	$\mathrm{Log}(\frac{nA}{1-n})$	pKa
8.50	5.30	5.81	0.51	0.6619	0.2919	8.7919
8.72	5.35	5.90	0.55	0.6357	0.2418	8.9618
9.00	5.40	6.00	0.60	0.6029	0.1813	9.1813
9.22	5.45	6.10	0.65	0.5701	0.1226	9.3426
9.51	5.50	6.20	0.70	0.5376	0.0654	9.5754
9.73	5.55	6.33	0.78	0.4851	-0.0259	9.7041
10.00	5.60	6.47	0.87	0.4262	-0.1291	9.8709
10.23	5.65	6.62	0.99	0.3609	-0.2481	9.9819
10.49	5.70	6.80	1.10	0.2759	-0.4690	10.0210

Average pKa = 9.4923± 0.4410

Metal-ligand stability constant (Log K)

The stabilityconstants require the accurate values of proton-ligand stability constants (Anil and Maroti, 2008). Metal titration curves crossed over ligand titration curve indicated the formation of complex upon proton release (Santosh, *et al.*, 2011). If the values of n- are within range 0.2-0.8 and 1.2-18 this indicates the formation of 1:1 and 1:2 complexes (Sayyed and Mazahar, 2012).

The metal (II)-humate stepwise stability constants (log k) at phenolic group (Tables 3-18)

Table 3: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$\log(\frac{n}{1-n})$	$\mathrm{Log}K_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

LogK_1 (Average value) = 2.4788± 0.2203

Table 4: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$\mathrm{Log}(\frac{n-1}{2-n})$	$\mathrm{Log}K_2$
9.51	5.50	6.66	6.73	0.07	1.3509	1.70	-0.2671	1.4329
9.73	5.55	6.78	6.85	0.07	1.6383	1.51	0.2467	1.7567
10.00	5.60	6.90	6.98	0.08	2.1783	1.31	-0.2158	1.0942
10.23	5.65	7.05	7.13	0.08	4.1904	1.27		
10.49	5.70	7.10	7.19	0.09	4.6920			

LogK_2(Average value) = 1.4280 ± 0.3312

Table 5:Point-wise method,Cu (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	Log($\frac{n}{n-1}$)	Log K$_1$
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430

LogK$_1$ **(Average value)** = 2.3059± 0.6153

Table 6:Point-wise method, Cu (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	V$_3$-V$_2$	n	pL	Log($\frac{n-1}{2-n}$)	Log K$_2$
9.73	5.55	6.33	6.42	0.09	0.9000	1.69		
10.00	5.60	6.47	6.58	0.11	1.2578	1.44	-0.4592	0.9808
10.23	5.65	6.62	6.84	0.12	1.6137	1.26	-0.2010	1.4610
10.49	5.70	6.80	6.92	0.12	2.1052	1.03		

LogK$_2$ **(Average value)** = 1.2209± 0.3398

Table 7:Point-wise method,Pb (Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	log($\frac{n}{1-n}$)	LogK$_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.60	0.05	0.8333	1.96	0.6989	2.6589

LogK$_1$ (Average value) = 2.5832 ±0.1614

Table 8:Point-wise method,Pb-(Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	log($\frac{n-1}{2-n}$)	logK$_2$
9.51	5.50	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.83	0.05	1.1702	1.44		
10.00	5.60	6.90	6.90	0.05	1.4864	1.22	-0.0237	1.1963
10.23	5.65	7.05	7.10	0.05	2.0190	1.09		
10.49	5.70	7.10	7.17	0.07	3.6492	1.00		

LogK$_2$(Average value) = 1.1963

Table 9:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	V$_3$-V$_2$	n	pL	Log ($\frac{n}{n-1}$)	Log K$_1$
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.5477	2.3123
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	0.0272	2.2072
9.51	5.50	6.20	6.26	0.07	0.6417	1.89	0.2530	2.1430
9.73	5.55	6.40	6.40	0.07	0.7000	1.67	0.3680	2.0380

LogK$_1$ **(Average value)** = 2.2364 ± 0.1602

Table 10:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	V$_3$-V$_2$	n	pL	Log($\frac{n-1}{2-n}$)	Log K$_2$
10.00	5.60	6.47	6.55	0.08	1.9503	1.41		
10.23	5.65	6.62	6.72	0.11	1.4792	1.26	-0.0361	1.2239

LogK$_2$ **(Average value)** = 1.2239

Table 11:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	log($\frac{n}{n-1}$)	LogK$_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4290	2.2110
8.72	5.35	6.37	6.39	0.02	0.2858	2.42	-0.3978	2.0222
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

LogK$_1$ (Average value)=2.1382**±**0.1046

Table 12:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	log($\frac{n-1}{2-n}$)	$LogK_2$
9.51	5.55	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.84	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.93	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.10		
10.49	5.70	7.10	7.18	0.07	3.6492	0.83		

$LogK_2$(Average value) = 1.5453 **±** 0.3450

Table 13:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$V_3\text{-}V_2$	n	pL	Log($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.3477	2.3123
9.00	5.40	6.00	6.04	0.04	0.3236	2.38	-0.3202	2.0598
9.22	5.45	6.10	6.15	0.05	0.4297	2.17	-0.1230	2.0470
9.51	5.50	6.20	6.26	0.06	0.5500	1.89	0.0871	1.9771
9.73	5.55	6.33	6.40	0.07	0.7000	1.67	0.3680	2.0380

$LogK_1$ **(Average value)** = 2.1568 ± 0.2069

Table 14:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$V_3\text{-}V_2$	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
10.00	5.60	6.47	6.55	0.08	0.9148	1.41		
10.23	5.65	6.62	6.71	0.09	1.2102	1.20	-0.5749	0.6251
10.49	5.70	6.80	6.92	0.09	1.5968	1.03	0.1703	1.2003

$LogK_2$ **(Average value)** = 0.9127± 0.4070

Table15:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	Log($\frac{n}{1-n}$)	$LogK_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4210	2.2190
8.72	5.35	6.37	6.40	0.03	0.4286	2.42	-0.1249	2.2951
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.96	0.3010	2.2610
9.51	5.55	6.66	6.70	0.04	0.7720	1.67	0.5297	2.1997

$LogK_1$ (Average value) = 2.2108± 0.0825

Table 16:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
9.73	5.55	6.78	6.83	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.95	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.09		
10.49	5.70	7.10	7.16	0.06	3.1429	0.89		

$LogK_2$ **(Average value)** = 1.5453± 0.3450

Table 17:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$V_3\text{-}V_2$	n	pL	Log($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.86	0.05	0.3717	2.88	-0.2280	2.6520
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.06	0.06	0.4853	2.38	-0.0255	2.3545
9.22	5.45	6.10	6.16	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430
9.73	5.55	6.33	6.41	0.08	0.8000	1.69	0.6020	2.2920

$LogK_1$ **(Average value)** = 2.2516± 0.5380

Table 18:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$\text{Log}(\frac{n-1}{2-n})$	Log K_2
10.00	5.60	6.47	6.57	0.10	1.1434	1.43		
10.23	5.65	6.62	6.72	0.10	1.3448	1.23	-0.2788	0.9512
10.49	5.70	6.80	6.90	0.10	1.7742	1.03	0.5351	1.5651

LogK_2 **(Average value)** = 1.2581± 0.4340

Table 19: Stepwise and overall Stability constants of thehydrolysed and unhydrolysed divalent metal (II) complexes

Chelates	LogK_1	LogK_2	Logβ
[Cu (Hydrolysed PSHA-1)$_2$]	2.4788	1.4280	3.9068
[Pb (Hydrolysed PSHA-1)$_2$]	2.5832	1.1963	3.7795
[Cd (Hydrolysed PSHA-1)$_2$]	2.2108	1.5453	3.7561
[Mg (Hydrolysed PSHA-1)$_2$]	2.1382	1.5453	3.6835
[Cu (Unhydrolysed PSHA-1)$_2$]	2.3059	1.2209	3.5268
[Pb (Unhydrolysed PSHA-1)$_2$]	2.2364	1.2239	3.4603
[Cd (Unhydrolysed PSHA-1)$_2$]	2.2516	1.2581	3.5097
[Mg (Unydrolysed PSHA-1)$_2$]	2.1568	0.9127	3.0695

The results obtained (Table19) shows the stepwise and overall stability constants to be not high indicating low stability of the complexes, because the solubility of most metal ions in the basic pH range is minimal due to metal hydroxide precipitation (Karimi, 2017). In general, the stepwise stability constants (K_1 and K_2) follow the order $K_1 > K_2$ for the copper, lead, magnesium and cadmium complexes respectively. The steady decrease of the values with increasing number of ligands is in agreement with the prediction made by researchers (Na'aliya, 2013). The decrease could be attributed to the fact that as the number of the ligands (Humate ions) that enters the coordination zone increases the aqua molecules available for replacement by the ligands become less. Thus, the metal ions become less electron loving with progressive intake of the ligand and this results in the decrease in the values of the constants (Na'aliya, 2013). Also the stability of the complexes is influenced by the size and number of the chelate rings(Mackay and Mackay,2002).All the complexes form rings in their structure as humate, a bidentate ligand, bond the metal ions in the ratio 1:2 (Boguta and Sokolowska, 2016) forming chelate rings. The values of the overall stability constants (logβ) obtained for humate complexes are not high indicating low stability as the values are not high. LogK values for copper-humates (Table 3 to 6) obtained in this study are lower than those reported for the complexes of humic acids (Pandey *et al*., 2015; Dinu, 2013; Kaschl *et al*., 2010 and Gilbeto and Jorg, 2001). The values of LogK(Table 7 to 10) forlead-humates are lower than those reported for the lead in the literature (Dinu, 2013; Gilbeto and Jorg 2001). Log K values(Table 11 to 14) for magnesium-humates obtained in this study are close to those reported by (Pandey *et al*., 2015). Log K values of cadmium-humates (Table 15 to 18) obtained in this work near to the one reported by (Dinu, 2013 and Pandey *et al*., 2015).The difference between the reported values and the values obtained in this study might be probably as a result of acid hydrolysis of humic acid. The values of the overall stability constants (log β) of the copper humates complexes presented in Table 19 is high than that of other metal humate complexes, show relatively high stability of Cu-HA complexes, show the following order of stability: Cu >Pb> Cd > Mg; which are in close agreement to the findings of (Dinu, 2013 and Pandey *et al*., 2015).The high stability of Cu-humate chelate could be attributed to the existence of coordinate covalent bond between the complexing agents and the Cu^{2+} ions. Since, Cu^{2+} being a metal of the transitional series with $3d^9$ electronic configurations can accept the electrons from the complexing agents. Similarly,the low stabilities of Pb,Cd and Mg -complexes could be explained by that Pb^{2+} with $6s^2$, Cd^{2+} with $4d^{10}$ and Mg^{2+} with $2p^6$ their electronic configuration has a completely filled d,p and s orbitals. Moreover, the stabilities of metal ions with hydrolysed humic acid from peat soil were higher than those with unhydrolysed humic acid from peat soil; which is ascribed to the high content of acidity in hydrolysed humic acid than unhydrolysed humic acid.

CONCLUSION

The values of logK for Cu(II) hydrolysed humic acid complex was higher followed by Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes as compared with metal(II) unhydrolysed humic acid complexes . This indicates acid hydrolysis of humic acid can enhance the complexation behavior of humic acid with metal (II) ions. However, the higher values of logβ for Cu(II), Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes indicates more stable stepwise complexes formed as compared with Cu(II), Pb(II), Cd(II) and Mg(II) unhydrolysed humic acid complexes.

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STABILITY CONSTANTS OF COMPLEXES OF METAL IONS WITH PEATSOIL HUMIC ACIDS UNDER NON-ACID-CONDITIONS

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ABSTRACT

Stability constants of complexes of four divalent metal ions viz. Cu^{2+}, Pb^{2+},Mg^{2+} and Cd^{2+} with humic acids (HA) were determined by potentiometric titration of humic acids with the corresponding salt of the divalent metals in aqueous media under non-acid-condition. The log K (logarithm of the stability constant) ranged from 1.0942 to 2.7471 for metal-humic acid complexes were determined using point-wise computational method. The order of stability constants were obtained as follows: Cu >Pb> Cd > Mg for metal -HA complexes respectively, indicating a higher degree of complexation with Cu metal ion.

Keywords: stability constant, humic acid, potentiometric titration, divalent metals, acid hydrolysis.

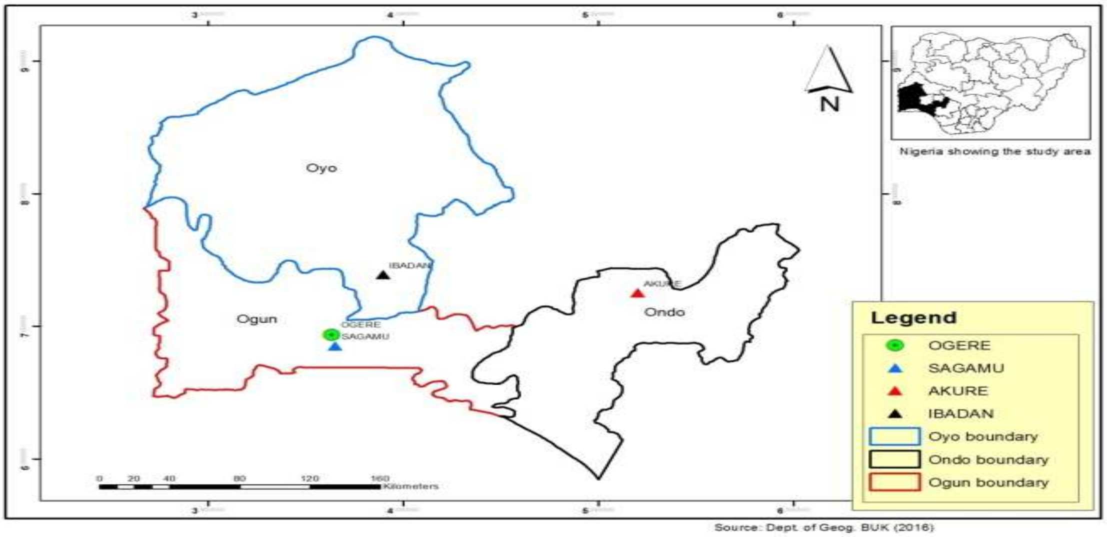
NTRODUCTION

The stability constant of a complex is the numerical expression of its stability and provides a quantitative measure of affinity of the metal ion to the complexing agent. An understanding of the relative stability of metal-complexes helps in predicting the behavior of metal ions in the soil (Ram and Raman, 1982). Extensive researches has been done to determine the stability constants of the complexes formed between humic acid (HA) with a number of metal ions. Ashok *et al*., (2000) reported that humic acid with hydroxyl, phenoxyl and carboxyl reactive groups can form coordination compound with metal ions at pH 3.5. The stability constants(Log K) for different metal-humic acid complexes indicated the following order of the stabilities of complexes formed between humic acid and metal ion, Cu >Fe >Pb> Ni > Co > Ca > Cd > Zn >Mn> Mg. Andelkovic *et al*., (2010) investigated the binding of Cd(II) to soil humic acid at pH 6.5 and in 0.1M KNO_3 ionic medium. The stability constant for binding indicating greater stability in the case when carboxyl groups are involved in complexation reaction. Kostic *et al*.,(2012) investigated the complexation of humic acid with certain heavy metal ions (Co(II), Ni(II),Cu(II), Zn(II), and Pb(II). The experiment was performed at 25°C, at pH 4.0 and ionic strength of 0.01M. Stability constant of complex between Pb(II) ions and humic acid is greater than stability constants of other investigated metal-humate complexes. Bogata and Sokolowska (2016) analyses the interaction between humic acids from different soils and Zn (II) ions at wide concentration ranges and at pH 5. Studies have showed significant impact of Zn concentration, pH and some properties of humic acids with zinc.But all of these studies were limited to acidic pH range. Therefore, the present study was carried out to determine and compare the stability constants of complexes of metal ions with hydrolysed peat soil humic acid and unhydrolysed peat soil humic under non-acid conditions.

MATERIALS AND METHODS

Analytical grade chemicals used includes hydrochloric acid (HCl), nitric acid (HNO_3), sodium hydroxide (NaOH), lead nitrate $Pb(NO_3)_2$, copper nitrate $Cu(NO_3)_2.3H_2O$, cadmium nitrate $Cd(NO_3)_2.4H_2O$, magnesium nitrate $Mg(NO_3)_2.6H_2O$, potassium nitrate (KNO_3), calcium chloride ($CaCl_2$), (sigma-Aldrich). Dowex 50WX8, (20-50 mesh) from Fluka.

Area of study



Source: Dept. of Geog. BUK (2016)

Figure 1: Map showing the sampling point at Sagamu Town, Ogun State.

Description of Sampling Area

Sagamu has geographical coordinates between 6°50′ north; 3° 38′ east is located in south western region of Nigeria. The region has tropical wet and dry climate with a lengthy wet season and relatively constant temperatures throughout the course of the year. Wet season runs from March to October, November to December forms the region dry season. The vegetation type of the region is savannah which is really grassland with small bushes and occasional big trees. Grassland soils have substantially higher organic matter content than forest soils (Novackova, 2011).

Sample Collection

The Peatsoil samples were collected from four different sampling points (0-10cm depth) in Sagamu into polyethylene bag with plastic spoons. Samples were taken to the laboratory, extraneous materials were removed; the samples were air-dried, crushed and ground to a fine powder in a mortar passed through a 0.20mm sieve. The samples were kept for analysis.

Isolation and purification of humic acid from peat soil sample

Peatsoil sample (100g) was mixed with 1000 cm^3 of 0.1M NaOH solution, shaken for 3hours and left to stand overnight. Dark-coloured supernatant was obtained and decanted from solid residue. The dark-coloured supernatant was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 6 hours. Yellowish brown supernatant and dark-brown precipitate were obtained. The yellowish brown supernatant was decanted followed by centrifuge and discarded. The dark-brown precipitate was mixed with $500cm^3$of 0.1M NaOH solution followed by passing through dowex resin. The dark-brown solution was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 3 hours. The dark-brown precipitate was washed several times with deionized water. The supernatant was treated with $AgNO_3$ solution until no white precipitate observed. The humic acid was transferred to weighed crucible and dried at 60°C in an oven for 12 hours. The humic acid was cooled and dried in the desiccator, weighed and recorded. The obtained humic acid was dried again at 60°C for additional 6 hours cooled and dried in the desiccator, weighed and recorded constant weight was obtained (Baruah *et al.*, 2015).

FT-IR analysis

FT-IR spectra of humic acid sample was analysed using Carry 630 FT-IR Agilent Technologies.

Unhydrolysed compost humic acid

The unhydrolysed humic acid was obtained after isolation and purification of compost humic acid and kept for investigation.

Acid hydrolysis of Peatsoil acid

Peatsoil humic acid sample (1g) was refluxed for 12 hours at (160°C) with $50cm^3$ of 6M HCl. The mixture was allowed to cool, decanted, and centrifuged after hydrolysis. The insoluble residues were washed with distilled water via centrifugation several times, and the supernatant was treated with $AgNO_3$ solution until no white precipitate was observed. The residue was thoroughly dried over $CaCl_2$ in a desiccator at room temperature (Chefetz *et al.*, 2002). Finally, the obtained hydrolysed humic acid was kept for investigation.

Potentiometric Titrations

Potentiometric measurements were carried out using a pH-meter Jenway (model 3510) with combine electrode, the sensitivity of the pH -meter is 0.01 units. The pH meter was switched on half an hour before starting the titration for initial warm up of the instrument. The instrument was calibrated with an aqueous standard buffer solution of pH 4.00 and 10.0 (borate buffer) prepared from a "Qualigens" buffer tablets.

The following sets of solutions were prepared in a 250cm^3 volumetric flask separately for pH metric titrations.

(i) 5 cm^3 0.1 M HCl + 40 cm^3 deionized water

(ii) 5 cm^3 0.1 M HCl + 39 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid

(iii) 5 cm^3 0.1 M HCl + 37 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid + 2 cm^3 0.01 M Cu(II)

The solutions were titrated against standardized 0.110MNaOH separately. The total volume of each mixture was adjusted to 50 cm^3 and the ionic strength of the solutions was maintained constant at by adding appropriate amount of stock solution of 1M KNO$_3$ (Gamal, 2015; Omar and Ali, 2015). A magnetic stirrer was used to achieve thorough mixing of the interacting solutions at 550 rpm. The same set of experimental conditions was applied for potentiometric titration of remaining samples.

Evaluation of pKa of Hydrolysed peat soil Humic Acids

The proton-ligand formation number n$_\mathbf{A}$ were calculated by Irving and Rossotti expression (Omar and Ali, 2015).

$$nA = Y - \frac{(V2-V1)(No-Eo)}{(Vo+V1)TcL} \quad ....1$$

Where: Y is number of dissociable proton, (V$_2$-V$_1$) is the measure of displacement of the ligand curve relative to acid curve, N^o and E^o are the resultant concentration of alkali solution, free acid solution, T$_{cL}$^{o} is the total ligand concentration, V^o is the total volume of titration solution,V$_1$ is the volume of alkali added to acid solution,V$_2$ is the volume of alkali added to acid solution + ligand solution, acid dissociation constants (pKa - values) of ligand were calculated by algebraic method point wise calculation (Tables 1). The dissociation constants (pKa) were calculated according to the following relation:

$$pKa = pH + \log\left(\frac{nA}{1-nA}\right) \quad ....2$$

Where: pKa is the acid dissociation constant, n$_A$is the Proton-ligand formation number and pH is the pH-values (Omar and Ali, 2015).

Determination of metal-ligand stability constants (log K) of complexes

The potentiometric measurement for the determination of stability constant of a complex in solution is based on the fact that the redox potential of the couple $\frac{M^{+(m-n)}}{M^{+m}}$ is shifted significantly on complexation of the metal ion with the ligand. This method involves change in hydrogen ion concentration [H$^+$] due to the displacement or association of one or more protons taking place during complexation reaction. This change can be found out by titrating the solutions containing free acid, acid with ligand, and acid with ligand and metal ion, individually against a standard alkali solution at a constant ionic strength or temperature. Either ionic strength or temperature may be varied for different sets of solutions. In all the cases, the change in the pH of the solution is measured after each addition of a known amount of alkali to the reaction cell which contains the reaction mixture. The titration curves are then drawn by plotting the measured pH values against the corresponding volume of alkali added and the stability constants of the complexes are determined from the titration curves by employing pH-metric titration technique given by (Irving and Rossoti).

Metal-ligand stability constants (Log K) were determined by using the following relations:

$$\bar{n} = \frac{(V_3 - V_2)(E^0 + N^0)}{(V^0 + V_2)\bar{n}_A T_m^0} \quad ....3$$

and

$$PL = \log_{10}\left\{\frac{1 + \beta_n^H \frac{1}{[anti\ \log pH]^n}}{T_L^0 - \bar{n} T_m^0} X \frac{(V^0 + V_3)}{V^0}\right\} \quad ....4$$

Where $T_{L,}$ T^{o}, E°, and V^{o}havethe same significance as in equation (1) above, T_m denotes the total concentration of metal present in solution, V_3 is the volume of metal ions present in solution and β^H is the overall proton ligand stability constant. The metal-ligand stability constants (log K) were determined by employing point wise computational Method (eq. 5 and 6).

$$\mathrm{Log}K_1 = \log\left(\frac{n}{1-n}\right) + pL \qquad \ldots\ldots\ldots\ldots.5$$

$$\mathrm{Log}K_2 = \log\left(\frac{1-n}{2-n}\right) + pL\ldots\ldots\ldots\ldots\ldots\ldots\ldots.6$$

Where: Log K is the metal-ligand stability constant, pL is the Free ligand exponent function, **n** is the Average number of ligand attached with metal ion (Janrao*et al*., 2014).The results obtained were analyzed by an ORIGIN 2016 program using titration data and then the proton-ligand stability constants (pKa) and Metal-ligand stability constant (LogK) calculated (Omar and Ali, 2015).

RESULTS AND DISCUSSION

Fourier transformed infrared (FT-IR) spectra of isolated humic acid from peat soils Figure 2 had distinct clear absorption bands indicating the presence of major humic acid structural elemental groups such as H bonded OH ($3680cm^{-1}$ peak), C=O of carbonyl ($1721cm^{-1}$ peak), functional groups of aliphatic components CH_2 ($2918cm^{-1}$ peak) and C-O stretching of polysaccharide ($1168cm^{-1}$ peak). The positions of the absorption bands of the spectra fell within typical major absorption bands of humic acid which is at frequencies 3680, 2918, 1721, 1168 cm^{-1}. The first peak centred in the vicinity of 3680 cm^{-1} region is attributed to phenol OH group bounded by intermolecular H bonds. The $2918cm^{-1}$ band usually has absorption maximum at 2918 cm^{-1} which is due to C–H stretching of alkane group (CH_2). The next major absorption band is 1721 cm^{-1}. This band has been commonly ascribed to C=O stretching of mainly carboxyl group (COOH) with trace amount of ketones. The last peak was observed at 1168 cm^{-1} due to C–O stretching of polysaccharides and this peak appeared also in the spectra of humic acid from peat soil. The FTIR spectra of the isolated humic acid contained all major characteristic absorption peaks of humic acid. These absorption peaks indicated the presence of the major structural elements of humic acid namely H bonded OH, C=C of aromatic ring, C=O of carbonyl group (both carboxyl and ketonic), CH_2 group. This strongly supports the presence of humic acid.

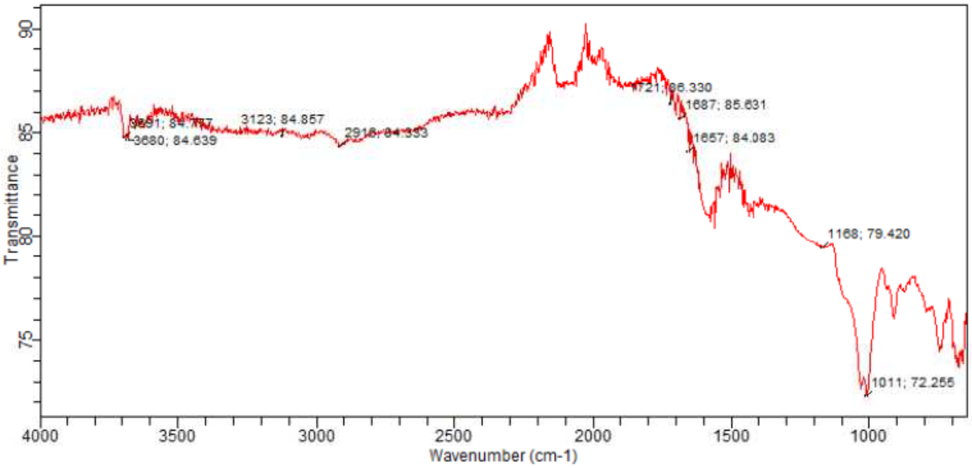


Fig. 2 : FT-IR spectraof peatsoilhumic acid (PSHA)

Evaluation of acid dissociation constant (pka) of acid hydrolysed peat soil humicacid at phenolic group

The value of the dissociation constant of the peat soil humic acid (PSHA) that underwent acidhydrolysis studied was found to be 8.9299 as shown Table 1, which is lower than the literaturevalues reported by Almeida and Szpoganics, (2015), Borges *et al*., (2005); Badr *et al*., (2012)and Fernandes *et al*,.(2009) of 9.73, 9.47 and 10.30. The difference between the obtained valuesand the reported values in this study might be probably as a result of acid hydrolysis of humicacid.

Table 1: PKa of (Hydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	log($\frac{nA}{1-nA}$)	pKa
8.50	5.30	6.29	0.99	0.3594	-0.2510	8.2490
8.72	5.35	6.37	1.02	0.3400	-0.2880	8.4320
9.00	5.40	6.46	1.06	0.3141	-0.3391	8.6609
9.22	5.45	6.55	1.10	0.2882	-0.3927	8.8273
9.51	5.50	6.66	1.16	0.2494	-0.4786	9.0314
9.73	5.55	6.78	1.23	0.2041	-0.5910	9.1390
10.00	5.60	6.90	1.30	0.1589	-0.7238	9.2762
10.23	5.65	7.05	1.40	0.0941	-0.9835	9.2465
10.49	5.70	7.10	1.40	0.0941	-0.9835	9.5065

Average pKa = 8.9299 ± 0.4186

Table 2: PKa of (Unhydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	Log($\frac{nA}{1-n}$)	pKa
8.50	5.30	5.81	0.51	0.6619	0.2919	8.7919
8.72	5.35	5.90	0.55	0.6357	0.2418	8.9618
9.00	5.40	6.00	0.60	0.6029	0.1813	9.1813
9.22	5.45	6.10	0.65	0.5701	0.1226	9.3426
9.51	5.50	6.20	0.70	0.5376	0.0654	9.5754
9.73	5.55	6.33	0.78	0.4851	-0.0259	9.7041
10.00	5.60	6.47	0.87	0.4262	-0.1291	9.8709
10.23	5.65	6.62	0.99	0.3609	-0.2481	9.9819
10.49	5.70	6.80	1.10	0.2759	-0.4690	10.0210

Average pKa = 9.4923± 0.4410

Metal-ligand stability constant (Log K)

The stabilityconstants require the accurate values of proton-ligand stability constants (Anil and Maroti, 2008). Metal titration curves crossed over ligand titration curve indicated the formation of complex upon proton release (Santosh, *et al.*, 2011). If the values of n- are within range 0.2-0.8 and 1.2-18 this indicates the formation of 1:1 and 1:2 complexes (Sayyed and Mazahar, 2012).

The metal (II)-humate stepwise stability constants (log k) at phenolic group (Tables 3-18)

Table 3: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n}{1-n}$)	$LogK_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

$LogK_1$ (Average value) = 2.4788± 0.2203

Table 4: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	Log($\frac{n-1}{2-n}$)	$LogK_2$
9.51	5.50	6.66	6.73	0.07	1.3509	1.70	-0.2671	1.4329
9.73	5.55	6.78	6.85	0.07	1.6383	1.51	0.2467	1.7567
10.00	5.60	6.90	6.98	0.08	2.1783	1.31	-0.2158	1.0942
10.23	5.65	7.05	7.13	0.08	4.1904	1.27		
10.49	5.70	7.10	7.19	0.09	4.6920			

$LogK_2$(Average value) = 1.4280 ± 0.3312

Table 5:Point-wise method,Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	Log($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430

$LogK_1$ **(Average value)** = 2.3059± 0.6153

Table 6:Point-wise method, Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
9.73	5.55	6.33	6.42	0.09	0.9000	1.69		
10.00	5.60	6.47	6.58	0.11	1.2578	1.44	-0.4592	0.9808
10.23	5.65	6.62	6.84	0.12	1.6137	1.26	-0.2010	1.4610
10.49	5.70	6.80	6.92	0.12	2.1052	1.03		

$LogK_2$ **(Average value)** = 1.2209± 0.3398

Table 7:Point-wise method,Pb (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n}{1-n}$)	$LogK_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.60	0.05	0.8333	1.96	0.6989	2.6589

$LogK_1$ (Average value) = 2.5832 ±0.1614

Table 8:Point-wise method,Pb-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n-1}{2-n}$)	$logK_2$
9.51	5.50	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.83	0.05	1.1702	1.44		
10.00	5.60	6.90	6.90	0.05	1.4864	1.22	-0.0237	1.1963
10.23	5.65	7.05	7.10	0.05	2.0190	1.09		
10.49	5.70	7.10	7.17	0.07	3.6492	1.00		

$LogK_2$(Average value) = 1.1963

Table 9:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log ($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.5477	2.3123
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	0.0272	2.2072
9.51	5.50	6.20	6.26	0.07	0.6417	1.89	0.2530	2.1430
9.73	5.55	6.40	6.40	0.07	0.7000	1.67	0.3680	2.0380

$LogK_1$ **(Average value)** = 2.2364 ± 0.1602

Table 10:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
10.00	5.60	6.47	6.55	0.08	1.9503	1.41		
10.23	5.65	6.62	6.72	0.11	1.4792	1.26	-0.0361	1.2239

$LogK_2$ **(Average value)** = 1.2239

Table 11:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n}{n-1}$)	$LogK_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4290	2.2110
8.72	5.35	6.37	6.39	0.02	0.2858	2.42	-0.3978	2.0222
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

$LogK_1$ (Average value)=2.1382**±**0.1046

Table 12:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	log$(\frac{n-1}{2-n})$	LogK$_2$
9.51	5.55	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.84	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.93	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.10		
10.49	5.70	7.10	7.18	0.07	3.6492	0.83		

LogK$_2$(Average value) = 1.5453 **±** 0.3450

Table 13:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	V$_3$-V$_2$	n	pL	Log$(\frac{n}{n-1})$	Log K$_1$
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.3477	2.3123
9.00	5.40	6.00	6.04	0.04	0.3236	2.38	-0.3202	2.0598
9.22	5.45	6.10	6.15	0.05	0.4297	2.17	-0.1230	2.0470
9.51	5.50	6.20	6.26	0.06	0.5500	1.89	0.0871	1.9771
9.73	5.55	6.33	6.40	0.07	0.7000	1.67	0.3680	2.0380

LogK$_1$ **(Average value)** = 2.1568 ± 0.2069

Table 14:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	V$_3$-V$_2$	n	pL	Log$(\frac{n-1}{2-n})$	Log K$_2$
10.00	5.60	6.47	6.55	0.08	0.9148	1.41		
10.23	5.65	6.62	6.71	0.09	1.2102	1.20	-0.5749	0.6251
10.49	5.70	6.80	6.92	0.09	1.5968	1.03	0.1703	1.2003

LogK$_2$ **(Average value)** = 0.9127± 0.4070

Table15:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	Log$(\frac{n}{1-n})$	LogK$_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4210	2.2190
8.72	5.35	6.37	6.40	0.03	0.4286	2.42	-0.1249	2.2951
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.96	0.3010	2.2610
9.51	5.55	6.66	6.70	0.04	0.7720	1.67	0.5297	2.1997

LogK$_1$ (Average value) = 2.2108± 0.0825

Table 16:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	Log$(\frac{n-1}{2-n})$	Log K$_2$
9.73	5.55	6.78	6.83	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.95	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.09		
10.49	5.70	7.10	7.16	0.06	3.1429	0.89		

LogK$_2$ **(Average value)** = 1.5453± 0.3450

Table 17:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	V$_3$-V$_2$	n	pL	Log$(\frac{n}{n-1})$	Log K$_1$
8.50	5.30	5.81	5.86	0.05	0.3717	2.88	-0.2280	2.6520
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.06	0.06	0.4853	2.38	-0.0255	2.3545
9.22	5.45	6.10	6.16	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430
9.73	5.55	6.33	6.41	0.08	0.8000	1.69	0.6020	2.2920

LogK$_1$ **(Average value)** = 2.2516± 0.5380

Table 18:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$\mathrm{Log}(\frac{n-1}{2-n})$	Log K_2
10.00	5.60	6.47	6.57	0.10	1.1434	1.43		
10.23	5.65	6.62	6.72	0.10	1.3448	1.23	-0.2788	0.9512
10.49	5.70	6.80	6.90	0.10	1.7742	1.03	0.5351	1.5651

LogK_2 **(Average value)** = 1.2581± 0.4340

Table 19: Stepwise and overall Stability constants of thehydrolysed and unhydrolysed divalent metal (II) complexes

Chelates	LogK₁	LogK₂	Logβ
[Cu (Hydrolysed PSHA-1)$_2$]	2.4788	1.4280	3.9068
[Pb (Hydrolysed PSHA-1)$_2$]	2.5832	1.1963	3.7795
[Cd (Hydrolysed PSHA-1)$_2$]	2.2108	1.5453	3.7561
[Mg (Hydrolysed PSHA-1)$_2$]	2.1382	1.5453	3.6835
[Cu (Unhydrolysed PSHA-1)$_2$]	2.3059	1.2209	3.5268
[Pb (Unhydrolysed PSHA-1)$_2$]	2.2364	1.2239	3.4603
[Cd (Unhydrolysed PSHA-1)$_2$]	2.2516	1.2581	3.5097
[Mg (Unydrolysed PSHA-1)$_2$]	2.1568	0.9127	3.0695

The results obtained (Table19) shows the stepwise and overall stability constants to be not high indicating low stability of the complexes, because the solubility of most metal ions in the basic pH range is minimal due to metal hydroxide precipitation (Karimi, 2017). In general, the stepwise stability constants (K_1 and K_2) follow the order $K_1 > K_2$ for the copper, lead, magnesium and cadmium complexes respectively. The steady decrease of the values with increasing number of ligands is in agreement with the prediction made by researchers (Na'aliya, 2013). The decrease could be attributed to the fact that as the number of the ligands (Humate ions) that enters the coordination zone increases the aqua molecules available for replacement by the ligands become less. Thus, the metal ions become less electron loving with progressive intake of the ligand and this results in the decrease in the values of the constants (Na'aliya, 2013). Also the stability of the complexes is influenced by the size and number of the chelate rings(Mackay and Mackay,2002).All the complexes form rings in their structure as humate, a bidentate ligand, bond the metal ions in the ratio 1:2 (Boguta and Sokolowska, 2016) forming chelate rings. The values of the overall stability constants (logβ) obtained for humate complexes are not high indicating low stability as the values are not high. LogK values for copper-humates (Table 3 to 6) obtained in this study are lower than those reported for the complexes of humic acids (Pandey *et al.*, 2015; Dinu, 2013; Kaschl *et al.*, 2010 and Gilbeto and Jorg, 2001). The values of LogK(Table 7 to 10) forlead-humates are lower than those reported for the lead in the literature (Dinu, 2013; Gilbeto and Jorg 2001). Log K values(Table 11 to 14) for magnesium-humates obtained in this study are close to those reported by (Pandey *et al.*, 2015). Log K values of cadmium-humates (Table 15 to 18) obtained in this work near to the one reported by (Dinu, 2013 and Pandey *et al.*, 2015).The difference between the reported values and the values obtained in this study might be probably as a result of acid hydrolysis of humic acid. The values of the overall stability constants (log β) of the copper humates complexes presented in Table 19 is high than that of other metal humate complexes, show relatively high stability of Cu-HA complexes, show the following order of stability: Cu >Pb> Cd > Mg; which are in close agreement to the findings of (Dinu, 2013 and Pandey *et al.*, 2015).The high stability of Cu-humate chelate could be attributed to the existence of coordinate covalent bond between the complexing agents and the Cu^{2+} ions. Since, Cu^{2+} being a metal of the transitional series with $3d^9$ electronic configurations can accept the electrons from the complexing agents. Similarly,the low stabilities of Pb,Cd and Mg - complexes could be explained by that Pb^{2+} with $6s^2$, Cd^{2+} with $4d^{10}$ and Mg^{2+} with $2p^6$ their electronic configuration has a completely filled d,p and s orbitals. Moreover, the stabilities of metal ions with hydrolysed humic acid from peat soil were higher than those with unhydrolysed humic acid from peat soil; which is ascribed to the high content of acidity in hydrolysed humic acid than unhydrolysed humic acid.

CONCLUSION

The values of logK for Cu(II) hydrolysed humic acid complex was higher followed by Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes as compared with metal(II) unhydrolysed humic acid complexes . This indicates acid hydrolysis of humic acid can enhance the complexation behavior of humic acid with metal (II) ions. However, the higher values of logβ for Cu(II), Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes indicates more stable stepwise complexes formed as compared with Cu(II), Pb(II), Cd(II) and Mg(II) unhydrolysed humic acid complexes.

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STABILITY CONSTANTS OF COMPLEXES OF METAL IONS WITH PEATSOIL HUMIC ACIDS UNDER NON-ACID-CONDITIONS

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ABSTRACT

Stability constants of complexes of four divalent metal ions viz. Cu^{2+}, Pb^{2+},Mg^{2+} and Cd^{2+} with humic acids (HA) were determined by potentiometric titration of humic acids with the corresponding salt of the divalent metals in aqueous media under non-acid-condition. The log K (logarithm of the stability constant) ranged from 1.0942 to 2.7471 for metal-humic acid complexes were determined using point-wise computational method. The order of stability constants were obtained as follows: Cu >Pb> Cd > Mg for metal -HA complexes respectively, indicating a higher degree of complexation with Cu metal ion.

Keywords: stability constant, humic acid, potentiometric titration, divalent metals, acid hydrolysis.

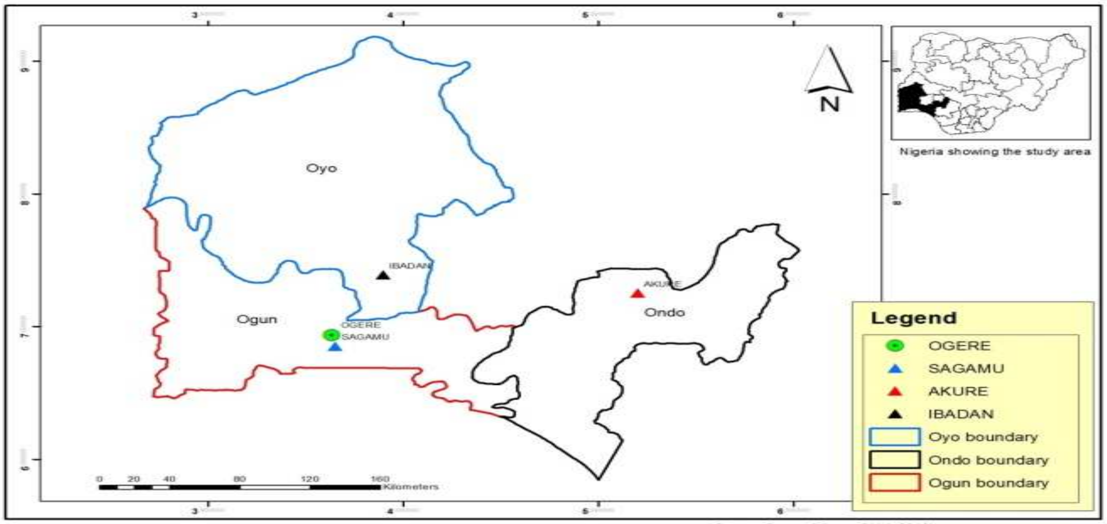
NTRODUCTION

The stability constant of a complex is the numerical expression of its stability and provides a quantitative measure of affinity of the metal ion to the complexing agent. An understanding of the relative stability of metal-complexes helps in predicting the behavior of metal ions in the soil (Ram and Raman, 1982). Extensive researches has been done to determine the stability constants of the complexes formed between humic acid (HA) with a number of metal ions. Ashok *et al*., (2000) reported that humic acid with hydroxyl, phenoxyl and carboxyl reactive groups can form coordination compound with metal ions at pH 3.5. The stability constants(Log K) for different metal-humic acid complexes indicated the following order of the stabilities of complexes formed between humic acid and metal ion, Cu >Fe >Pb> Ni > Co > Ca > Cd > Zn >Mn> Mg. Andelkovic *et al*., (2010) investigated the binding of Cd(II) to soil humic acid at pH 6.5 and in 0.1M KNO_3 ionic medium. The stability constant for binding indicating greater stability in the case when carboxyl groups are involved in complexation reaction. Kostic *et al*.,(2012) investigated the complexation of humic acid with certain heavy metal ions (Co(II), Ni(II),Cu(II), Zn(II), and Pb(II). The experiment was performed at 25°C, at pH 4.0 and ionic strength of 0.01M. Stability constant of complex between Pb(II) ions and humic acid is greater than stability constants of other investigated metal-humate complexes. Bogata and Sokolowska (2016) analyses the interaction between humic acids from different soils and Zn (II) ions at wide concentration ranges and at pH 5. Studies have showed significant impact of Zn concentration, pH and some properties of humic acids with zinc.But all of these studies were limited to acidic pH range. Therefore, the present study was carried out to determine and compare the stability constants of complexes of metal ions with hydrolysed peat soil humic acid and unhydrolysed peat soil humic under non-acid conditions.

MATERIALS AND METHODS

Analytical grade chemicals used includes hydrochloric acid (HCl), nitric acid (HNO_3), sodium hydroxide (NaOH), lead nitrate $Pb(NO_3)_2$, copper nitrate $Cu(NO_3)_2.3H_2O$, cadmium nitrate $Cd(NO_3)_2.4H_2O$, magnesium nitrate $Mg(NO_3)_2.6H_2O$, potassium nitrate (KNO_3), calcium chloride ($CaCl_2$), (sigma-Aldrich). Dowex 50WX8, (20-50 mesh) from Fluka.

Area of study



Source: Dept. of Geog. BUK (2016)

Figure 1: Map showing the sampling point at Sagamu Town, Ogun State.

Description of Sampling Area

Sagamu has geographical coordinates between 6°50′ north; 3° 38′ east is located in south western region of Nigeria. The region has tropical wet and dry climate with a lengthy wet season and relatively constant temperatures throughout the course of the year. Wet season runs from March to October, November to December forms the region dry season. The vegetation type of the region is savannah which is really grassland with small bushes and occasional big trees. Grassland soils have substantially higher organic matter content than forest soils (Novackova, 2011).

Sample Collection

The Peatsoil samples were collected from four different sampling points (0-10cm depth) in Sagamu into polyethylene bag with plastic spoons. Samples were taken to the laboratory, extraneous materials were removed; the samples were air-dried, crushed and ground to a fine powder in a mortar passed through a 0.20mm sieve. The samples were kept for analysis.

Isolation and purification of humic acid from peat soil sample

Peatsoil sample (100g) was mixed with 1000 cm^3 of 0.1M NaOH solution, shaken for 3hours and left to stand overnight. Dark-coloured supernatant was obtained and decanted from solid residue. The dark-coloured supernatant was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 6 hours. Yellowish brown supernatant and dark-brown precipitate were obtained. The yellowish brown supernatant was decanted followed by centrifuge and discarded. The dark-brown precipitate was mixed with $500cm^3$of 0.1M NaOH solution followed by passing through dowex resin. The dark-brown solution was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 3 hours. The dark-brown precipitate was washed several times with deionized water. The supernatant was treated with $AgNO_3$ solution until no white precipitate observed. The humic acid was transferred to weighed crucible and dried at 60°C in an oven for 12 hours. The humic acid was cooled and dried in the desiccator, weighed and recorded. The obtained humic acid was dried again at 60°C for additional 6 hours cooled and dried in the desiccator, weighed and recorded constant weight was obtained (Baruah *et al*., 2015).

FT-IR analysis

FT-IR spectra of humic acid sample was analysed using Carry 630 FT-IR Agilent Technologies.

Unhydrolysed compost humic acid

The unhydrolysed humic acid was obtained after isolation and purification of compost humic acid and kept for investigation.

Acid hydrolysis of Peatsoil acid

Peatsoil humic acid sample (1g) was refluxed for 12 hours at (160°C) with $50cm^3$ of 6M HCl. The mixture was allowed to cool, decanted, and centrifuged after hydrolysis. The insoluble residues were washed with distilled water via centrifugation several times, and the supernatant was treated with $AgNO_3$ solution until no white precipitate was observed. The residue was thoroughly dried over $CaCl_2$ in a desiccator at room temperature (Chefetz *et al*., 2002). Finally, the obtained hydrolysed humic acid was kept for investigation.

Potentiometric Titrations

Potentiometric measurements were carried out using a pH-meter Jenway (model 3510) with combine electrode, the sensitivity of the pH - meter is 0.01 units. The pH meter was switched on half an hour before starting the titration for initial warm up of the instrument. The instrument was calibrated with an aqueous standard buffer solution of pH 4.00 and 10.0 (borate buffer) prepared from a "Qualigens" buffer tablets.

The following sets of solutions were prepared in a 250cm^3 volumetric flask separately for pH metric titrations.

(i) 5 cm^3 0.1 M HCl + 40 cm^3 deionized water

(ii) 5 cm^3 0.1 M HCl + 39 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid

(iii) 5 cm^3 0.1 M HCl + 37 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid + 2 cm^3 0.01 M Cu(II)

The solutions were titrated against standardized 0.110MNaOH separately. The total volume of each mixture was adjusted to 50 cm^3 and the ionic strength of the solutions was maintained constant at by adding appropriate amount of stock solution of 1M KNO_3 (Gamal, 2015; Omar and Ali, 2015). A magnetic stirrer was used to achieve thorough mixing of the interacting solutions at 550 rpm. The same set of experimental conditions was applied for potentiometric titration of remaining samples.

Evaluation of pKa of Hydrolysed peat soil Humic Acids

The proton-ligand formation number n_A were calculated by Irving and Rossotti expression (Omar and Ali, 2015).

$$nA = Y - \frac{(V2-V1)(No-Eo)}{(Vo+V1)TcL} \quad \text{……………………………}1$$

Where: Y is number of dissociable proton, (V_2-V_1) is the measure of displacement of the ligand curve relative to acid curve, N^o and E^o are the resultant concentration of alkali solution, free acid solution, $T_{cL}{}^o$ is the total ligand concentration, V^o is the total volume of titration solution,V_1 is the volume of alkali added to acid solution,V_2 is the volume of alkali added to acid solution + ligand solution, acid dissociation constants (pKa - values) of ligand were calculated by algebraic method point wise calculation (Tables 1). The dissociation constants (pKa) were calculated according to the following relation:

$$pKa = pH + \log(\frac{nA}{1-nA}) \quad \text{…………………………}2$$

Where: pKa is the acid dissociation constant, $n_A$is the Proton-ligand formation number and pH is the pH-values (Omar and Ali, 2015).

Determination of metal-ligand stability constants (log K) of complexes

The potentiometric measurement for the determination of stability constant of a complex in solution is based on the fact that the redox potential of the couple $\frac{M^{+(m-n)}}{M^{+m}}$ is shifted significantly on complexation of the metal ion with the ligand. This method involves change in hydrogen ion concentration [H$^+$] due to the displacement or association of one or more protons taking place during complexation reaction. This change can be found out by titrating the solutions containing free acid, acid with ligand, and acid with ligand and metal ion, individually against a standard alkali solution at a constant ionic strength or temperature. Either ionic strength or temperature may be varied for different sets of solutions. In all the cases, the change in the pH of the solution is measured after each addition of a known amount of alkali to the reaction cell which contains the reaction mixture. The titration curves are then drawn by plotting the measured pH values against the corresponding volume of alkali added and the stability constants of the complexes are determined from the titration curves by employing pH-metric titration technique given by (Irving and Rossoti).

Metal-ligand stability constants (Log K) were determined by using the following relations:

$$\bar{n} = \frac{(V_3 - V_2)(E^0 + N^0)}{(V^0 + V_2)\bar{n}_A T_m^0} \quad \text{…………………………………………………………………}3$$

and

$$PL = \log_{10}\{\frac{1+\beta_n^H \frac{1}{[anti\ \log pH]^n}}{T_L^0 - \bar{n}T_m^0} X \frac{(V^0+V_3)}{V^0}\} \quad \text{……………………………………………………}4$$

Where $T_{L,}$ T^o, E°, and V^ohavethe same significance as in equation (1) above, T_m denotes the total concentration of metal present in solution, V_3 is the volume of metal ions present in solution and β^H is the overall proton ligand stability constant. The metal-ligand stability constants (log K) were determined by employing point wise computational Method (eq. 5 and 6).

$$\text{LogK}_1 = \log\left(\frac{n}{1-n}\right) + \text{pL} \qquad \ldots\ldots\ldots\ldots.5$$

$$\text{LogK}_2 = \log\left(\frac{1-n}{2-n}\right) + \text{pL}\ldots\ldots\ldots\ldots\ldots\ldots\ldots.6$$

Where: Log K is the metal-ligand stability constant, pL is the Free ligand exponent function, **n** is the Average number of ligand attached with metal ion (Janrao*et al.*, 2014).The results obtained were analyzed by an ORIGIN 2016 program using titration data and then the proton-ligand stability constants (pKa) and Metal-ligand stability constant (LogK) calculated (Omar and Ali, 2015).

RESULTS AND DISCUSSION

Fourier transformed infrared (FT-IR) spectra of isolated humic acid from peat soils Figure 2 had distinct clear absorption bands indicating the presence of major humic acid structural elemental groups such as H bonded OH ($3680cm^{-1}$ peak), C=O of carbonyl ($1721cm^{-1}$ peak), functional groups of aliphatic components CH_2 ($2918cm^{-1}$ peak) and C-O stretching of polysaccharide ($1168cm^{-1}$ peak). The positions of the absorption bands of the spectra fell within typical major absorption bands of humic acid which is at frequencies 3680, 2918, 1721, 1168 cm^{-1}. The first peak centred in the vicinity of 3680 cm^{-1} region is attributed to phenol OH group bounded by intermolecular H bonds. The $2918cm^{-1}$ band usually has absorption maximum at 2918 cm^{-1} which is due to C–H stretching of alkane group (CH_2). The next major absorption band is 1721 cm^{-1}. This band has been commonly ascribed to C=O stretching of mainly carboxyl group (COOH) with trace amount of ketones. The last peak was observed at 1168 cm^{-1} due to C–O stretching of polysaccharides and this peak appeared also in the spectra of humic acid from peat soil. The FTIR spectra of the isolated humic acid contained all major characteristic absorption peaks of humic acid. These absorption peaks indicated the presence of the major structural elements of humic acid namely H bonded OH, C=C of aromatic ring, C=O of carbonyl group (both carboxyl and ketonic), CH_2 group. This strongly supports the presence of humic acid.

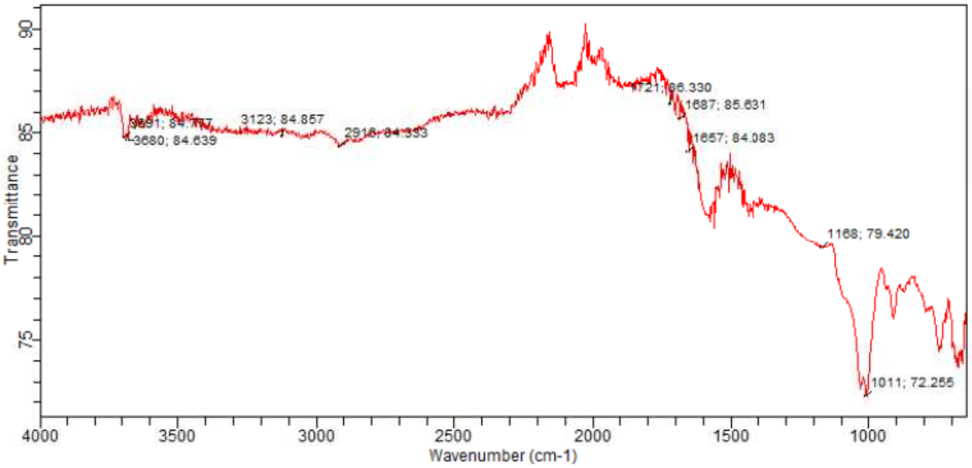


Fig. 2 : FT-IR spectraof peatsoilhumic acid (PSHA)

Evaluation of acid dissociation constant (pka) of acid hydrolysed peat soil humicacid at phenolic group

The value of the dissociation constant of the peat soil humic acid (PSHA) that underwent acidhydrolysis studied was found to be 8.9299 as shown Table 1, which is lower than the literaturevalues reported by Almeida and Szpoganics, (2015), Borges *et al.*, (2005); Badr *et al.*, (2012)and Fernandes *et al*,.(2009) of 9.73, 9.47 and 10.30. The difference between the obtained valuesand the reported values in this study might be probably as a result of acid hydrolysis of humicacid.

Table 1: PKa of (Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	V$_2$-V$_1$	nA	log($\frac{nA}{1-nA}$)	pKa
8.50	5.30	6.29	0.99	0.3594	-0.2510	8.2490
8.72	5.35	6.37	1.02	0.3400	-0.2880	8.4320
9.00	5.40	6.46	1.06	0.3141	-0.3391	8.6609
9.22	5.45	6.55	1.10	0.2882	-0.3927	8.8273
9.51	5.50	6.66	1.16	0.2494	-0.4786	9.0314
9.73	5.55	6.78	1.23	0.2041	-0.5910	9.1390
10.00	5.60	6.90	1.30	0.1589	-0.7238	9.2762
10.23	5.65	7.05	1.40	0.0941	-0.9835	9.2465
10.49	5.70	7.10	1.40	0.0941	-0.9835	9.5065

Average pKa = 8.9299 ± 0.4186

Table 2: PKa of (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	V$_2$-V$_1$	nA	Log($\frac{nA}{1-n}$)	pKa
8.50	5.30	5.81	0.51	0.6619	0.2919	8.7919
8.72	5.35	5.90	0.55	0.6357	0.2418	8.9618
9.00	5.40	6.00	0.60	0.6029	0.1813	9.1813
9.22	5.45	6.10	0.65	0.5701	0.1226	9.3426
9.51	5.50	6.20	0.70	0.5376	0.0654	9.5754
9.73	5.55	6.33	0.78	0.4851	-0.0259	9.7041
10.00	5.60	6.47	0.87	0.4262	-0.1291	9.8709
10.23	5.65	6.62	0.99	0.3609	-0.2481	9.9819
10.49	5.70	6.80	1.10	0.2759	-0.4690	10.0210

Average pKa = 9.4923± 0.4410

Metal-ligand stability constant (Log K)

The stabilityconstants require the accurate values of proton-ligand stability constants (Anil and Maroti, 2008). Metal titration curves crossed over ligand titration curve indicated the formation of complex upon proton release (Santosh, *et al.*, 2011). If the values of n- are within range 0.2-0.8 and 1.2-18 this indicates the formation of 1:1 and 1:2 complexes (Sayyed and Mazahar, 2012).

The metal (II)-humate stepwise stability constants (log k) at phenolic group (Tables 3-18)

Table 3: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	log($\frac{n}{1-n}$)	LogK$_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

LogK$_1$ (Average value) = 2.4788± 0.2203

Table 4: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	Log($\frac{n-1}{2-n}$)	LogK$_2$
9.51	5.50	6.66	6.73	0.07	1.3509	1.70	-0.2671	1.4329
9.73	5.55	6.78	6.85	0.07	1.6383	1.51	0.2467	1.7567
10.00	5.60	6.90	6.98	0.08	2.1783	1.31	-0.2158	1.0942
10.23	5.65	7.05	7.13	0.08	4.1904	1.27		
10.49	5.70	7.10	7.19	0.09	4.6920			

LogK$_2$(Average value) = 1.4280 ± 0.3312

Table 5:Point-wise method,Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	$\text{Log}(\frac{n}{n-1})$	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430

LogK_1 **(Average value)** = 2.3059± 0.6153

Table 6:Point-wise method, Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$V_3\text{-}V_2$	n	pL	$\text{Log}(\frac{n-1}{2-n})$	Log K_2
9.73	5.55	6.33	6.42	0.09	0.9000	1.69		
10.00	5.60	6.47	6.58	0.11	1.2578	1.44	-0.4592	0.9808
10.23	5.65	6.62	6.84	0.12	1.6137	1.26	-0.2010	1.4610
10.49	5.70	6.80	6.92	0.12	2.1052	1.03		

LogK_2 **(Average value)** = 1.2209± 0.3398

Table 7:Point-wise method,Pb (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	$\log(\frac{n}{1-n})$	LogK_1
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.60	0.05	0.8333	1.96	0.6989	2.6589

LogK_1 (Average value) = 2.5832 ±0.1614

Table 8:Point-wise method,Pb-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	$\log(\frac{n-1}{2-n})$	logK_2
9.51	5.50	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.83	0.05	1.1702	1.44		
10.00	5.60	6.90	6.90	0.05	1.4864	1.22	-0.0237	1.1963
10.23	5.65	7.05	7.10	0.05	2.0190	1.09		
10.49	5.70	7.10	7.17	0.07	3.6492	1.00		

LogK_2(Average value) = 1.1963

Table 9:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$V_3\text{-}V_2$	n	pL	Log $(\frac{n}{n-1})$	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.5477	2.3123
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	0.0272	2.2072
9.51	5.50	6.20	6.26	0.07	0.6417	1.89	0.2530	2.1430
9.73	5.55	6.40	6.40	0.07	0.7000	1.67	0.3680	2.0380

LogK_1 **(Average value)** = 2.2364 ± 0.1602

Table 10:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$V_3\text{-}V_2$	n	pL	$\text{Log}(\frac{n-1}{2-n})$	Log K_2
10.00	5.60	6.47	6.55	0.08	1.9503	1.41		
10.23	5.65	6.62	6.72	0.11	1.4792	1.26	-0.0361	1.2239

LogK_2 **(Average value)** = 1.2239

Table 11:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	$\log(\frac{n}{n-1})$	LogK_1
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4290	2.2110
8.72	5.35	6.37	6.39	0.02	0.2858	2.42	-0.3978	2.0222
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

LogK_1 (Average value)=2.1382**±**0.1046

Table 12:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$\log(\frac{n-1}{2-n})$	$LogK_2$
9.51	5.55	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.84	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.93	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.10		
10.49	5.70	7.10	7.18	0.07	3.6492	0.83		

$LogK_2$(Average value) = 1.5453 **±** 0.3450

Table 13:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$Log(\frac{n}{n-1})$	$Log\ K_1$
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.3477	2.3123
9.00	5.40	6.00	6.04	0.04	0.3236	2.38	-0.3202	2.0598
9.22	5.45	6.10	6.15	0.05	0.4297	2.17	-0.1230	2.0470
9.51	5.50	6.20	6.26	0.06	0.5500	1.89	0.0871	1.9771
9.73	5.55	6.33	6.40	0.07	0.7000	1.67	0.3680	2.0380

$LogK_1$ **(Average value)** = 2.1568 ± 0.2069

Table 14:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$Log(\frac{n-1}{2-n})$	$Log\ K_2$
10.00	5.60	6.47	6.55	0.08	0.9148	1.41		
10.23	5.65	6.62	6.71	0.09	1.2102	1.20	-0.5749	0.6251
10.49	5.70	6.80	6.92	0.09	1.5968	1.03	0.1703	1.2003

$LogK_2$ **(Average value)** = 0.9127± 0.4070

Table15:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$Log(\frac{n}{1-n})$	$LogK_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4210	2.2190
8.72	5.35	6.37	6.40	0.03	0.4286	2.42	-0.1249	2.2951
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.96	0.3010	2.2610
9.51	5.55	6.66	6.70	0.04	0.7720	1.67	0.5297	2.1997

$LogK_1$ (Average value) = 2.2108± 0.0825

Table 16:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$Log(\frac{n-1}{2-n})$	$Log\ K_2$
9.73	5.55	6.78	6.83	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.95	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.09		
10.49	5.70	7.10	7.16	0.06	3.1429	0.89		

$LogK_2$ **(Average value)** = 1.5453± 0.3450

Table 17:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$Log(\frac{n}{n-1})$	$Log\ K_1$
8.50	5.30	5.81	5.86	0.05	0.3717	2.88	-0.2280	2.6520
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.06	0.06	0.4853	2.38	-0.0255	2.3545
9.22	5.45	6.10	6.16	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430
9.73	5.55	6.33	6.41	0.08	0.8000	1.69	0.6020	2.2920

$LogK_1$ **(Average value)** = 2.2516± 0.5380

Table 18:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$\text{Log}(\frac{n-1}{2-n})$	Log K_2
10.00	5.60	6.47	6.57	0.10	1.1434	1.43		
10.23	5.65	6.62	6.72	0.10	1.3448	1.23	-0.2788	0.9512
10.49	5.70	6.80	6.90	0.10	1.7742	1.03	0.5351	1.5651

LogK_2 **(Average value)** = 1.2581± 0.4340

Table 19: Stepwise and overall Stability constants of thehydrolysed and unhydrolysed divalent metal (II) complexes

Chelates	**LogK_1**	**LogK_2**	**Logβ**
[Cu (Hydrolysed PSHA-1)$_2$]	2.4788	1.4280	3.9068
[Pb (Hydrolysed PSHA-1)$_2$]	2.5832	1.1963	3.7795
[Cd (Hydrolysed PSHA-1)$_2$]	2.2108	1.5453	3.7561
[Mg (Hydrolysed PSHA-1)$_2$]	2.1382	1.5453	3.6835
[Cu (Unhydrolysed PSHA-1)$_2$]	2.3059	1.2209	3.5268
[Pb (Unhydrolysed PSHA-1)$_2$]	2.2364	1.2239	3.4603
[Cd (Unhydrolysed PSHA-1)$_2$]	2.2516	1.2581	3.5097
[Mg (Unydrolysed PSHA-1)$_2$]	2.1568	0.9127	3.0695

The results obtained (Table19) shows the stepwise and overall stability constants to be not high indicating low stability of the complexes, because the solubility of most metal ions in the basic pH range is minimal due to metal hydroxide precipitation (Karimi, 2017). In general, the stepwise stability constants (K_1 and K_2) follow the order $K_1 > K_2$ for the copper, lead, magnesium and cadmium complexes respectively. The steady decrease of the values with increasing number of ligands is in agreement with the prediction made by researchers (Na'aliya, 2013). The decrease could be attributed to the fact that as the number of the ligands (Humate ions) that enters the coordination zone increases the aqua molecules available for replacement by the ligands become less. Thus, the metal ions become less electron loving with progressive intake of the ligand and this results in the decrease in the values of the constants (Na'aliya, 2013). Also the stability of the complexes is influenced by the size and number of the chelate rings(Mackay and Mackay,2002).All the complexes form rings in their structure as humate, a bidentate ligand, bond the metal ions in the ratio 1:2 (Boguta and Sokolowska, 2016) forming chelate rings. The values of the overall stability constants (logβ) obtained for humate complexes are not high indicating low stability as the values are not high. LogK values for copper-humates (Table 3 to 6) obtained in this study are lower than those reported for the complexes of humic acids (Pandey *et al.*, 2015; Dinu, 2013; Kaschl *et al.*, 2010 and Gilbeto and Jorg, 2001). The values of LogK(Table 7 to 10) forlead-humates are lower than those reported for the lead in the literature (Dinu, 2013; Gilbeto and Jorg 2001). Log K values(Table 11 to 14) for magnesium-humates obtained in this study are close to those reported by (Pandey *et al.*, 2015). Log K values of cadmium-humates (Table 15 to 18) obtained in this work near to the one reported by (Dinu, 2013 and Pandey *et al.*, 2015).The difference between the reported values and the values obtained in this study might be probably as a result of acid hydrolysis of humic acid. The values of the overall stability constants (log β) of the copper humates complexes presented in Table 19 is high than that of other metal humate complexes, show relatively high stability of Cu-HA complexes, show the following order of stability: Cu >Pb> Cd > Mg; which are in close agreement to the findings of (Dinu, 2013 and Pandey *et al.*, 2015).The high stability of Cu-humate chelate could be attributed to the existence of coordinate covalent bond between the complexing agents and the Cu^{2+} ions. Since, Cu^{2+} being a metal of the transitional series with $3d^9$ electronic configurations can accept the electrons from the complexing agents. Similarly,the low stabilities of Pb,Cd and Mg - complexes could be explained by that Pb^{2+} with $6s^2$, Cd^{2+} with $4d^{10}$ and Mg^{2+} with $2p^6$ their electronic configuration has a completely filled d,p and s orbitals. Moreover, the stabilities of metal ions with hydrolysed humic acid from peat soil were higher than those with unhydrolysed humic acid from peat soil; which is ascribed to the high content of acidity in hydrolysed humic acid than unhydrolysed humic acid.

CONCLUSION

The values of logK for Cu(II) hydrolysed humic acid complex was higher followed by Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes as compared with metal(II) unhydrolysed humic acid complexes . This indicates acid hydrolysis of humic acid can enhance the complexation behavior of humic acid with metal (II) ions. However, the higher values of logβ for Cu(II), Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes indicates more stable stepwise complexes formed as compared with Cu(II), Pb(II), Cd(II) and Mg(II) unhydrolysed humic acid complexes.

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STABILITY CONSTANTS OF COMPLEXES OF METAL IONS WITH PEATSOIL HUMIC ACIDS UNDER NON-ACID-CONDITIONS

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ABSTRACT

Stability constants of complexes of four divalent metal ions viz. Cu^{2+}, Pb^{2+},Mg^{2+} and Cd^{2+} with humic acids (HA) were determined by potentiometric titration of humic acids with the corresponding salt of the divalent metals in aqueous media under non-acid-condition. The log K (logarithm of the stability constant) ranged from 1.0942 to 2.7471 for metal-humic acid complexes were determined using point-wise computational method. The order of stability constants were obtained as follows: Cu >Pb> Cd > Mg for metal -HA complexes respectively, indicating a higher degree of complexation with Cu metal ion.

Keywords: stability constant, humic acid, potentiometric titration, divalent metals, acid hydrolysis.

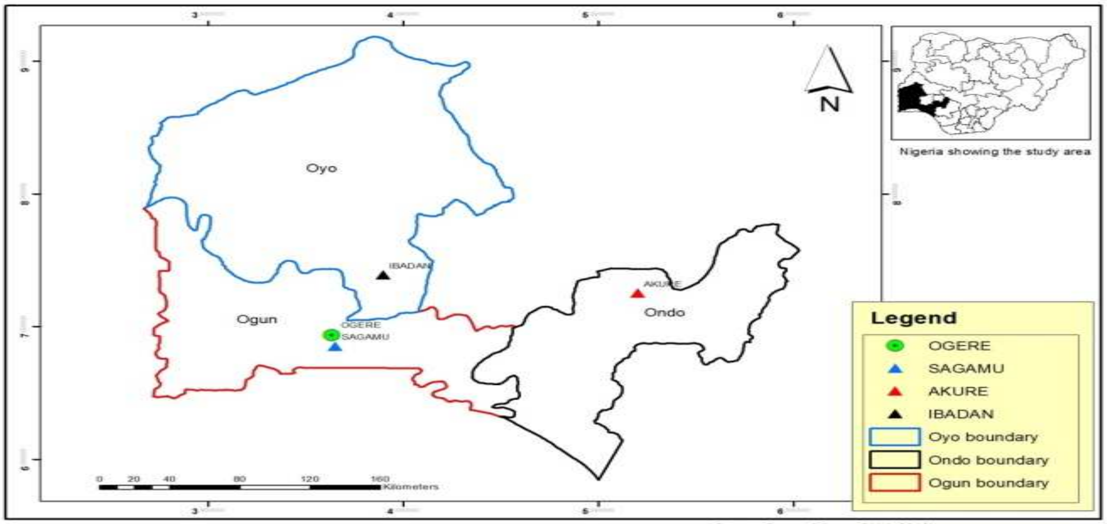
NTRODUCTION

The stability constant of a complex is the numerical expression of its stability and provides a quantitative measure of affinity of the metal ion to the complexing agent. An understanding of the relative stability of metal-complexes helps in predicting the behavior of metal ions in the soil (Ram and Raman, 1982). Extensive researches has been done to determine the stability constants of the complexes formed between humic acid (HA) with a number of metal ions. Ashok *et al.*, (2000) reported that humic acid with hydroxyl, phenoxyl and carboxyl reactive groups can form coordination compound with metal ions at pH 3.5. The stability constants(Log K) for different metal-humic acid complexes indicated the following order of the stabilities of complexes formed between humic acid and metal ion, Cu >Fe >Pb> Ni > Co > Ca > Cd > Zn >Mn> Mg. Andelkovic *et al.*, (2010) investigated the binding of Cd(II) to soil humic acid at pH 6.5 and in 0.1M KNO_3 ionic medium. The stability constant for binding indicating greater stability in the case when carboxyl groups are involved in complexation reaction. Kostic *et al.*,(2012) investigated the complexation of humic acid with certain heavy metal ions (Co(II), Ni(II),Cu(II), Zn(II), and Pb(II). The experiment was performed at 25°C, at pH 4.0 and ionic strength of 0.01M. Stability constant of complex between Pb(II) ions and humic acid is greater than stability constants of other investigated metal-humate complexes. Bogata and Sokolowska (2016) analyses the interaction between humic acids from different soils and Zn (II) ions at wide concentration ranges and at pH 5. Studies have showed significant impact of Zn concentration, pH and some properties of humic acids with zinc.But all of these studies were limited to acidic pH range. Therefore, the present study was carried out to determine and compare the stability constants of complexes of metal ions with hydrolysed peat soil humic acid and unhydrolysed peat soil humic under non-acid conditions.

MATERIALS AND METHODS

Analytical grade chemicals used includes hydrochloric acid (HCl), nitric acid (HNO_3), sodium hydroxide (NaOH), lead nitrate $Pb(NO_3)_2$, copper nitrate $Cu(NO_3)_2.3H_2O$, cadmium nitrate $Cd(NO_3)_2.4H_2O$, magnesium nitrate $Mg(NO_3)_2.6H_2O$, potassium nitrate (KNO_3), calcium chloride ($CaCl_2$), (sigma-Aldrich). Dowex 50WX8, (20-50 mesh) from Fluka.

Area of study



Source: Dept. of Geog. BUK (2016)

Figure 1: Map showing the sampling point at Sagamu Town, Ogun State.

Description of Sampling Area

Sagamu has geographical coordinates between 6°50′ north; 3° 38′ east is located in south western region of Nigeria. The region has tropical wet and dry climate with a lengthy wet season and relatively constant temperatures throughout the course of the year. Wet season runs from March to October, November to December forms the region dry season. The vegetation type of the region is savannah which is really grassland with small bushes and occasional big trees. Grassland soils have substantially higher organic matter content than forest soils (Novackova, 2011).

Sample Collection

The Peatsoil samples were collected from four different sampling points (0-10cm depth) in Sagamu into polyethylene bag with plastic spoons. Samples were taken to the laboratory, extraneous materials were removed; the samples were air-dried, crushed and ground to a fine powder in a mortar passed through a 0.20mm sieve. The samples were kept for analysis.

Isolation and purification of humic acid from peat soil sample

Peatsoil sample (100g) was mixed with 1000 cm^3 of 0.1M NaOH solution, shaken for 3hours and left to stand overnight. Dark-coloured supernatant was obtained and decanted from solid residue. The dark-coloured supernatant was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 6 hours. Yellowish brown supernatant and dark-brown precipitate were obtained. The yellowish brown supernatant was decanted followed by centrifuge and discarded. The dark-brown precipitate was mixed with 500$cm^3$of 0.1M NaOH solution followed by passing through dowex resin. The dark-brown solution was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 3 hours. The dark-brown precipitate was washed several times with deionized water. The supernatant was treated with $AgNO_3$ solution until no white precipitate observed. The humic acid was transferred to weighed crucible and dried at 60°C in an oven for 12 hours. The humic acid was cooled and dried in the desiccator, weighed and recorded. The obtained humic acid was dried again at 60°C for additional 6 hours cooled and dried in the desiccator, weighed and recorded constant weight was obtained (Baruah *et al.*, 2015).

FT-IR analysis

FT-IR spectra of humic acid sample was analysed using Carry 630 FT-IR Agilent Technologies.

Unhydrolysed compost humic acid

The unhydrolysed humic acid was obtained after isolation and purification of compost humic acid and kept for investigation.

Acid hydrolysis of Peatsoil acid

Peatsoil humic acid sample (1g) was refluxed for 12 hours at (160°C) with 50cm^3 of 6M HCl. The mixture was allowed to cool, decanted, and centrifuged after hydrolysis. The insoluble residues were washed with distilled water via centrifugation several times, and the supernatant was treated with $AgNO_3$ solution until no white precipitate was observed. The residue was thoroughly dried over $CaCl_2$ in a desiccator at room temperature (Chefetz *et al.*, 2002). Finally, the obtained hydrolysed humic acid was kept for investigation.

Potentiometric Titrations

Potentiometric measurements were carried out using a pH-meter Jenway (model 3510) with combine electrode, the sensitivity of the pH - meter is 0.01 units. The pH meter was switched on half an hour before starting the titration for initial warm up of the instrument. The instrument was calibrated with an aqueous standard buffer solution of pH 4.00 and 10.0 (borate buffer) prepared from a "Qualigens" buffer tablets.

The following sets of solutions were prepared in a 250cm^3 volumetric flask separately for pH metric titrations.

(i) 5 cm^3 0.1 M HCl + 40 cm^3 deionized water

(ii) 5 cm^3 0.1 M HCl + 39 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid

(iii) 5 cm^3 0.1 M HCl + 37 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid + 2 cm^3 0.01 M Cu(II)

The solutions were titrated against standardized 0.110MNaOH separately. The total volume of each mixture was adjusted to 50 cm^3 and the ionic strength of the solutions was maintained constant at by adding appropriate amount of stock solution of 1M KNO_3 (Gamal, 2015; Omar and Ali, 2015). A magnetic stirrer was used to achieve thorough mixing of the interacting solutions at 550 rpm. The same set of experimental conditions was applied for potentiometric titration of remaining samples.

Evaluation of pKa of Hydrolysed peat soil Humic Acids

The proton-ligand formation number $n_{\mathbf{A}}$ were calculated by Irving and Rossotti expression (Omar and Ali, 2015).

$$nA = Y - \frac{(V2-V1)(No-Eo)}{(Vo+V1)TcL} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 1$$

Where: Y is number of dissociable proton, (V_2-V_1) is the measure of displacement of the ligand curve relative to acid curve, N^o and E^o are the resultant concentration of alkali solution, free acid solution, $T_{cL}{}^o$ is the total ligand concentration, V^o is the total volume of titration solution,V_1 is the volume of alkali added to acid solution,V_2 is the volume of alkali added to acid solution + ligand solution, acid dissociation constants (pKa - values) of ligand were calculated by algebraic method point wise calculation (Tables 1). The dissociation constants (pKa) were calculated according to the following relation:

$$pKa = pH + \log(\frac{nA}{1-nA}) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 2$$

Where: pKa is the acid dissociation constant, $n_A$is the Proton-ligand formation number and pH is the pH-values (Omar and Ali, 2015).

Determination of metal-ligand stability constants (log K) of complexes

The potentiometric measurement for the determination of stability constant of a complex in solution is based on the fact that the redox potential of the couple $\frac{M^{+(m-n)}}{M^{+m}}$ is shifted significantly on complexation of the metal ion with the ligand. This method involves change in hydrogen ion concentration [H^+] due to the displacement or association of one or more protons taking place during complexation reaction. This change can be found out by titrating the solutions containing free acid, acid with ligand, and acid with ligand and metal ion, individually against a standard alkali solution at a constant ionic strength or temperature. Either ionic strength or temperature may be varied for different sets of solutions. In all the cases, the change in the pH of the solution is measured after each addition of a known amount of alkali to the reaction cell which contains the reaction mixture. The titration curves are then drawn by plotting the measured pH values against the corresponding volume of alkali added and the stability constants of the complexes are determined from the titration curves by employing pH-metric titration technique given by (Irving and Rossoti).

Metal-ligand stability constants (Log K) were determined by using the following relations:

$$\bar{n} = \frac{(V_3 - V_2)(E^0 + N^0)}{(V^0 + V_2)\bar{n}_A T_m^0} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 3$$

and

$$PL = \log_{10}\{\frac{1+\beta_n^H \dfrac{1}{[anti\ \log pH]^n}}{T_L^0 - \bar{n}T_m^0} X \frac{(V^0+V_3)}{V^0}\} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 4$$

Where $T_{L,}$ T^o, E°, and V^ohavethe same significance as in equation (1) above, T_m denotes the total concentration of metal present in solution, V_3 is the volume of metal ions present in solution and β^H is the overall proton ligand stability constant. The metal-ligand stability constants (log K) were determined by employing point wise computational Method (eq. 5 and 6).

$\text{LogK}_1 = \log \left(\frac{n}{1-n}\right) + \text{pL}$ 5

$\text{LogK}_2 = \log \left(\frac{1-n}{2-n}\right) + \text{pL}$.......................6

Where: Log K is the metal-ligand stability constant, pL is the Free ligand exponent function, **n** is the Average number of ligand attached with metal ion (Janrao*et al*., 2014).The results obtained were analyzed by an ORIGIN 2016 program using titration data and then the proton-ligand stability constants (pKa) and Metal-ligand stability constant (LogK) calculated (Omar and Ali, 2015).

RESULTS AND DISCUSSION

Fourier transformed infrared (FT-IR) spectra of isolated humic acid from peat soils Figure 2 had distinct clear absorption bands indicating the presence of major humic acid structural elemental groups such as H bonded OH ($3680cm^{-1}$ peak), C=O of carbonyl ($1721cm^{-1}$ peak), functional groups of aliphatic components CH_2 ($2918cm^{-1}$ peak) and C-O stretching of polysaccharide ($1168cm^{-1}$ peak). The positions of the absorption bands of the spectra fell within typical major absorption bands of humic acid which is at frequencies 3680, 2918, 1721, 1168 cm^{-1}. The first peak centred in the vicinity of 3680 cm^{-1} region is attributed to phenol OH group bounded by intermolecular H bonds. The $2918cm^{-1}$ band usually has absorption maximum at 2918 cm^{-1} which is due to C–H stretching of alkane group (CH_2). The next major absorption band is 1721 cm^{-1}. This band has been commonly ascribed to C=O stretching of mainly carboxyl group (COOH) with trace amount of ketones. The last peak was observed at 1168 cm^{-1} due to C–O stretching of polysaccharides and this peak appeared also in the spectra of humic acid from peat soil. The FTIR spectra of the isolated humic acid contained all major characteristic absorption peaks of humic acid. These absorption peaks indicated the presence of the major structural elements of humic acid namely H bonded OH, C=C of aromatic ring, C=O of carbonyl group (both carboxyl and ketonic), CH_2 group. This strongly supports the presence of humic acid.

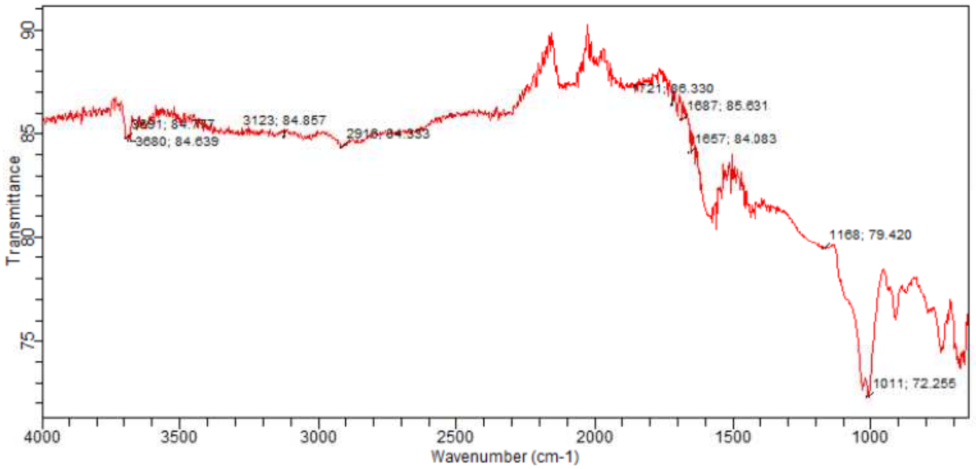


Fig. 2 : FT-IR spectraof peatsoilhumic acid (PSHA)

Evaluation of acid dissociation constant (pka) of acid hydrolysed peat soil humicacid at phenolic group

The value of the dissociation constant of the peat soil humic acid (PSHA) that underwent acidhydrolysis studied was found to be 8.9299 as shown Table 1, which is lower than the literaturevalues reported by Almeida and Szpoganics, (2015), Borges *et al*., (2005); Badr *et al*., (2012)and Fernandes *et al*,.(2009) of 9.73, 9.47 and 10.30. The difference between the obtained valuesand the reported values in this study might be probably as a result of acid hydrolysis of humicacid.

Table 1: PKa of (Hydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	$\log(\frac{nA}{1-nA})$	pKa
8.50	5.30	6.29	0.99	0.3594	-0.2510	8.2490
8.72	5.35	6.37	1.02	0.3400	-0.2880	8.4320
9.00	5.40	6.46	1.06	0.3141	-0.3391	8.6609
9.22	5.45	6.55	1.10	0.2882	-0.3927	8.8273
9.51	5.50	6.66	1.16	0.2494	-0.4786	9.0314
9.73	5.55	6.78	1.23	0.2041	-0.5910	9.1390
10.00	5.60	6.90	1.30	0.1589	-0.7238	9.2762
10.23	5.65	7.05	1.40	0.0941	-0.9835	9.2465
10.49	5.70	7.10	1.40	0.0941	-0.9835	9.5065

Average pKa = 8.9299 ± 0.4186

Table 2: PKa of (Unhydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	$\text{Log}(\frac{nA}{1-n})$	pKa
8.50	5.30	5.81	0.51	0.6619	0.2919	8.7919
8.72	5.35	5.90	0.55	0.6357	0.2418	8.9618
9.00	5.40	6.00	0.60	0.6029	0.1813	9.1813
9.22	5.45	6.10	0.65	0.5701	0.1226	9.3426
9.51	5.50	6.20	0.70	0.5376	0.0654	9.5754
9.73	5.55	6.33	0.78	0.4851	-0.0259	9.7041
10.00	5.60	6.47	0.87	0.4262	-0.1291	9.8709
10.23	5.65	6.62	0.99	0.3609	-0.2481	9.9819
10.49	5.70	6.80	1.10	0.2759	-0.4690	10.0210

Average pKa = 9.4923± 0.4410

Metal-ligand stability constant (Log K)

The stabilityconstants require the accurate values of proton-ligand stability constants (Anil and Maroti, 2008). Metal titration curves crossed over ligand titration curve indicated the formation of complex upon proton release (Santosh, *et al.*, 2011). If the values of n- are within range 0.2-0.8 and 1.2-18 this indicates the formation of 1:1 and 1:2 complexes (Sayyed and Mazahar, 2012).

The metal (II)-humate stepwise stability constants (log k) at phenolic group (Tables 3-18)

Table 3: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$\log(\frac{n}{1-n})$	LogK_1
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

LogK_1 (Average value) = 2.4788± 0.2203

Table 4: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$\text{Log}(\frac{n-1}{2-n})$	LogK_2
9.51	5.50	6.66	6.73	0.07	1.3509	1.70	-0.2671	1.4329
9.73	5.55	6.78	6.85	0.07	1.6383	1.51	0.2467	1.7567
10.00	5.60	6.90	6.98	0.08	2.1783	1.31	-0.2158	1.0942
10.23	5.65	7.05	7.13	0.08	4.1904	1.27		
10.49	5.70	7.10	7.19	0.09	4.6920			

LogK_2(Average value) = 1.4280 ± 0.3312

Table 5:Point-wise method,Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	Log($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430

$LogK_1$ **(Average value)** = 2.3059± 0.6153

Table 6:Point-wise method, Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
9.73	5.55	6.33	6.42	0.09	0.9000	1.69		
10.00	5.60	6.47	6.58	0.11	1.2578	1.44	-0.4592	0.9808
10.23	5.65	6.62	6.84	0.12	1.6137	1.26	-0.2010	1.4610
10.49	5.70	6.80	6.92	0.12	2.1052	1.03		

$LogK_2$ **(Average value)** = 1.2209± 0.3398

Table 7:Point-wise method,Pb (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n}{1-n}$)	$LogK_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.60	0.05	0.8333	1.96	0.6989	2.6589

$LogK_1$ (Average value) = 2.5832 ±0.1614

Table 8:Point-wise method,Pb-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n-1}{2-n}$)	$logK_2$
9.51	5.50	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.83	0.05	1.1702	1.44		
10.00	5.60	6.90	6.90	0.05	1.4864	1.22	-0.0237	1.1963
10.23	5.65	7.05	7.10	0.05	2.0190	1.09		
10.49	5.70	7.10	7.17	0.07	3.6492	1.00		

$LogK_2$(Average value) = 1.1963

Table 9:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log ($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.5477	2.3123
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	0.0272	2.2072
9.51	5.50	6.20	6.26	0.07	0.6417	1.89	0.2530	2.1430
9.73	5.55	6.40	6.40	0.07	0.7000	1.67	0.3680	2.0380

$LogK_1$ **(Average value)** = 2.2364 ± 0.1602

Table 10:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
10.00	5.60	6.47	6.55	0.08	1.9503	1.41		
10.23	5.65	6.62	6.72	0.11	1.4792	1.26	-0.0361	1.2239

$LogK_2$ **(Average value)** = 1.2239

Table 11:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n}{n-1}$)	$LogK_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4290	2.2110
8.72	5.35	6.37	6.39	0.02	0.2858	2.42	-0.3978	2.0222
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

$LogK_1$ (Average value)=2.1382**±**0.1046

Table 12:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n-1}{2-n}$)	$LogK_2$
9.51	5.55	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.84	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.93	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.10		
10.49	5.70	7.10	7.18	0.07	3.6492	0.83		

$LogK_2$(Average value) = 1.5453 **±** 0.3450

Table 13:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.3477	2.3123
9.00	5.40	6.00	6.04	0.04	0.3236	2.38	-0.3202	2.0598
9.22	5.45	6.10	6.15	0.05	0.4297	2.17	-0.1230	2.0470
9.51	5.50	6.20	6.26	0.06	0.5500	1.89	0.0871	1.9771
9.73	5.55	6.33	6.40	0.07	0.7000	1.67	0.3680	2.0380

$LogK_1$ **(Average value)** = 2.1568 ± 0.2069

Table 14:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
10.00	5.60	6.47	6.55	0.08	0.9148	1.41		
10.23	5.65	6.62	6.71	0.09	1.2102	1.20	-0.5749	0.6251
10.49	5.70	6.80	6.92	0.09	1.5968	1.03	0.1703	1.2003

$LogK_2$ **(Average value)** = 0.9127± 0.4070

Table15:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	Log($\frac{n}{1-n}$)	$LogK_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4210	2.2190
8.72	5.35	6.37	6.40	0.03	0.4286	2.42	-0.1249	2.2951
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.96	0.3010	2.2610
9.51	5.55	6.66	6.70	0.04	0.7720	1.67	0.5297	2.1997

$LogK_1$ (Average value) = 2.2108± 0.0825

Table 16:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
9.73	5.55	6.78	6.83	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.95	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.09		
10.49	5.70	7.10	7.16	0.06	3.1429	0.89		

$LogK_2$ **(Average value)** = 1.5453± 0.3450

Table 17:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.86	0.05	0.3717	2.88	-0.2280	2.6520
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.06	0.06	0.4853	2.38	-0.0255	2.3545
9.22	5.45	6.10	6.16	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430
9.73	5.55	6.33	6.41	0.08	0.8000	1.69	0.6020	2.2920

$LogK_1$ **(Average value)** = 2.2516± 0.5380

Table 18:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$\mathrm{Log}(\frac{n-1}{2-n})$	Log K_2
10.00	5.60	6.47	6.57	0.10	1.1434	1.43		
10.23	5.65	6.62	6.72	0.10	1.3448	1.23	-0.2788	0.9512
10.49	5.70	6.80	6.90	0.10	1.7742	1.03	0.5351	1.5651

LogK_2 **(Average value)** = 1.2581± 0.4340

Table 19: Stepwise and overall Stability constants of thehydrolysed and unhydrolysed divalent metal (II) complexes

Chelates	**LogK_1**	**LogK_2**	**Logβ**
[Cu (Hydrolysed PSHA-1)$_2$]	2.4788	1.4280	3.9068
[Pb (Hydrolysed PSHA-1)$_2$]	2.5832	1.1963	3.7795
[Cd (Hydrolysed PSHA-1)$_2$]	2.2108	1.5453	3.7561
[Mg (Hydrolysed PSHA-1)$_2$]	2.1382	1.5453	3.6835
[Cu (Unhydrolysed PSHA-1)$_2$]	2.3059	1.2209	3.5268
[Pb (Unhydrolysed PSHA-1)$_2$]	2.2364	1.2239	3.4603
[Cd (Unhydrolysed PSHA-1)$_2$]	2.2516	1.2581	3.5097
[Mg (Unydrolysed PSHA-1)$_2$]	2.1568	0.9127	3.0695

The results obtained (Table19) shows the stepwise and overall stability constants to be not high indicating low stability of the complexes, because the solubility of most metal ions in the basic pH range is minimal due to metal hydroxide precipitation (Karimi, 2017). In general, the stepwise stability constants (K_1 and K_2) follow the order $K_1 > K_2$ for the copper, lead, magnesium and cadmium complexes respectively. The steady decrease of the values with increasing number of ligands is in agreement with the prediction made by researchers (Na'aliya, 2013). The decrease could be attributed to the fact that as the number of the ligands (Humate ions) that enters the coordination zone increases the aqua molecules available for replacement by the ligands become less. Thus, the metal ions become less electron loving with progressive intake of the ligand and this results in the decrease in the values of the constants (Na'aliya, 2013). Also the stability of the complexes is influenced by the size and number of the chelate rings(Mackay and Mackay,2002).All the complexes form rings in their structure as humate, a bidentate ligand, bond the metal ions in the ratio 1:2 (Boguta and Sokolowska, 2016) forming chelate rings. The values of the overall stability constants (logβ) obtained for humate complexes are not high indicating low stability as the values are not high. LogK values for copper-humates (Table 3 to 6) obtained in this study are lower than those reported for the complexes of humic acids (Pandey *et al.*, 2015; Dinu, 2013; Kaschl *et al.*, 2010 and Gilbeto and Jorg, 2001). The values of LogK(Table 7 to 10) forlead-humates are lower than those reported for the lead in the literature (Dinu, 2013; Gilbeto and Jorg 2001). Log K values(Table 11 to 14) for magnesium-humates obtained in this study are close to those reported by (Pandey *et al.*, 2015). Log K values of cadmium-humates (Table 15 to 18) obtained in this work near to the one reported by (Dinu, 2013 and Pandey *et al.*, 2015).The difference between the reported values and the values obtained in this study might be probably as a result of acid hydrolysis of humic acid. The values of the overall stability constants (log β) of the copper humates complexes presented in Table 19 is high than that of other metal humate complexes, show relatively high stability of Cu-HA complexes, show the following order of stability: Cu >Pb> Cd > Mg; which are in close agreement to the findings of (Dinu, 2013 and Pandey *et al.*, 2015).The high stability of Cu-humate chelate could be attributed to the existence of coordinate covalent bond between the complexing agents and the Cu^{2+} ions. Since, Cu^{2+} being a metal of the transitional series with $3d^9$ electronic configurations can accept the electrons from the complexing agents. Similarly,the low stabilities of Pb,Cd and Mg -complexes could be explained by that Pb^{2+} with $6s^2$, Cd^{2+} with $4d^{10}$ and Mg^{2+} with $2p^6$ their electronic configuration has a completely filled d,p and s orbitals. Moreover, the stabilities of metal ions with hydrolysed humic acid from peat soil were higher than those with unhydrolysed humic acid from peat soil; which is ascribed to the high content of acidity in hydrolysed humic acid than unhydrolysed humic acid.

CONCLUSION

The values of logK for Cu(II) hydrolysed humic acid complex was higher followed by Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes as compared with metal(II) unhydrolysed humic acid complexes . This indicates acid hydrolysis of humic acid can enhance the complexation behavior of humic acid with metal (II) ions. However, the higher values of logβ for Cu(II), Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes indicates more stable stepwise complexes formed as compared with Cu(II), Pb(II), Cd(II) and Mg(II) unhydrolysed humic acid complexes.

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STABILITY CONSTANTS OF COMPLEXES OF METAL IONS WITH PEATSOIL HUMIC ACIDS UNDER NON-ACID-CONDITIONS

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ABSTRACT

Stability constants of complexes of four divalent metal ions viz. Cu^{2+}, Pb^{2+},Mg^{2+} and Cd^{2+} with humic acids (HA) were determined by potentiometric titration of humic acids with the corresponding salt of the divalent metals in aqueous media under non-acid-condition. The log K (logarithm of the stability constant) ranged from 1.0942 to 2.7471 for metal-humic acid complexes were determined using point-wise computational method. The order of stability constants were obtained as follows: Cu >Pb> Cd > Mg for metal -HA complexes respectively, indicating a higher degree of complexation with Cu metal ion.

Keywords: stability constant, humic acid, potentiometric titration, divalent metals, acid hydrolysis.

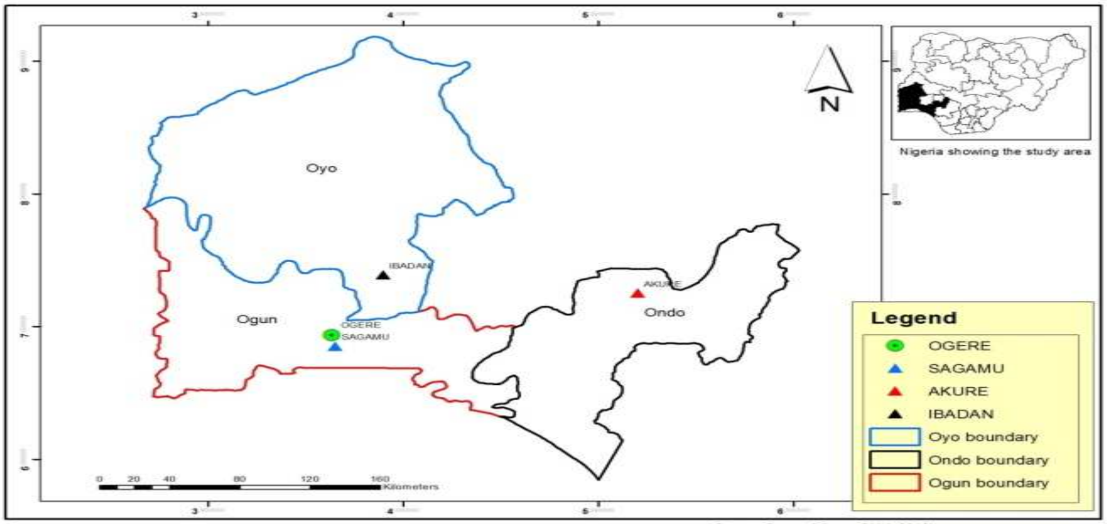
NTRODUCTION

The stability constant of a complex is the numerical expression of its stability and provides a quantitative measure of affinity of the metal ion to the complexing agent. An understanding of the relative stability of metal-complexes helps in predicting the behavior of metal ions in the soil (Ram and Raman, 1982). Extensive researches has been done to determine the stability constants of the complexes formed between humic acid (HA) with a number of metal ions. Ashok *et al*., (2000) reported that humic acid with hydroxyl, phenoxyl and carboxyl reactive groups can form coordination compound with metal ions at pH 3.5. The stability constants(Log K) for different metal-humic acid complexes indicated the following order of the stabilities of complexes formed between humic acid and metal ion, Cu >Fe >Pb> Ni > Co > Ca > Cd > Zn >Mn> Mg. Andelkovic *et al*., (2010) investigated the binding of Cd(II) to soil humic acid at pH 6.5 and in 0.1M KNO_3 ionic medium. The stability constant for binding indicating greater stability in the case when carboxyl groups are involved in complexation reaction. Kostic *et al*.,(2012) investigated the complexation of humic acid with certain heavy metal ions (Co(II), Ni(II),Cu(II), Zn(II), and Pb(II). The experiment was performed at 25°C, at pH 4.0 and ionic strength of 0.01M. Stability constant of complex between Pb(II) ions and humic acid is greater than stability constants of other investigated metal-humate complexes. Bogata and Sokolowska (2016) analyses the interaction between humic acids from different soils and Zn (II) ions at wide concentration ranges and at pH 5. Studies have showed significant impact of Zn concentration, pH and some properties of humic acids with zinc.But all of these studies were limited to acidic pH range. Therefore, the present study was carried out to determine and compare the stability constants of complexes of metal ions with hydrolysed peat soil humic acid and unhydrolysed peat soil humic under non-acid conditions.

MATERIALS AND METHODS

Analytical grade chemicals used includes hydrochloric acid (HCl), nitric acid (HNO_3), sodium hydroxide (NaOH), lead nitrate $Pb(NO_3)_2$, copper nitrate $Cu(NO_3)_2.3H_2O$, cadmium nitrate $Cd(NO_3)_2.4H_2O$, magnesium nitrate $Mg(NO_3)_2.6H_2O$, potassium nitrate (KNO_3), calcium chloride ($CaCl_2$), (sigma-Aldrich). Dowex 50WX8, (20-50 mesh) from Fluka.

Area of study



Source: Dept. of Geog. BUK (2016)

Figure 1: Map showing the sampling point at Sagamu Town, Ogun State.

Description of Sampling Area

Sagamu has geographical coordinates between 6°50′ north; 3° 38′ east is located in south western region of Nigeria. The region has tropical wet and dry climate with a lengthy wet season and relatively constant temperatures throughout the course of the year. Wet season runs from March to October, November to December forms the region dry season. The vegetation type of the region is savannah which is really grassland with small bushes and occasional big trees. Grassland soils have substantially higher organic matter content than forest soils (Novackova, 2011).

Sample Collection

The Peatsoil samples were collected from four different sampling points (0-10cm depth) in Sagamu into polyethylene bag with plastic spoons. Samples were taken to the laboratory, extraneous materials were removed; the samples were air-dried, crushed and ground to a fine powder in a mortar passed through a 0.20mm sieve. The samples were kept for analysis.

Isolation and purification of humic acid from peat soil sample

Peatsoil sample (100g) was mixed with 1000 cm^3 of 0.1M NaOH solution, shaken for 3hours and left to stand overnight. Dark-coloured supernatant was obtained and decanted from solid residue. The dark-coloured supernatant was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 6 hours. Yellowish brown supernatant and dark-brown precipitate were obtained. The yellowish brown supernatant was decanted followed by centrifuge and discarded. The dark-brown precipitate was mixed with $500cm^3$of 0.1M NaOH solution followed by passing through dowex resin. The dark-brown solution was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 3 hours. The dark-brown precipitate was washed several times with deionized water. The supernatant was treated with $AgNO_3$ solution until no white precipitate observed. The humic acid was transferred to weighed crucible and dried at 60°C in an oven for 12 hours. The humic acid was cooled and dried in the desiccator, weighed and recorded. The obtained humic acid was dried again at 60°C for additional 6 hours cooled and dried in the desiccator, weighed and recorded constant weight was obtained (Baruah *et al*., 2015).

FT-IR analysis

FT-IR spectra of humic acid sample was analysed using Carry 630 FT-IR Agilent Technologies.

Unhydrolysed compost humic acid

The unhydrolysed humic acid was obtained after isolation and purification of compost humic acid and kept for investigation.

Acid hydrolysis of Peatsoil acid

Peatsoil humic acid sample (1g) was refluxed for 12 hours at (160°C) with $50cm^3$ of 6M HCl. The mixture was allowed to cool, decanted, and centrifuged after hydrolysis. The insoluble residues were washed with distilled water via centrifugation several times, and the supernatant was treated with $AgNO_3$ solution until no white precipitate was observed. The residue was thoroughly dried over $CaCl_2$ in a desiccator at room temperature (Chefetz *et al*., 2002). Finally, the obtained hydrolysed humic acid was kept for investigation.

Potentiometric Titrations

Potentiometric measurements were carried out using a pH-meter Jenway (model 3510) with combine electrode, the sensitivity of the pH - meter is 0.01 units. The pH meter was switched on half an hour before starting the titration for initial warm up of the instrument. The instrument was calibrated with an aqueous standard buffer solution of pH 4.00 and 10.0 (borate buffer) prepared from a "Qualigens" buffer tablets.

The following sets of solutions were prepared in a 250cm^3 volumetric flask separately for pH metric titrations.

(i) 5 cm^3 0.1 M HCl + 40 cm^3 deionized water
(ii) 5 cm^3 0.1 M HCl + 39 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid
(iii) 5 cm^3 0.1 M HCl + 37 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid + 2 cm^3 0.01 M Cu(II)

The solutions were titrated against standardized 0.110MNaOH separately. The total volume of each mixture was adjusted to 50 cm^3 and the ionic strength of the solutions was maintained constant at by adding appropriate amount of stock solution of 1M KNO$_3$ (Gamal, 2015; Omar and Ali, 2015). A magnetic stirrer was used to achieve thorough mixing of the interacting solutions at 550 rpm. The same set of experimental conditions was applied for potentiometric titration of remaining samples.

Evaluation of pKa of Hydrolysed peat soil Humic Acids

The proton-ligand formation number n$_\mathbf{A}$ were calculated by Irving and Rossotti expression (Omar and Ali, 2015).

$$nA = Y - \frac{(V2-V1)(No-Eo)}{(Vo+V1)TcL} \quad \text{.................................}1$$

Where: Y is number of dissociable proton, (V$_2$-V$_1$) is the measure of displacement of the ligand curve relative to acid curve, N^o and E^o are the resultant concentration of alkali solution, free acid solution, T$_{cL}$^{o} is the total ligand concentration, V^o is the total volume of titration solution,V$_1$ is the volume of alkali added to acid solution,V$_2$ is the volume of alkali added to acid solution + ligand solution, acid dissociation constants (pKa - values) of ligand were calculated by algebraic method point wise calculation (Tables 1). The dissociation constants (pKa) were calculated according to the following relation:

$$pKa = pH + \log\left(\frac{nA}{1-nA}\right) \quad \text{.............................}2$$

Where: pKa is the acid dissociation constant, n$_A$is the Proton-ligand formation number and pH is the pH-values (Omar and Ali, 2015).

Determination of metal-ligand stability constants (log K) of complexes

The potentiometric measurement for the determination of stability constant of a complex in solution is based on the fact that the redox potential of the couple $\frac{M^{+(m-n)}}{M^{+m}}$ is shifted significantly on complexation of the metal ion with the ligand. This method involves change in hydrogen ion concentration [H$^+$] due to the displacement or association of one or more protons taking place during complexation reaction. This change can be found out by titrating the solutions containing free acid, acid with ligand, and acid with ligand and metal ion, individually against a standard alkali solution at a constant ionic strength or temperature. Either ionic strength or temperature may be varied for different sets of solutions. In all the cases, the change in the pH of the solution is measured after each addition of a known amount of alkali to the reaction cell which contains the reaction mixture. The titration curves are then drawn by plotting the measured pH values against the corresponding volume of alkali added and the stability constants of the complexes are determined from the titration curves by employing pH-metric titration technique given by (Irving and Rossoti).

Metal-ligand stability constants (Log K) were determined by using the following relations:

$$\bar{n} = \frac{(V_3 - V_2)(E^0 + N^0)}{(V^0 + V_2)\bar{n}_A T_m^0} \quad \text{..}3$$

and

$$PL = \log_{10}\left\{\frac{1 + \beta_n^H \frac{1}{[anti\ \log pH]^n}}{T_L^0 - \bar{n}T_m^0} X \frac{(V^0 + V_3)}{V^0}\right\} \quad \text{..}4$$

Where $T_{L,}$ T^{o}, E°, and V^{o}havethe same significance as in equation (1) above, T_m denotes the total concentration of metal present in solution, V_3 is the volume of metal ions present in solution and β^H is the overall proton ligand stability constant. The metal-ligand stability constants (log K) were determined by employing point wise computational Method (eq. 5 and 6).

$LogK_1 = \log\left(\frac{n}{1-n}\right) + pL$ 5

$LogK_2 = \log\left(\frac{1-n}{2-n}\right) + pL$.......................6

Where: Log K is the metal-ligand stability constant, pL is the Free ligand exponent function, **n** is the Average number of ligand attached with metal ion (Janrao*et al.*, 2014).The results obtained were analyzed by an ORIGIN 2016 program using titration data and then the proton-ligand stability constants (pKa) and Metal-ligand stability constant (LogK) calculated (Omar and Ali, 2015).

RESULTS AND DISCUSSION

Fourier transformed infrared (FT-IR) spectra of isolated humic acid from peat soils Figure 2 had distinct clear absorption bands indicating the presence of major humic acid structural elemental groups such as H bonded OH ($3680cm^{-1}$ peak), C=O of carbonyl ($1721cm^{-1}$ peak), functional groups of aliphatic components CH_2 ($2918cm^{-1}$ peak) and C-O stretching of polysaccharide ($1168cm^{-1}$ peak). The positions of the absorption bands of the spectra fell within typical major absorption bands of humic acid which is at frequencies 3680, 2918, 1721, 1168 cm^{-1}. The first peak centred in the vicinity of 3680 cm^{-1} region is attributed to phenol OH group bounded by intermolecular H bonds. The $2918cm^{-1}$ band usually has absorption maximum at 2918 cm^{-1} which is due to C–H stretching of alkane group (CH_2). The next major absorption band is 1721 cm^{-1}. This band has been commonly ascribed to C=O stretching of mainly carboxyl group (COOH) with trace amount of ketones. The last peak was observed at 1168 cm^{-1} due to C–O stretching of polysaccharides and this peak appeared also in the spectra of humic acid from peat soil. The FTIR spectra of the isolated humic acid contained all major characteristic absorption peaks of humic acid. These absorption peaks indicated the presence of the major structural elements of humic acid namely H bonded OH, C=C of aromatic ring, C=O of carbonyl group (both carboxyl and ketonic), CH_2 group. This strongly supports the presence of humic acid.

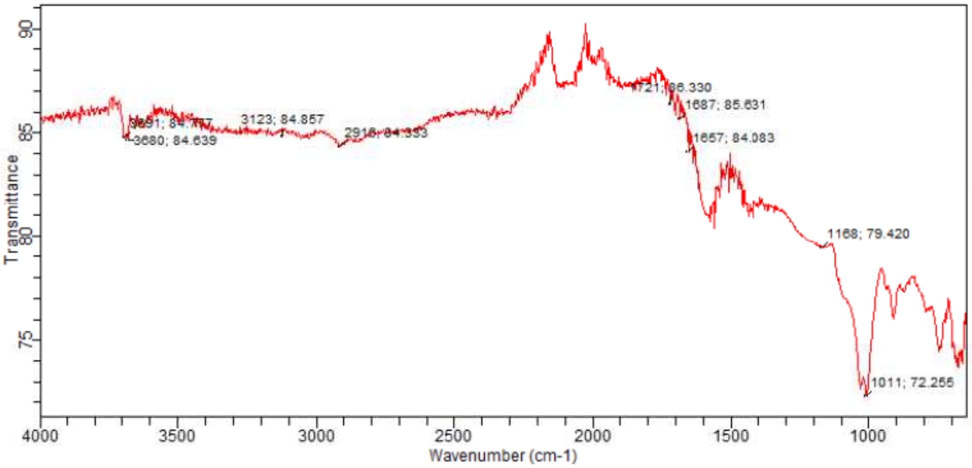


Fig. 2 : FT-IR spectraof peatsoilhumic acid (PSHA)

Evaluation of acid dissociation constant (pka) of acid hydrolysed peat soil humicacid at phenolic group

The value of the dissociation constant of the peat soil humic acid (PSHA) that underwent acidhydrolysis studied was found to be 8.9299 as shown Table 1, which is lower than the literaturevalues reported by Almeida and Szpoganics, (2015), Borges *et al.*, (2005); Badr *et al.*, (2012)and Fernandes *et al*,.(2009) of 9.73, 9.47 and 10.30. The difference between the obtained valuesand the reported values in this study might be probably as a result of acid hydrolysis of humicacid.

Table 1: PKa of (Hydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	$\log(\frac{nA}{1-nA})$	pKa
8.50	5.30	6.29	0.99	0.3594	-0.2510	8.2490
8.72	5.35	6.37	1.02	0.3400	-0.2880	8.4320
9.00	5.40	6.46	1.06	0.3141	-0.3391	8.6609
9.22	5.45	6.55	1.10	0.2882	-0.3927	8.8273
9.51	5.50	6.66	1.16	0.2494	-0.4786	9.0314
9.73	5.55	6.78	1.23	0.2041	-0.5910	9.1390
10.00	5.60	6.90	1.30	0.1589	-0.7238	9.2762
10.23	5.65	7.05	1.40	0.0941	-0.9835	9.2465
10.49	5.70	7.10	1.40	0.0941	-0.9835	9.5065

Average pKa = 8.9299 ± 0.4186

Table 2: PKa of (Unhydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	$\mathrm{Log}(\frac{nA}{1-n})$	pKa
8.50	5.30	5.81	0.51	0.6619	0.2919	8.7919
8.72	5.35	5.90	0.55	0.6357	0.2418	8.9618
9.00	5.40	6.00	0.60	0.6029	0.1813	9.1813
9.22	5.45	6.10	0.65	0.5701	0.1226	9.3426
9.51	5.50	6.20	0.70	0.5376	0.0654	9.5754
9.73	5.55	6.33	0.78	0.4851	-0.0259	9.7041
10.00	5.60	6.47	0.87	0.4262	-0.1291	9.8709
10.23	5.65	6.62	0.99	0.3609	-0.2481	9.9819
10.49	5.70	6.80	1.10	0.2759	-0.4690	10.0210

Average pKa = 9.4923± 0.4410

Metal-ligand stability constant (Log K)

The stabilityconstants require the accurate values of proton-ligand stability constants (Anil and Maroti, 2008). Metal titration curves crossed over ligand titration curve indicated the formation of complex upon proton release (Santosh, *et al.*, 2011). If the values of n- are within range 0.2-0.8 and 1.2-18 this indicates the formation of 1:1 and 1:2 complexes (Sayyed and Mazahar, 2012).

The metal (II)-humate stepwise stability constants (log k) at phenolic group (Tables 3-18)

Table 3: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3$-$V_2)$	n	pL	$\log(\frac{n}{1-n})$	LogK_1
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

LogK_1 (Average value) = 2.4788± 0.2203

Table 4: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3$-$V_2)$	n	pL	$\mathrm{Log}(\frac{n-1}{2-n})$	LogK_2
9.51	5.50	6.66	6.73	0.07	1.3509	1.70	-0.2671	1.4329
9.73	5.55	6.78	6.85	0.07	1.6383	1.51	0.2467	1.7567
10.00	5.60	6.90	6.98	0.08	2.1783	1.31	-0.2158	1.0942
10.23	5.65	7.05	7.13	0.08	4.1904	1.27		
10.49	5.70	7.10	7.19	0.09	4.6920			

LogK_2(Average value) = 1.4280 ± 0.3312

Table 5:Point-wise method,Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$\text{Log}(\frac{n}{n-1})$	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430

$\text{Log}K_1$ **(Average value)** = 2.3059± 0.6153

Table 6:Point-wise method, Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$\text{Log}(\frac{n-1}{2-n})$	Log K_2
9.73	5.55	6.33	6.42	0.09	0.9000	1.69		
10.00	5.60	6.47	6.58	0.11	1.2578	1.44	-0.4592	0.9808
10.23	5.65	6.62	6.84	0.12	1.6137	1.26	-0.2010	1.4610
10.49	5.70	6.80	6.92	0.12	2.1052	1.03		

$\text{Log}K_2$ **(Average value)** = 1.2209± 0.3398

Table 7:Point-wise method,Pb (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$\log(\frac{n}{1-n})$	$\text{Log}K_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.60	0.05	0.8333	1.96	0.6989	2.6589

$\text{Log}K_1$ (Average value) = 2.5832 ±0.1614

Table 8:Point-wise method,Pb-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$\log(\frac{n-1}{2-n})$	$\log K_2$
9.51	5.50	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.83	0.05	1.1702	1.44		
10.00	5.60	6.90	6.90	0.05	1.4864	1.22	-0.0237	1.1963
10.23	5.65	7.05	7.10	0.05	2.0190	1.09		
10.49	5.70	7.10	7.17	0.07	3.6492	1.00		

$\text{Log}K_2$(Average value) = 1.1963

Table 9:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log $(\frac{n}{n-1})$	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.5477	2.3123
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	0.0272	2.2072
9.51	5.50	6.20	6.26	0.07	0.6417	1.89	0.2530	2.1430
9.73	5.55	6.40	6.40	0.07	0.7000	1.67	0.3680	2.0380

$\text{Log}K_1$ **(Average value)** = 2.2364 ± 0.1602

Table 10:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$\text{Log}(\frac{n-1}{2-n})$	Log K_2
10.00	5.60	6.47	6.55	0.08	1.9503	1.41		
10.23	5.65	6.62	6.72	0.11	1.4792	1.26	-0.0361	1.2239

$\text{Log}K_2$ **(Average value)** = 1.2239

Table 11:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$\log(\frac{n}{n-1})$	$\text{Log}K_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4290	2.2110
8.72	5.35	6.37	6.39	0.02	0.2858	2.42	-0.3978	2.0222
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

$\text{Log}K_1$ (Average value)=2.1382**±**0.1046

Table 12:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	$\log(\frac{n-1}{2-n})$	$LogK_2$
9.51	5.55	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.84	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.93	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.10		
10.49	5.70	7.10	7.18	0.07	3.6492	0.83		

$LogK_2$(Average value) = 1.5453 **±** 0.3450

Table 13:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$V_3\text{-}V_2$	n	pL	$Log(\frac{n}{n-1})$	$Log\ K_1$
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.3477	2.3123
9.00	5.40	6.00	6.04	0.04	0.3236	2.38	-0.3202	2.0598
9.22	5.45	6.10	6.15	0.05	0.4297	2.17	-0.1230	2.0470
9.51	5.50	6.20	6.26	0.06	0.5500	1.89	0.0871	1.9771
9.73	5.55	6.33	6.40	0.07	0.7000	1.67	0.3680	2.0380

$LogK_1$ **(Average value)** = 2.1568 ± 0.2069

Table 14:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$V_3\text{-}V_2$	n	pL	$Log(\frac{n-1}{2-n})$	$Log\ K_2$
10.00	5.60	6.47	6.55	0.08	0.9148	1.41		
10.23	5.65	6.62	6.71	0.09	1.2102	1.20	-0.5749	0.6251
10.49	5.70	6.80	6.92	0.09	1.5968	1.03	0.1703	1.2003

$LogK_2$ **(Average value)** = 0.9127± 0.4070

Table15:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	$Log(\frac{n}{1-n})$	$LogK_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4210	2.2190
8.72	5.35	6.37	6.40	0.03	0.4286	2.42	-0.1249	2.2951
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.96	0.3010	2.2610
9.51	5.55	6.66	6.70	0.04	0.7720	1.67	0.5297	2.1997

$LogK_1$ (Average value) = 2.2108± 0.0825

Table 16:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	$Log(\frac{n-1}{2-n})$	$Log\ K_2$
9.73	5.55	6.78	6.83	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.95	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.09		
10.49	5.70	7.10	7.16	0.06	3.1429	0.89		

$LogK_2$ **(Average value)** = 1.5453± 0.3450

Table 17:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$V_3\text{-}V_2$	n	pL	$Log(\frac{n}{n-1})$	$Log\ K_1$
8.50	5.30	5.81	5.86	0.05	0.3717	2.88	-0.2280	2.6520
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.06	0.06	0.4853	2.38	-0.0255	2.3545
9.22	5.45	6.10	6.16	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430
9.73	5.55	6.33	6.41	0.08	0.8000	1.69	0.6020	2.2920

$LogK_1$ **(Average value)** = 2.2516± 0.5380

Table 18:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$\text{Log}(\frac{n-1}{2-n})$	Log K_2
10.00	5.60	6.47	6.57	0.10	1.1434	1.43		
10.23	5.65	6.62	6.72	0.10	1.3448	1.23	-0.2788	0.9512
10.49	5.70	6.80	6.90	0.10	1.7742	1.03	0.5351	1.5651

LogK_2 **(Average value)** = 1.2581± 0.4340

Table 19: Stepwise and overall Stability constants of thehydrolysed and unhydrolysed divalent metal (II) complexes

Chelates	**LogK_1**	**LogK_2**	**Logβ**
[Cu (Hydrolysed PSHA-1)$_2$]	2.4788	1.4280	3.9068
[Pb (Hydrolysed PSHA-1)$_2$]	2.5832	1.1963	3.7795
[Cd (Hydrolysed PSHA-1)$_2$]	2.2108	1.5453	3.7561
[Mg (Hydrolysed PSHA-1)$_2$]	2.1382	1.5453	3.6835
[Cu (Unhydrolysed PSHA-1)$_2$]	2.3059	1.2209	3.5268
[Pb (Unhydrolysed PSHA-1)$_2$]	2.2364	1.2239	3.4603
[Cd (Unhydrolysed PSHA-1)$_2$]	2.2516	1.2581	3.5097
[Mg (Unydrolysed PSHA-1)$_2$]	2.1568	0.9127	3.0695

The results obtained (Table19) shows the stepwise and overall stability constants to be not high indicating low stability of the complexes, because the solubility of most metal ions in the basic pH range is minimal due to metal hydroxide precipitation (Karimi, 2017). In general, the stepwise stability constants (K_1 and K_2) follow the order $K_1 > K_2$ for the copper, lead, magnesium and cadmium complexes respectively. The steady decrease of the values with increasing number of ligands is in agreement with the prediction made by researchers (Na'aliya, 2013). The decrease could be attributed to the fact that as the number of the ligands (Humate ions) that enters the coordination zone increases the aqua molecules available for replacement by the ligands become less. Thus, the metal ions become less electron loving with progressive intake of the ligand and this results in the decrease in the values of the constants (Na'aliya, 2013). Also the stability of the complexes is influenced by the size and number of the chelate rings(Mackay and Mackay,2002).All the complexes form rings in their structure as humate, a bidentate ligand, bond the metal ions in the ratio 1:2 (Boguta and Sokolowska, 2016) forming chelate rings. The values of the overall stability constants (logβ) obtained for humate complexes are not high indicating low stability as the values are not high. LogK values for copper-humates (Table 3 to 6) obtained in this study are lower than those reported for the complexes of humic acids (Pandey *et al*., 2015; Dinu, 2013; Kaschl *et al*., 2010 and Gilbeto and Jorg, 2001). The values of LogK(Table 7 to 10) forlead-humates are lower than those reported for the lead in the literature (Dinu, 2013; Gilbeto and Jorg 2001). Log K values(Table 11 to 14) for magnesium-humates obtained in this study are close to those reported by (Pandey *et al*., 2015). Log K values of cadmium-humates (Table 15 to 18) obtained in this work near to the one reported by (Dinu, 2013 and Pandey *et al*., 2015).The difference between the reported values and the values obtained in this study might be probably as a result of acid hydrolysis of humic acid. The values of the overall stability constants (log β) of the copper humates complexes presented in Table 19 is high than that of other metal humate complexes, show relatively high stability of Cu-HA complexes, show the following order of stability: Cu >Pb> Cd > Mg; which are in close agreement to the findings of (Dinu, 2013 and Pandey *et al*., 2015).The high stability of Cu-humate chelate could be attributed to the existence of coordinate covalent bond between the complexing agents and the Cu^{2+} ions. Since, Cu^{2+} being a metal of the transitional series with $3d^9$ electronic configurations can accept the electrons from the complexing agents. Similarly,the low stabilities of Pb,Cd and Mg -complexes could be explained by that Pb^{2+} with $6s^2$, Cd^{2+} with $4d^{10}$ and Mg^{2+} with $2p^6$ their electronic configuration has a completely filled d,p and s orbitals. Moreover, the stabilities of metal ions with hydrolysed humic acid from peat soil were higher than those with unhydrolysed humic acid from peat soil; which is ascribed to the high content of acidity in hydrolysed humic acid than unhydrolysed humic acid.

CONCLUSION

The values of logK for Cu(II) hydrolysed humic acid complex was higher followed by Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes as compared with metal(II) unhydrolysed humic acid complexes . This indicates acid hydrolysis of humic acid can enhance the complexation behavior of humic acid with metal (II) ions. However, the higher values of logβ for Cu(II), Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes indicates more stable stepwise complexes formed as compared with Cu(II), Pb(II), Cd(II) and Mg(II) unhydrolysed humic acid complexes.

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STABILITY CONSTANTS OF COMPLEXES OF METAL IONS WITH PEATSOIL HUMIC ACIDS UNDER NON-ACID-CONDITIONS

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ABSTRACT

Stability constants of complexes of four divalent metal ions viz. Cu^{2+}, Pb^{2+},Mg^{2+} and Cd^{2+} with humic acids (HA) were determined by potentiometric titration of humic acids with the corresponding salt of the divalent metals in aqueous media under non-acid-condition. The log K (logarithm of the stability constant) ranged from 1.0942 to 2.7471 for metal-humic acid complexes were determined using point-wise computational method. The order of stability constants were obtained as follows: Cu >Pb> Cd > Mg for metal -HA complexes respectively, indicating a higher degree of complexation with Cu metal ion.

Keywords: stability constant, humic acid, potentiometric titration, divalent metals, acid hydrolysis.

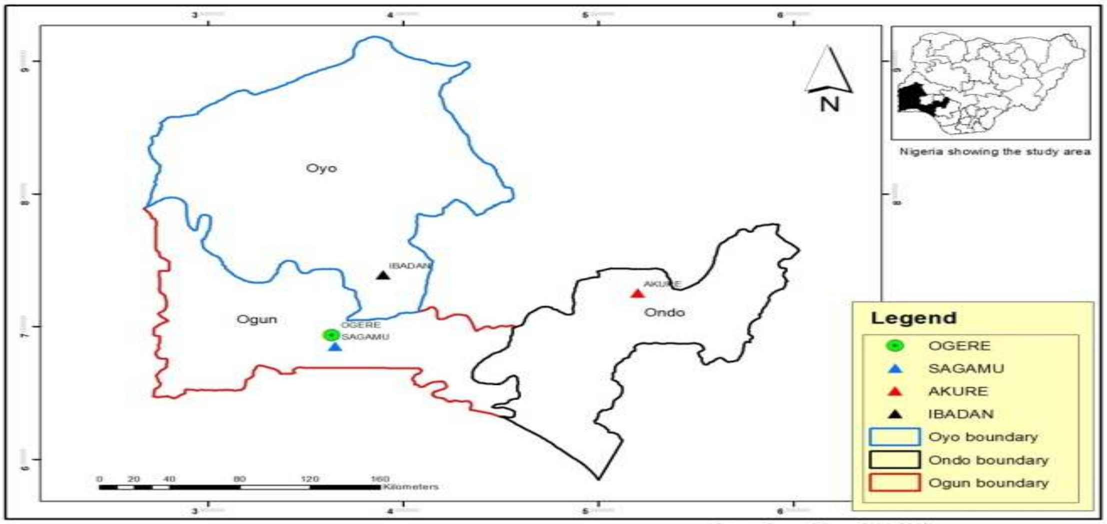
NTRODUCTION

The stability constant of a complex is the numerical expression of its stability and provides a quantitative measure of affinity of the metal ion to the complexing agent. An understanding of the relative stability of metal-complexes helps in predicting the behavior of metal ions in the soil (Ram and Raman, 1982). Extensive researches has been done to determine the stability constants of the complexes formed between humic acid (HA) with a number of metal ions. Ashok *et al.*, (2000) reported that humic acid with hydroxyl, phenoxyl and carboxyl reactive groups can form coordination compound with metal ions at pH 3.5. The stability constants(Log K) for different metal-humic acid complexes indicated the following order of the stabilities of complexes formed between humic acid and metal ion, Cu >Fe >Pb> Ni > Co > Ca > Cd > Zn >Mn> Mg. Andelkovic *et al.*, (2010) investigated the binding of Cd(II) to soil humic acid at pH 6.5 and in 0.1M KNO_3 ionic medium. The stability constant for binding indicating greater stability in the case when carboxyl groups are involved in complexation reaction. Kostic *et al.*,(2012) investigated the complexation of humic acid with certain heavy metal ions (Co(II), Ni(II),Cu(II), Zn(II), and Pb(II). The experiment was performed at 25°C, at pH 4.0 and ionic strength of 0.01M. Stability constant of complex between Pb(II) ions and humic acid is greater than stability constants of other investigated metal-humate complexes. Bogata and Sokolowska (2016) analyses the interaction between humic acids from different soils and Zn (II) ions at wide concentration ranges and at pH 5. Studies have showed significant impact of Zn concentration, pH and some properties of humic acids with zinc.But all of these studies were limited to acidic pH range. Therefore, the present study was carried out to determine and compare the stability constants of complexes of metal ions with hydrolysed peat soil humic acid and unhydrolysed peat soil humic under non-acid conditions.

MATERIALS AND METHODS

Analytical grade chemicals used includes hydrochloric acid (HCl), nitric acid (HNO_3), sodium hydroxide (NaOH), lead nitrate $Pb(NO_3)_2$, copper nitrate $Cu(NO_3)_2.3H_2O$, cadmium nitrate $Cd(NO_3)_2.4H_2O$, magnesium nitrate $Mg(NO_3)_2.6H_2O$, potassium nitrate (KNO_3), calcium chloride ($CaCl_2$), (sigma-Aldrich). Dowex 50WX8, (20-50 mesh) from Fluka.

Area of study



Source: Dept. of Geog. BUK (2016)

Figure 1: Map showing the sampling point at Sagamu Town, Ogun State.

Description of Sampling Area

Sagamu has geographical coordinates between 6°50′ north; 3° 38′ east is located in south western region of Nigeria. The region has tropical wet and dry climate with a lengthy wet season and relatively constant temperatures throughout the course of the year. Wet season runs from March to October, November to December forms the region dry season. The vegetation type of the region is savannah which is really grassland with small bushes and occasional big trees. Grassland soils have substantially higher organic matter content than forest soils (Novackova, 2011).

Sample Collection

The Peatsoil samples were collected from four different sampling points (0-10cm depth) in Sagamu into polyethylene bag with plastic spoons. Samples were taken to the laboratory, extraneous materials were removed; the samples were air-dried, crushed and ground to a fine powder in a mortar passed through a 0.20mm sieve. The samples were kept for analysis.

Isolation and purification of humic acid from peat soil sample

Peatsoil sample (100g) was mixed with 1000 cm^3 of 0.1M NaOH solution, shaken for 3hours and left to stand overnight. Dark-coloured supernatant was obtained and decanted from solid residue. The dark-coloured supernatant was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 6 hours. Yellowish brown supernatant and dark-brown precipitate were obtained. The yellowish brown supernatant was decanted followed by centrifuge and discarded. The dark-brown precipitate was mixed with $500cm^3$of 0.1M NaOH solution followed by passing through dowex resin. The dark-brown solution was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 3 hours. The dark-brown precipitate was washed several times with deionized water. The supernatant was treated with $AgNO_3$ solution until no white precipitate observed. The humic acid was transferred to weighed crucible and dried at 60°C in an oven for 12 hours. The humic acid was cooled and dried in the desiccator, weighed and recorded. The obtained humic acid was dried again at 60°C for additional 6 hours cooled and dried in the desiccator, weighed and recorded constant weight was obtained (Baruah *et al.*, 2015).

FT-IR analysis

FT-IR spectra of humic acid sample was analysed using Carry 630 FT-IR Agilent Technologies.

Unhydrolysed compost humic acid

The unhydrolysed humic acid was obtained after isolation and purification of compost humic acid and kept for investigation.

Acid hydrolysis of Peatsoil acid

Peatsoil humic acid sample (1g) was refluxed for 12 hours at (160°C) with $50cm^3$ of 6M HCl. The mixture was allowed to cool, decanted, and centrifuged after hydrolysis. The insoluble residues were washed with distilled water via centrifugation several times, and the supernatant was treated with $AgNO_3$ solution until no white precipitate was observed. The residue was thoroughly dried over $CaCl_2$ in a desiccator at room temperature (Chefetz *et al.*, 2002). Finally, the obtained hydrolysed humic acid was kept for investigation.

Potentiometric Titrations

Potentiometric measurements were carried out using a pH-meter Jenway (model 3510) with combine electrode, the sensitivity of the pH - meter is 0.01 units. The pH meter was switched on half an hour before starting the titration for initial warm up of the instrument. The instrument was calibrated with an aqueous standard buffer solution of pH 4.00 and 10.0 (borate buffer) prepared from a "Qualigens" buffer tablets.

The following sets of solutions were prepared in a 250cm^3 volumetric flask separately for pH metric titrations.

(i) 5 cm^3 0.1 M HCl + 40 cm^3 deionized water
(ii) 5 cm^3 0.1 M HCl + 39 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid
(iii) 5 cm^3 0.1 M HCl + 37 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid + 2 cm^3 0.01 M Cu(II)

The solutions were titrated against standardized 0.110MNaOH separately. The total volume of each mixture was adjusted to 50 cm^3 and the ionic strength of the solutions was maintained constant at by adding appropriate amount of stock solution of 1M KNO_3 (Gamal, 2015; Omar and Ali, 2015). A magnetic stirrer was used to achieve thorough mixing of the interacting solutions at 550 rpm. The same set of experimental conditions was applied for potentiometric titration of remaining samples.

Evaluation of pKa of Hydrolysed peat soil Humic Acids

The proton-ligand formation number $n_{\mathbf{A}}$ were calculated by Irving and Rossotti expression (Omar and Ali, 2015).

$$nA = Y- \frac{(V2-V1)(No-Eo)}{(Vo+V1)TcL} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 1$$

Where: Y is number of dissociable proton, (V_2-V_1) is the measure of displacement of the ligand curve relative to acid curve, N^o and E^o are the resultant concentration of alkali solution, free acid solution, $T_{cL}{}^o$ is the total ligand concentration, V^o is the total volume of titration solution,V_1 is the volume of alkali added to acid solution,V_2 is the volume of alkali added to acid solution + ligand solution, acid dissociation constants (pKa - values) of ligand were calculated by algebraic method point wise calculation (Tables 1). The dissociation constants (pKa) were calculated according to the following relation:

$$\text{pKa} = \text{pH} + \log\left(\frac{nA}{1-nA}\right) \quad \ldots\ldots\ldots\ldots\ldots\ldots 2$$

Where: pKa is the acid dissociation constant, $n_A$is the Proton-ligand formation number and pH is the pH-values (Omar and Ali, 2015).

Determination of metal-ligand stability constants (log K) of complexes

The potentiometric measurement for the determination of stability constant of a complex in solution is based on the fact that the redox potential of the couple $\frac{M^{+(m-n)}}{M^{+m}}$ is shifted significantly on complexation of the metal ion with the ligand. This method involves change in hydrogen ion concentration [H$^+$] due to the displacement or association of one or more protons taking place during complexation reaction. This change can be found out by titrating the solutions containing free acid, acid with ligand, and acid with ligand and metal ion, individually against a standard alkali solution at a constant ionic strength or temperature. Either ionic strength or temperature may be varied for different sets of solutions. In all the cases, the change in the pH of the solution is measured after each addition of a known amount of alkali to the reaction cell which contains the reaction mixture. The titration curves are then drawn by plotting the measured pH values against the corresponding volume of alkali added and the stability constants of the complexes are determined from the titration curves by employing pH-metric titration technique given by (Irving and Rossoti).

Metal-ligand stability constants (Log K) were determined by using the following relations:

$$\bar{n} = \frac{(V_3 - V_2)(E^0 + N^0)}{(V^0 + V_2)\bar{n}_A T_m^0} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 3$$

and

$$PL = \log_{10}\{\frac{1 + \beta_n^H \frac{1}{[anti\ \log \text{pH}]^n}}{T_L^0 - \bar{n}T_m^0} \text{X} \frac{(V^0 + V_3)}{V^0}\} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots 4$$

Where $T_{L,}$ T^{o}, E°, and V^{o}havethe same significance as in equation (1) above, T_m denotes the total concentration of metal present in solution, V_3 is the volume of metal ions present in solution and β^H is the overall proton ligand stability constant. The metal-ligand stability constants (log K) were determined by employing point wise computational Method (eq. 5 and 6).

$LogK_1 = \log\left(\frac{n}{1-n}\right) + pL$ 5

$LogK_2 = \log\left(\frac{1-n}{2-n}\right) + pL$........................6

Where: Log K is the metal-ligand stability constant, pL is the Free ligand exponent function, **n** is the Average number of ligand attached with metal ion (Janrao*et al.*, 2014).The results obtained were analyzed by an ORIGIN 2016 program using titration data and then the proton-ligand stability constants (pKa) and Metal-ligand stability constant (LogK) calculated (Omar and Ali, 2015).

RESULTS AND DISCUSSION

Fourier transformed infrared (FT-IR) spectra of isolated humic acid from peat soils Figure 2 had distinct clear absorption bands indicating the presence of major humic acid structural elemental groups such as H bonded OH ($3680cm^{-1}$ peak), C=O of carbonyl ($1721cm^{-1}$ peak), functional groups of aliphatic components CH_2 ($2918cm^{-1}$ peak) and C-O stretching of polysaccharide ($1168cm^{-1}$ peak). The positions of the absorption bands of the spectra fell within typical major absorption bands of humic acid which is at frequencies 3680, 2918, 1721, 1168 cm^{-1}. The first peak centred in the vicinity of 3680 cm^{-1} region is attributed to phenol OH group bounded by intermolecular H bonds. The $2918cm^{-1}$ band usually has absorption maximum at 2918 cm^{-1} which is due to C–H stretching of alkane group (CH_2). The next major absorption band is 1721 cm^{-1}. This band has been commonly ascribed to C=O stretching of mainly carboxyl group (COOH) with trace amount of ketones. The last peak was observed at 1168 cm^{-1} due to C–O stretching of polysaccharides and this peak appeared also in the spectra of humic acid from peat soil. The FTIR spectra of the isolated humic acid contained all major characteristic absorption peaks of humic acid. These absorption peaks indicated the presence of the major structural elements of humic acid namely H bonded OH, C=C of aromatic ring, C=O of carbonyl group (both carboxyl and ketonic), CH_2 group. This strongly supports the presence of humic acid.

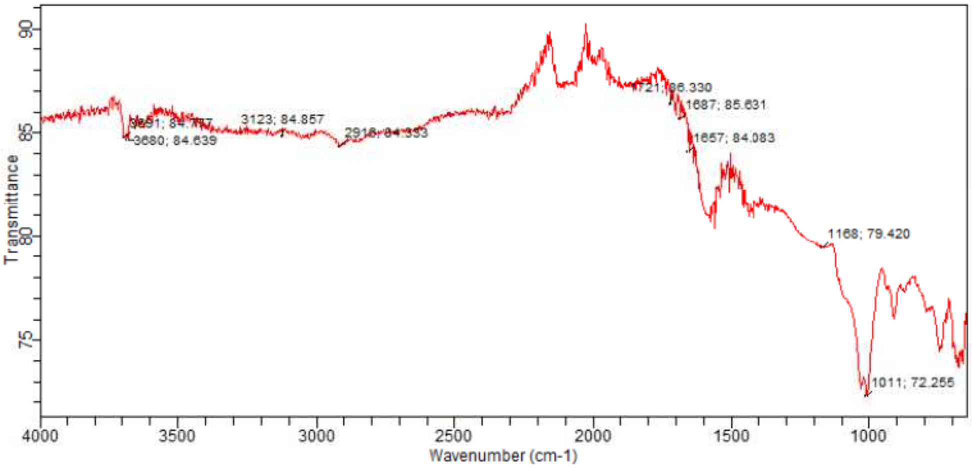


Fig. 2 : FT-IR spectraof peatsoilhumic acid (PSHA)

Evaluation of acid dissociation constant (pka) of acid hydrolysed peat soil humicacid at phenolic group

The value of the dissociation constant of the peat soil humic acid (PSHA) that underwent acidhydrolysis studied was found to be 8.9299 as shown Table 1, which is lower than the literaturevalues reported by Almeida and Szpoganics, (2015), Borges *et al.*, (2005); Badr *et al.*, (2012)and Fernandes *et al*,.(2009) of 9.73, 9.47 and 10.30. The difference between the obtained valuesand the reported values in this study might be probably as a result of acid hydrolysis of humicacid.

Table 1: PKa of (Hydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	log($\frac{nA}{1-nA}$)	pKa
8.50	5.30	6.29	0.99	0.3594	-0.2510	8.2490
8.72	5.35	6.37	1.02	0.3400	-0.2880	8.4320
9.00	5.40	6.46	1.06	0.3141	-0.3391	8.6609
9.22	5.45	6.55	1.10	0.2882	-0.3927	8.8273
9.51	5.50	6.66	1.16	0.2494	-0.4786	9.0314
9.73	5.55	6.78	1.23	0.2041	-0.5910	9.1390
10.00	5.60	6.90	1.30	0.1589	-0.7238	9.2762
10.23	5.65	7.05	1.40	0.0941	-0.9835	9.2465
10.49	5.70	7.10	1.40	0.0941	-0.9835	9.5065

Average pKa = 8.9299 ± 0.4186

Table 2: PKa of (Unhydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	Log($\frac{nA}{1-n}$)	pKa
8.50	5.30	5.81	0.51	0.6619	0.2919	8.7919
8.72	5.35	5.90	0.55	0.6357	0.2418	8.9618
9.00	5.40	6.00	0.60	0.6029	0.1813	9.1813
9.22	5.45	6.10	0.65	0.5701	0.1226	9.3426
9.51	5.50	6.20	0.70	0.5376	0.0654	9.5754
9.73	5.55	6.33	0.78	0.4851	-0.0259	9.7041
10.00	5.60	6.47	0.87	0.4262	-0.1291	9.8709
10.23	5.65	6.62	0.99	0.3609	-0.2481	9.9819
10.49	5.70	6.80	1.10	0.2759	-0.4690	10.0210

Average pKa = 9.4923± 0.4410

Metal-ligand stability constant (Log K)

The stabilityconstants require the accurate values of proton-ligand stability constants (Anil and Maroti, 2008). Metal titration curves crossed over ligand titration curve indicated the formation of complex upon proton release (Santosh, *et al.*, 2011). If the values of n- are within range 0.2-0.8 and 1.2-18 this indicates the formation of 1:1 and 1:2 complexes (Sayyed and Mazahar, 2012).

The metal (II)-humate stepwise stability constants (log k) at phenolic group (Tables 3-18)

Table 3: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n}{1-n}$)	$LogK_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

$LogK_1$ (Average value) = 2.4788± 0.2203

Table 4: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	Log($\frac{n-1}{2-n}$)	$LogK_2$
9.51	5.50	6.66	6.73	0.07	1.3509	1.70	-0.2671	1.4329
9.73	5.55	6.78	6.85	0.07	1.6383	1.51	0.2467	1.7567
10.00	5.60	6.90	6.98	0.08	2.1783	1.31	-0.2158	1.0942
10.23	5.65	7.05	7.13	0.08	4.1904	1.27		
10.49	5.70	7.10	7.19	0.09	4.6920			

$LogK_2$(Average value) = 1.4280 ± 0.3312

Table 5:Point-wise method,Cu (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	Log($\frac{n}{n-1}$)	Log K$_1$
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430

LogK$_1$ **(Average value)** = 2.3059± 0.6153

Table 6:Point-wise method, Cu (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	V$_3$-V$_2$	n	pL	Log($\frac{n-1}{2-n}$)	Log K$_2$
9.73	5.55	6.33	6.42	0.09	0.9000	1.69		
10.00	5.60	6.47	6.58	0.11	1.2578	1.44	-0.4592	0.9808
10.23	5.65	6.62	6.84	0.12	1.6137	1.26	-0.2010	1.4610
10.49	5.70	6.80	6.92	0.12	2.1052	1.03		

LogK$_2$ **(Average value)** = 1.2209± 0.3398

Table 7:Point-wise method,Pb (Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	log($\frac{n}{1-n}$)	LogK$_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.60	0.05	0.8333	1.96	0.6989	2.6589

LogK$_1$ (Average value) = 2.5832 ±0.1614

Table 8:Point-wise method,Pb-(Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	log($\frac{n-1}{2-n}$)	logK$_2$
9.51	5.50	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.83	0.05	1.1702	1.44		
10.00	5.60	6.90	6.90	0.05	1.4864	1.22	-0.0237	1.1963
10.23	5.65	7.05	7.10	0.05	2.0190	1.09		
10.49	5.70	7.10	7.17	0.07	3.6492	1.00		

LogK$_2$(Average value) = 1.1963

Table 9:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	V$_3$-V$_2$	n	pL	Log ($\frac{n}{n-1}$)	Log K$_1$
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.5477	2.3123
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	0.0272	2.2072
9.51	5.50	6.20	6.26	0.07	0.6417	1.89	0.2530	2.1430
9.73	5.55	6.40	6.40	0.07	0.7000	1.67	0.3680	2.0380

LogK$_1$ **(Average value)** = 2.2364 ± 0.1602

Table 10:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	V$_3$-V$_2$	n	pL	Log($\frac{n-1}{2-n}$)	Log K$_2$
10.00	5.60	6.47	6.55	0.08	1.9503	1.41		
10.23	5.65	6.62	6.72	0.11	1.4792	1.26	-0.0361	1.2239

LogK$_2$ **(Average value)** = 1.2239

Table 11:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	log($\frac{n}{n-1}$)	LogK$_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4290	2.2110
8.72	5.35	6.37	6.39	0.02	0.2858	2.42	-0.3978	2.0222
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

LogK$_1$ (Average value)=2.1382**±**0.1046

Table 12:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	log($\frac{n-1}{2-n}$)	LogK$_2$
9.51	5.55	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.84	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.93	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.10		
10.49	5.70	7.10	7.18	0.07	3.6492	0.83		

LogK$_2$(Average value) = 1.5453 **±** 0.3450

Table 13:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	V$_3$-V$_2$	n	pL	Log($\frac{n}{n-1}$)	Log K$_1$
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.3477	2.3123
9.00	5.40	6.00	6.04	0.04	0.3236	2.38	-0.3202	2.0598
9.22	5.45	6.10	6.15	0.05	0.4297	2.17	-0.1230	2.0470
9.51	5.50	6.20	6.26	0.06	0.5500	1.89	0.0871	1.9771
9.73	5.55	6.33	6.40	0.07	0.7000	1.67	0.3680	2.0380

LogK$_1$ **(Average value)** = 2.1568 ± 0.2069

Table 14:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	V$_3$-V$_2$	n	pL	Log($\frac{n-1}{2-n}$)	Log K$_2$
10.00	5.60	6.47	6.55	0.08	0.9148	1.41		
10.23	5.65	6.62	6.71	0.09	1.2102	1.20	-0.5749	0.6251
10.49	5.70	6.80	6.92	0.09	1.5968	1.03	0.1703	1.2003

LogK$_2$ **(Average value)** = 0.9127± 0.4070

Table15:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	Log($\frac{n}{1-n}$)	LogK$_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4210	2.2190
8.72	5.35	6.37	6.40	0.03	0.4286	2.42	-0.1249	2.2951
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.96	0.3010	2.2610
9.51	5.55	6.66	6.70	0.04	0.7720	1.67	0.5297	2.1997

LogK$_1$ (Average value) = 2.2108± 0.0825

Table 16:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	Log($\frac{n-1}{2-n}$)	Log K$_2$
9.73	5.55	6.78	6.83	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.95	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.09		
10.49	5.70	7.10	7.16	0.06	3.1429	0.89		

LogK$_2$ **(Average value)** = 1.5453± 0.3450

Table 17:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	V$_3$-V$_2$	n	pL	Log($\frac{n}{n-1}$)	Log K$_1$
8.50	5.30	5.81	5.86	0.05	0.3717	2.88	-0.2280	2.6520
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.06	0.06	0.4853	2.38	-0.0255	2.3545
9.22	5.45	6.10	6.16	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430
9.73	5.55	6.33	6.41	0.08	0.8000	1.69	0.6020	2.2920

LogK$_1$ **(Average value)** = 2.2516± 0.5380

Table 18:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$Log(\frac{n-1}{2-n})$	Log K_2
10.00	5.60	6.47	6.57	0.10	1.1434	1.43		
10.23	5.65	6.62	6.72	0.10	1.3448	1.23	-0.2788	0.9512
10.49	5.70	6.80	6.90	0.10	1.7742	1.03	0.5351	1.5651

$LogK_2$ **(Average value)** = 1.2581± 0.4340

Table 19: Stepwise and overall Stability constants of thehydrolysed and unhydrolysed divalent metal (II) complexes

Chelates	**$LogK_1$**	**$LogK_2$**	**Logβ**
[Cu (Hydrolysed PSHA-1)$_2$]	2.4788	1.4280	3.9068
[Pb (Hydrolysed PSHA-1)$_2$]	2.5832	1.1963	3.7795
[Cd (Hydrolysed PSHA-1)$_2$]	2.2108	1.5453	3.7561
[Mg (Hydrolysed PSHA-1)$_2$]	2.1382	1.5453	3.6835
[Cu (Unhydrolysed PSHA-1)$_2$]	2.3059	1.2209	3.5268
[Pb (Unhydrolysed PSHA-1)$_2$]	2.2364	1.2239	3.4603
[Cd (Unhydrolysed PSHA-1)$_2$]	2.2516	1.2581	3.5097
[Mg (Unydrolysed PSHA-1)$_2$]	2.1568	0.9127	3.0695

The results obtained (Table19) shows the stepwise and overall stability constants to be not high indicating low stability of the complexes, because the solubility of most metal ions in the basic pH range is minimal due to metal hydroxide precipitation (Karimi, 2017). In general, the stepwise stability constants (K_1 and K_2) follow the order $K_1 > K_2$ for the copper, lead, magnesium and cadmium complexes respectively. The steady decrease of the values with increasing number of ligands is in agreement with the prediction made by researchers (Na'aliya, 2013). The decrease could be attributed to the fact that as the number of the ligands (Humate ions) that enters the coordination zone increases the aqua molecules available for replacement by the ligands become less. Thus, the metal ions become less electron loving with progressive intake of the ligand and this results in the decrease in the values of the constants (Na'aliya, 2013). Also the stability of the complexes is influenced by the size and number of the chelate rings(Mackay and Mackay,2002).All the complexes form rings in their structure as humate, a bidentate ligand, bond the metal ions in the ratio 1:2 (Boguta and Sokolowska, 2016) forming chelate rings. The values of the overall stability constants (logβ) obtained for humate complexes are not high indicating low stability as the values are not high. LogK values for copper-humates (Table 3 to 6) obtained in this study are lower than those reported for the complexes of humic acids (Pandey *et al.*, 2015; Dinu, 2013; Kaschl *et al.*, 2010 and Gilbeto and Jorg, 2001). The values of LogK(Table 7 to 10) forlead-humates are lower than those reported for the lead in the literature (Dinu, 2013; Gilbeto and Jorg 2001). Log K values(Table 11 to 14) for magnesium-humates obtained in this study are close to those reported by (Pandey *et al.*, 2015). Log K values of cadmium-humates (Table 15 to 18) obtained in this work near to the one reported by (Dinu, 2013 and Pandey *et al.*, 2015).The difference between the reported values and the values obtained in this study might be probably as a result of acid hydrolysis of humic acid. The values of the overall stability constants (log β) of the copper humates complexes presented in Table 19 is high than that of other metal humate complexes, show relatively high stability of Cu-HA complexes, show the following order of stability: Cu >Pb> Cd > Mg; which are in close agreement to the findings of (Dinu, 2013 and Pandey *et al.*, 2015).The high stability of Cu-humate chelate could be attributed to the existence of coordinate covalent bond between the complexing agents and the Cu^{2+} ions. Since, Cu^{2+} being a metal of the transitional series with $3d^9$ electronic configurations can accept the electrons from the complexing agents. Similarly,the low stabilities of Pb,Cd and Mg - complexes could be explained by that Pb^{2+} with $6s^2$, Cd^{2+} with $4d^{10}$ and Mg^{2+} with $2p^6$ their electronic configuration has a completely filled d,p and s orbitals. Moreover, the stabilities of metal ions with hydrolysed humic acid from peat soil were higher than those with unhydrolysed humic acid from peat soil; which is ascribed to the high content of acidity in hydrolysed humic acid than unhydrolysed humic acid.

CONCLUSION

The values of logK for Cu(II) hydrolysed humic acid complex was higher followed by Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes as compared with metal(II) unhydrolysed humic acid complexes . This indicates acid hydrolysis of humic acid can enhance the complexation behavior of humic acid with metal (II) ions. However, the higher values of logβ for Cu(II), Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes indicates more stable stepwise complexes formed as compared with Cu(II), Pb(II), Cd(II) and Mg(II) unhydrolysed humic acid complexes.

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STABILITY CONSTANTS OF COMPLEXES OF METAL IONS WITH PEATSOIL HUMIC ACIDS UNDER NON-ACID-CONDITIONS

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ABSTRACT

Stability constants of complexes of four divalent metal ions viz. Cu^{2+}, Pb^{2+},Mg^{2+} and Cd^{2+} with humic acids (HA) were determined by potentiometric titration of humic acids with the corresponding salt of the divalent metals in aqueous media under non-acid-condition. The log K (logarithm of the stability constant) ranged from 1.0942 to 2.7471 for metal-humic acid complexes were determined using point-wise computational method. The order of stability constants were obtained as follows: Cu >Pb> Cd > Mg for metal -HA complexes respectively, indicating a higher degree of complexation with Cu metal ion.

Keywords: stability constant, humic acid, potentiometric titration, divalent metals, acid hydrolysis.

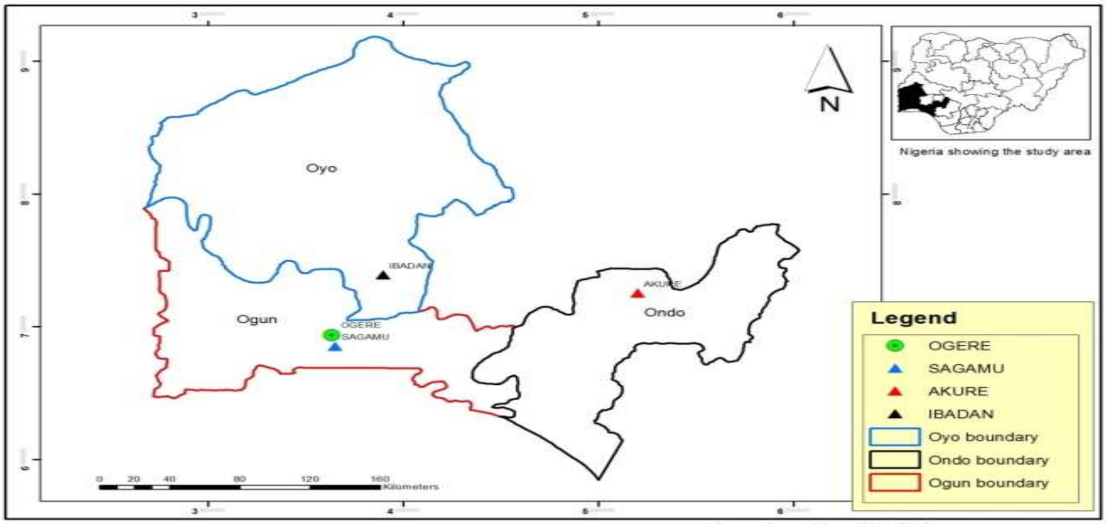
NTRODUCTION

The stability constant of a complex is the numerical expression of its stability and provides a quantitative measure of affinity of the metal ion to the complexing agent. An understanding of the relative stability of metal-complexes helps in predicting the behavior of metal ions in the soil (Ram and Raman, 1982). Extensive researches has been done to determine the stability constants of the complexes formed between humic acid (HA) with a number of metal ions. Ashok *et al*., (2000) reported that humic acid with hydroxyl, phenoxyl and carboxyl reactive groups can form coordination compound with metal ions at pH 3.5. The stability constants(Log K) for different metal-humic acid complexes indicated the following order of the stabilities of complexes formed between humic acid and metal ion, Cu >Fe >Pb> Ni > Co > Ca > Cd > Zn >Mn> Mg. Andelkovic *et al*., (2010) investigated the binding of Cd(II) to soil humic acid at pH 6.5 and in 0.1M KNO_3 ionic medium. The stability constant for binding indicating greater stability in the case when carboxyl groups are involved in complexation reaction. Kostic *et al*.,(2012) investigated the complexation of humic acid with certain heavy metal ions (Co(II), Ni(II),Cu(II), Zn(II), and Pb(II). The experiment was performed at 25°C, at pH 4.0 and ionic strength of 0.01M. Stability constant of complex between Pb(II) ions and humic acid is greater than stability constants of other investigated metal-humate complexes. Bogata and Sokolowska (2016) analyses the interaction between humic acids from different soils and Zn (II) ions at wide concentration ranges and at pH 5. Studies have showed significant impact of Zn concentration, pH and some properties of humic acids with zinc.But all of these studies were limited to acidic pH range. Therefore, the present study was carried out to determine and compare the stability constants of complexes of metal ions with hydrolysed peat soil humic acid and unhydrolysed peat soil humic under non-acid conditions.

MATERIALS AND METHODS

Analytical grade chemicals used includes hydrochloric acid (HCl), nitric acid (HNO_3), sodium hydroxide (NaOH), lead nitrate $Pb(NO_3)_2$, copper nitrate $Cu(NO_3)_2.3H_2O$, cadmium nitrate $Cd(NO_3)_2.4H_2O$, magnesium nitrate $Mg(NO_3)_2.6H_2O$, potassium nitrate (KNO_3), calcium chloride ($CaCl_2$), (sigma-Aldrich). Dowex 50WX8, (20-50 mesh) from Fluka.

Area of study



Source: Dept. of Geog. BUK (2016)

Figure 1: Map showing the sampling point at Sagamu Town, Ogun State.

Description of Sampling Area

Sagamu has geographical coordinates between 6°50′ north; 3° 38′ east is located in south western region of Nigeria. The region has tropical wet and dry climate with a lengthy wet season and relatively constant temperatures throughout the course of the year. Wet season runs from March to October, November to December forms the region dry season. The vegetation type of the region is savannah which is really grassland with small bushes and occasional big trees. Grassland soils have substantially higher organic matter content than forest soils (Novackova, 2011).

Sample Collection

The Peatsoil samples were collected from four different sampling points (0-10cm depth) in Sagamu into polyethylene bag with plastic spoons. Samples were taken to the laboratory, extraneous materials were removed; the samples were air-dried, crushed and ground to a fine powder in a mortar passed through a 0.20mm sieve. The samples were kept for analysis.

Isolation and purification of humic acid from peat soil sample

Peatsoil sample (100g) was mixed with 1000 cm^3 of 0.1M NaOH solution, shaken for 3hours and left to stand overnight. Dark-coloured supernatant was obtained and decanted from solid residue. The dark-coloured supernatant was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 6 hours. Yellowish brown supernatant and dark-brown precipitate were obtained. The yellowish brown supernatant was decanted followed by centrifuge and discarded. The dark-brown precipitate was mixed with 500cm^{3}of 0.1M NaOH solution followed by passing through dowex resin. The dark-brown solution was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 3 hours. The dark-brown precipitate was washed several times with deionized water. The supernatant was treated with $AgNO_3$ solution until no white precipitate observed. The humic acid was transferred to weighed crucible and dried at 60^oC in an oven for 12 hours. The humic acid was cooled and dried in the desiccator, weighed and recorded. The obtained humic acid was dried again at 60^oC for additional 6 hours cooled and dried in the desiccator, weighed and recorded constant weight was obtained (Baruah *et al*., 2015).

FT-IR analysis

FT-IR spectra of humic acid sample was analysed using Carry 630 FT-IR Agilent Technologies.

Unhydrolysed compost humic acid

The unhydrolysed humic acid was obtained after isolation and purification of compost humic acid and kept for investigation.

Acid hydrolysis of Peatsoil acid

Peatsoil humic acid sample (1g) was refluxed for 12 hours at (160^oC) with 50cm^3 of 6M HCl. The mixture was allowed to cool, decanted, and centrifuged after hydrolysis. The insoluble residues were washed with distilled water via centrifugation several times, and the supernatant was treated with $AgNO_3$ solution until no white precipitate was observed. The residue was thoroughly dried over $CaCl_2$ in a desiccator at room temperature (Chefetz *et al*., 2002). Finally, the obtained hydrolysed humic acid was kept for investigation.

Potentiometric Titrations

Potentiometric measurements were carried out using a pH-meter Jenway (model 3510) with combine electrode, the sensitivity of the pH - meter is 0.01 units. The pH meter was switched on half an hour before starting the titration for initial warm up of the instrument. The instrument was calibrated with an aqueous standard buffer solution of pH 4.00 and 10.0 (borate buffer) prepared from a "Qualigens" buffer tablets.

The following sets of solutions were prepared in a 250cm^3 volumetric flask separately for pH metric titrations.

(i) 5 cm^3 0.1 M HCl + 40 cm^3 deionized water

(ii) 5 cm^3 0.1 M HCl + 39 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid

(iii) 5 cm^3 0.1 M HCl + 37 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid + 2 cm^3 0.01 M Cu(II)

The solutions were titrated against standardized 0.110MNaOH separately. The total volume of each mixture was adjusted to 50 cm^3 and the ionic strength of the solutions was maintained constant at by adding appropriate amount of stock solution of 1M KNO_3 (Gamal, 2015; Omar and Ali, 2015). A magnetic stirrer was used to achieve thorough mixing of the interacting solutions at 550 rpm. The same set of experimental conditions was applied for potentiometric titration of remaining samples.

Evaluation of pKa of Hydrolysed peat soil Humic Acids

The proton-ligand formation number n_A were calculated by Irving and Rossotti expression (Omar and Ali, 2015).

$$nA = Y- \frac{(V2-V1)(No-Eo)}{(Vo+V1)TcL} \text{ ....1}$$

Where: Y is number of dissociable proton, (V_2-V_1) is the measure of displacement of the ligand curve relative to acid curve, N^o and E^o are the resultant concentration of alkali solution, free acid solution, $T_{cL}{}^o$ is the total ligand concentration, V^o is the total volume of titration solution,V_1 is the volume of alkali added to acid solution,V_2 is the volume of alkali added to acid solution + ligand solution, acid dissociation constants (pKa - values) of ligand were calculated by algebraic method point wise calculation (Tables 1). The dissociation constants (pKa) were calculated according to the following relation:

$$pKa = pH + \log(\frac{nA}{1-nA}) \text{ ....2}$$

Where: pKa is the acid dissociation constant, $n_A$is the Proton-ligand formation number and pH is the pH-values (Omar and Ali, 2015).

Determination of metal-ligand stability constants (log K) of complexes

The potentiometric measurement for the determination of stability constant of a complex in solution is based on the fact that the redox potential of the couple $\frac{M^{+(m-n)}}{M^{+m}}$ is shifted significantly on complexation of the metal ion with the ligand. This method involves change in hydrogen ion concentration [H$^+$] due to the displacement or association of one or more protons taking place during complexation reaction. This change can be found out by titrating the solutions containing free acid, acid with ligand, and acid with ligand and metal ion, individually against a standard alkali solution at a constant ionic strength or temperature. Either ionic strength or temperature may be varied for different sets of solutions. In all the cases, the change in the pH of the solution is measured after each addition of a known amount of alkali to the reaction cell which contains the reaction mixture. The titration curves are then drawn by plotting the measured pH values against the corresponding volume of alkali added and the stability constants of the complexes are determined from the titration curves by employing pH-metric titration technique given by (Irving and Rossoti).

Metal-ligand stability constants (Log K) were determined by using the following relations:

$$\bar{n} = \frac{(V_3 - V_2)(E^0 + N^0)}{(V^0 + V_2)\bar{n}_A T_m^0} \text{ ....3}$$

and

$$PL = \log_{10}\{\frac{1+\beta_n^H \frac{1}{[anti\ \log pH]^n}}{T_L^0 - \bar{n}T_m^0} X \frac{(V^0+V_3)}{V^0}\} \text{ ....4}$$

Where $T_{L,}$ T^{o}, E°, and V^{o}havethe same significance as in equation (1) above, T_{m} denotes the total concentration of metal present in solution, V_3 is the volume of metal ions present in solution and β^{H} is the overall proton ligand stability constant. The metal-ligand stability constants (log K) were determined by employing point wise computational Method (eq. 5 and 6).

$$LogK_1 = \log\left(\frac{n}{1-n}\right) + pL \qquad ....5$$

$$LogK_2 = \log\left(\frac{1-n}{2-n}\right) + pL.......................6$$

Where: Log K is the metal-ligand stability constant, pL is the Free ligand exponent function, **n** is the Average number of ligand attached with metal ion (Janrao*et al.*, 2014).The results obtained were analyzed by an ORIGIN 2016 program using titration data and then the proton-ligand stability constants (pKa) and Metal-ligand stability constant (LogK) calculated (Omar and Ali, 2015).

RESULTS AND DISCUSSION

Fourier transformed infrared (FT-IR) spectra of isolated humic acid from peat soils Figure 2 had distinct clear absorption bands indicating the presence of major humic acid structural elemental groups such as H bonded OH ($3680cm^{-1}$ peak), C=O of carbonyl ($1721cm^{-1}$ peak), functional groups of aliphatic components CH_2 ($2918cm^{-1}$ peak) and C-O stretching of polysaccharide ($1168cm^{-1}$ peak). The positions of the absorption bands of the spectra fell within typical major absorption bands of humic acid which is at frequencies 3680, 2918, 1721, 1168 cm^{-1}. The first peak centred in the vicinity of 3680 cm^{-1} region is attributed to phenol OH group bounded by intermolecular H bonds. The $2918cm^{-1}$ band usually has absorption maximum at 2918 cm^{-1} which is due to C–H stretching of alkane group (CH_2). The next major absorption band is 1721 cm^{-1}. This band has been commonly ascribed to C=O stretching of mainly carboxyl group (COOH) with trace amount of ketones. The last peak was observed at 1168 cm^{-1} due to C–O stretching of polysaccharides and this peak appeared also in the spectra of humic acid from peat soil. The FTIR spectra of the isolated humic acid contained all major characteristic absorption peaks of humic acid. These absorption peaks indicated the presence of the major structural elements of humic acid namely H bonded OH, C=C of aromatic ring, C=O of carbonyl group (both carboxyl and ketonic), CH_2 group. This strongly supports the presence of humic acid.

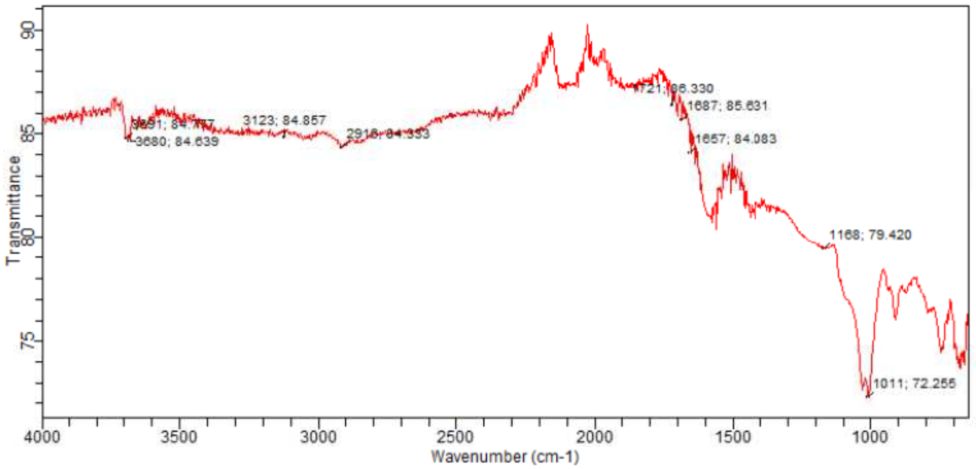


Fig. 2 : FT-IR spectraof peatsoilhumic acid (PSHA)

Evaluation of acid dissociation constant (pka) of acid hydrolysed peat soil humicacid at phenolic group

The value of the dissociation constant of the peat soil humic acid (PSHA) that underwent acidhydrolysis studied was found to be 8.9299 as shown Table 1, which is lower than the literaturevalues reported by Almeida and Szpoganics, (2015), Borges *et al.*, (2005); Badr *et al.*, (2012)and Fernandes *et al*,.(2009) of 9.73, 9.47 and 10.30. The difference between the obtained valuesand the reported values in this study might be probably as a result of acid hydrolysis of humicacid.

Table 1: PKa of (Hydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	$\log(\frac{nA}{1-nA})$	pKa
8.50	5.30	6.29	0.99	0.3594	-0.2510	8.2490
8.72	5.35	6.37	1.02	0.3400	-0.2880	8.4320
9.00	5.40	6.46	1.06	0.3141	-0.3391	8.6609
9.22	5.45	6.55	1.10	0.2882	-0.3927	8.8273
9.51	5.50	6.66	1.16	0.2494	-0.4786	9.0314
9.73	5.55	6.78	1.23	0.2041	-0.5910	9.1390
10.00	5.60	6.90	1.30	0.1589	-0.7238	9.2762
10.23	5.65	7.05	1.40	0.0941	-0.9835	9.2465
10.49	5.70	7.10	1.40	0.0941	-0.9835	9.5065

Average pKa = 8.9299 ± 0.4186

Table 2: PKa of (Unhydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	$\text{Log}(\frac{nA}{1-n})$	pKa
8.50	5.30	5.81	0.51	0.6619	0.2919	8.7919
8.72	5.35	5.90	0.55	0.6357	0.2418	8.9618
9.00	5.40	6.00	0.60	0.6029	0.1813	9.1813
9.22	5.45	6.10	0.65	0.5701	0.1226	9.3426
9.51	5.50	6.20	0.70	0.5376	0.0654	9.5754
9.73	5.55	6.33	0.78	0.4851	-0.0259	9.7041
10.00	5.60	6.47	0.87	0.4262	-0.1291	9.8709
10.23	5.65	6.62	0.99	0.3609	-0.2481	9.9819
10.49	5.70	6.80	1.10	0.2759	-0.4690	10.0210

Average pKa = 9.4923± 0.4410

Metal-ligand stability constant (Log K)

The stabilityconstants require the accurate values of proton-ligand stability constants (Anil and Maroti, 2008). Metal titration curves crossed over ligand titration curve indicated the formation of complex upon proton release (Santosh, *et al.*, 2011). If the values of n- are within range 0.2-0.8 and 1.2-18 this indicates the formation of 1:1 and 1:2 complexes (Sayyed and Mazahar, 2012).

The metal (II)-humate stepwise stability constants (log k) at phenolic group (Tables 3-18)

Table 3: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$\log(\frac{n}{1-n})$	LogK_1
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

LogK_1 (Average value) = 2.4788± 0.2203

Table 4: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$\text{Log}(\frac{n-1}{2-n})$	LogK_2
9.51	5.50	6.66	6.73	0.07	1.3509	1.70	-0.2671	1.4329
9.73	5.55	6.78	6.85	0.07	1.6383	1.51	0.2467	1.7567
10.00	5.60	6.90	6.98	0.08	2.1783	1.31	-0.2158	1.0942
10.23	5.65	7.05	7.13	0.08	4.1904	1.27		
10.49	5.70	7.10	7.19	0.09	4.6920			

LogK_2(Average value) = 1.4280 ± 0.3312

Table 5:Point-wise method,Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	Log($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430

$LogK_1$ **(Average value)** = 2.3059± 0.6153

Table 6:Point-wise method, Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
9.73	5.55	6.33	6.42	0.09	0.9000	1.69		
10.00	5.60	6.47	6.58	0.11	1.2578	1.44	-0.4592	0.9808
10.23	5.65	6.62	6.84	0.12	1.6137	1.26	-0.2010	1.4610
10.49	5.70	6.80	6.92	0.12	2.1052	1.03		

$LogK_2$ **(Average value)** = 1.2209± 0.3398

Table 7:Point-wise method,Pb (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n}{1-n}$)	$LogK_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.60	0.05	0.8333	1.96	0.6989	2.6589

$LogK_1$ (Average value) = 2.5832 ±0.1614

Table 8:Point-wise method,Pb-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n-1}{2-n}$)	$logK_2$
9.51	5.50	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.83	0.05	1.1702	1.44		
10.00	5.60	6.90	6.90	0.05	1.4864	1.22	-0.0237	1.1963
10.23	5.65	7.05	7.10	0.05	2.0190	1.09		
10.49	5.70	7.10	7.17	0.07	3.6492	1.00		

$LogK_2$(Average value) = 1.1963

Table 9:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log ($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.5477	2.3123
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	0.0272	2.2072
9.51	5.50	6.20	6.26	0.07	0.6417	1.89	0.2530	2.1430
9.73	5.55	6.40	6.40	0.07	0.7000	1.67	0.3680	2.0380

$LogK_1$ **(Average value)** = 2.2364 ± 0.1602

Table 10:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
10.00	5.60	6.47	6.55	0.08	1.9503	1.41		
10.23	5.65	6.62	6.72	0.11	1.4792	1.26	-0.0361	1.2239

$LogK_2$ **(Average value)** = 1.2239

Table 11:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n}{n-1}$)	$LogK_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4290	2.2110
8.72	5.35	6.37	6.39	0.02	0.2858	2.42	-0.3978	2.0222
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

$LogK_1$ (Average value)=2.1382±0.1046

Table 12:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	log($\frac{n-1}{2-n}$)	LogK$_2$
9.51	5.55	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.84	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.93	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.10		
10.49	5.70	7.10	7.18	0.07	3.6492	0.83		

LogK$_2$(Average value) = 1.5453 **±** 0.3450

Table 13:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	V$_3$-V$_2$	n	pL	Log($\frac{n}{n-1}$)	Log K$_1$
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.3477	2.3123
9.00	5.40	6.00	6.04	0.04	0.3236	2.38	-0.3202	2.0598
9.22	5.45	6.10	6.15	0.05	0.4297	2.17	-0.1230	2.0470
9.51	5.50	6.20	6.26	0.06	0.5500	1.89	0.0871	1.9771
9.73	5.55	6.33	6.40	0.07	0.7000	1.67	0.3680	2.0380

LogK$_1$ **(Average value)** = 2.1568 ± 0.2069

Table 14:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	V$_3$-V$_2$	n	pL	Log($\frac{n-1}{2-n}$)	Log K$_2$
10.00	5.60	6.47	6.55	0.08	0.9148	1.41		
10.23	5.65	6.62	6.71	0.09	1.2102	1.20	-0.5749	0.6251
10.49	5.70	6.80	6.92	0.09	1.5968	1.03	0.1703	1.2003

LogK$_2$ **(Average value)** = 0.9127± 0.4070

Table15:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	Log($\frac{n}{1-n}$)	LogK$_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4210	2.2190
8.72	5.35	6.37	6.40	0.03	0.4286	2.42	-0.1249	2.2951
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.96	0.3010	2.2610
9.51	5.55	6.66	6.70	0.04	0.7720	1.67	0.5297	2.1997

LogK$_1$ (Average value) = 2.2108± 0.0825

Table 16:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	Log($\frac{n-1}{2-n}$)	Log K$_2$
9.73	5.55	6.78	6.83	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.95	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.09		
10.49	5.70	7.10	7.16	0.06	3.1429	0.89		

LogK$_2$ **(Average value)** = 1.5453± 0.3450

Table 17:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	V$_3$-V$_2$	n	pL	Log($\frac{n}{n-1}$)	Log K$_1$
8.50	5.30	5.81	5.86	0.05	0.3717	2.88	-0.2280	2.6520
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.06	0.06	0.4853	2.38	-0.0255	2.3545
9.22	5.45	6.10	6.16	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430
9.73	5.55	6.33	6.41	0.08	0.8000	1.69	0.6020	2.2920

LogK$_1$ **(Average value)** = 2.2516± 0.5380

Table 18:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$\text{Log}(\frac{n-1}{2-n})$	Log K_2
10.00	5.60	6.47	6.57	0.10	1.1434	1.43		
10.23	5.65	6.62	6.72	0.10	1.3448	1.23	-0.2788	0.9512
10.49	5.70	6.80	6.90	0.10	1.7742	1.03	0.5351	1.5651

LogK_2 **(Average value)** = 1.2581± 0.4340

Table 19: Stepwise and overall Stability constants of thehydrolysed and unhydrolysed divalent metal (II) complexes

Chelates	**LogK_1**	**LogK_2**	**Logβ**
[Cu (Hydrolysed PSHA-1)$_2$]	2.4788	1.4280	3.9068
[Pb (Hydrolysed PSHA-1)$_2$]	2.5832	1.1963	3.7795
[Cd (Hydrolysed PSHA-1)$_2$]	2.2108	1.5453	3.7561
[Mg (Hydrolysed PSHA-1)$_2$]	2.1382	1.5453	3.6835
[Cu (Unhydrolysed PSHA-1)$_2$]	2.3059	1.2209	3.5268
[Pb (Unhydrolysed PSHA-1)$_2$]	2.2364	1.2239	3.4603
[Cd (Unhydrolysed PSHA-1)$_2$]	2.2516	1.2581	3.5097
[Mg (Unydrolysed PSHA-1)$_2$]	2.1568	0.9127	3.0695

The results obtained (Table19) shows the stepwise and overall stability constants to be not high indicating low stability of the complexes, because the solubility of most metal ions in the basic pH range is minimal due to metal hydroxide precipitation (Karimi, 2017). In general, the stepwise stability constants (K_1 and K_2) follow the order $K_1 > K_2$ for the copper, lead, magnesium and cadmium complexes respectively. The steady decrease of the values with increasing number of ligands is in agreement with the prediction made by researchers (Na'aliya, 2013). The decrease could be attributed to the fact that as the number of the ligands (Humate ions) that enters the coordination zone increases the aqua molecules available for replacement by the ligands become less. Thus, the metal ions become less electron loving with progressive intake of the ligand and this results in the decrease in the values of the constants (Na'aliya, 2013). Also the stability of the complexes is influenced by the size and number of the chelate rings(Mackay and Mackay,2002).All the complexes form rings in their structure as humate, a bidentate ligand, bond the metal ions in the ratio 1:2 (Boguta and Sokolowska, 2016) forming chelate rings. The values of the overall stability constants (logβ) obtained for humate complexes are not high indicating low stability as the values are not high. LogK values for copper-humates (Table 3 to 6) obtained in this study are lower than those reported for the complexes of humic acids (Pandey *et al*., 2015; Dinu, 2013; Kaschl *et al*., 2010 and Gilbeto and Jorg, 2001). The values of LogK(Table 7 to 10) forlead-humates are lower than those reported for the lead in the literature (Dinu, 2013; Gilbeto and Jorg 2001). Log K values(Table 11 to 14) for magnesium-humates obtained in this study are close to those reported by (Pandey *et al*., 2015). Log K values of cadmium-humates (Table 15 to 18) obtained in this work near to the one reported by (Dinu, 2013 and Pandey *et al*., 2015).The difference between the reported values and the values obtained in this study might be probably as a result of acid hydrolysis of humic acid. The values of the overall stability constants (log β) of the copper humates complexes presented in Table 19 is high than that of other metal humate complexes, show relatively high stability of Cu-HA complexes, show the following order of stability: Cu >Pb> Cd > Mg; which are in close agreement to the findings of (Dinu, 2013 and Pandey *et al*., 2015).The high stability of Cu-humate chelate could be attributed to the existence of coordinate covalent bond between the complexing agents and the Cu^{2+} ions. Since, Cu^{2+} being a metal of the transitional series with $3d^9$ electronic configurations can accept the electrons from the complexing agents. Similarly,the low stabilities of Pb,Cd and Mg -complexes could be explained by that Pb^{2+} with $6s^2$, Cd^{2+} with $4d^{10}$ and Mg^{2+} with $2p^6$ their electronic configuration has a completely filled d,p and s orbitals. Moreover, the stabilities of metal ions with hydrolysed humic acid from peat soil were higher than those with unhydrolysed humic acid from peat soil; which is ascribed to the high content of acidity in hydrolysed humic acid than unhydrolysed humic acid.

CONCLUSION

The values of logK for Cu(II) hydrolysed humic acid complex was higher followed by Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes as compared with metal(II) unhydrolysed humic acid complexes . This indicates acid hydrolysis of humic acid can enhance the complexation behavior of humic acid with metal (II) ions. However, the higher values of logβ for Cu(II), Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes indicates more stable stepwise complexes formed as compared with Cu(II), Pb(II), Cd(II) and Mg(II) unhydrolysed humic acid complexes.

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STABILITY CONSTANTS OF COMPLEXES OF METAL IONS WITH PEATSOIL HUMIC ACIDS UNDER NON-ACID-CONDITIONS

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ABSTRACT

Stability constants of complexes of four divalent metal ions viz. Cu^{2+}, Pb^{2+},Mg^{2+} and Cd^{2+} with humic acids (HA) were determined by potentiometric titration of humic acids with the corresponding salt of the divalent metals in aqueous media under non-acid-condition. The log K (logarithm of the stability constant) ranged from 1.0942 to 2.7471 for metal-humic acid complexes were determined using point-wise computational method. The order of stability constants were obtained as follows: Cu >Pb> Cd > Mg for metal -HA complexes respectively, indicating a higher degree of complexation with Cu metal ion.

Keywords: stability constant, humic acid, potentiometric titration, divalent metals, acid hydrolysis.

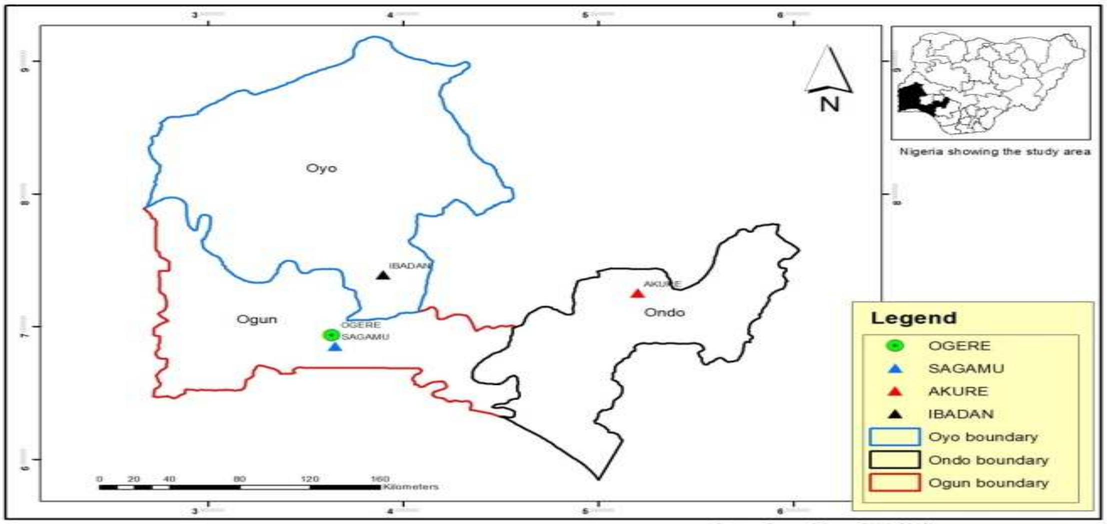
NTRODUCTION

The stability constant of a complex is the numerical expression of its stability and provides a quantitative measure of affinity of the metal ion to the complexing agent. An understanding of the relative stability of metal-complexes helps in predicting the behavior of metal ions in the soil (Ram and Raman, 1982). Extensive researches has been done to determine the stability constants of the complexes formed between humic acid (HA) with a number of metal ions. Ashok *et al.*, (2000) reported that humic acid with hydroxyl, phenoxyl and carboxyl reactive groups can form coordination compound with metal ions at pH 3.5. The stability constants(Log K) for different metal-humic acid complexes indicated the following order of the stabilities of complexes formed between humic acid and metal ion, Cu >Fe >Pb> Ni > Co > Ca > Cd > Zn >Mn> Mg. Andelkovic *et al.*, (2010) investigated the binding of Cd(II) to soil humic acid at pH 6.5 and in 0.1M KNO_3 ionic medium. The stability constant for binding indicating greater stability in the case when carboxyl groups are involved in complexation reaction. Kostic *et al.*,(2012) investigated the complexation of humic acid with certain heavy metal ions (Co(II), Ni(II),Cu(II), Zn(II), and Pb(II). The experiment was performed at 25°C, at pH 4.0 and ionic strength of 0.01M. Stability constant of complex between Pb(II) ions and humic acid is greater than stability constants of other investigated metal-humate complexes. Bogata and Sokolowska (2016) analyses the interaction between humic acids from different soils and Zn (II) ions at wide concentration ranges and at pH 5. Studies have showed significant impact of Zn concentration, pH and some properties of humic acids with zinc.But all of these studies were limited to acidic pH range. Therefore, the present study was carried out to determine and compare the stability constants of complexes of metal ions with hydrolysed peat soil humic acid and unhydrolysed peat soil humic under non-acid conditions.

MATERIALS AND METHODS

Analytical grade chemicals used includes hydrochloric acid (HCl), nitric acid (HNO_3), sodium hydroxide (NaOH), lead nitrate $Pb(NO_3)_2$, copper nitrate $Cu(NO_3)_2.3H_2O$, cadmium nitrate $Cd(NO_3)_2.4H_2O$, magnesium nitrate $Mg(NO_3)_2.6H_2O$, potassium nitrate (KNO_3), calcium chloride ($CaCl_2$), (sigma-Aldrich). Dowex 50WX8, (20-50 mesh) from Fluka.

Area of study



Source: Dept. of Geog. BUK (2016)

Figure 1: Map showing the sampling point at Sagamu Town, Ogun State.

Description of Sampling Area

Sagamu has geographical coordinates between 6°50′ north; 3° 38′ east is located in south western region of Nigeria. The region has tropical wet and dry climate with a lengthy wet season and relatively constant temperatures throughout the course of the year. Wet season runs from March to October, November to December forms the region dry season. The vegetation type of the region is savannah which is really grassland with small bushes and occasional big trees. Grassland soils have substantially higher organic matter content than forest soils (Novackova, 2011).

Sample Collection

The Peatsoil samples were collected from four different sampling points (0-10cm depth) in Sagamu into polyethylene bag with plastic spoons. Samples were taken to the laboratory, extraneous materials were removed; the samples were air-dried, crushed and ground to a fine powder in a mortar passed through a 0.20mm sieve. The samples were kept for analysis.

Isolation and purification of humic acid from peat soil sample

Peatsoil sample (100g) was mixed with 1000 cm^3 of 0.1M NaOH solution, shaken for 3hours and left to stand overnight. Dark-coloured supernatant was obtained and decanted from solid residue. The dark-coloured supernatant was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 6 hours. Yellowish brown supernatant and dark-brown precipitate were obtained. The yellowish brown supernatant was decanted followed by centrifuge and discarded. The dark-brown precipitate was mixed with 500$cm^3$of 0.1M NaOH solution followed by passing through dowex resin. The dark-brown solution was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 3 hours. The dark-brown precipitate was washed several times with deionized water. The supernatant was treated with $AgNO_3$ solution until no white precipitate observed. The humic acid was transferred to weighed crucible and dried at 60°C in an oven for 12 hours. The humic acid was cooled and dried in the desiccator, weighed and recorded. The obtained humic acid was dried again at 60°C for additional 6 hours cooled and dried in the desiccator, weighed and recorded constant weight was obtained (Baruah *et al*., 2015).

FT-IR analysis

FT-IR spectra of humic acid sample was analysed using Carry 630 FT-IR Agilent Technologies.

Unhydrolysed compost humic acid

The unhydrolysed humic acid was obtained after isolation and purification of compost humic acid and kept for investigation.

Acid hydrolysis of Peatsoil acid

Peatsoil humic acid sample (1g) was refluxed for 12 hours at (160°C) with 50cm^3 of 6M HCl. The mixture was allowed to cool, decanted, and centrifuged after hydrolysis. The insoluble residues were washed with distilled water via centrifugation several times, and the supernatant was treated with $AgNO_3$ solution until no white precipitate was observed. The residue was thoroughly dried over $CaCl_2$ in a desiccator at room temperature (Chefetz *et al*., 2002). Finally, the obtained hydrolysed humic acid was kept for investigation.

Potentiometric Titrations

Potentiometric measurements were carried out using a pH-meter Jenway (model 3510) with combine electrode, the sensitivity of the pH - meter is 0.01 units. The pH meter was switched on half an hour before starting the titration for initial warm up of the instrument. The instrument was calibrated with an aqueous standard buffer solution of pH 4.00 and 10.0 (borate buffer) prepared from a "Qualigens" buffer tablets.

The following sets of solutions were prepared in a 250cm^3 volumetric flask separately for pH metric titrations.

(i) 5 cm^3 0.1 M HCl + 40 cm^3 deionized water

(ii) 5 cm^3 0.1 M HCl + 39 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid

(iii) 5 cm^3 0.1 M HCl + 37 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid + 2 cm^3 0.01 M Cu(II)

The solutions were titrated against standardized 0.110MNaOH separately. The total volume of each mixture was adjusted to 50 cm^3 and the ionic strength of the solutions was maintained constant at by adding appropriate amount of stock solution of 1M KNO$_3$ (Gamal, 2015; Omar and Ali, 2015). A magnetic stirrer was used to achieve thorough mixing of the interacting solutions at 550 rpm. The same set of experimental conditions was applied for potentiometric titration of remaining samples.

Evaluation of pKa of Hydrolysed peat soil Humic Acids

The proton-ligand formation number n$_\mathbf{A}$ were calculated by Irving and Rossotti expression (Omar and Ali, 2015).

$$nA = Y- \frac{(V2-V1)(No-Eo)}{(Vo+V1)TcL} \text{ ………………………………1}$$

Where: Y is number of dissociable proton, (V$_2$-V$_1$) is the measure of displacement of the ligand curve relative to acid curve, N^o and E^o are the resultant concentration of alkali solution, free acid solution, T$_{cL}$^{o} is the total ligand concentration, V^o is the total volume of titration solution,V$_1$ is the volume of alkali added to acid solution,V$_2$ is the volume of alkali added to acid solution + ligand solution, acid dissociation constants (pKa - values) of ligand were calculated by algebraic method point wise calculation (Tables 1). The dissociation constants (pKa) were calculated according to the following relation:

$$pKa = pH + \log(\frac{nA}{1-nA}) \text{ …………………………2}$$

Where: pKa is the acid dissociation constant, n$_A$is the Proton-ligand formation number and pH is the pH-values (Omar and Ali, 2015).

Determination of metal-ligand stability constants (log K) of complexes

The potentiometric measurement for the determination of stability constant of a complex in solution is based on the fact that the redox potential of the couple $\frac{M^{+(m-n)}}{M^{+m}}$ is shifted significantly on complexation of the metal ion with the ligand. This method involves change in hydrogen ion concentration [H$^+$] due to the displacement or association of one or more protons taking place during complexation reaction. This change can be found out by titrating the solutions containing free acid, acid with ligand, and acid with ligand and metal ion, individually against a standard alkali solution at a constant ionic strength or temperature. Either ionic strength or temperature may be varied for different sets of solutions. In all the cases, the change in the pH of the solution is measured after each addition of a known amount of alkali to the reaction cell which contains the reaction mixture. The titration curves are then drawn by plotting the measured pH values against the corresponding volume of alkali added and the stability constants of the complexes are determined from the titration curves by employing pH-metric titration technique given by (Irving and Rossoti).

Metal-ligand stability constants (Log K) were determined by using the following relations:

$$\bar{n} = \frac{(V_3 - V_2)(E^0 + N^0)}{(V^0 + V_2)\bar{n}_A T_m^0} \text{ ………………………………………………………………………3}$$

and

$$PL = \log_{10}\{\frac{1+\beta_n^H \frac{1}{[anti\ \log pH]^n}}{T_L^0 - \bar{n}T_m^0} X \frac{(V^0+V_3)}{V^0}\} \text{ ……………………………………………………4}$$

Where $T_{L,}$ T^{o}, E°, and V^{o}havethe same significance as in equation (1) above, T_m denotes the total concentration of metal present in solution, V_3 is the volume of metal ions present in solution and β^H is the overall proton ligand stability constant. The metal-ligand stability constants (log K) were determined by employing point wise computational Method (eq. 5 and 6).

$$\text{Log}K_1 = \log\left(\frac{n}{1-n}\right) + pL \qquad \ldots\ldots\ldots\ldots.5$$

$$\text{Log}K_2 = \log\left(\frac{1-n}{2-n}\right) + pL\ldots\ldots\ldots\ldots\ldots\ldots\ldots.6$$

Where: Log K is the metal-ligand stability constant, pL is the Free ligand exponent function, **n** is the Average number of ligand attached with metal ion (Janrao*et al.*, 2014).The results obtained were analyzed by an ORIGIN 2016 program using titration data and then the proton-ligand stability constants (pKa) and Metal-ligand stability constant (LogK) calculated (Omar and Ali, 2015).

RESULTS AND DISCUSSION

Fourier transformed infrared (FT-IR) spectra of isolated humic acid from peat soils Figure 2 had distinct clear absorption bands indicating the presence of major humic acid structural elemental groups such as H bonded OH (3680cm^{-1} peak), C=O of carbonyl (1721cm^{-1} peak), functional groups of aliphatic components CH_2 (2918cm^{-1} peak) and C-O stretching of polysaccharide (1168cm^{-1} peak). The positions of the absorption bands of the spectra fell within typical major absorption bands of humic acid which is at frequencies 3680, 2918, 1721, 1168 cm^{-1}. The first peak centred in the vicinity of 3680 cm^{-1} region is attributed to phenol OH group bounded by intermolecular H bonds. The 2918cm^{-1} band usually has absorption maximum at 2918 cm^{-1} which is due to C–H stretching of alkane group (CH_2). The next major absorption band is 1721 cm^{-1}. This band has been commonly ascribed to C=O stretching of mainly carboxyl group (COOH) with trace amount of ketones. The last peak was observed at 1168 cm^{-1} due to C–O stretching of polysaccharides and this peak appeared also in the spectra of humic acid from peat soil. The FTIR spectra of the isolated humic acid contained all major characteristic absorption peaks of humic acid. These absorption peaks indicated the presence of the major structural elements of humic acid namely H bonded OH, C=C of aromatic ring, C=O of carbonyl group (both carboxyl and ketonic), CH_2 group. This strongly supports the presence of humic acid.

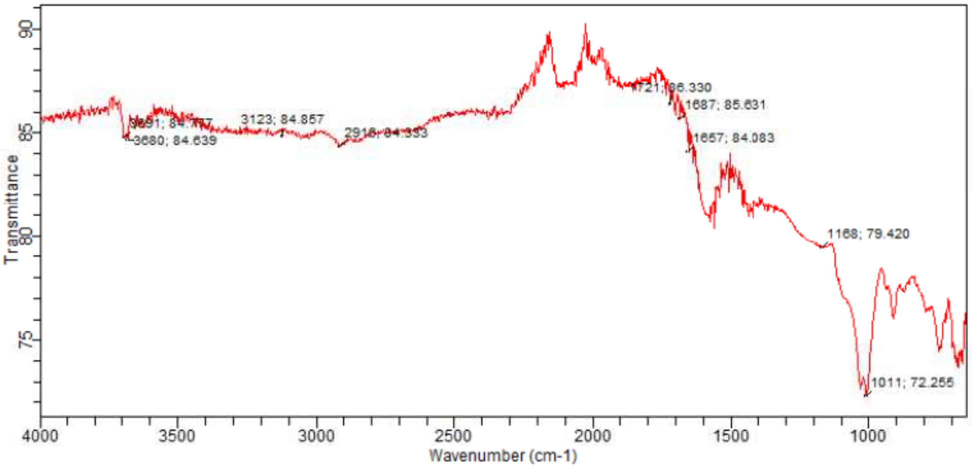


Fig. 2 : FT-IR spectraof peatsoilhumic acid (PSHA)

Evaluation of acid dissociation constant (pka) of acid hydrolysed peat soil humicacid at phenolic group

The value of the dissociation constant of the peat soil humic acid (PSHA) that underwent acidhydrolysis studied was found to be 8.9299 as shown Table 1, which is lower than the literaturevalues reported by Almeida and Szpoganics, (2015), Borges *et al.*, (2005); Badr *et al.*, (2012)and Fernandes *et al*,.(2009) of 9.73, 9.47 and 10.30. The difference between the obtained valuesand the reported values in this study might be probably as a result of acid hydrolysis of humicacid.

Table 1: PKa of (Hydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	$\log(\frac{nA}{1-nA})$	pKa
8.50	5.30	6.29	0.99	0.3594	-0.2510	8.2490
8.72	5.35	6.37	1.02	0.3400	-0.2880	8.4320
9.00	5.40	6.46	1.06	0.3141	-0.3391	8.6609
9.22	5.45	6.55	1.10	0.2882	-0.3927	8.8273
9.51	5.50	6.66	1.16	0.2494	-0.4786	9.0314
9.73	5.55	6.78	1.23	0.2041	-0.5910	9.1390
10.00	5.60	6.90	1.30	0.1589	-0.7238	9.2762
10.23	5.65	7.05	1.40	0.0941	-0.9835	9.2465
10.49	5.70	7.10	1.40	0.0941	-0.9835	9.5065

Average pKa = 8.9299 ± 0.4186

Table 2: PKa of (Unhydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	$\mathrm{Log}(\frac{nA}{1-n})$	pKa
8.50	5.30	5.81	0.51	0.6619	0.2919	8.7919
8.72	5.35	5.90	0.55	0.6357	0.2418	8.9618
9.00	5.40	6.00	0.60	0.6029	0.1813	9.1813
9.22	5.45	6.10	0.65	0.5701	0.1226	9.3426
9.51	5.50	6.20	0.70	0.5376	0.0654	9.5754
9.73	5.55	6.33	0.78	0.4851	-0.0259	9.7041
10.00	5.60	6.47	0.87	0.4262	-0.1291	9.8709
10.23	5.65	6.62	0.99	0.3609	-0.2481	9.9819
10.49	5.70	6.80	1.10	0.2759	-0.4690	10.0210

Average pKa = 9.4923± 0.4410

Metal-ligand stability constant (Log K)

The stabilityconstants require the accurate values of proton-ligand stability constants (Anil and Maroti, 2008). Metal titration curves crossed over ligand titration curve indicated the formation of complex upon proton release (Santosh, *et al.*, 2011). If the values of n- are within range 0.2-0.8 and 1.2-18 this indicates the formation of 1:1 and 1:2 complexes (Sayyed and Mazahar, 2012).

The metal (II)-humate stepwise stability constants (log k) at phenolic group (Tables 3-18)

Table 3: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$\log(\frac{n}{1-n})$	$\mathrm{Log}K_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

LogK_1 (Average value) = 2.4788± 0.2203

Table 4: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$\mathrm{Log}(\frac{n-1}{2-n})$	$\mathrm{Log}K_2$
9.51	5.50	6.66	6.73	0.07	1.3509	1.70	-0.2671	1.4329
9.73	5.55	6.78	6.85	0.07	1.6383	1.51	0.2467	1.7567
10.00	5.60	6.90	6.98	0.08	2.1783	1.31	-0.2158	1.0942
10.23	5.65	7.05	7.13	0.08	4.1904	1.27		
10.49	5.70	7.10	7.19	0.09	4.6920			

LogK_2(Average value) = 1.4280 ± 0.3312

Table 5:Point-wise method,Cu (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	Log($\frac{n}{n-1}$)	Log K$_1$
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430

LogK$_1$ **(Average value)** = 2.3059± 0.6153

Table 6:Point-wise method, Cu (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	V$_3$-V$_2$	n	pL	Log($\frac{n-1}{2-n}$)	Log K$_2$
9.73	5.55	6.33	6.42	0.09	0.9000	1.69		
10.00	5.60	6.47	6.58	0.11	1.2578	1.44	-0.4592	0.9808
10.23	5.65	6.62	6.84	0.12	1.6137	1.26	-0.2010	1.4610
10.49	5.70	6.80	6.92	0.12	2.1052	1.03		

LogK$_2$ **(Average value)** = 1.2209± 0.3398

Table 7:Point-wise method,Pb (Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	log($\frac{n}{1-n}$)	LogK$_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.60	0.05	0.8333	1.96	0.6989	2.6589

LogK$_1$ (Average value) = 2.5832 ±0.1614

Table 8:Point-wise method,Pb-(Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	log($\frac{n-1}{2-n}$)	logK$_2$
9.51	5.50	6.66	6.71	0.05	0.9650	1.67	-0.0237	1.1963
9.73	5.55	6.78	6.83	0.05	1.1702	1.44		
10.00	5.60	6.90	6.90	0.05	1.4864	1.22		
10.23	5.65	7.05	7.10	0.05	2.0190	1.09		
10.49	5.70	7.10	7.17	0.07	3.6492	1.00		

LogK$_2$(Average value) = 1.1963

Table 9:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	V$_3$-V$_2$	n	pL	Log ($\frac{n}{n-1}$)	Log K$_1$
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.5477	2.3123
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	0.0272	2.2072
9.51	5.50	6.20	6.26	0.07	0.6417	1.89	0.2530	2.1430
9.73	5.55	6.40	6.40	0.07	0.7000	1.67	0.3680	2.0380

LogK$_1$ **(Average value)** = 2.2364 ± 0.1602

Table 10:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	V$_3$-V$_2$	n	pL	Log($\frac{n-1}{2-n}$)	Log K$_2$
10.00	5.60	6.47	6.55	0.08	1.9503	1.41		
10.23	5.65	6.62	6.72	0.11	1.4792	1.26	-0.0361	1.2239

LogK$_2$ **(Average value)** = 1.2239

Table 11:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	log($\frac{n}{n-1}$)	LogK$_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4290	2.2110
8.72	5.35	6.37	6.39	0.02	0.2858	2.42	-0.3978	2.0222
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

LogK$_1$ (Average value)=2.1382**±**0.1046

Table 12:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n-1}{2-n}$)	$LogK_2$
9.51	5.55	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.84	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.93	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.10		
10.49	5.70	7.10	7.18	0.07	3.6492	0.83		

$LogK_2$(Average value) = 1.5453 **±** 0.3450

Table 13:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.3477	2.3123
9.00	5.40	6.00	6.04	0.04	0.3236	2.38	-0.3202	2.0598
9.22	5.45	6.10	6.15	0.05	0.4297	2.17	-0.1230	2.0470
9.51	5.50	6.20	6.26	0.06	0.5500	1.89	0.0871	1.9771
9.73	5.55	6.33	6.40	0.07	0.7000	1.67	0.3680	2.0380

$LogK_1$ **(Average value)** = 2.1568 ± 0.2069

Table 14:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
10.00	5.60	6.47	6.55	0.08	0.9148	1.41		
10.23	5.65	6.62	6.71	0.09	1.2102	1.20	-0.5749	0.6251
10.49	5.70	6.80	6.92	0.09	1.5968	1.03	0.1703	1.2003

$LogK_2$ **(Average value)** = 0.9127± 0.4070

Table15:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	Log($\frac{n}{1-n}$)	$LogK_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4210	2.2190
8.72	5.35	6.37	6.40	0.03	0.4286	2.42	-0.1249	2.2951
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.96	0.3010	2.2610
9.51	5.55	6.66	6.70	0.04	0.7720	1.67	0.5297	2.1997

$LogK_1$ (Average value) = 2.2108± 0.0825

Table 16:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
9.73	5.55	6.78	6.83	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.95	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.09		
10.49	5.70	7.10	7.16	0.06	3.1429	0.89		

$LogK_2$ **(Average value)** = 1.5453± 0.3450

Table 17:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.86	0.05	0.3717	2.88	-0.2280	2.6520
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.06	0.06	0.4853	2.38	-0.0255	2.3545
9.22	5.45	6.10	6.16	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430
9.73	5.55	6.33	6.41	0.08	0.8000	1.69	0.6020	2.2920

$LogK_1$ **(Average value)** = 2.2516± 0.5380

Table 18:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$\text{Log}(\frac{n-1}{2-n})$	Log K_2
10.00	5.60	6.47	6.57	0.10	1.1434	1.43		
10.23	5.65	6.62	6.72	0.10	1.3448	1.23	-0.2788	0.9512
10.49	5.70	6.80	6.90	0.10	1.7742	1.03	0.5351	1.5651

LogK_2 **(Average value)** = 1.2581± 0.4340

Table 19: Stepwise and overall Stability constants of thehydrolysed and unhydrolysed divalent metal (II) complexes

Chelates	**LogK_1**	**LogK_2**	**Logβ**
[Cu (Hydrolysed PSHA-1)$_2$]	2.4788	1.4280	3.9068
[Pb (Hydrolysed PSHA-1)$_2$]	2.5832	1.1963	3.7795
[Cd (Hydrolysed PSHA-1)$_2$]	2.2108	1.5453	3.7561
[Mg (Hydrolysed PSHA-1)$_2$]	2.1382	1.5453	3.6835
[Cu (Unhydrolysed PSHA-1)$_2$]	2.3059	1.2209	3.5268
[Pb (Unhydrolysed PSHA-1)$_2$]	2.2364	1.2239	3.4603
[Cd (Unhydrolysed PSHA-1)$_2$]	2.2516	1.2581	3.5097
[Mg (Unydrolysed PSHA-1)$_2$]	2.1568	0.9127	3.0695

The results obtained (Table19) shows the stepwise and overall stability constants to be not high indicating low stability of the complexes, because the solubility of most metal ions in the basic pH range is minimal due to metal hydroxide precipitation (Karimi, 2017). In general, the stepwise stability constants (K_1 and K_2) follow the order $K_1 > K_2$ for the copper, lead, magnesium and cadmium complexes respectively. The steady decrease of the values with increasing number of ligands is in agreement with the prediction made by researchers (Na'aliya, 2013). The decrease could be attributed to the fact that as the number of the ligands (Humate ions) that enters the coordination zone increases the aqua molecules available for replacement by the ligands become less. Thus, the metal ions become less electron loving with progressive intake of the ligand and this results in the decrease in the values of the constants (Na'aliya, 2013). Also the stability of the complexes is influenced by the size and number of the chelate rings(Mackay and Mackay,2002).All the complexes form rings in their structure as humate, a bidentate ligand, bond the metal ions in the ratio 1:2 (Boguta and Sokolowska, 2016) forming chelate rings. The values of the overall stability constants (logβ) obtained for humate complexes are not high indicating low stability as the values are not high. LogK values for copper-humates (Table 3 to 6) obtained in this study are lower than those reported for the complexes of humic acids (Pandey *et al*., 2015; Dinu, 2013; Kaschl *et al*., 2010 and Gilbeto and Jorg, 2001). The values of LogK(Table 7 to 10) forlead-humates are lower than those reported for the lead in the literature (Dinu, 2013; Gilbeto and Jorg 2001). Log K values(Table 11 to 14) for magnesium-humates obtained in this study are close to those reported by (Pandey *et al*., 2015). Log K values of cadmium-humates (Table 15 to 18) obtained in this work near to the one reported by (Dinu, 2013 and Pandey *et al*., 2015).The difference between the reported values and the values obtained in this study might be probably as a result of acid hydrolysis of humic acid. The values of the overall stability constants (log β) of the copper humates complexes presented in Table 19 is high than that of other metal humate complexes, show relatively high stability of Cu-HA complexes, show the following order of stability: Cu >Pb> Cd > Mg; which are in close agreement to the findings of (Dinu, 2013 and Pandey *et al*., 2015).The high stability of Cu-humate chelate could be attributed to the existence of coordinate covalent bond between the complexing agents and the Cu^{2+} ions. Since, Cu^{2+} being a metal of the transitional series with $3d^9$ electronic configurations can accept the electrons from the complexing agents. Similarly,the low stabilities of Pb,Cd and Mg -complexes could be explained by that Pb^{2+} with $6s^2$, Cd^{2+} with $4d^{10}$ and Mg^{2+} with $2p^6$ their electronic configuration has a completely filled d,p and s orbitals. Moreover, the stabilities of metal ions with hydrolysed humic acid from peat soil were higher than those with unhydrolysed humic acid from peat soil; which is ascribed to the high content of acidity in hydrolysed humic acid than unhydrolysed humic acid.

CONCLUSION

The values of logK for Cu(II) hydrolysed humic acid complex was higher followed by Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes as compared with metal(II) unhydrolysed humic acid complexes . This indicates acid hydrolysis of humic acid can enhance the complexation behavior of humic acid with metal (II) ions. However, the higher values of logβ for Cu(II), Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes indicates more stable stepwise complexes formed as compared with Cu(II), Pb(II), Cd(II) and Mg(II) unhydrolysed humic acid complexes.

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STABILITY CONSTANTS OF COMPLEXES OF METAL IONS WITH PEATSOIL HUMIC ACIDS UNDER NON-ACID-CONDITIONS

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ABSTRACT

Stability constants of complexes of four divalent metal ions viz. Cu^{2+}, Pb^{2+},Mg^{2+} and Cd^{2+} with humic acids (HA) were determined by potentiometric titration of humic acids with the corresponding salt of the divalent metals in aqueous media under non-acid-condition. The log K (logarithm of the stability constant) ranged from 1.0942 to 2.7471 for metal-humic acid complexes were determined using point-wise computational method. The order of stability constants were obtained as follows: Cu >Pb> Cd > Mg for metal -HA complexes respectively, indicating a higher degree of complexation with Cu metal ion.

Keywords: stability constant, humic acid, potentiometric titration, divalent metals, acid hydrolysis.

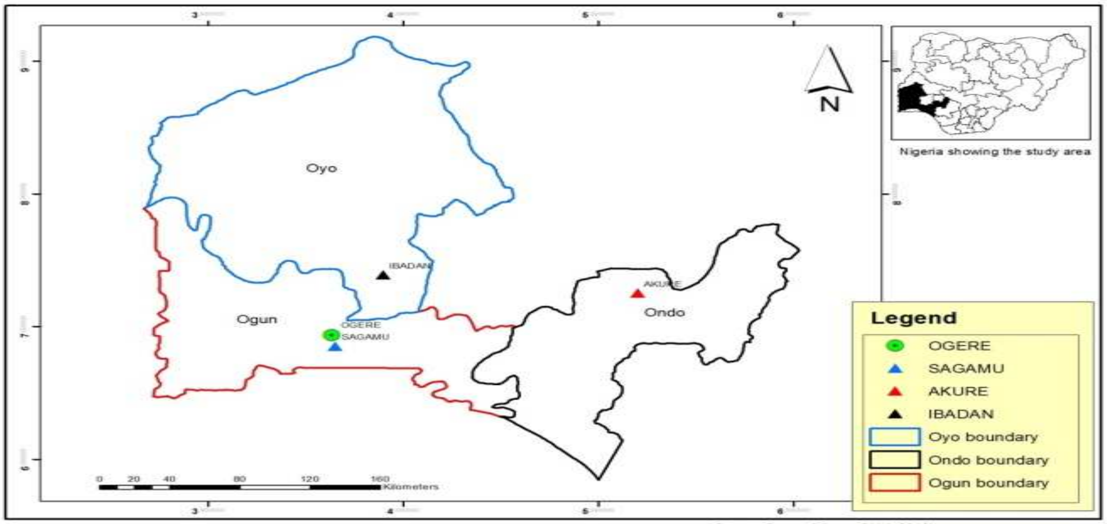
NTRODUCTION

The stability constant of a complex is the numerical expression of its stability and provides a quantitative measure of affinity of the metal ion to the complexing agent. An understanding of the relative stability of metal-complexes helps in predicting the behavior of metal ions in the soil (Ram and Raman, 1982). Extensive researches has been done to determine the stability constants of the complexes formed between humic acid (HA) with a number of metal ions. Ashok *et al.*, (2000) reported that humic acid with hydroxyl, phenoxyl and carboxyl reactive groups can form coordination compound with metal ions at pH 3.5. The stability constants(Log K) for different metal-humic acid complexes indicated the following order of the stabilities of complexes formed between humic acid and metal ion, Cu >Fe >Pb> Ni > Co > Ca > Cd > Zn >Mn> Mg. Andelkovic *et al.*, (2010) investigated the binding of Cd(II) to soil humic acid at pH 6.5 and in 0.1M KNO_3 ionic medium. The stability constant for binding indicating greater stability in the case when carboxyl groups are involved in complexation reaction. Kostic *et al.*,(2012) investigated the complexation of humic acid with certain heavy metal ions (Co(II), Ni(II),Cu(II), Zn(II), and Pb(II). The experiment was performed at 25°C, at pH 4.0 and ionic strength of 0.01M. Stability constant of complex between Pb(II) ions and humic acid is greater than stability constants of other investigated metal-humate complexes. Bogata and Sokolowska (2016) analyses the interaction between humic acids from different soils and Zn (II) ions at wide concentration ranges and at pH 5. Studies have showed significant impact of Zn concentration, pH and some properties of humic acids with zinc.But all of these studies were limited to acidic pH range. Therefore, the present study was carried out to determine and compare the stability constants of complexes of metal ions with hydrolysed peat soil humic acid and unhydrolysed peat soil humic under non-acid conditions.

MATERIALS AND METHODS

Analytical grade chemicals used includes hydrochloric acid (HCl), nitric acid (HNO_3), sodium hydroxide (NaOH), lead nitrate $Pb(NO_3)_2$, copper nitrate $Cu(NO_3)_2.3H_2O$, cadmium nitrate $Cd(NO_3)_2.4H_2O$, magnesium nitrate $Mg(NO_3)_2.6H_2O$, potassium nitrate (KNO_3), calcium chloride ($CaCl_2$), (sigma-Aldrich). Dowex 50WX8, (20-50 mesh) from Fluka.

Area of study



Source: Dept. of Geog. BUK (2016)

Figure 1: Map showing the sampling point at Sagamu Town, Ogun State.

Description of Sampling Area

Sagamu has geographical coordinates between 6°50′ north; 3° 38′ east is located in south western region of Nigeria. The region has tropical wet and dry climate with a lengthy wet season and relatively constant temperatures throughout the course of the year. Wet season runs from March to October, November to December forms the region dry season. The vegetation type of the region is savannah which is really grassland with small bushes and occasional big trees. Grassland soils have substantially higher organic matter content than forest soils (Novackova, 2011).

Sample Collection

The Peatsoil samples were collected from four different sampling points (0-10cm depth) in Sagamu into polyethylene bag with plastic spoons. Samples were taken to the laboratory, extraneous materials were removed; the samples were air-dried, crushed and ground to a fine powder in a mortar passed through a 0.20mm sieve. The samples were kept for analysis.

Isolation and purification of humic acid from peat soil sample

Peatsoil sample (100g) was mixed with 1000 cm^3 of 0.1M NaOH solution, shaken for 3hours and left to stand overnight. Dark-coloured supernatant was obtained and decanted from solid residue. The dark-coloured supernatant was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 6 hours. Yellowish brown supernatant and dark-brown precipitate were obtained. The yellowish brown supernatant was decanted followed by centrifuge and discarded. The dark-brown precipitate was mixed with $500cm^3$of 0.1M NaOH solution followed by passing through dowex resin. The dark-brown solution was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 3 hours. The dark-brown precipitate was washed several times with deionized water. The supernatant was treated with $AgNO_3$ solution until no white precipitate observed. The humic acid was transferred to weighed crucible and dried at 60^oC in an oven for 12 hours. The humic acid was cooled and dried in the desiccator, weighed and recorded. The obtained humic acid was dried again at 60^oC for additional 6 hours cooled and dried in the desiccator, weighed and recorded constant weight was obtained (Baruah *et al*., 2015).

FT-IR analysis

FT-IR spectra of humic acid sample was analysed using Carry 630 FT-IR Agilent Technologies.

Unhydrolysed compost humic acid

The unhydrolysed humic acid was obtained after isolation and purification of compost humic acid and kept for investigation.

Acid hydrolysis of Peatsoil acid

Peatsoil humic acid sample (1g) was refluxed for 12 hours at (160^oC) with $50cm^3$ of 6M HCl. The mixture was allowed to cool, decanted, and centrifuged after hydrolysis. The insoluble residues were washed with distilled water via centrifugation several times, and the supernatant was treated with $AgNO_3$ solution until no white precipitate was observed. The residue was thoroughly dried over $CaCl_2$ in a desiccator at room temperature (Chefetz *et al*., 2002). Finally, the obtained hydrolysed humic acid was kept for investigation.

Potentiometric Titrations

Potentiometric measurements were carried out using a pH-meter Jenway (model 3510) with combine electrode, the sensitivity of the pH - meter is 0.01 units. The pH meter was switched on half an hour before starting the titration for initial warm up of the instrument. The instrument was calibrated with an aqueous standard buffer solution of pH 4.00 and 10.0 (borate buffer) prepared from a "Qualigens" buffer tablets.

The following sets of solutions were prepared in a 250cm^3 volumetric flask separately for pH metric titrations.

(i) 5 cm^3 0.1 M HCl + 40 cm^3 deionized water

(ii) 5 cm^3 0.1 M HCl + 39 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid

(iii) 5 cm^3 0.1 M HCl + 37 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid + 2 cm^3 0.01 M Cu(II)

The solutions were titrated against standardized 0.110MNaOH separately. The total volume of each mixture was adjusted to 50 cm^3 and the ionic strength of the solutions was maintained constant at by adding appropriate amount of stock solution of 1M KNO_3 (Gamal, 2015; Omar and Ali, 2015). A magnetic stirrer was used to achieve thorough mixing of the interacting solutions at 550 rpm. The same set of experimental conditions was applied for potentiometric titration of remaining samples.

Evaluation of pKa of Hydrolysed peat soil Humic Acids

The proton-ligand formation number n_A were calculated by Irving and Rossotti expression (Omar and Ali, 2015).

$$nA = Y- \frac{(V2-V1)(No-Eo)}{(Vo+V1)TcL} \quad \text{.....................................1}$$

Where: Y is number of dissociable proton, (V_2-V_1) is the measure of displacement of the ligand curve relative to acid curve, N^o and E^o are the resultant concentration of alkali solution, free acid solution, $T_{cL}{}^o$ is the total ligand concentration, V^o is the total volume of titration solution,V_1 is the volume of alkali added to acid solution,V_2 is the volume of alkali added to acid solution + ligand solution, acid dissociation constants (pKa - values) of ligand were calculated by algebraic method point wise calculation (Tables 1). The dissociation constants (pKa) were calculated according to the following relation:

$$pKa = pH + \log(\frac{nA}{1-nA}) \quad \text{..............................2}$$

Where: pKa is the acid dissociation constant, $n_A$is the Proton-ligand formation number and pH is the pH-values (Omar and Ali, 2015).

Determination of metal-ligand stability constants (log K) of complexes

The potentiometric measurement for the determination of stability constant of a complex in solution is based on the fact that the redox potential of the couple $\frac{M^{+(m-n)}}{M^{+m}}$ is shifted significantly on complexation of the metal ion with the ligand. This method involves change in hydrogen ion concentration [H$^+$] due to the displacement or association of one or more protons taking place during complexation reaction. This change can be found out by titrating the solutions containing free acid, acid with ligand, and acid with ligand and metal ion, individually against a standard alkali solution at a constant ionic strength or temperature. Either ionic strength or temperature may be varied for different sets of solutions. In all the cases, the change in the pH of the solution is measured after each addition of a known amount of alkali to the reaction cell which contains the reaction mixture. The titration curves are then drawn by plotting the measured pH values against the corresponding volume of alkali added and the stability constants of the complexes are determined from the titration curves by employing pH-metric titration technique given by (Irving and Rossoti).

Metal-ligand stability constants (Log K) were determined by using the following relations:

$$\bar{n} = \frac{(V_3 - V_2)(E^0 + N^0)}{(V^0 + V_2)\bar{n}_A T_m^0} \quad \text{..3}$$

and

$$PL = \log_{10}\{\frac{1+\beta_n^H \frac{1}{[anti\ \log \text{pH}]^n}}{T_L^0 - \bar{n}T_m^0} X \frac{(V^0+V_3)}{V^0}\} \quad \text{..4}$$

Where $T_{L,}$ T^{o}, E°, and V^{o}havethe same significance as in equation (1) above, T_m denotes the total concentration of metal present in solution, V_3 is the volume of metal ions present in solution and β^{H} is the overall proton ligand stability constant. The metal-ligand stability constants (log K) were determined by employing point wise computational Method (eq. 5 and 6).

$$LogK_1 = \log\left(\frac{n}{1-n}\right) + pL \quad ....5$$

$$LogK_2 = \log\left(\frac{1-n}{2-n}\right) + pL.......................6$$

Where: Log K is the metal-ligand stability constant, pL is the Free ligand exponent function, **n** is the Average number of ligand attached with metal ion (Janrao*et al.*, 2014).The results obtained were analyzed by an ORIGIN 2016 program using titration data and then the proton-ligand stability constants (pKa) and Metal-ligand stability constant (LogK) calculated (Omar and Ali, 2015).

RESULTS AND DISCUSSION

Fourier transformed infrared (FT-IR) spectra of isolated humic acid from peat soils Figure 2 had distinct clear absorption bands indicating the presence of major humic acid structural elemental groups such as H bonded OH ($3680cm^{-1}$ peak), C=O of carbonyl ($1721cm^{-1}$ peak), functional groups of aliphatic components CH_2 ($2918cm^{-1}$ peak) and C-O stretching of polysaccharide ($1168cm^{-1}$ peak). The positions of the absorption bands of the spectra fell within typical major absorption bands of humic acid which is at frequencies 3680, 2918, 1721, 1168 cm^{-1}. The first peak centred in the vicinity of 3680 cm^{-1} region is attributed to phenol OH group bounded by intermolecular H bonds. The $2918cm^{-1}$ band usually has absorption maximum at 2918 cm^{-1} which is due to C–H stretching of alkane group (CH_2). The next major absorption band is 1721 cm^{-1}. This band has been commonly ascribed to C=O stretching of mainly carboxyl group (COOH) with trace amount of ketones. The last peak was observed at 1168 cm^{-1} due to C–O stretching of polysaccharides and this peak appeared also in the spectra of humic acid from peat soil. The FTIR spectra of the isolated humic acid contained all major characteristic absorption peaks of humic acid. These absorption peaks indicated the presence of the major structural elements of humic acid namely H bonded OH, C=C of aromatic ring, C=O of carbonyl group (both carboxyl and ketonic), CH_2 group. This strongly supports the presence of humic acid.

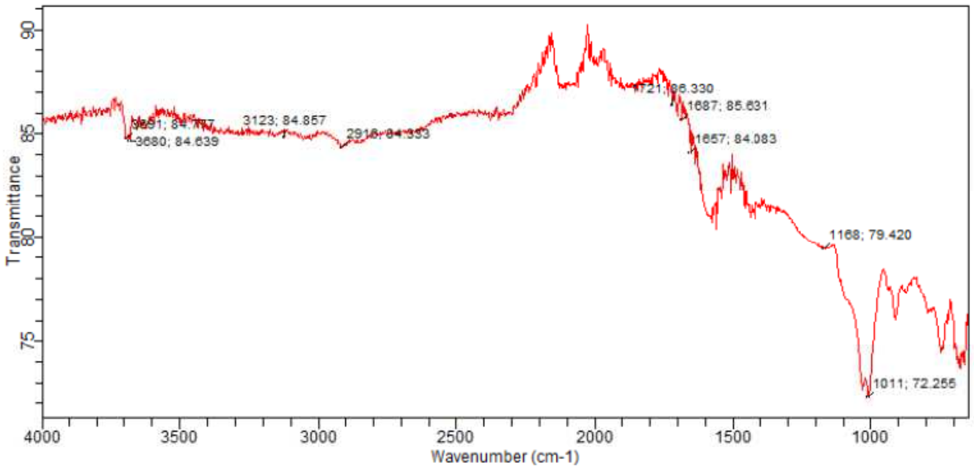


Fig. 2 : FT-IR spectraof peatsoilhumic acid (PSHA)

Evaluation of acid dissociation constant (pka) of acid hydrolysed peat soil humicacid at phenolic group

The value of the dissociation constant of the peat soil humic acid (PSHA) that underwent acidhydrolysis studied was found to be 8.9299 as shown Table 1, which is lower than the literaturevalues reported by Almeida and Szpoganics, (2015), Borges *et al.*, (2005); Badr *et al.*, (2012)and Fernandes *et al*,.(2009) of 9.73, 9.47 and 10.30. The difference between the obtained valuesand the reported values in this study might be probably as a result of acid hydrolysis of humicacid.

Table 1: PKa of (Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	V$_2$-V$_1$	nA	log($\frac{nA}{1-nA}$)	pKa
8.50	5.30	6.29	0.99	0.3594	-0.2510	8.2490
8.72	5.35	6.37	1.02	0.3400	-0.2880	8.4320
9.00	5.40	6.46	1.06	0.3141	-0.3391	8.6609
9.22	5.45	6.55	1.10	0.2882	-0.3927	8.8273
9.51	5.50	6.66	1.16	0.2494	-0.4786	9.0314
9.73	5.55	6.78	1.23	0.2041	-0.5910	9.1390
10.00	5.60	6.90	1.30	0.1589	-0.7238	9.2762
10.23	5.65	7.05	1.40	0.0941	-0.9835	9.2465
10.49	5.70	7.10	1.40	0.0941	-0.9835	9.5065

Average pKa = 8.9299 ± 0.4186

Table 2: PKa of (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	V$_2$-V$_1$	nA	Log($\frac{nA}{1-n}$)	pKa
8.50	5.30	5.81	0.51	0.6619	0.2919	8.7919
8.72	5.35	5.90	0.55	0.6357	0.2418	8.9618
9.00	5.40	6.00	0.60	0.6029	0.1813	9.1813
9.22	5.45	6.10	0.65	0.5701	0.1226	9.3426
9.51	5.50	6.20	0.70	0.5376	0.0654	9.5754
9.73	5.55	6.33	0.78	0.4851	-0.0259	9.7041
10.00	5.60	6.47	0.87	0.4262	-0.1291	9.8709
10.23	5.65	6.62	0.99	0.3609	-0.2481	9.9819
10.49	5.70	6.80	1.10	0.2759	-0.4690	10.0210

Average pKa = 9.4923± 0.4410

Metal-ligand stability constant (Log K)

The stabilityconstants require the accurate values of proton-ligand stability constants (Anil and Maroti, 2008). Metal titration curves crossed over ligand titration curve indicated the formation of complex upon proton release (Santosh, *et al.*, 2011). If the values of n- are within range 0.2-0.8 and 1.2-18 this indicates the formation of 1:1 and 1:2 complexes (Sayyed and Mazahar, 2012).

The metal (II)-humate stepwise stability constants (log k) at phenolic group (Tables 3-18)

Table 3: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	log($\frac{n}{1-n}$)	LogK$_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

LogK$_1$ (Average value) = 2.4788± 0.2203

Table 4: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	Log($\frac{n-1}{2-n}$)	LogK$_2$
9.51	5.50	6.66	6.73	0.07	1.3509	1.70	-0.2671	1.4329
9.73	5.55	6.78	6.85	0.07	1.6383	1.51	0.2467	1.7567
10.00	5.60	6.90	6.98	0.08	2.1783	1.31	-0.2158	1.0942
10.23	5.65	7.05	7.13	0.08	4.1904	1.27		
10.49	5.70	7.10	7.19	0.09	4.6920			

LogK$_2$(Average value) = 1.4280 ± 0.3312

Table 5:Point-wise method,Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	Log($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430

$LogK_1$ **(Average value)** = 2.3059± 0.6153

Table 6:Point-wise method, Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
9.73	5.55	6.33	6.42	0.09	0.9000	1.69		
10.00	5.60	6.47	6.58	0.11	1.2578	1.44	-0.4592	0.9808
10.23	5.65	6.62	6.84	0.12	1.6137	1.26	-0.2010	1.4610
10.49	5.70	6.80	6.92	0.12	2.1052	1.03		

$LogK_2$ **(Average value)** = 1.2209± 0.3398

Table 7:Point-wise method,Pb (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n}{1-n}$)	$LogK_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.60	0.05	0.8333	1.96	0.6989	2.6589

$LogK_1$ (Average value) = 2.5832 ±0.1614

Table 8:Point-wise method,Pb-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n-1}{2-n}$)	$logK_2$
9.51	5.50	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.83	0.05	1.1702	1.44		
10.00	5.60	6.90	6.90	0.05	1.4864	1.22	-0.0237	1.1963
10.23	5.65	7.05	7.10	0.05	2.0190	1.09		
10.49	5.70	7.10	7.17	0.07	3.6492	1.00		

$LogK_2$(Average value) = 1.1963

Table 9:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log ($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.5477	2.3123
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	0.0272	2.2072
9.51	5.50	6.20	6.26	0.07	0.6417	1.89	0.2530	2.1430
9.73	5.55	6.40	6.40	0.07	0.7000	1.67	0.3680	2.0380

$LogK_1$ **(Average value)** = 2.2364 ± 0.1602

Table 10:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
10.00	5.60	6.47	6.55	0.08	1.9503	1.41		
10.23	5.65	6.62	6.72	0.11	1.4792	1.26	-0.0361	1.2239

$LogK_2$ **(Average value)** = 1.2239

Table 11:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n}{n-1}$)	$LogK_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4290	2.2110
8.72	5.35	6.37	6.39	0.02	0.2858	2.42	-0.3978	2.0222
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

$LogK_1$ (Average value)=2.1382**±**0.1046

Table 12:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	log$(\frac{n-1}{2-n})$	LogK$_2$
9.51	5.55	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.84	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.93	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.10		
10.49	5.70	7.10	7.18	0.07	3.6492	0.83		

LogK$_2$(Average value) = 1.5453 **±** 0.3450

Table 13:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	V$_3$-V$_2$	n	pL	Log$(\frac{n}{n-1})$	Log K$_1$
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.3477	2.3123
9.00	5.40	6.00	6.04	0.04	0.3236	2.38	-0.3202	2.0598
9.22	5.45	6.10	6.15	0.05	0.4297	2.17	-0.1230	2.0470
9.51	5.50	6.20	6.26	0.06	0.5500	1.89	0.0871	1.9771
9.73	5.55	6.33	6.40	0.07	0.7000	1.67	0.3680	2.0380

LogK$_1$ **(Average value)** = 2.1568 ± 0.2069

Table 14:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	V$_3$-V$_2$	n	pL	Log$(\frac{n-1}{2-n})$	Log K$_2$
10.00	5.60	6.47	6.55	0.08	0.9148	1.41		
10.23	5.65	6.62	6.71	0.09	1.2102	1.20	-0.5749	0.6251
10.49	5.70	6.80	6.92	0.09	1.5968	1.03	0.1703	1.2003

LogK$_2$ **(Average value)** = 0.9127± 0.4070

Table15:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	Log$(\frac{n}{1-n})$	LogK$_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4210	2.2190
8.72	5.35	6.37	6.40	0.03	0.4286	2.42	-0.1249	2.2951
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.96	0.3010	2.2610
9.51	5.55	6.66	6.70	0.04	0.7720	1.67	0.5297	2.1997

LogK$_1$ (Average value) = 2.2108± 0.0825

Table 16:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	Log$(\frac{n-1}{2-n})$	Log K$_2$
9.73	5.55	6.78	6.83	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.95	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.09		
10.49	5.70	7.10	7.16	0.06	3.1429	0.89		

LogK$_2$ **(Average value)** = 1.5453± 0.3450

Table 17:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	V$_3$-V$_2$	n	pL	Log$(\frac{n}{n-1})$	Log K$_1$
8.50	5.30	5.81	5.86	0.05	0.3717	2.88	-0.2280	2.6520
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.06	0.06	0.4853	2.38	-0.0255	2.3545
9.22	5.45	6.10	6.16	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430
9.73	5.55	6.33	6.41	0.08	0.8000	1.69	0.6020	2.2920

LogK$_1$ **(Average value)** = 2.2516± 0.5380

Table 18:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$Log(\frac{n-1}{2-n})$	Log K_2
10.00	5.60	6.47	6.57	0.10	1.1434	1.43		
10.23	5.65	6.62	6.72	0.10	1.3448	1.23	-0.2788	0.9512
10.49	5.70	6.80	6.90	0.10	1.7742	1.03	0.5351	1.5651

$LogK_2$ **(Average value)** = 1.2581± 0.4340

Table 19: Stepwise and overall Stability constants of thehydrolysed and unhydrolysed divalent metal (II) complexes

Chelates	**$LogK_1$**	**$LogK_2$**	**Logβ**
[Cu (Hydrolysed PSHA-1)$_2$]	2.4788	1.4280	3.9068
[Pb (Hydrolysed PSHA-1)$_2$]	2.5832	1.1963	3.7795
[Cd (Hydrolysed PSHA-1)$_2$]	2.2108	1.5453	3.7561
[Mg (Hydrolysed PSHA-1)$_2$]	2.1382	1.5453	3.6835
[Cu (Unhydrolysed PSHA-1)$_2$]	2.3059	1.2209	3.5268
[Pb (Unhydrolysed PSHA-1)$_2$]	2.2364	1.2239	3.4603
[Cd (Unhydrolysed PSHA-1)$_2$]	2.2516	1.2581	3.5097
[Mg (Unydrolysed PSHA-1)$_2$]	2.1568	0.9127	3.0695

The results obtained (Table19) shows the stepwise and overall stability constants to be not high indicating low stability of the complexes, because the solubility of most metal ions in the basic pH range is minimal due to metal hydroxide precipitation (Karimi, 2017). In general, the stepwise stability constants (K_1 and K_2) follow the order $K_1 > K_2$ for the copper, lead, magnesium and cadmium complexes respectively. The steady decrease of the values with increasing number of ligands is in agreement with the prediction made by researchers (Na'aliya, 2013). The decrease could be attributed to the fact that as the number of the ligands (Humate ions) that enters the coordination zone increases the aqua molecules available for replacement by the ligands become less. Thus, the metal ions become less electron loving with progressive intake of the ligand and this results in the decrease in the values of the constants (Na'aliya, 2013). Also the stability of the complexes is influenced by the size and number of the chelate rings(Mackay and Mackay,2002).All the complexes form rings in their structure as humate, a bidentate ligand, bond the metal ions in the ratio 1:2 (Boguta and Sokolowska, 2016) forming chelate rings. The values of the overall stability constants (logβ) obtained for humate complexes are not high indicating low stability as the values are not high. LogK values for copper-humates (Table 3 to 6) obtained in this study are lower than those reported for the complexes of humic acids (Pandey *et al.*, 2015; Dinu, 2013; Kaschl *et al.*, 2010 and Gilbeto and Jorg, 2001). The values of LogK(Table 7 to 10) forlead-humates are lower than those reported for the lead in the literature (Dinu, 2013; Gilbeto and Jorg 2001). Log K values(Table 11 to 14) for magnesium-humates obtained in this study are close to those reported by (Pandey *et al.*, 2015). Log K values of cadmium-humates (Table 15 to 18) obtained in this work near to the one reported by (Dinu, 2013 and Pandey *et al.*, 2015).The difference between the reported values and the values obtained in this study might be probably as a result of acid hydrolysis of humic acid. The values of the overall stability constants (log β) of the copper humates complexes presented in Table 19 is high than that of other metal humate complexes, show relatively high stability of Cu-HA complexes, show the following order of stability: Cu >Pb> Cd > Mg; which are in close agreement to the findings of (Dinu, 2013 and Pandey *et al.*, 2015).The high stability of Cu-humate chelate could be attributed to the existence of coordinate covalent bond between the complexing agents and the Cu^{2+} ions. Since, Cu^{2+} being a metal of the transitional series with $3d^9$ electronic configurations can accept the electrons from the complexing agents. Similarly,the low stabilities of Pb,Cd and Mg - complexes could be explained by that Pb^{2+} with $6s^2$, Cd^{2+} with $4d^{10}$ and Mg^{2+} with $2p^6$ their electronic configuration has a completely filled d,p and s orbitals. Moreover, the stabilities of metal ions with hydrolysed humic acid from peat soil were higher than those with unhydrolysed humic acid from peat soil; which is ascribed to the high content of acidity in hydrolysed humic acid than unhydrolysed humic acid.

CONCLUSION

The values of logK for Cu(II) hydrolysed humic acid complex was higher followed by Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes as compared with metal(II) unhydrolysed humic acid complexes . This indicates acid hydrolysis of humic acid can enhance the complexation behavior of humic acid with metal (II) ions. However, the higher values of logβ for Cu(II), Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes indicates more stable stepwise complexes formed as compared with Cu(II), Pb(II), Cd(II) and Mg(II) unhydrolysed humic acid complexes.

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STABILITY CONSTANTS OF COMPLEXES OF METAL IONS WITH PEATSOIL HUMIC ACIDS UNDER NON-ACID-CONDITIONS

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ABSTRACT

Stability constants of complexes of four divalent metal ions viz. Cu^{2+}, Pb^{2+},Mg^{2+} and Cd^{2+} with humic acids (HA) were determined by potentiometric titration of humic acids with the corresponding salt of the divalent metals in aqueous media under non-acid-condition. The log K (logarithm of the stability constant) ranged from 1.0942 to 2.7471 for metal-humic acid complexes were determined using point-wise computational method. The order of stability constants were obtained as follows: Cu >Pb> Cd > Mg for metal -HA complexes respectively, indicating a higher degree of complexation with Cu metal ion.

Keywords: stability constant, humic acid, potentiometric titration, divalent metals, acid hydrolysis.

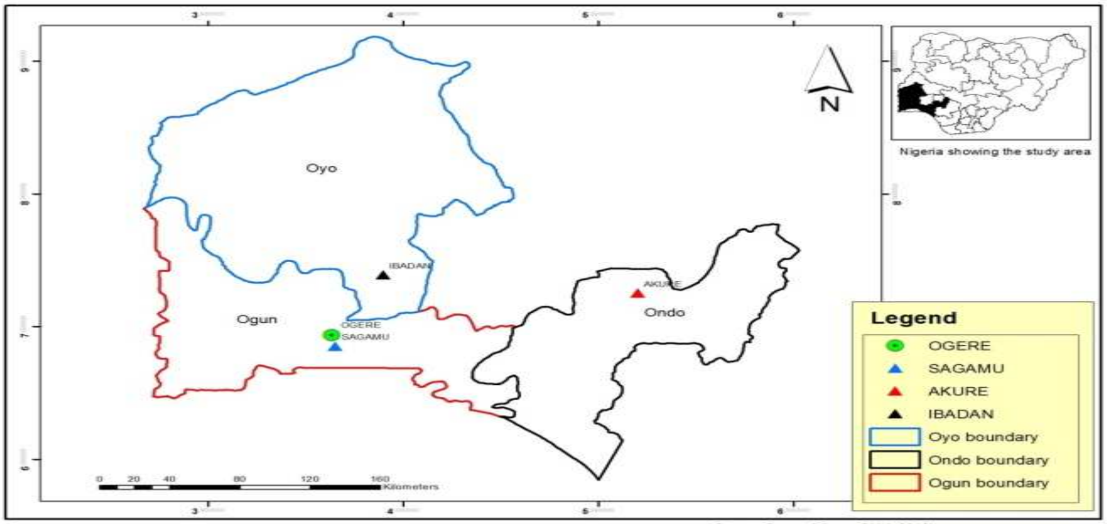
NTRODUCTION

The stability constant of a complex is the numerical expression of its stability and provides a quantitative measure of affinity of the metal ion to the complexing agent. An understanding of the relative stability of metal-complexes helps in predicting the behavior of metal ions in the soil (Ram and Raman, 1982). Extensive researches has been done to determine the stability constants of the complexes formed between humic acid (HA) with a number of metal ions. Ashok *et al.*, (2000) reported that humic acid with hydroxyl, phenoxyl and carboxyl reactive groups can form coordination compound with metal ions at pH 3.5. The stability constants(Log K) for different metal-humic acid complexes indicated the following order of the stabilities of complexes formed between humic acid and metal ion, Cu >Fe >Pb> Ni > Co > Ca > Cd > Zn >Mn> Mg. Andelkovic *et al.*, (2010) investigated the binding of Cd(II) to soil humic acid at pH 6.5 and in 0.1M KNO_3 ionic medium. The stability constant for binding indicating greater stability in the case when carboxyl groups are involved in complexation reaction. Kostic *et al.*,(2012) investigated the complexation of humic acid with certain heavy metal ions (Co(II), Ni(II),Cu(II), Zn(II), and Pb(II). The experiment was performed at 25°C, at pH 4.0 and ionic strength of 0.01M. Stability constant of complex between Pb(II) ions and humic acid is greater than stability constants of other investigated metal-humate complexes. Bogata and Sokolowska (2016) analyses the interaction between humic acids from different soils and Zn (II) ions at wide concentration ranges and at pH 5. Studies have showed significant impact of Zn concentration, pH and some properties of humic acids with zinc.But all of these studies were limited to acidic pH range. Therefore, the present study was carried out to determine and compare the stability constants of complexes of metal ions with hydrolysed peat soil humic acid and unhydrolysed peat soil humic under non-acid conditions.

MATERIALS AND METHODS

Analytical grade chemicals used includes hydrochloric acid (HCl), nitric acid (HNO_3), sodium hydroxide (NaOH), lead nitrate $Pb(NO_3)_2$, copper nitrate $Cu(NO_3)_2.3H_2O$, cadmium nitrate $Cd(NO_3)_2.4H_2O$, magnesium nitrate $Mg(NO_3)_2.6H_2O$, potassium nitrate (KNO_3), calcium chloride ($CaCl_2$), (sigma-Aldrich). Dowex 50WX8, (20-50 mesh) from Fluka.

Area of study



Source: Dept. of Geog. BUK (2016)

Figure 1: Map showing the sampling point at Sagamu Town, Ogun State.

Description of Sampling Area

Sagamu has geographical coordinates between 6°50′ north; 3° 38′ east is located in south western region of Nigeria. The region has tropical wet and dry climate with a lengthy wet season and relatively constant temperatures throughout the course of the year. Wet season runs from March to October, November to December forms the region dry season. The vegetation type of the region is savannah which is really grassland with small bushes and occasional big trees. Grassland soils have substantially higher organic matter content than forest soils (Novackova, 2011).

Sample Collection

The Peatsoil samples were collected from four different sampling points (0-10cm depth) in Sagamu into polyethylene bag with plastic spoons. Samples were taken to the laboratory, extraneous materials were removed; the samples were air-dried, crushed and ground to a fine powder in a mortar passed through a 0.20mm sieve. The samples were kept for analysis.

Isolation and purification of humic acid from peat soil sample

Peatsoil sample (100g) was mixed with 1000 cm^3 of 0.1M NaOH solution, shaken for 3hours and left to stand overnight. Dark-coloured supernatant was obtained and decanted from solid residue. The dark-coloured supernatant was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 6 hours. Yellowish brown supernatant and dark-brown precipitate were obtained. The yellowish brown supernatant was decanted followed by centrifuge and discarded. The dark-brown precipitate was mixed with $500cm^3$of 0.1M NaOH solution followed by passing through dowex resin. The dark-brown solution was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 3 hours. The dark-brown precipitate was washed several times with deionized water. The supernatant was treated with $AgNO_3$ solution until no white precipitate observed. The humic acid was transferred to weighed crucible and dried at 60°C in an oven for 12 hours. The humic acid was cooled and dried in the desiccator, weighed and recorded. The obtained humic acid was dried again at 60°C for additional 6 hours cooled and dried in the desiccator, weighed and recorded constant weight was obtained (Baruah *et al.*, 2015).

FT-IR analysis

FT-IR spectra of humic acid sample was analysed using Carry 630 FT-IR Agilent Technologies.

Unhydrolysed compost humic acid

The unhydrolysed humic acid was obtained after isolation and purification of compost humic acid and kept for investigation.

Acid hydrolysis of Peatsoil acid

Peatsoil humic acid sample (1g) was refluxed for 12 hours at (160°C) with $50cm^3$ of 6M HCl. The mixture was allowed to cool, decanted, and centrifuged after hydrolysis. The insoluble residues were washed with distilled water via centrifugation several times, and the supernatant was treated with $AgNO_3$ solution until no white precipitate was observed. The residue was thoroughly dried over $CaCl_2$ in a desiccator at room temperature (Chefetz *et al.*, 2002). Finally, the obtained hydrolysed humic acid was kept for investigation.

Potentiometric Titrations

Potentiometric measurements were carried out using a pH-meter Jenway (model 3510) with combine electrode, the sensitivity of the pH -meter is 0.01 units. The pH meter was switched on half an hour before starting the titration for initial warm up of the instrument. The instrument was calibrated with an aqueous standard buffer solution of pH 4.00 and 10.0 (borate buffer) prepared from a "Qualigens" buffer tablets.

The following sets of solutions were prepared in a 250cm^3 volumetric flask separately for pH metric titrations.

(i) 5 cm^3 0.1 M HCl + 40 cm^3 deionized water

(ii) 5 cm^3 0.1 M HCl + 39 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid

(iii) 5 cm^3 0.1 M HCl + 37 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid
+ 2 cm^3 0.01 M Cu(II)

The solutions were titrated against standardized 0.110MNaOH separately. The total volume of each mixture was adjusted to 50 cm^3 and the ionic strength of the solutions was maintained constant at by adding appropriate amount of stock solution of 1M KNO$_3$ (Gamal, 2015; Omar and Ali, 2015). A magnetic stirrer was used to achieve thorough mixing of the interacting solutions at 550 rpm. The same set of experimental conditions was applied for potentiometric titration of remaining samples.

Evaluation of pKa of Hydrolysed peat soil Humic Acids

The proton-ligand formation number n$_{\mathbf{A}}$ were calculated by Irving and Rossotti expression (Omar and Ali, 2015).

$$nA = Y - \frac{(V2-V1)(No-Eo)}{(Vo+V1)TcL} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 1$$

Where: Y is number of dissociable proton, (V$_2$-V$_1$) is the measure of displacement of the ligand curve relative to acid curve, N^o and E^o are the resultant concentration of alkali solution, free acid solution, T$_{cL}$^{o} is the total ligand concentration, V^o is the total volume of titration solution,V$_1$ is the volume of alkali added to acid solution,V$_2$ is the volume of alkali added to acid solution + ligand solution, acid dissociation constants (pKa - values) of ligand were calculated by algebraic method point wise calculation (Tables 1). The dissociation constants (pKa) were calculated according to the following relation:

$$pKa = pH + \log(\frac{nA}{1-nA}) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 2$$

Where: pKa is the acid dissociation constant, n$_A$is the Proton-ligand formation number and pH is the pH-values (Omar and Ali, 2015).

Determination of metal-ligand stability constants (log K) of complexes

The potentiometric measurement for the determination of stability constant of a complex in solution is based on the fact that the redox potential of the couple $\frac{M^{+(m-n)}}{M^{+m}}$ is shifted significantly on complexation of the metal ion with the ligand. This method involves change in hydrogen ion concentration [H$^+$] due to the displacement or association of one or more protons taking place during complexation reaction. This change can be found out by titrating the solutions containing free acid, acid with ligand, and acid with ligand and metal ion, individually against a standard alkali solution at a constant ionic strength or temperature. Either ionic strength or temperature may be varied for different sets of solutions. In all the cases, the change in the pH of the solution is measured after each addition of a known amount of alkali to the reaction cell which contains the reaction mixture. The titration curves are then drawn by plotting the measured pH values against the corresponding volume of alkali added and the stability constants of the complexes are determined from the titration curves by employing pH-metric titration technique given by (Irving and Rossoti).

Metal-ligand stability constants (Log K) were determined by using the following relations:

$$\bar{n} = \frac{(V_3 - V_2)(E^0 + N^0)}{(V^0 + V_2)\bar{n}_A T_m^0} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 3$$

and

$$PL = \log_{10}\{\frac{1 + \beta_n^H \frac{1}{[anti\ \log pH]^n}}{T_L^0 - \bar{n}T_m^0} X \frac{(V^0 + V_3)}{V^0}\} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 4$$

Where $T_{L,}$ T^o, E°, and V^ohavethe same significance as in equation (1) above, T_m denotes the total concentration of metal present in solution, V_3 is the volume of metal ions present in solution and β^H is the overall proton ligand stability constant. The metal-ligand stability constants (log K) were determined by employing point wise computational Method (eq. 5 and 6).

$\text{LogK}_1 = \log\left(\frac{n}{1-n}\right) + \text{pL}$ 5

$\text{LogK}_2 = \log\left(\frac{1-n}{2-n}\right) + \text{pL}$........................6

Where: Log K is the metal-ligand stability constant, pL is the Free ligand exponent function, **n** is the Average number of ligand attached with metal ion (Janrao*et al*., 2014).The results obtained were analyzed by an ORIGIN 2016 program using titration data and then the proton-ligand stability constants (pKa) and Metal-ligand stability constant (LogK) calculated (Omar and Ali, 2015).

RESULTS AND DISCUSSION

Fourier transformed infrared (FT-IR) spectra of isolated humic acid from peat soils Figure 2 had distinct clear absorption bands indicating the presence of major humic acid structural elemental groups such as H bonded OH ($3680cm^{-1}$ peak), C=O of carbonyl ($1721cm^{-1}$ peak), functional groups of aliphatic components CH_2 ($2918cm^{-1}$ peak) and C-O stretching of polysaccharide ($1168cm^{-1}$ peak). The positions of the absorption bands of the spectra fell within typical major absorption bands of humic acid which is at frequencies 3680, 2918, 1721, 1168 cm^{-1}. The first peak centred in the vicinity of 3680 cm^{-1} region is attributed to phenol OH group bounded by intermolecular H bonds. The $2918cm^{-1}$ band usually has absorption maximum at 2918 cm^{-1} which is due to C–H stretching of alkane group (CH_2). The next major absorption band is 1721 cm^{-1}. This band has been commonly ascribed to C=O stretching of mainly carboxyl group (COOH) with trace amount of ketones. The last peak was observed at 1168 cm^{-1} due to C–O stretching of polysaccharides and this peak appeared also in the spectra of humic acid from peat soil. The FTIR spectra of the isolated humic acid contained all major characteristic absorption peaks of humic acid. These absorption peaks indicated the presence of the major structural elements of humic acid namely H bonded OH, C=C of aromatic ring, C=O of carbonyl group (both carboxyl and ketonic), CH_2 group. This strongly supports the presence of humic acid.

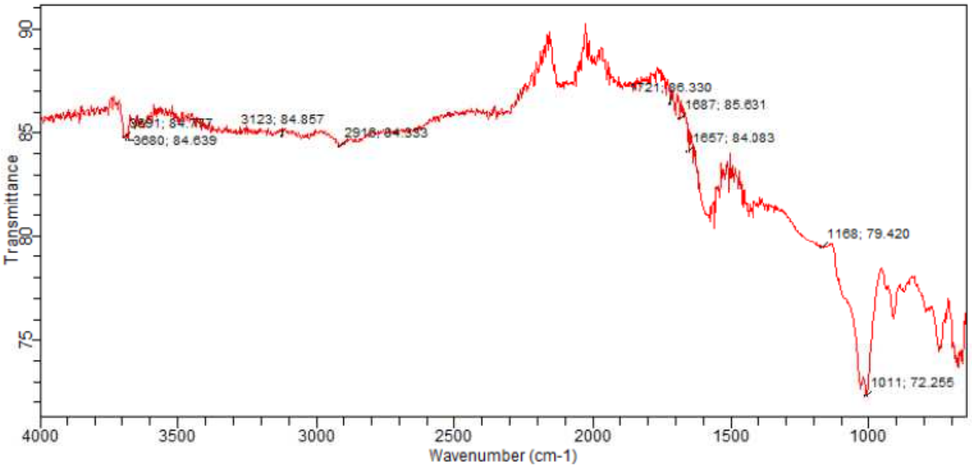


Fig. 2 : FT-IR spectraof peatsoilhumic acid (PSHA)

Evaluation of acid dissociation constant (pka) of acid hydrolysed peat soil humicacid at phenolic group

The value of the dissociation constant of the peat soil humic acid (PSHA) that underwent acidhydrolysis studied was found to be 8.9299 as shown Table 1, which is lower than the literaturevalues reported by Almeida and Szpoganics, (2015), Borges *et al*., (2005); Badr *et al*., (2012)and Fernandes *et al*,.(2009) of 9.73, 9.47 and 10.30. The difference between the obtained valuesand the reported values in this study might be probably as a result of acid hydrolysis of humicacid.

Table 1: PKa of (Hydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	$\log(\frac{nA}{1-nA})$	pKa
8.50	5.30	6.29	0.99	0.3594	-0.2510	8.2490
8.72	5.35	6.37	1.02	0.3400	-0.2880	8.4320
9.00	5.40	6.46	1.06	0.3141	-0.3391	8.6609
9.22	5.45	6.55	1.10	0.2882	-0.3927	8.8273
9.51	5.50	6.66	1.16	0.2494	-0.4786	9.0314
9.73	5.55	6.78	1.23	0.2041	-0.5910	9.1390
10.00	5.60	6.90	1.30	0.1589	-0.7238	9.2762
10.23	5.65	7.05	1.40	0.0941	-0.9835	9.2465
10.49	5.70	7.10	1.40	0.0941	-0.9835	9.5065

Average pKa = 8.9299 ± 0.4186

Table 2: PKa of (Unhydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	$\mathrm{Log}(\frac{nA}{1-n})$	pKa
8.50	5.30	5.81	0.51	0.6619	0.2919	8.7919
8.72	5.35	5.90	0.55	0.6357	0.2418	8.9618
9.00	5.40	6.00	0.60	0.6029	0.1813	9.1813
9.22	5.45	6.10	0.65	0.5701	0.1226	9.3426
9.51	5.50	6.20	0.70	0.5376	0.0654	9.5754
9.73	5.55	6.33	0.78	0.4851	-0.0259	9.7041
10.00	5.60	6.47	0.87	0.4262	-0.1291	9.8709
10.23	5.65	6.62	0.99	0.3609	-0.2481	9.9819
10.49	5.70	6.80	1.10	0.2759	-0.4690	10.0210

Average pKa = 9.4923± 0.4410

Metal-ligand stability constant (Log K)

The stabilityconstants require the accurate values of proton-ligand stability constants (Anil and Maroti, 2008). Metal titration curves crossed over ligand titration curve indicated the formation of complex upon proton release (Santosh, *et al.*, 2011). If the values of n- are within range 0.2-0.8 and 1.2-18 this indicates the formation of 1:1 and 1:2 complexes (Sayyed and Mazahar, 2012).

The metal (II)-humate stepwise stability constants (log k) at phenolic group (Tables 3-18)

Table 3: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$\log(\frac{n}{1-n})$	$\mathrm{Log}K_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

LogK_1 (Average value) = 2.4788± 0.2203

Table 4: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$\mathrm{Log}(\frac{n-1}{2-n})$	$\mathrm{Log}K_2$
9.51	5.50	6.66	6.73	0.07	1.3509	1.70	-0.2671	1.4329
9.73	5.55	6.78	6.85	0.07	1.6383	1.51	0.2467	1.7567
10.00	5.60	6.90	6.98	0.08	2.1783	1.31	-0.2158	1.0942
10.23	5.65	7.05	7.13	0.08	4.1904	1.27		
10.49	5.70	7.10	7.19	0.09	4.6920			

LogK_2(Average value) = 1.4280 ± 0.3312

Table 5:Point-wise method,Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	Log$(\frac{n}{n-1})$	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430

$LogK_1$ **(Average value)** = 2.3059± 0.6153

Table 6:Point-wise method, Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log$(\frac{n-1}{2-n})$	Log K_2
9.73	5.55	6.33	6.42	0.09	0.9000	1.69		
10.00	5.60	6.47	6.58	0.11	1.2578	1.44	-0.4592	0.9808
10.23	5.65	6.62	6.84	0.12	1.6137	1.26	-0.2010	1.4610
10.49	5.70	6.80	6.92	0.12	2.1052	1.03		

$LogK_2$ **(Average value)** = 1.2209± 0.3398

Table 7:Point-wise method,Pb (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log$(\frac{n}{1-n})$	$LogK_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.60	0.05	0.8333	1.96	0.6989	2.6589

$LogK_1$ (Average value) = 2.5832 ±0.1614

Table 8:Point-wise method,Pb-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log$(\frac{n-1}{2-n})$	$logK_2$
9.51	5.50	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.83	0.05	1.1702	1.44		
10.00	5.60	6.90	6.90	0.05	1.4864	1.22	-0.0237	1.1963
10.23	5.65	7.05	7.10	0.05	2.0190	1.09		
10.49	5.70	7.10	7.17	0.07	3.6492	1.00		

$LogK_2$(Average value) = 1.1963

Table 9:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log $(\frac{n}{n-1})$	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.5477	2.3123
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	0.0272	2.2072
9.51	5.50	6.20	6.26	0.07	0.6417	1.89	0.2530	2.1430
9.73	5.55	6.40	6.40	0.07	0.7000	1.67	0.3680	2.0380

$LogK_1$ **(Average value)** = 2.2364 ± 0.1602

Table 10:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log$(\frac{n-1}{2-n})$	Log K_2
10.00	5.60	6.47	6.55	0.08	1.9503	1.41		
10.23	5.65	6.62	6.72	0.11	1.4792	1.26	-0.0361	1.2239

$LogK_2$ **(Average value)** = 1.2239

Table 11:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log$(\frac{n}{n-1})$	$LogK_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4290	2.2110
8.72	5.35	6.37	6.39	0.02	0.2858	2.42	-0.3978	2.0222
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

$LogK_1$ (Average value)=2.1382**±**0.1046

Table 12:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$\log(\frac{n-1}{2-n})$	$LogK_2$
9.51	5.55	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.84	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.93	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.10		
10.49	5.70	7.10	7.18	0.07	3.6492	0.83		

$LogK_2$(Average value) = 1.5453 **±** 0.3450

Table 13:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$Log(\frac{n}{n-1})$	$Log\ K_1$
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.3477	2.3123
9.00	5.40	6.00	6.04	0.04	0.3236	2.38	-0.3202	2.0598
9.22	5.45	6.10	6.15	0.05	0.4297	2.17	-0.1230	2.0470
9.51	5.50	6.20	6.26	0.06	0.5500	1.89	0.0871	1.9771
9.73	5.55	6.33	6.40	0.07	0.7000	1.67	0.3680	2.0380

$LogK_1$ **(Average value)** = 2.1568 ± 0.2069

Table 14:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$Log(\frac{n-1}{2-n})$	$Log\ K_2$
10.00	5.60	6.47	6.55	0.08	0.9148	1.41		
10.23	5.65	6.62	6.71	0.09	1.2102	1.20	-0.5749	0.6251
10.49	5.70	6.80	6.92	0.09	1.5968	1.03	0.1703	1.2003

$LogK_2$ **(Average value)** = 0.9127± 0.4070

Table15:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$Log(\frac{n}{1-n})$	$LogK_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4210	2.2190
8.72	5.35	6.37	6.40	0.03	0.4286	2.42	-0.1249	2.2951
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.96	0.3010	2.2610
9.51	5.55	6.66	6.70	0.04	0.7720	1.67	0.5297	2.1997

$LogK_1$ (Average value) = 2.2108± 0.0825

Table 16:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$Log(\frac{n-1}{2-n})$	$Log\ K_2$
9.73	5.55	6.78	6.83	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.95	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.09		
10.49	5.70	7.10	7.16	0.06	3.1429	0.89		

$LogK_2$ **(Average value)** = 1.5453± 0.3450

Table 17:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$Log(\frac{n}{n-1})$	$Log\ K_1$
8.50	5.30	5.81	5.86	0.05	0.3717	2.88	-0.2280	2.6520
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.06	0.06	0.4853	2.38	-0.0255	2.3545
9.22	5.45	6.10	6.16	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430
9.73	5.55	6.33	6.41	0.08	0.8000	1.69	0.6020	2.2920

$LogK_1$ **(Average value)** = 2.2516± 0.5380

Table 18:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$\text{Log}(\frac{n-1}{2-n})$	Log K_2
10.00	5.60	6.47	6.57	0.10	1.1434	1.43		
10.23	5.65	6.62	6.72	0.10	1.3448	1.23	-0.2788	0.9512
10.49	5.70	6.80	6.90	0.10	1.7742	1.03	0.5351	1.5651

LogK_2 **(Average value)** = 1.2581± 0.4340

Table 19: Stepwise and overall Stability constants of thehydrolysed and unhydrolysed divalent metal (II) complexes

Chelates	LogK_1	LogK_2	Logβ
[Cu (Hydrolysed PSHA-1)$_2$]	2.4788	1.4280	3.9068
[Pb (Hydrolysed PSHA-1)$_2$]	2.5832	1.1963	3.7795
[Cd (Hydrolysed PSHA-1)$_2$]	2.2108	1.5453	3.7561
[Mg (Hydrolysed PSHA-1)$_2$]	2.1382	1.5453	3.6835
[Cu (Unhydrolysed PSHA-1)$_2$]	2.3059	1.2209	3.5268
[Pb (Unhydrolysed PSHA-1)$_2$]	2.2364	1.2239	3.4603
[Cd (Unhydrolysed PSHA-1)$_2$]	2.2516	1.2581	3.5097
[Mg (Unydrolysed PSHA-1)$_2$]	2.1568	0.9127	3.0695

The results obtained (Table19) shows the stepwise and overall stability constants to be not high indicating low stability of the complexes, because the solubility of most metal ions in the basic pH range is minimal due to metal hydroxide precipitation (Karimi, 2017). In general, the stepwise stability constants (K_1 and K_2) follow the order $K_1 > K_2$ for the copper, lead, magnesium and cadmium complexes respectively. The steady decrease of the values with increasing number of ligands is in agreement with the prediction made by researchers (Na'aliya, 2013). The decrease could be attributed to the fact that as the number of the ligands (Humate ions) that enters the coordination zone increases the aqua molecules available for replacement by the ligands become less. Thus, the metal ions become less electron loving with progressive intake of the ligand and this results in the decrease in the values of the constants (Na'aliya, 2013). Also the stability of the complexes is influenced by the size and number of the chelate rings(Mackay and Mackay,2002).All the complexes form rings in their structure as humate, a bidentate ligand, bond the metal ions in the ratio 1:2 (Boguta and Sokolowska, 2016) forming chelate rings. The values of the overall stability constants (logβ) obtained for humate complexes are not high indicating low stability as the values are not high. LogK values for copper-humates (Table 3 to 6) obtained in this study are lower than those reported for the complexes of humic acids (Pandey *et al*., 2015; Dinu, 2013; Kaschl *et al*., 2010 and Gilbeto and Jorg, 2001). The values of LogK(Table 7 to 10) forlead-humates are lower than those reported for the lead in the literature (Dinu, 2013; Gilbeto and Jorg 2001). Log K values(Table 11 to 14) for magnesium-humates obtained in this study are close to those reported by (Pandey *et al*., 2015). Log K values of cadmium-humates (Table 15 to 18) obtained in this work near to the one reported by (Dinu, 2013 and Pandey *et al*., 2015).The difference between the reported values and the values obtained in this study might be probably as a result of acid hydrolysis of humic acid. The values of the overall stability constants (log β) of the copper humates complexes presented in Table 19 is high than that of other metal humate complexes, show relatively high stability of Cu-HA complexes, show the following order of stability: Cu >Pb> Cd > Mg; which are in close agreement to the findings of (Dinu, 2013 and Pandey *et al*., 2015).The high stability of Cu-humate chelate could be attributed to the existence of coordinate covalent bond between the complexing agents and the Cu^{2+} ions. Since, Cu^{2+} being a metal of the transitional series with $3d^9$ electronic configurations can accept the electrons from the complexing agents. Similarly,the low stabilities of Pb,Cd and Mg - complexes could be explained by that Pb^{2+} with $6s^2$, Cd^{2+} with $4d^{10}$ and Mg^{2+} with $2p^6$ their electronic configuration has a completely filled d,p and s orbitals. Moreover, the stabilities of metal ions with hydrolysed humic acid from peat soil were higher than those with unhydrolysed humic acid from peat soil; which is ascribed to the high content of acidity in hydrolysed humic acid than unhydrolysed humic acid.

CONCLUSION

The values of logK for Cu(II) hydrolysed humic acid complex was higher followed by Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes as compared with metal(II) unhydrolysed humic acid complexes . This indicates acid hydrolysis of humic acid can enhance the complexation behavior of humic acid with metal (II) ions. However, the higher values of logβ for Cu(II), Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes indicates more stable stepwise complexes formed as compared with Cu(II), Pb(II), Cd(II) and Mg(II) unhydrolysed humic acid complexes.

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STABILITY CONSTANTS OF COMPLEXES OF METAL IONS WITH PEATSOIL HUMIC ACIDS UNDER NON-ACID-CONDITIONS

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ABSTRACT

Stability constants of complexes of four divalent metal ions viz. Cu^{2+}, Pb^{2+},Mg^{2+} and Cd^{2+} with humic acids (HA) were determined by potentiometric titration of humic acids with the corresponding salt of the divalent metals in aqueous media under non-acid-condition. The log K (logarithm of the stability constant) ranged from 1.0942 to 2.7471 for metal-humic acid complexes were determined using point-wise computational method. The order of stability constants were obtained as follows: Cu >Pb> Cd > Mg for metal -HA complexes respectively, indicating a higher degree of complexation with Cu metal ion.

Keywords: stability constant, humic acid, potentiometric titration, divalent metals, acid hydrolysis.

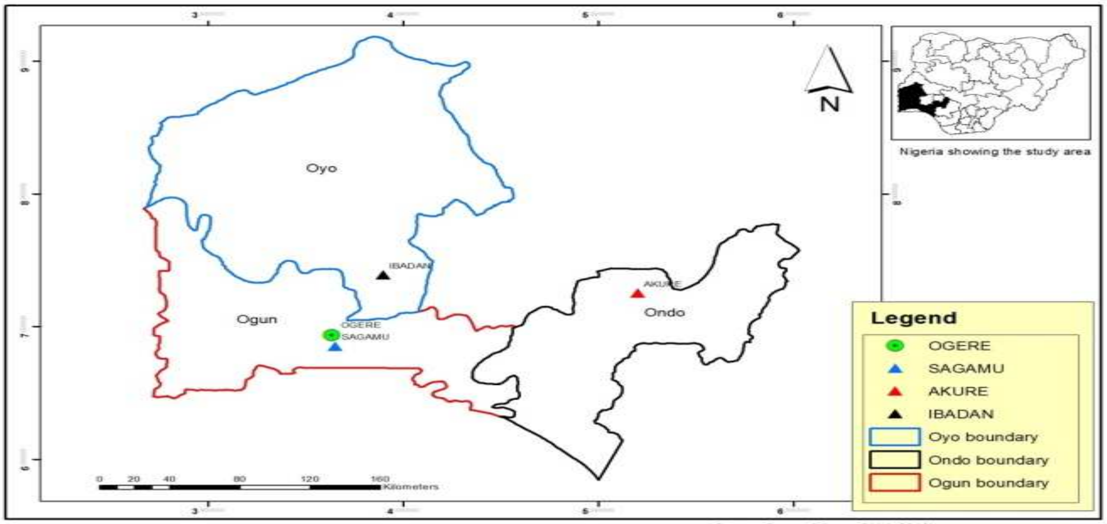
NTRODUCTION

The stability constant of a complex is the numerical expression of its stability and provides a quantitative measure of affinity of the metal ion to the complexing agent. An understanding of the relative stability of metal-complexes helps in predicting the behavior of metal ions in the soil (Ram and Raman, 1982). Extensive researches has been done to determine the stability constants of the complexes formed between humic acid (HA) with a number of metal ions. Ashok *et al*., (2000) reported that humic acid with hydroxyl, phenoxyl and carboxyl reactive groups can form coordination compound with metal ions at pH 3.5. The stability constants(Log K) for different metal-humic acid complexes indicated the following order of the stabilities of complexes formed between humic acid and metal ion, Cu >Fe >Pb> Ni > Co > Ca > Cd > Zn >Mn> Mg. Andelkovic *et al*., (2010) investigated the binding of Cd(II) to soil humic acid at pH 6.5 and in 0.1M KNO_3 ionic medium. The stability constant for binding indicating greater stability in the case when carboxyl groups are involved in complexation reaction. Kostic *et al*.,(2012) investigated the complexation of humic acid with certain heavy metal ions (Co(II), Ni(II),Cu(II), Zn(II), and Pb(II). The experiment was performed at 25°C, at pH 4.0 and ionic strength of 0.01M. Stability constant of complex between Pb(II) ions and humic acid is greater than stability constants of other investigated metal-humate complexes. Bogata and Sokolowska (2016) analyses the interaction between humic acids from different soils and Zn (II) ions at wide concentration ranges and at pH 5. Studies have showed significant impact of Zn concentration, pH and some properties of humic acids with zinc.But all of these studies were limited to acidic pH range. Therefore, the present study was carried out to determine and compare the stability constants of complexes of metal ions with hydrolysed peat soil humic acid and unhydrolysed peat soil humic under non-acid conditions.

MATERIALS AND METHODS

Analytical grade chemicals used includes hydrochloric acid (HCl), nitric acid (HNO_3), sodium hydroxide (NaOH), lead nitrate $Pb(NO_3)_2$, copper nitrate $Cu(NO_3)_2.3H_2O$, cadmium nitrate $Cd(NO_3)_2.4H_2O$, magnesium nitrate $Mg(NO_3)_2.6H_2O$, potassium nitrate (KNO_3), calcium chloride ($CaCl_2$), (sigma-Aldrich). Dowex 50WX8, (20-50 mesh) from Fluka.

Area of study



Source: Dept. of Geog. BUK (2016)

Figure 1: Map showing the sampling point at Sagamu Town, Ogun State.

Description of Sampling Area

Sagamu has geographical coordinates between 6°50′ north; 3° 38′ east is located in south western region of Nigeria. The region has tropical wet and dry climate with a lengthy wet season and relatively constant temperatures throughout the course of the year. Wet season runs from March to October, November to December forms the region dry season. The vegetation type of the region is savannah which is really grassland with small bushes and occasional big trees. Grassland soils have substantially higher organic matter content than forest soils (Novackova, 2011).

Sample Collection

The Peatsoil samples were collected from four different sampling points (0-10cm depth) in Sagamu into polyethylene bag with plastic spoons. Samples were taken to the laboratory, extraneous materials were removed; the samples were air-dried, crushed and ground to a fine powder in a mortar passed through a 0.20mm sieve. The samples were kept for analysis.

Isolation and purification of humic acid from peat soil sample

Peatsoil sample (100g) was mixed with 1000 cm^3 of 0.1M NaOH solution, shaken for 3hours and left to stand overnight. Dark-coloured supernatant was obtained and decanted from solid residue. The dark-coloured supernatant was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 6 hours. Yellowish brown supernatant and dark-brown precipitate were obtained. The yellowish brown supernatant was decanted followed by centrifuge and discarded. The dark-brown precipitate was mixed with $500cm^3$of 0.1M NaOH solution followed by passing through dowex resin. The dark-brown solution was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 3 hours. The dark-brown precipitate was washed several times with deionized water. The supernatant was treated with $AgNO_3$ solution until no white precipitate observed. The humic acid was transferred to weighed crucible and dried at 60°C in an oven for 12 hours. The humic acid was cooled and dried in the desiccator, weighed and recorded. The obtained humic acid was dried again at 60°C for additional 6 hours cooled and dried in the desiccator, weighed and recorded constant weight was obtained (Baruah *et al*., 2015).

FT-IR analysis

FT-IR spectra of humic acid sample was analysed using Carry 630 FT-IR Agilent Technologies.

Unhydrolysed compost humic acid

The unhydrolysed humic acid was obtained after isolation and purification of compost humic acid and kept for investigation.

Acid hydrolysis of Peatsoil acid

Peatsoil humic acid sample (1g) was refluxed for 12 hours at (160°C) with $50cm^3$ of 6M HCl. The mixture was allowed to cool, decanted, and centrifuged after hydrolysis. The insoluble residues were washed with distilled water via centrifugation several times, and the supernatant was treated with $AgNO_3$ solution until no white precipitate was observed. The residue was thoroughly dried over $CaCl_2$ in a desiccator at room temperature (Chefetz *et al*., 2002). Finally, the obtained hydrolysed humic acid was kept for investigation.

Potentiometric Titrations

Potentiometric measurements were carried out using a pH-meter Jenway (model 3510) with combine electrode, the sensitivity of the pH -meter is 0.01 units. The pH meter was switched on half an hour before starting the titration for initial warm up of the instrument. The instrument was calibrated with an aqueous standard buffer solution of pH 4.00 and 10.0 (borate buffer) prepared from a "Qualigens" buffer tablets.

The following sets of solutions were prepared in a 250cm^3 volumetric flask separately for pH metric titrations.

(i) 5 cm^3 0.1 M HCl + 40 cm^3 deionized water

(ii) 5 cm^3 0.1 M HCl + 39 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid

(iii) 5 cm^3 0.1 M HCl + 37 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid + 2 cm^3 0.01 M Cu(II)

The solutions were titrated against standardized 0.110MNaOH separately. The total volume of each mixture was adjusted to 50 cm^3 and the ionic strength of the solutions was maintained constant at by adding appropriate amount of stock solution of 1M KNO_3 (Gamal, 2015; Omar and Ali, 2015). A magnetic stirrer was used to achieve thorough mixing of the interacting solutions at 550 rpm. The same set of experimental conditions was applied for potentiometric titration of remaining samples.

Evaluation of pKa of Hydrolysed peat soil Humic Acids

The proton-ligand formation number n$_{\mathbf{A}}$ were calculated by Irving and Rossotti expression (Omar and Ali, 2015).

$$nA = Y - \frac{(V2-V1)(No-Eo)}{(Vo+V1)TcL} \quad \text{.................................}1$$

Where: Y is number of dissociable proton, (V_2-V_1) is the measure of displacement of the ligand curve relative to acid curve, N^o and E^o are the resultant concentration of alkali solution, free acid solution, $T_{cL}{}^o$ is the total ligand concentration, V^o is the total volume of titration solution,V_1 is the volume of alkali added to acid solution,V_2 is the volume of alkali added to acid solution + ligand solution, acid dissociation constants (pKa - values) of ligand were calculated by algebraic method point wise calculation (Tables 1). The dissociation constants (pKa) were calculated according to the following relation:

$$pKa = pH + \log\left(\frac{nA}{1-nA}\right) \quad \text{.............................}2$$

Where: pKa is the acid dissociation constant, $n_A$is the Proton-ligand formation number and pH is the pH-values (Omar and Ali, 2015).

Determination of metal-ligand stability constants (log K) of complexes

The potentiometric measurement for the determination of stability constant of a complex in solution is based on the fact that the redox potential of the couple $\frac{M^{+(m-n)}}{M^{+m}}$ is shifted significantly on complexation of the metal ion with the ligand. This method involves change in hydrogen ion concentration [H$^+$] due to the displacement or association of one or more protons taking place during complexation reaction. This change can be found out by titrating the solutions containing free acid, acid with ligand, and acid with ligand and metal ion, individually against a standard alkali solution at a constant ionic strength or temperature. Either ionic strength or temperature may be varied for different sets of solutions. In all the cases, the change in the pH of the solution is measured after each addition of a known amount of alkali to the reaction cell which contains the reaction mixture. The titration curves are then drawn by plotting the measured pH values against the corresponding volume of alkali added and the stability constants of the complexes are determined from the titration curves by employing pH-metric titration technique given by (Irving and Rossoti).

Metal-ligand stability constants (Log K) were determined by using the following relations:

$$\bar{n} = \frac{(V_3 - V_2)(E^0 + N^0)}{(V^0 + V_2)\bar{n}_A T_m^0} \quad \text{..}3$$

and

$$PL = \log_{10}\left\{\frac{1 + \beta_n^H \frac{1}{[anti\ \log \mathrm{pH}]^n}}{\mathrm{T}_\mathrm{L}^0 - \bar{n} T_m^0} \mathrm{X} \frac{(V^0 + V_3)}{V^0}\right\} \quad \text{...}4$$

Where $T_{L,}$ T^{o}, $E°$, and V^{o}havethe same significance as in equation (1) above, T_{m} denotes the total concentration of metal present in solution, V_{3} is the volume of metal ions present in solution and β^{H} is the overall proton ligand stability constant. The metal-ligand stability constants (log K) were determined by employing point wise computational Method (eq. 5 and 6).

$$\text{LogK}_1 = \log\left(\frac{n}{1-n}\right) + \text{pL} \quad \text{.............}5$$

$$\text{LogK}_2 = \log\left(\frac{1-n}{2-n}\right) + \text{pL}\text{.......................}6$$

Where: Log K is the metal-ligand stability constant, pL is the Free ligand exponent function, **n** is the Average number of ligand attached with metal ion (Janrao*et al.*, 2014).The results obtained were analyzed by an ORIGIN 2016 program using titration data and then the proton-ligand stability constants (pKa) and Metal-ligand stability constant (LogK) calculated (Omar and Ali, 2015).

RESULTS AND DISCUSSION

Fourier transformed infrared (FT-IR) spectra of isolated humic acid from peat soils Figure 2 had distinct clear absorption bands indicating the presence of major humic acid structural elemental groups such as H bonded OH ($3680cm^{-1}$ peak), C=O of carbonyl ($1721cm^{-1}$ peak), functional groups of aliphatic components CH_2 ($2918cm^{-1}$ peak) and C-O stretching of polysaccharide ($1168cm^{-1}$ peak). The positions of the absorption bands of the spectra fell within typical major absorption bands of humic acid which is at frequencies 3680, 2918, 1721, 1168 cm^{-1}. The first peak centred in the vicinity of 3680 cm^{-1} region is attributed to phenol OH group bounded by intermolecular H bonds. The $2918cm^{-1}$ band usually has absorption maximum at 2918 cm^{-1} which is due to C–H stretching of alkane group (CH_2). The next major absorption band is 1721 cm^{-1}. This band has been commonly ascribed to C=O stretching of mainly carboxyl group (COOH) with trace amount of ketones. The last peak was observed at 1168 cm^{-1} due to C–O stretching of polysaccharides and this peak appeared also in the spectra of humic acid from peat soil. The FTIR spectra of the isolated humic acid contained all major characteristic absorption peaks of humic acid. These absorption peaks indicated the presence of the major structural elements of humic acid namely H bonded OH, C=C of aromatic ring, C=O of carbonyl group (both carboxyl and ketonic), CH_2 group. This strongly supports the presence of humic acid.

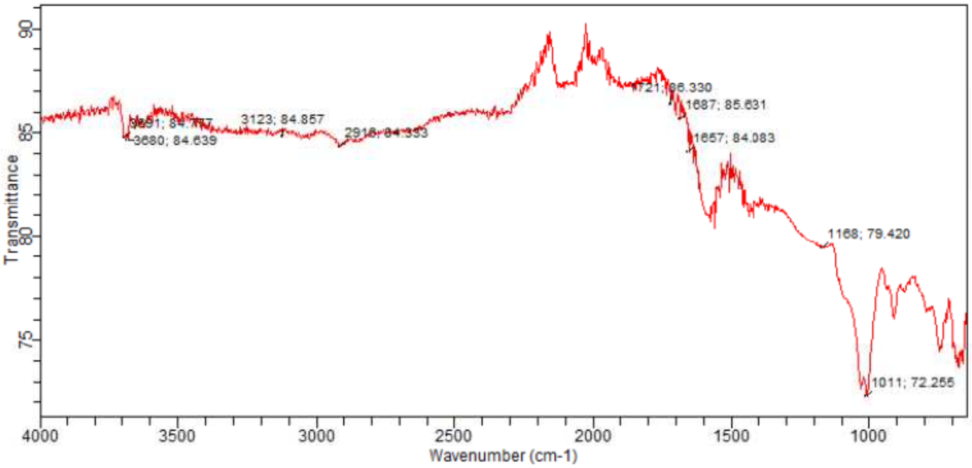


Fig. 2 : FT-IR spectraof peatsoilhumic acid (PSHA)

Evaluation of acid dissociation constant (pka) of acid hydrolysed peat soil humicacid at phenolic group

The value of the dissociation constant of the peat soil humic acid (PSHA) that underwent acidhydrolysis studied was found to be 8.9299 as shown Table 1, which is lower than the literaturevalues reported by Almeida and Szpoganics, (2015), Borges *et al.*, (2005); Badr *et al.*, (2012)and Fernandes *et al*,.(2009) of 9.73, 9.47 and 10.30. The difference between the obtained valuesand the reported values in this study might be probably as a result of acid hydrolysis of humicacid.

Table 1: PKa of (Hydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	$\log(\frac{nA}{1-nA})$	pKa
8.50	5.30	6.29	0.99	0.3594	-0.2510	8.2490
8.72	5.35	6.37	1.02	0.3400	-0.2880	8.4320
9.00	5.40	6.46	1.06	0.3141	-0.3391	8.6609
9.22	5.45	6.55	1.10	0.2882	-0.3927	8.8273
9.51	5.50	6.66	1.16	0.2494	-0.4786	9.0314
9.73	5.55	6.78	1.23	0.2041	-0.5910	9.1390
10.00	5.60	6.90	1.30	0.1589	-0.7238	9.2762
10.23	5.65	7.05	1.40	0.0941	-0.9835	9.2465
10.49	5.70	7.10	1.40	0.0941	-0.9835	9.5065

Average pKa = 8.9299 ± 0.4186

Table 2: PKa of (Unhydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	$\text{Log}(\frac{nA}{1-n})$	pKa
8.50	5.30	5.81	0.51	0.6619	0.2919	8.7919
8.72	5.35	5.90	0.55	0.6357	0.2418	8.9618
9.00	5.40	6.00	0.60	0.6029	0.1813	9.1813
9.22	5.45	6.10	0.65	0.5701	0.1226	9.3426
9.51	5.50	6.20	0.70	0.5376	0.0654	9.5754
9.73	5.55	6.33	0.78	0.4851	-0.0259	9.7041
10.00	5.60	6.47	0.87	0.4262	-0.1291	9.8709
10.23	5.65	6.62	0.99	0.3609	-0.2481	9.9819
10.49	5.70	6.80	1.10	0.2759	-0.4690	10.0210

Average pKa = 9.4923± 0.4410

Metal-ligand stability constant (Log K)

The stabilityconstants require the accurate values of proton-ligand stability constants (Anil and Maroti, 2008). Metal titration curves crossed over ligand titration curve indicated the formation of complex upon proton release (Santosh, *et al.*, 2011). If the values of n- are within range 0.2-0.8 and 1.2-18 this indicates the formation of 1:1 and 1:2 complexes (Sayyed and Mazahar, 2012).

The metal (II)-humate stepwise stability constants (log k) at phenolic group (Tables 3-18)

Table 3: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$\log(\frac{n}{1-n})$	LogK_1
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

LogK_1 (Average value) = 2.4788± 0.2203

Table 4: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$\text{Log}(\frac{n-1}{2-n})$	LogK_2
9.51	5.50	6.66	6.73	0.07	1.3509	1.70	-0.2671	1.4329
9.73	5.55	6.78	6.85	0.07	1.6383	1.51	0.2467	1.7567
10.00	5.60	6.90	6.98	0.08	2.1783	1.31	-0.2158	1.0942
10.23	5.65	7.05	7.13	0.08	4.1904	1.27		
10.49	5.70	7.10	7.19	0.09	4.6920			

LogK_2(Average value) = 1.4280 ± 0.3312

Table 5:Point-wise method,Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	Log($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430

$LogK_1$ **(Average value)** = 2.3059± 0.6153

Table 6:Point-wise method, Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
9.73	5.55	6.33	6.42	0.09	0.9000	1.69		
10.00	5.60	6.47	6.58	0.11	1.2578	1.44	-0.4592	0.9808
10.23	5.65	6.62	6.84	0.12	1.6137	1.26	-0.2010	1.4610
10.49	5.70	6.80	6.92	0.12	2.1052	1.03		

$LogK_2$ **(Average value)** = 1.2209± 0.3398

Table 7:Point-wise method,Pb (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n}{1-n}$)	$LogK_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.60	0.05	0.8333	1.96	0.6989	2.6589

$LogK_1$ (Average value) = 2.5832 ±0.1614

Table 8:Point-wise method,Pb-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n-1}{2-n}$)	$logK_2$
9.51	5.50	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.83	0.05	1.1702	1.44		
10.00	5.60	6.90	6.90	0.05	1.4864	1.22	-0.0237	1.1963
10.23	5.65	7.05	7.10	0.05	2.0190	1.09		
10.49	5.70	7.10	7.17	0.07	3.6492	1.00		

$LogK_2$(Average value) = 1.1963

Table 9:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log ($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.5477	2.3123
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	0.0272	2.2072
9.51	5.50	6.20	6.26	0.07	0.6417	1.89	0.2530	2.1430
9.73	5.55	6.40	6.40	0.07	0.7000	1.67	0.3680	2.0380

$LogK_1$ **(Average value)** = 2.2364 ± 0.1602

Table 10:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
10.00	5.60	6.47	6.55	0.08	1.9503	1.41		
10.23	5.65	6.62	6.72	0.11	1.4792	1.26	-0.0361	1.2239

$LogK_2$ **(Average value)** = 1.2239

Table 11:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n}{n-1}$)	$LogK_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4290	2.2110
8.72	5.35	6.37	6.39	0.02	0.2858	2.42	-0.3978	2.0222
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

$LogK_1$ (Average value)=2.1382±0.1046

Table 12:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	log($\frac{n-1}{2-n}$)	LogK$_2$
9.51	5.55	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.84	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.93	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.10		
10.49	5.70	7.10	7.18	0.07	3.6492	0.83		

LogK$_2$(Average value) = 1.5453 **±** 0.3450

Table 13:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	V$_3$-V$_2$	n	pL	Log($\frac{n}{n-1}$)	Log K$_1$
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.3477	2.3123
9.00	5.40	6.00	6.04	0.04	0.3236	2.38	-0.3202	2.0598
9.22	5.45	6.10	6.15	0.05	0.4297	2.17	-0.1230	2.0470
9.51	5.50	6.20	6.26	0.06	0.5500	1.89	0.0871	1.9771
9.73	5.55	6.33	6.40	0.07	0.7000	1.67	0.3680	2.0380

LogK$_1$ **(Average value)** = 2.1568 ± 0.2069

Table 14:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	V$_3$-V$_2$	n	pL	Log($\frac{n-1}{2-n}$)	Log K$_2$
10.00	5.60	6.47	6.55	0.08	0.9148	1.41		
10.23	5.65	6.62	6.71	0.09	1.2102	1.20	-0.5749	0.6251
10.49	5.70	6.80	6.92	0.09	1.5968	1.03	0.1703	1.2003

LogK$_2$ **(Average value)** = 0.9127± 0.4070

Table15:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	Log($\frac{n}{1-n}$)	LogK$_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4210	2.2190
8.72	5.35	6.37	6.40	0.03	0.4286	2.42	-0.1249	2.2951
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.96	0.3010	2.2610
9.51	5.55	6.66	6.70	0.04	0.7720	1.67	0.5297	2.1997

LogK$_1$ (Average value) = 2.2108± 0.0825

Table 16:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	Log($\frac{n-1}{2-n}$)	Log K$_2$
9.73	5.55	6.78	6.83	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.95	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.09		
10.49	5.70	7.10	7.16	0.06	3.1429	0.89		

LogK$_2$ **(Average value)** = 1.5453± 0.3450

Table 17:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	V$_3$-V$_2$	n	pL	Log($\frac{n}{n-1}$)	Log K$_1$
8.50	5.30	5.81	5.86	0.05	0.3717	2.88	-0.2280	2.6520
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.06	0.06	0.4853	2.38	-0.0255	2.3545
9.22	5.45	6.10	6.16	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430
9.73	5.55	6.33	6.41	0.08	0.8000	1.69	0.6020	2.2920

LogK$_1$ **(Average value)** = 2.2516± 0.5380

Table 18:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$\text{Log}(\frac{n-1}{2-n})$	Log K_2
10.00	5.60	6.47	6.57	0.10	1.1434	1.43		
10.23	5.65	6.62	6.72	0.10	1.3448	1.23	-0.2788	0.9512
10.49	5.70	6.80	6.90	0.10	1.7742	1.03	0.5351	1.5651

LogK_2 **(Average value)** = 1.2581± 0.4340

Table 19: Stepwise and overall Stability constants of thehydrolysed and unhydrolysed divalent metal (II) complexes

Chelates	**LogK_1**	**LogK_2**	**Logβ**
[Cu (Hydrolysed PSHA-1)$_2$]	2.4788	1.4280	3.9068
[Pb (Hydrolysed PSHA-1)$_2$]	2.5832	1.1963	3.7795
[Cd (Hydrolysed PSHA-1)$_2$]	2.2108	1.5453	3.7561
[Mg (Hydrolysed PSHA-1)$_2$]	2.1382	1.5453	3.6835
[Cu (Unhydrolysed PSHA-1)$_2$]	2.3059	1.2209	3.5268
[Pb (Unhydrolysed PSHA-1)$_2$]	2.2364	1.2239	3.4603
[Cd (Unhydrolysed PSHA-1)$_2$]	2.2516	1.2581	3.5097
[Mg (Unydrolysed PSHA-1)$_2$]	2.1568	0.9127	3.0695

The results obtained (Table19) shows the stepwise and overall stability constants to be not high indicating low stability of the complexes, because the solubility of most metal ions in the basic pH range is minimal due to metal hydroxide precipitation (Karimi, 2017). In general, the stepwise stability constants (K_1 and K_2) follow the order $K_1 > K_2$ for the copper, lead, magnesium and cadmium complexes respectively. The steady decrease of the values with increasing number of ligands is in agreement with the prediction made by researchers (Na'aliya, 2013). The decrease could be attributed to the fact that as the number of the ligands (Humate ions) that enters the coordination zone increases the aqua molecules available for replacement by the ligands become less. Thus, the metal ions become less electron loving with progressive intake of the ligand and this results in the decrease in the values of the constants (Na'aliya, 2013). Also the stability of the complexes is influenced by the size and number of the chelate rings(Mackay and Mackay,2002).All the complexes form rings in their structure as humate, a bidentate ligand, bond the metal ions in the ratio 1:2 (Boguta and Sokolowska, 2016) forming chelate rings. The values of the overall stability constants (logβ) obtained for humate complexes are not high indicating low stability as the values are not high. LogK values for copper-humates (Table 3 to 6) obtained in this study are lower than those reported for the complexes of humic acids (Pandey *et al*., 2015; Dinu, 2013; Kaschl *et al*., 2010 and Gilbeto and Jorg, 2001). The values of LogK(Table 7 to 10) forlead-humates are lower than those reported for the lead in the literature (Dinu, 2013; Gilbeto and Jorg 2001). Log K values(Table 11 to 14) for magnesium-humates obtained in this study are close to those reported by (Pandey *et al*., 2015). Log K values of cadmium-humates (Table 15 to 18) obtained in this work near to the one reported by (Dinu, 2013 and Pandey *et al*., 2015).The difference between the reported values and the values obtained in this study might be probably as a result of acid hydrolysis of humic acid. The values of the overall stability constants (log β) of the copper humates complexes presented in Table 19 is high than that of other metal humate complexes, show relatively high stability of Cu-HA complexes, show the following order of stability: Cu >Pb> Cd > Mg; which are in close agreement to the findings of (Dinu, 2013 and Pandey *et al*., 2015).The high stability of Cu-humate chelate could be attributed to the existence of coordinate covalent bond between the complexing agents and the Cu^{2+} ions. Since, Cu^{2+} being a metal of the transitional series with $3d^9$ electronic configurations can accept the electrons from the complexing agents. Similarly,the low stabilities of Pb,Cd and Mg -complexes could be explained by that Pb^{2+} with $6s^2$, Cd^{2+} with $4d^{10}$ and Mg^{2+} with $2p^6$ their electronic configuration has a completely filled d,p and s orbitals. Moreover, the stabilities of metal ions with hydrolysed humic acid from peat soil were higher than those with unhydrolysed humic acid from peat soil; which is ascribed to the high content of acidity in hydrolysed humic acid than unhydrolysed humic acid.

CONCLUSION

The values of logK for Cu(II) hydrolysed humic acid complex was higher followed by Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes as compared with metal(II) unhydrolysed humic acid complexes . This indicates acid hydrolysis of humic acid can enhance the complexation behavior of humic acid with metal (II) ions. However, the higher values of logβ for Cu(II), Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes indicates more stable stepwise complexes formed as compared with Cu(II), Pb(II), Cd(II) and Mg(II) unhydrolysed humic acid complexes.

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STABILITY CONSTANTS OF COMPLEXES OF METAL IONS WITH PEATSOIL HUMIC ACIDS UNDER NON-ACID-CONDITIONS

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ABSTRACT

Stability constants of complexes of four divalent metal ions viz. Cu^{2+}, Pb^{2+},Mg^{2+} and Cd^{2+} with humic acids (HA) were determined by potentiometric titration of humic acids with the corresponding salt of the divalent metals in aqueous media under non-acid-condition. The log K (logarithm of the stability constant) ranged from 1.0942 to 2.7471 for metal-humic acid complexes were determined using point-wise computational method. The order of stability constants were obtained as follows: Cu >Pb> Cd > Mg for metal -HA complexes respectively, indicating a higher degree of complexation with Cu metal ion.

Keywords: stability constant, humic acid, potentiometric titration, divalent metals, acid hydrolysis.

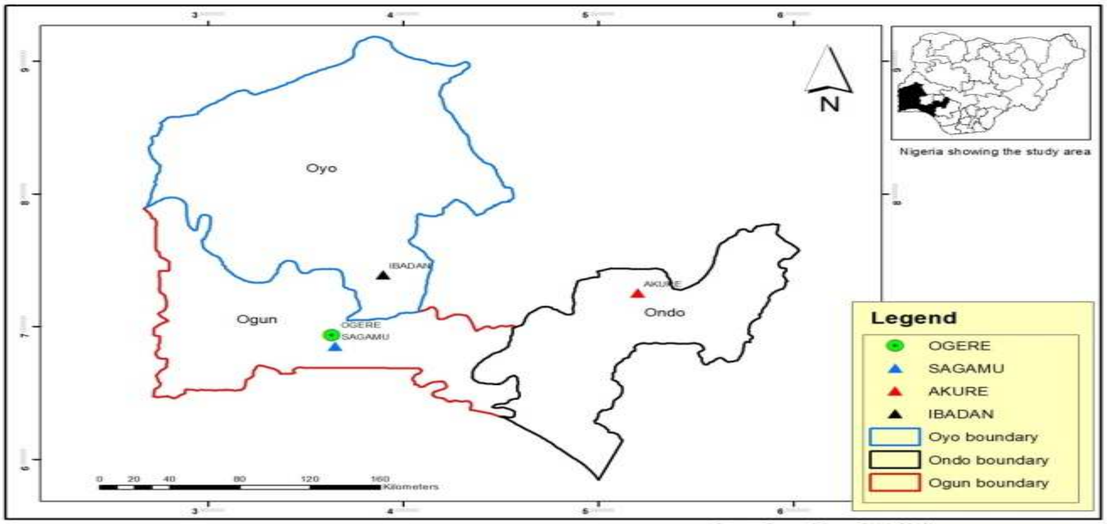
NTRODUCTION

The stability constant of a complex is the numerical expression of its stability and provides a quantitative measure of affinity of the metal ion to the complexing agent. An understanding of the relative stability of metal-complexes helps in predicting the behavior of metal ions in the soil (Ram and Raman, 1982). Extensive researches has been done to determine the stability constants of the complexes formed between humic acid (HA) with a number of metal ions. Ashok *et al*., (2000) reported that humic acid with hydroxyl, phenoxyl and carboxyl reactive groups can form coordination compound with metal ions at pH 3.5. The stability constants(Log K) for different metal-humic acid complexes indicated the following order of the stabilities of complexes formed between humic acid and metal ion, Cu >Fe >Pb> Ni > Co > Ca > Cd > Zn >Mn> Mg. Andelkovic *et al*., (2010) investigated the binding of Cd(II) to soil humic acid at pH 6.5 and in 0.1M KNO_3 ionic medium. The stability constant for binding indicating greater stability in the case when carboxyl groups are involved in complexation reaction. Kostic *et al*.,(2012) investigated the complexation of humic acid with certain heavy metal ions (Co(II), Ni(II),Cu(II), Zn(II), and Pb(II). The experiment was performed at 25°C, at pH 4.0 and ionic strength of 0.01M. Stability constant of complex between Pb(II) ions and humic acid is greater than stability constants of other investigated metal-humate complexes. Bogata and Sokolowska (2016) analyses the interaction between humic acids from different soils and Zn (II) ions at wide concentration ranges and at pH 5. Studies have showed significant impact of Zn concentration, pH and some properties of humic acids with zinc.But all of these studies were limited to acidic pH range. Therefore, the present study was carried out to determine and compare the stability constants of complexes of metal ions with hydrolysed peat soil humic acid and unhydrolysed peat soil humic under non-acid conditions.

MATERIALS AND METHODS

Analytical grade chemicals used includes hydrochloric acid (HCl), nitric acid (HNO_3), sodium hydroxide (NaOH), lead nitrate $Pb(NO_3)_2$, copper nitrate $Cu(NO_3)_2.3H_2O$, cadmium nitrate $Cd(NO_3)_2.4H_2O$, magnesium nitrate $Mg(NO_3)_2.6H_2O$, potassium nitrate (KNO_3), calcium chloride ($CaCl_2$), (sigma-Aldrich). Dowex 50WX8, (20-50 mesh) from Fluka.

Area of study



Source: Dept. of Geog. BUK (2016)

Figure 1: Map showing the sampling point at Sagamu Town, Ogun State.

Description of Sampling Area

Sagamu has geographical coordinates between 6°50′ north; 3° 38′ east is located in south western region of Nigeria. The region has tropical wet and dry climate with a lengthy wet season and relatively constant temperatures throughout the course of the year. Wet season runs from March to October, November to December forms the region dry season. The vegetation type of the region is savannah which is really grassland with small bushes and occasional big trees. Grassland soils have substantially higher organic matter content than forest soils (Novackova, 2011).

Sample Collection

The Peatsoil samples were collected from four different sampling points (0-10cm depth) in Sagamu into polyethylene bag with plastic spoons. Samples were taken to the laboratory, extraneous materials were removed; the samples were air-dried, crushed and ground to a fine powder in a mortar passed through a 0.20mm sieve. The samples were kept for analysis.

Isolation and purification of humic acid from peat soil sample

Peatsoil sample (100g) was mixed with 1000 cm^3 of 0.1M NaOH solution, shaken for 3hours and left to stand overnight. Dark-coloured supernatant was obtained and decanted from solid residue. The dark-coloured supernatant was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 6 hours. Yellowish brown supernatant and dark-brown precipitate were obtained. The yellowish brown supernatant was decanted followed by centrifuge and discarded. The dark-brown precipitate was mixed with 500$cm^3$of 0.1M NaOH solution followed by passing through dowex resin. The dark-brown solution was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 3 hours. The dark-brown precipitate was washed several times with deionized water. The supernatant was treated with $AgNO_3$ solution until no white precipitate observed. The humic acid was transferred to weighed crucible and dried at 60°C in an oven for 12 hours. The humic acid was cooled and dried in the desiccator, weighed and recorded. The obtained humic acid was dried again at 60°C for additional 6 hours cooled and dried in the desiccator, weighed and recorded constant weight was obtained (Baruah *et al*., 2015).

FT-IR analysis

FT-IR spectra of humic acid sample was analysed using Carry 630 FT-IR Agilent Technologies.

Unhydrolysed compost humic acid

The unhydrolysed humic acid was obtained after isolation and purification of compost humic acid and kept for investigation.

Acid hydrolysis of Peatsoil acid

Peatsoil humic acid sample (1g) was refluxed for 12 hours at (160°C) with 50cm^3 of 6M HCl. The mixture was allowed to cool, decanted, and centrifuged after hydrolysis. The insoluble residues were washed with distilled water via centrifugation several times, and the supernatant was treated with $AgNO_3$ solution until no white precipitate was observed. The residue was thoroughly dried over $CaCl_2$ in a desiccator at room temperature (Chefetz *et al*., 2002). Finally, the obtained hydrolysed humic acid was kept for investigation.

Potentiometric Titrations

Potentiometric measurements were carried out using a pH-meter Jenway (model 3510) with combine electrode, the sensitivity of the pH - meter is 0.01 units. The pH meter was switched on half an hour before starting the titration for initial warm up of the instrument. The instrument was calibrated with an aqueous standard buffer solution of pH 4.00 and 10.0 (borate buffer) prepared from a "Qualigens" buffer tablets.

The following sets of solutions were prepared in a 250cm^3 volumetric flask separately for pH metric titrations.

(i) 5 cm^3 0.1 M HCl + 40 cm^3 deionized water

(ii) 5 cm^3 0.1 M HCl + 39 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid

(iii) 5 cm^3 0.1 M HCl + 37 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid + 2 cm^3 0.01 M Cu(II)

The solutions were titrated against standardized 0.110MNaOH separately. The total volume of each mixture was adjusted to 50 cm^3 and the ionic strength of the solutions was maintained constant at by adding appropriate amount of stock solution of 1M KNO_3 (Gamal, 2015; Omar and Ali, 2015). A magnetic stirrer was used to achieve thorough mixing of the interacting solutions at 550 rpm. The same set of experimental conditions was applied for potentiometric titration of remaining samples.

Evaluation of pKa of Hydrolysed peat soil Humic Acids

The proton-ligand formation number $n_{\mathbf{A}}$ were calculated by Irving and Rossotti expression (Omar and Ali, 2015).

$$nA = Y- \frac{(V2-V1)(No-Eo)}{(Vo+V1)TcL} \quad \text{..................................1}$$

Where: Y is number of dissociable proton, (V_2-V_1) is the measure of displacement of the ligand curve relative to acid curve, N^o and E^o are the resultant concentration of alkali solution, free acid solution, $T_{cL}{}^o$ is the total ligand concentration, V^o is the total volume of titration solution,V_1 is the volume of alkali added to acid solution,V_2 is the volume of alkali added to acid solution + ligand solution, acid dissociation constants (pKa - values) of ligand were calculated by algebraic method point wise calculation (Tables 1). The dissociation constants (pKa) were calculated according to the following relation:

$$pKa = pH + \log(\frac{nA}{1-nA}) \quad \text{.............................2}$$

Where: pKa is the acid dissociation constant, $n_A$is the Proton-ligand formation number and pH is the pH-values (Omar and Ali, 2015).

Determination of metal-ligand stability constants (log K) of complexes

The potentiometric measurement for the determination of stability constant of a complex in solution is based on the fact that the redox potential of the couple $\frac{M^{+(m-n)}}{M^{+m}}$ is shifted significantly on complexation of the metal ion with the ligand. This method involves change in hydrogen ion concentration [H$^+$] due to the displacement or association of one or more protons taking place during complexation reaction. This change can be found out by titrating the solutions containing free acid, acid with ligand, and acid with ligand and metal ion, individually against a standard alkali solution at a constant ionic strength or temperature. Either ionic strength or temperature may be varied for different sets of solutions. In all the cases, the change in the pH of the solution is measured after each addition of a known amount of alkali to the reaction cell which contains the reaction mixture. The titration curves are then drawn by plotting the measured pH values against the corresponding volume of alkali added and the stability constants of the complexes are determined from the titration curves by employing pH-metric titration technique given by (Irving and Rossoti).

Metal-ligand stability constants (Log K) were determined by using the following relations:

$$\bar{n} = \frac{(V_3 - V_2)(E^0 + N^0)}{(V^0 + V_2)\bar{n}_A T_m^0} \quad \text{...3}$$

and

$$PL = \log_{10}\{\frac{1 + \beta_n^H \frac{1}{[anti\ \log pH]^n}}{T_L^0 - \bar{n} T_m^0} X \frac{(V^0 + V_3)}{V^0}\} \quad \text{..4}$$

Where $T_{L,}$ T^o, E°, and V^ohavethe same significance as in equation (1) above, T_m denotes the total concentration of metal present in solution, V_3 is the volume of metal ions present in solution and β^H is the overall proton ligand stability constant. The metal-ligand stability constants (log K) were determined by employing point wise computational Method (eq. 5 and 6).

$$\text{Log}K_1 = \log\left(\frac{n}{1-n}\right) + pL \qquad ....5$$

$$\text{Log}K_2 = \log\left(\frac{1-n}{2-n}\right) + pL.......................6$$

Where: Log K is the metal-ligand stability constant, pL is the Free ligand exponent function, **n** is the Average number of ligand attached with metal ion (Janrao*et al.*, 2014).The results obtained were analyzed by an ORIGIN 2016 program using titration data and then the proton-ligand stability constants (pKa) and Metal-ligand stability constant (LogK) calculated (Omar and Ali, 2015).

RESULTS AND DISCUSSION

Fourier transformed infrared (FT-IR) spectra of isolated humic acid from peat soils Figure 2 had distinct clear absorption bands indicating the presence of major humic acid structural elemental groups such as H bonded OH (3680cm^{-1} peak), C=O of carbonyl (1721cm^{-1} peak), functional groups of aliphatic components CH_2 (2918cm^{-1} peak) and C-O stretching of polysaccharide (1168cm^{-1} peak). The positions of the absorption bands of the spectra fell within typical major absorption bands of humic acid which is at frequencies 3680, 2918, 1721, 1168 cm^{-1}. The first peak centred in the vicinity of 3680 cm^{-1} region is attributed to phenol OH group bounded by intermolecular H bonds. The 2918cm^{-1} band usually has absorption maximum at 2918 cm^{-1} which is due to C–H stretching of alkane group (CH_2). The next major absorption band is 1721 cm^{-1}. This band has been commonly ascribed to C=O stretching of mainly carboxyl group (COOH) with trace amount of ketones. The last peak was observed at 1168 cm^{-1} due to C–O stretching of polysaccharides and this peak appeared also in the spectra of humic acid from peat soil. The FTIR spectra of the isolated humic acid contained all major characteristic absorption peaks of humic acid. These absorption peaks indicated the presence of the major structural elements of humic acid namely H bonded OH, C=C of aromatic ring, C=O of carbonyl group (both carboxyl and ketonic), CH_2 group. This strongly supports the presence of humic acid.

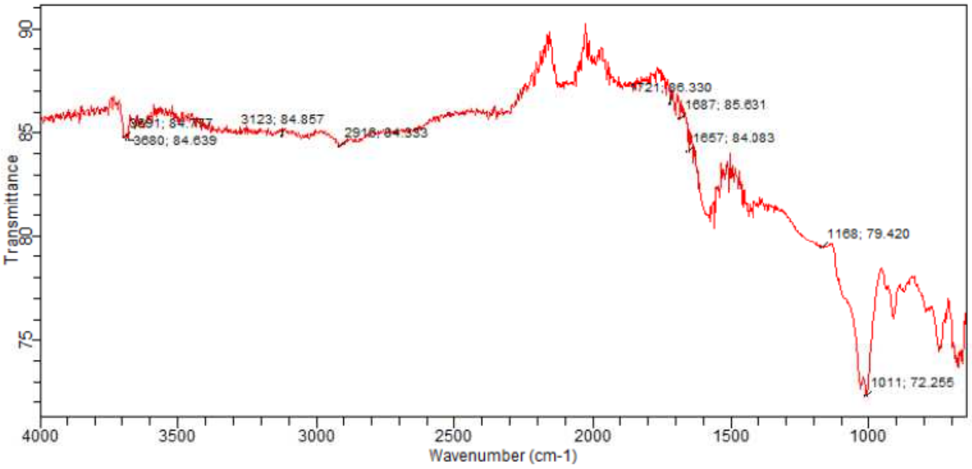


Fig. 2 : FT-IR spectraof peatsoilhumic acid (PSHA)

Evaluation of acid dissociation constant (pka) of acid hydrolysed peat soil humicacid at phenolic group

The value of the dissociation constant of the peat soil humic acid (PSHA) that underwent acidhydrolysis studied was found to be 8.9299 as shown Table 1, which is lower than the literaturevalues reported by Almeida and Szpoganics, (2015), Borges *et al.*, (2005); Badr *et al.*, (2012)and Fernandes *et al*,.(2009) of 9.73, 9.47 and 10.30. The difference between the obtained valuesand the reported values in this study might be probably as a result of acid hydrolysis of humicacid.

Table 1: PKa of (Hydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	$\log(\frac{nA}{1-nA})$	pKa
8.50	5.30	6.29	0.99	0.3594	-0.2510	8.2490
8.72	5.35	6.37	1.02	0.3400	-0.2880	8.4320
9.00	5.40	6.46	1.06	0.3141	-0.3391	8.6609
9.22	5.45	6.55	1.10	0.2882	-0.3927	8.8273
9.51	5.50	6.66	1.16	0.2494	-0.4786	9.0314
9.73	5.55	6.78	1.23	0.2041	-0.5910	9.1390
10.00	5.60	6.90	1.30	0.1589	-0.7238	9.2762
10.23	5.65	7.05	1.40	0.0941	-0.9835	9.2465
10.49	5.70	7.10	1.40	0.0941	-0.9835	9.5065

Average pKa = 8.9299 ± 0.4186

Table 2: PKa of (Unhydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	$\text{Log}(\frac{nA}{1-n})$	pKa
8.50	5.30	5.81	0.51	0.6619	0.2919	8.7919
8.72	5.35	5.90	0.55	0.6357	0.2418	8.9618
9.00	5.40	6.00	0.60	0.6029	0.1813	9.1813
9.22	5.45	6.10	0.65	0.5701	0.1226	9.3426
9.51	5.50	6.20	0.70	0.5376	0.0654	9.5754
9.73	5.55	6.33	0.78	0.4851	-0.0259	9.7041
10.00	5.60	6.47	0.87	0.4262	-0.1291	9.8709
10.23	5.65	6.62	0.99	0.3609	-0.2481	9.9819
10.49	5.70	6.80	1.10	0.2759	-0.4690	10.0210

Average pKa = 9.4923± 0.4410

Metal-ligand stability constant (Log K)

The stabilityconstants require the accurate values of proton-ligand stability constants (Anil and Maroti, 2008). Metal titration curves crossed over ligand titration curve indicated the formation of complex upon proton release (Santosh, *et al.*, 2011). If the values of n- are within range 0.2-0.8 and 1.2-18 this indicates the formation of 1:1 and 1:2 complexes (Sayyed and Mazahar, 2012).

The metal (II)-humate stepwise stability constants (log k) at phenolic group (Tables 3-18)

Table 3: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$\log(\frac{n}{1-n})$	$\text{Log}K_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

LogK_1 (Average value) = 2.4788± 0.2203

Table 4: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$\text{Log}(\frac{n-1}{2-n})$	$\text{Log}K_2$
9.51	5.50	6.66	6.73	0.07	1.3509	1.70	-0.2671	1.4329
9.73	5.55	6.78	6.85	0.07	1.6383	1.51	0.2467	1.7567
10.00	5.60	6.90	6.98	0.08	2.1783	1.31	-0.2158	1.0942
10.23	5.65	7.05	7.13	0.08	4.1904	1.27		
10.49	5.70	7.10	7.19	0.09	4.6920			

LogK_2(Average value) = 1.4280 ± 0.3312

Table 5:Point-wise method,Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	$\text{Log}(\frac{n}{n-1})$	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430

LogK_1 **(Average value)** = 2.3059± 0.6153

Table 6:Point-wise method, Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$V_3\text{-}V_2$	n	pL	$\text{Log}(\frac{n-1}{2-n})$	Log K_2
9.73	5.55	6.33	6.42	0.09	0.9000	1.69		
10.00	5.60	6.47	6.58	0.11	1.2578	1.44	-0.4592	0.9808
10.23	5.65	6.62	6.84	0.12	1.6137	1.26	-0.2010	1.4610
10.49	5.70	6.80	6.92	0.12	2.1052	1.03		

LogK_2 **(Average value)** = 1.2209± 0.3398

Table 7:Point-wise method,Pb (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	$\log(\frac{n}{1-n})$	LogK_1
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.60	0.05	0.8333	1.96	0.6989	2.6589

LogK_1 (Average value) = 2.5832 ±0.1614

Table 8:Point-wise method,Pb-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	$\log(\frac{n-1}{2-n})$	logK_2
9.51	5.50	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.83	0.05	1.1702	1.44		
10.00	5.60	6.90	6.90	0.05	1.4864	1.22	-0.0237	1.1963
10.23	5.65	7.05	7.10	0.05	2.0190	1.09		
10.49	5.70	7.10	7.17	0.07	3.6492	1.00		

LogK_2(Average value) = 1.1963

Table 9:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$V_3\text{-}V_2$	n	pL	$\text{Log}(\frac{n}{n-1})$	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.5477	2.3123
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	0.0272	2.2072
9.51	5.50	6.20	6.26	0.07	0.6417	1.89	0.2530	2.1430
9.73	5.55	6.40	6.40	0.07	0.7000	1.67	0.3680	2.0380

LogK_1 **(Average value)** = 2.2364 ± 0.1602

Table 10:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$V_3\text{-}V_2$	n	pL	$\text{Log}(\frac{n-1}{2-n})$	Log K_2
10.00	5.60	6.47	6.55	0.08	1.9503	1.41		
10.23	5.65	6.62	6.72	0.11	1.4792	1.26	-0.0361	1.2239

LogK_2 **(Average value)** = 1.2239

Table 11:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	$\log(\frac{n}{n-1})$	LogK_1
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4290	2.2110
8.72	5.35	6.37	6.39	0.02	0.2858	2.42	-0.3978	2.0222
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

LogK_1 (Average value)=2.1382**±**0.1046

Table 12:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$\log(\frac{n-1}{2-n})$	$LogK_2$
9.51	5.55	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.84	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.93	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.10		
10.49	5.70	7.10	7.18	0.07	3.6492	0.83		

$LogK_2$(Average value) = 1.5453 **±** 0.3450

Table 13:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$Log(\frac{n}{n-1})$	$Log\ K_1$
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.3477	2.3123
9.00	5.40	6.00	6.04	0.04	0.3236	2.38	-0.3202	2.0598
9.22	5.45	6.10	6.15	0.05	0.4297	2.17	-0.1230	2.0470
9.51	5.50	6.20	6.26	0.06	0.5500	1.89	0.0871	1.9771
9.73	5.55	6.33	6.40	0.07	0.7000	1.67	0.3680	2.0380

$LogK_1$ **(Average value)** = 2.1568 ± 0.2069

Table 14:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$Log(\frac{n-1}{2-n})$	$Log\ K_2$
10.00	5.60	6.47	6.55	0.08	0.9148	1.41		
10.23	5.65	6.62	6.71	0.09	1.2102	1.20	-0.5749	0.6251
10.49	5.70	6.80	6.92	0.09	1.5968	1.03	0.1703	1.2003

$LogK_2$ **(Average value)** = 0.9127± 0.4070

Table15:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$Log(\frac{n}{1-n})$	$LogK_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4210	2.2190
8.72	5.35	6.37	6.40	0.03	0.4286	2.42	-0.1249	2.2951
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.96	0.3010	2.2610
9.51	5.55	6.66	6.70	0.04	0.7720	1.67	0.5297	2.1997

$LogK_1$ (Average value) = 2.2108± 0.0825

Table 16:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$Log(\frac{n-1}{2-n})$	$Log\ K_2$
9.73	5.55	6.78	6.83	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.95	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.09		
10.49	5.70	7.10	7.16	0.06	3.1429	0.89		

$LogK_2$ **(Average value)** = 1.5453± 0.3450

Table 17:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$Log(\frac{n}{n-1})$	$Log\ K_1$
8.50	5.30	5.81	5.86	0.05	0.3717	2.88	-0.2280	2.6520
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.06	0.06	0.4853	2.38	-0.0255	2.3545
9.22	5.45	6.10	6.16	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430
9.73	5.55	6.33	6.41	0.08	0.8000	1.69	0.6020	2.2920

$LogK_1$ **(Average value)** = 2.2516± 0.5380

Table 18:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$\text{Log}(\frac{n-1}{2-n})$	Log K_2
10.00	5.60	6.47	6.57	0.10	1.1434	1.43		
10.23	5.65	6.62	6.72	0.10	1.3448	1.23	-0.2788	0.9512
10.49	5.70	6.80	6.90	0.10	1.7742	1.03	0.5351	1.5651

LogK_2 **(Average value)** = 1.2581± 0.4340

Table 19: Stepwise and overall Stability constants of thehydrolysed and unhydrolysed divalent metal (II) complexes

Chelates	LogK₁	LogK₂	Logβ
[Cu (Hydrolysed PSHA-1)$_2$]	2.4788	1.4280	3.9068
[Pb (Hydrolysed PSHA-1)$_2$]	2.5832	1.1963	3.7795
[Cd (Hydrolysed PSHA-1)$_2$]	2.2108	1.5453	3.7561
[Mg (Hydrolysed PSHA-1)$_2$]	2.1382	1.5453	3.6835
[Cu (Unhydrolysed PSHA-1)$_2$]	2.3059	1.2209	3.5268
[Pb (Unhydrolysed PSHA-1)$_2$]	2.2364	1.2239	3.4603
[Cd (Unhydrolysed PSHA-1)$_2$]	2.2516	1.2581	3.5097
[Mg (Unydrolysed PSHA-1)$_2$]	2.1568	0.9127	3.0695

The results obtained (Table19) shows the stepwise and overall stability constants to be not high indicating low stability of the complexes, because the solubility of most metal ions in the basic pH range is minimal due to metal hydroxide precipitation (Karimi, 2017). In general, the stepwise stability constants (K_1 and K_2) follow the order $K_1 > K_2$ for the copper, lead, magnesium and cadmium complexes respectively. The steady decrease of the values with increasing number of ligands is in agreement with the prediction made by researchers (Na'aliya, 2013). The decrease could be attributed to the fact that as the number of the ligands (Humate ions) that enters the coordination zone increases the aqua molecules available for replacement by the ligands become less. Thus, the metal ions become less electron loving with progressive intake of the ligand and this results in the decrease in the values of the constants (Na'aliya, 2013). Also the stability of the complexes is influenced by the size and number of the chelate rings(Mackay and Mackay,2002).All the complexes form rings in their structure as humate, a bidentate ligand, bond the metal ions in the ratio 1:2 (Boguta and Sokolowska, 2016) forming chelate rings. The values of the overall stability constants (logβ) obtained for humate complexes are not high indicating low stability as the values are not high. LogK values for copper-humates (Table 3 to 6) obtained in this study are lower than those reported for the complexes of humic acids (Pandey *et al.*, 2015; Dinu, 2013; Kaschl *et al.*, 2010 and Gilbeto and Jorg, 2001). The values of LogK(Table 7 to 10) forlead-humates are lower than those reported for the lead in the literature (Dinu, 2013; Gilbeto and Jorg 2001). Log K values(Table 11 to 14) for magnesium-humates obtained in this study are close to those reported by (Pandey *et al.*, 2015). Log K values of cadmium-humates (Table 15 to 18) obtained in this work near to the one reported by (Dinu, 2013 and Pandey *et al.*, 2015).The difference between the reported values and the values obtained in this study might be probably as a result of acid hydrolysis of humic acid. The values of the overall stability constants (log β) of the copper humates complexes presented in Table 19 is high than that of other metal humate complexes, show relatively high stability of Cu-HA complexes, show the following order of stability: Cu >Pb> Cd > Mg; which are in close agreement to the findings of (Dinu, 2013 and Pandey *et al.*, 2015).The high stability of Cu-humate chelate could be attributed to the existence of coordinate covalent bond between the complexing agents and the Cu^{2+} ions. Since, Cu^{2+} being a metal of the transitional series with $3d^9$ electronic configurations can accept the electrons from the complexing agents. Similarly,the low stabilities of Pb,Cd and Mg -complexes could be explained by that Pb^{2+} with $6s^2$, Cd^{2+} with $4d^{10}$ and Mg^{2+} with $2p^6$ their electronic configuration has a completely filled d,p and s orbitals. Moreover, the stabilities of metal ions with hydrolysed humic acid from peat soil were higher than those with unhydrolysed humic acid from peat soil; which is ascribed to the high content of acidity in hydrolysed humic acid than unhydrolysed humic acid.

CONCLUSION

The values of logK for Cu(II) hydrolysed humic acid complex was higher followed by Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes as compared with metal(II) unhydrolysed humic acid complexes . This indicates acid hydrolysis of humic acid can enhance the complexation behavior of humic acid with metal (II) ions. However, the higher values of logβ for Cu(II), Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes indicates more stable stepwise complexes formed as compared with Cu(II), Pb(II), Cd(II) and Mg(II) unhydrolysed humic acid complexes.

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STABILITY CONSTANTS OF COMPLEXES OF METAL IONS WITH PEATSOIL HUMIC ACIDS UNDER NON-ACID-CONDITIONS

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ABSTRACT

Stability constants of complexes of four divalent metal ions viz. Cu^{2+}, Pb^{2+},Mg^{2+} and Cd^{2+} with humic acids (HA) were determined by potentiometric titration of humic acids with the corresponding salt of the divalent metals in aqueous media under non-acid-condition. The log K (logarithm of the stability constant) ranged from 1.0942 to 2.7471 for metal-humic acid complexes were determined using point-wise computational method. The order of stability constants were obtained as follows: Cu >Pb> Cd > Mg for metal -HA complexes respectively, indicating a higher degree of complexation with Cu metal ion.

Keywords: stability constant, humic acid, potentiometric titration, divalent metals, acid hydrolysis.

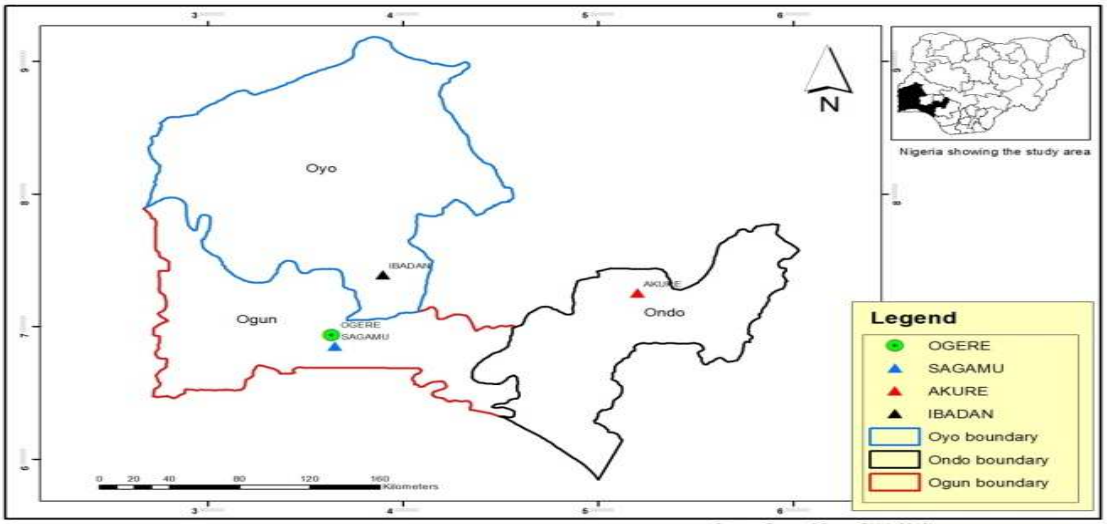
NTRODUCTION

The stability constant of a complex is the numerical expression of its stability and provides a quantitative measure of affinity of the metal ion to the complexing agent. An understanding of the relative stability of metal-complexes helps in predicting the behavior of metal ions in the soil (Ram and Raman, 1982). Extensive researches has been done to determine the stability constants of the complexes formed between humic acid (HA) with a number of metal ions. Ashok *et al*., (2000) reported that humic acid with hydroxyl, phenoxyl and carboxyl reactive groups can form coordination compound with metal ions at pH 3.5. The stability constants(Log K) for different metal-humic acid complexes indicated the following order of the stabilities of complexes formed between humic acid and metal ion, Cu >Fe >Pb> Ni > Co > Ca > Cd > Zn >Mn> Mg. Andelkovic *et al*., (2010) investigated the binding of Cd(II) to soil humic acid at pH 6.5 and in 0.1M KNO_3 ionic medium. The stability constant for binding indicating greater stability in the case when carboxyl groups are involved in complexation reaction. Kostic *et al*.,(2012) investigated the complexation of humic acid with certain heavy metal ions (Co(II), Ni(II),Cu(II), Zn(II), and Pb(II). The experiment was performed at 25°C, at pH 4.0 and ionic strength of 0.01M. Stability constant of complex between Pb(II) ions and humic acid is greater than stability constants of other investigated metal-humate complexes. Bogata and Sokolowska (2016) analyses the interaction between humic acids from different soils and Zn (II) ions at wide concentration ranges and at pH 5. Studies have showed significant impact of Zn concentration, pH and some properties of humic acids with zinc.But all of these studies were limited to acidic pH range. Therefore, the present study was carried out to determine and compare the stability constants of complexes of metal ions with hydrolysed peat soil humic acid and unhydrolysed peat soil humic under non-acid conditions.

MATERIALS AND METHODS

Analytical grade chemicals used includes hydrochloric acid (HCl), nitric acid (HNO_3), sodium hydroxide (NaOH), lead nitrate $Pb(NO_3)_2$, copper nitrate $Cu(NO_3)_2.3H_2O$, cadmium nitrate $Cd(NO_3)_2.4H_2O$, magnesium nitrate $Mg(NO_3)_2.6H_2O$, potassium nitrate (KNO_3), calcium chloride ($CaCl_2$), (sigma-Aldrich). Dowex 50WX8, (20-50 mesh) from Fluka.

Area of study



Source: Dept. of Geog. BUK (2016)

Figure 1: Map showing the sampling point at Sagamu Town, Ogun State.

Description of Sampling Area

Sagamu has geographical coordinates between 6°50′ north; 3° 38′ east is located in south western region of Nigeria. The region has tropical wet and dry climate with a lengthy wet season and relatively constant temperatures throughout the course of the year. Wet season runs from March to October, November to December forms the region dry season. The vegetation type of the region is savannah which is really grassland with small bushes and occasional big trees. Grassland soils have substantially higher organic matter content than forest soils (Novackova, 2011).

Sample Collection

The Peatsoil samples were collected from four different sampling points (0-10cm depth) in Sagamu into polyethylene bag with plastic spoons. Samples were taken to the laboratory, extraneous materials were removed; the samples were air-dried, crushed and ground to a fine powder in a mortar passed through a 0.20mm sieve. The samples were kept for analysis.

Isolation and purification of humic acid from peat soil sample

Peatsoil sample (100g) was mixed with 1000 cm^3 of 0.1M NaOH solution, shaken for 3hours and left to stand overnight. Dark-coloured supernatant was obtained and decanted from solid residue. The dark-coloured supernatant was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 6 hours. Yellowish brown supernatant and dark-brown precipitate were obtained. The yellowish brown supernatant was decanted followed by centrifuge and discarded. The dark-brown precipitate was mixed with $500cm^3$of 0.1M NaOH solution followed by passing through dowex resin. The dark-brown solution was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 3 hours. The dark-brown precipitate was washed several times with deionized water. The supernatant was treated with $AgNO_3$ solution until no white precipitate observed. The humic acid was transferred to weighed crucible and dried at 60^oC in an oven for 12 hours. The humic acid was cooled and dried in the desiccator, weighed and recorded. The obtained humic acid was dried again at 60^oC for additional 6 hours cooled and dried in the desiccator, weighed and recorded constant weight was obtained (Baruah *et al*., 2015).

FT-IR analysis

FT-IR spectra of humic acid sample was analysed using Carry 630 FT-IR Agilent Technologies.

Unhydrolysed compost humic acid

The unhydrolysed humic acid was obtained after isolation and purification of compost humic acid and kept for investigation.

Acid hydrolysis of Peatsoil acid

Peatsoil humic acid sample (1g) was refluxed for 12 hours at (160^oC) with $50cm^3$ of 6M HCl. The mixture was allowed to cool, decanted, and centrifuged after hydrolysis. The insoluble residues were washed with distilled water via centrifugation several times, and the supernatant was treated with $AgNO_3$ solution until no white precipitate was observed. The residue was thoroughly dried over $CaCl_2$ in a desiccator at room temperature (Chefetz *et al*., 2002). Finally, the obtained hydrolysed humic acid was kept for investigation.

Potentiometric Titrations

Potentiometric measurements were carried out using a pH-meter Jenway (model 3510) with combine electrode, the sensitivity of the pH - meter is 0.01 units. The pH meter was switched on half an hour before starting the titration for initial warm up of the instrument. The instrument was calibrated with an aqueous standard buffer solution of pH 4.00 and 10.0 (borate buffer) prepared from a "Qualigens" buffer tablets.

The following sets of solutions were prepared in a 250cm^3 volumetric flask separately for pH metric titrations.

(i) 5 cm^3 0.1 M HCl + 40 cm^3 deionized water

(ii) 5 cm^3 0.1 M HCl + 39 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid

(iii) 5 cm^3 0.1 M HCl + 37 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid + 2 cm^3 0.01 M Cu(II)

The solutions were titrated against standardized 0.110MNaOH separately. The total volume of each mixture was adjusted to 50 cm^3 and the ionic strength of the solutions was maintained constant at by adding appropriate amount of stock solution of 1M KNO_3 (Gamal, 2015; Omar and Ali, 2015). A magnetic stirrer was used to achieve thorough mixing of the interacting solutions at 550 rpm. The same set of experimental conditions was applied for potentiometric titration of remaining samples.

Evaluation of pKa of Hydrolysed peat soil Humic Acids

The proton-ligand formation number n$_{\mathbf{A}}$ were calculated by Irving and Rossotti expression (Omar and Ali, 2015).

$$nA = Y- \frac{(V2-V1)(No-Eo)}{(Vo+V1)TcL} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots1$$

Where: Y is number of dissociable proton, (V_2-V_1) is the measure of displacement of the ligand curve relative to acid curve, N^o and E^o are the resultant concentration of alkali solution, free acid solution, $T_{cL}{}^o$ is the total ligand concentration, V^o is the total volume of titration solution,V_1 is the volume of alkali added to acid solution,V_2 is the volume of alkali added to acid solution + ligand solution, acid dissociation constants (pKa - values) of ligand were calculated by algebraic method point wise calculation (Tables 1). The dissociation constants (pKa) were calculated according to the following relation:

$$pKa = pH + \log(\frac{nA}{1-nA}) \quad \ldots\ldots\ldots\ldots\ldots\ldots2$$

Where: pKa is the acid dissociation constant, n$_A$is the Proton-ligand formation number and pH is the pH-values (Omar and Ali, 2015).

Determination of metal-ligand stability constants (log K) of complexes

The potentiometric measurement for the determination of stability constant of a complex in solution is based on the fact that the redox potential of the couple $\frac{M^{+(m-n)}}{M^{+m}}$ is shifted significantly on complexation of the metal ion with the ligand. This method involves change in hydrogen ion concentration [H$^+$] due to the displacement or association of one or more protons taking place during complexation reaction. This change can be found out by titrating the solutions containing free acid, acid with ligand, and acid with ligand and metal ion, individually against a standard alkali solution at a constant ionic strength or temperature. Either ionic strength or temperature may be varied for different sets of solutions. In all the cases, the change in the pH of the solution is measured after each addition of a known amount of alkali to the reaction cell which contains the reaction mixture. The titration curves are then drawn by plotting the measured pH values against the corresponding volume of alkali added and the stability constants of the complexes are determined from the titration curves by employing pH-metric titration technique given by (Irving and Rossoti).

Metal-ligand stability constants (Log K) were determined by using the following relations:

$$\bar{n} = \frac{(V_3 - V_2)(E^0 + N^0)}{(V^0 + V_2)\bar{n}_A T_m^0} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots3$$

and

$$PL = \log_{10}\{\frac{1+\beta_n^H \frac{1}{[anti\ \log pH]^n}}{T_L^0 - \bar{n}T_m^0} X \frac{(V^0 + V_3)}{V^0}\} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots4$$

Where $T_{L,}$ T^o, E°, and V^ohavethe same significance as in equation (1) above, T_m denotes the total concentration of metal present in solution, V_3 is the volume of metal ions present in solution and β^H is the overall proton ligand stability constant. The metal-ligand stability constants (log K) were determined by employing point wise computational Method (eq. 5 and 6).

$$\mathrm{Log}K_1 = \log\left(\frac{n}{1-n}\right) + pL \qquad \ldots\ldots\ldots\ldots.5$$

$$\mathrm{Log}K_2 = \log\left(\frac{1-n}{2-n}\right) + pL\ldots\ldots\ldots\ldots\ldots\ldots\ldots.6$$

Where: Log K is the metal-ligand stability constant, pL is the Free ligand exponent function, **n** is the Average number of ligand attached with metal ion (Janrao*et al*., 2014).The results obtained were analyzed by an ORIGIN 2016 program using titration data and then the proton-ligand stability constants (pKa) and Metal-ligand stability constant (LogK) calculated (Omar and Ali, 2015).

RESULTS AND DISCUSSION

Fourier transformed infrared (FT-IR) spectra of isolated humic acid from peat soils Figure 2 had distinct clear absorption bands indicating the presence of major humic acid structural elemental groups such as H bonded OH ($3680cm^{-1}$ peak), C=O of carbonyl ($1721cm^{-1}$ peak), functional groups of aliphatic components CH_2 ($2918cm^{-1}$ peak) and C-O stretching of polysaccharide ($1168cm^{-1}$ peak). The positions of the absorption bands of the spectra fell within typical major absorption bands of humic acid which is at frequencies 3680, 2918, 1721, 1168 cm^{-1}. The first peak centred in the vicinity of 3680 cm^{-1} region is attributed to phenol OH group bounded by intermolecular H bonds. The $2918cm^{-1}$ band usually has absorption maximum at 2918 cm^{-1} which is due to C–H stretching of alkane group (CH_2). The next major absorption band is 1721 cm^{-1}. This band has been commonly ascribed to C=O stretching of mainly carboxyl group (COOH) with trace amount of ketones. The last peak was observed at 1168 cm^{-1} due to C–O stretching of polysaccharides and this peak appeared also in the spectra of humic acid from peat soil. The FTIR spectra of the isolated humic acid contained all major characteristic absorption peaks of humic acid. These absorption peaks indicated the presence of the major structural elements of humic acid namely H bonded OH, C=C of aromatic ring, C=O of carbonyl group (both carboxyl and ketonic), CH_2 group. This strongly supports the presence of humic acid.

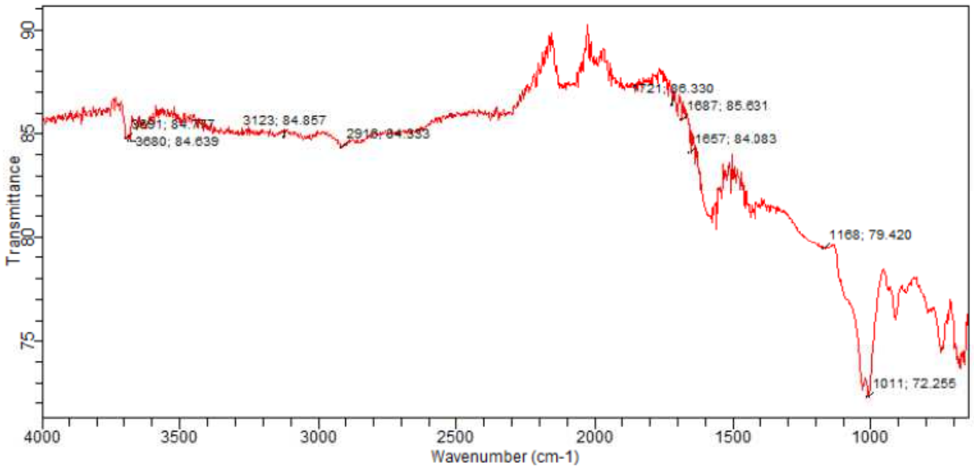


Fig. 2 : FT-IR spectraof peatsoilhumic acid (PSHA)

Evaluation of acid dissociation constant (pka) of acid hydrolysed peat soil humicacid at phenolic group

The value of the dissociation constant of the peat soil humic acid (PSHA) that underwent acidhydrolysis studied was found to be 8.9299 as shown Table 1, which is lower than the literaturevalues reported by Almeida and Szpoganics, (2015), Borges *et al*., (2005); Badr *et al*., (2012)and Fernandes *et al*,.(2009) of 9.73, 9.47 and 10.30. The difference between the obtained valuesand the reported values in this study might be probably as a result of acid hydrolysis of humicacid.

Table 1: PKa of (Hydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	log($\frac{nA}{1-nA}$)	pKa
8.50	5.30	6.29	0.99	0.3594	-0.2510	8.2490
8.72	5.35	6.37	1.02	0.3400	-0.2880	8.4320
9.00	5.40	6.46	1.06	0.3141	-0.3391	8.6609
9.22	5.45	6.55	1.10	0.2882	-0.3927	8.8273
9.51	5.50	6.66	1.16	0.2494	-0.4786	9.0314
9.73	5.55	6.78	1.23	0.2041	-0.5910	9.1390
10.00	5.60	6.90	1.30	0.1589	-0.7238	9.2762
10.23	5.65	7.05	1.40	0.0941	-0.9835	9.2465
10.49	5.70	7.10	1.40	0.0941	-0.9835	9.5065

Average pKa = 8.9299 ± 0.4186

Table 2: PKa of (Unhydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	Log($\frac{nA}{1-n}$)	pKa
8.50	5.30	5.81	0.51	0.6619	0.2919	8.7919
8.72	5.35	5.90	0.55	0.6357	0.2418	8.9618
9.00	5.40	6.00	0.60	0.6029	0.1813	9.1813
9.22	5.45	6.10	0.65	0.5701	0.1226	9.3426
9.51	5.50	6.20	0.70	0.5376	0.0654	9.5754
9.73	5.55	6.33	0.78	0.4851	-0.0259	9.7041
10.00	5.60	6.47	0.87	0.4262	-0.1291	9.8709
10.23	5.65	6.62	0.99	0.3609	-0.2481	9.9819
10.49	5.70	6.80	1.10	0.2759	-0.4690	10.0210

Average pKa = 9.4923± 0.4410

Metal-ligand stability constant (Log K)

The stabilityconstants require the accurate values of proton-ligand stability constants (Anil and Maroti, 2008). Metal titration curves crossed over ligand titration curve indicated the formation of complex upon proton release (Santosh, *et al.*, 2011). If the values of n- are within range 0.2-0.8 and 1.2-18 this indicates the formation of 1:1 and 1:2 complexes (Sayyed and Mazahar, 2012).

The metal (II)-humate stepwise stability constants (log k) at phenolic group (Tables 3-18)

Table 3: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n}{1-n}$)	$LogK_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

$LogK_1$ (Average value) = 2.4788± 0.2203

Table 4: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	Log($\frac{n-1}{2-n}$)	$LogK_2$
9.51	5.50	6.66	6.73	0.07	1.3509	1.70	-0.2671	1.4329
9.73	5.55	6.78	6.85	0.07	1.6383	1.51	0.2467	1.7567
10.00	5.60	6.90	6.98	0.08	2.1783	1.31	-0.2158	1.0942
10.23	5.65	7.05	7.13	0.08	4.1904	1.27		
10.49	5.70	7.10	7.19	0.09	4.6920			

$LogK_2$(Average value) = 1.4280 ± 0.3312

Table 5:Point-wise method,Cu (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	Log($\frac{n}{n-1}$)	Log K$_1$
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430

LogK$_1$ **(Average value)** = 2.3059± 0.6153

Table 6:Point-wise method, Cu (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	V$_3$-V$_2$	n	pL	Log($\frac{n-1}{2-n}$)	Log K$_2$
9.73	5.55	6.33	6.42	0.09	0.9000	1.69		
10.00	5.60	6.47	6.58	0.11	1.2578	1.44	-0.4592	0.9808
10.23	5.65	6.62	6.84	0.12	1.6137	1.26	-0.2010	1.4610
10.49	5.70	6.80	6.92	0.12	2.1052	1.03		

LogK$_2$ **(Average value)** = 1.2209± 0.3398

Table 7:Point-wise method,Pb (Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	log($\frac{n}{1-n}$)	LogK$_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.60	0.05	0.8333	1.96	0.6989	2.6589

LogK$_1$ (Average value) = 2.5832 ±0.1614

Table 8:Point-wise method,Pb-(Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	log($\frac{n-1}{2-n}$)	logK$_2$
9.51	5.50	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.83	0.05	1.1702	1.44		
10.00	5.60	6.90	6.90	0.05	1.4864	1.22	-0.0237	1.1963
10.23	5.65	7.05	7.10	0.05	2.0190	1.09		
10.49	5.70	7.10	7.17	0.07	3.6492	1.00		

LogK$_2$(Average value) = 1.1963

Table 9:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	V$_3$-V$_2$	n	pL	Log ($\frac{n}{n-1}$)	Log K$_1$
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.5477	2.3123
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	0.0272	2.2072
9.51	5.50	6.20	6.26	0.07	0.6417	1.89	0.2530	2.1430
9.73	5.55	6.40	6.40	0.07	0.7000	1.67	0.3680	2.0380

LogK$_1$ **(Average value)** = 2.2364 ± 0.1602

Table 10:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	V$_3$-V$_2$	n	pL	Log($\frac{n-1}{2-n}$)	Log K$_2$
10.00	5.60	6.47	6.55	0.08	1.9503	1.41		
10.23	5.65	6.62	6.72	0.11	1.4792	1.26	-0.0361	1.2239

LogK$_2$ **(Average value)** = 1.2239

Table 11:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	log($\frac{n}{n-1}$)	LogK$_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4290	2.2110
8.72	5.35	6.37	6.39	0.02	0.2858	2.42	-0.3978	2.0222
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

LogK$_1$ (Average value)=2.1382**±**0.1046

Table 12:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	log($\frac{n-1}{2-n}$)	LogK$_2$
9.51	5.55	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.84	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.93	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.10		
10.49	5.70	7.10	7.18	0.07	3.6492	0.83		

LogK$_2$(Average value) = 1.5453 **±** 0.3450

Table 13:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	V$_3$-V$_2$	n	pL	Log($\frac{n}{n-1}$)	Log K$_1$
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.3477	2.3123
9.00	5.40	6.00	6.04	0.04	0.3236	2.38	-0.3202	2.0598
9.22	5.45	6.10	6.15	0.05	0.4297	2.17	-0.1230	2.0470
9.51	5.50	6.20	6.26	0.06	0.5500	1.89	0.0871	1.9771
9.73	5.55	6.33	6.40	0.07	0.7000	1.67	0.3680	2.0380

LogK$_1$ **(Average value)** = 2.1568 ± 0.2069

Table 14:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	V$_3$-V$_2$	n	pL	Log($\frac{n-1}{2-n}$)	Log K$_2$
10.00	5.60	6.47	6.55	0.08	0.9148	1.41		
10.23	5.65	6.62	6.71	0.09	1.2102	1.20	-0.5749	0.6251
10.49	5.70	6.80	6.92	0.09	1.5968	1.03	0.1703	1.2003

LogK$_2$ **(Average value)** = 0.9127± 0.4070

Table15:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	Log($\frac{n}{1-n}$)	LogK$_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4210	2.2190
8.72	5.35	6.37	6.40	0.03	0.4286	2.42	-0.1249	2.2951
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.96	0.3010	2.2610
9.51	5.55	6.66	6.70	0.04	0.7720	1.67	0.5297	2.1997

LogK$_1$ (Average value) = 2.2108± 0.0825

Table 16:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	Log($\frac{n-1}{2-n}$)	Log K$_2$
9.73	5.55	6.78	6.83	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.95	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.09		
10.49	5.70	7.10	7.16	0.06	3.1429	0.89		

LogK$_2$ **(Average value)** = 1.5453± 0.3450

Table 17:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	V$_3$-V$_2$	n	pL	Log($\frac{n}{n-1}$)	Log K$_1$
8.50	5.30	5.81	5.86	0.05	0.3717	2.88	-0.2280	2.6520
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.06	0.06	0.4853	2.38	-0.0255	2.3545
9.22	5.45	6.10	6.16	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430
9.73	5.55	6.33	6.41	0.08	0.8000	1.69	0.6020	2.2920

LogK$_1$ **(Average value)** = 2.2516± 0.5380

Table 18:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log$(\frac{n-1}{2-n})$	Log K_2
10.00	5.60	6.47	6.57	0.10	1.1434	1.43		
10.23	5.65	6.62	6.72	0.10	1.3448	1.23	-0.2788	0.9512
10.49	5.70	6.80	6.90	0.10	1.7742	1.03	0.5351	1.5651

LogK_2 **(Average value)** = 1.2581± 0.4340

Table 19: Stepwise and overall Stability constants of thehydrolysed and unhydrolysed divalent metal (II) complexes

Chelates	**LogK_1**	**LogK_2**	**Logβ**
[Cu (Hydrolysed PSHA-1)$_2$]	2.4788	1.4280	3.9068
[Pb (Hydrolysed PSHA-1)$_2$]	2.5832	1.1963	3.7795
[Cd (Hydrolysed PSHA-1)$_2$]	2.2108	1.5453	3.7561
[Mg (Hydrolysed PSHA-1)$_2$]	2.1382	1.5453	3.6835
[Cu (Unhydrolysed PSHA-1)$_2$]	2.3059	1.2209	3.5268
[Pb (Unhydrolysed PSHA-1)$_2$]	2.2364	1.2239	3.4603
[Cd (Unhydrolysed PSHA-1)$_2$]	2.2516	1.2581	3.5097
[Mg (Unydrolysed PSHA-1)$_2$]	2.1568	0.9127	3.0695

The results obtained (Table19) shows the stepwise and overall stability constants to be not high indicating low stability of the complexes, because the solubility of most metal ions in the basic pH range is minimal due to metal hydroxide precipitation (Karimi, 2017). In general, the stepwise stability constants (K_1 and K_2) follow the order $K_1 > K_2$ for the copper, lead, magnesium and cadmium complexes respectively. The steady decrease of the values with increasing number of ligands is in agreement with the prediction made by researchers (Na'aliya, 2013). The decrease could be attributed to the fact that as the number of the ligands (Humate ions) that enters the coordination zone increases the aqua molecules available for replacement by the ligands become less. Thus, the metal ions become less electron loving with progressive intake of the ligand and this results in the decrease in the values of the constants (Na'aliya, 2013). Also the stability of the complexes is influenced by the size and number of the chelate rings(Mackay and Mackay,2002).All the complexes form rings in their structure as humate, a bidentate ligand, bond the metal ions in the ratio 1:2 (Boguta and Sokolowska, 2016) forming chelate rings. The values of the overall stability constants (logβ) obtained for humate complexes are not high indicating low stability as the values are not high. LogK values for copper-humates (Table 3 to 6) obtained in this study are lower than those reported for the complexes of humic acids (Pandey *et al*., 2015; Dinu, 2013; Kaschl *et al*., 2010 and Gilbeto and Jorg, 2001). The values of LogK(Table 7 to 10) forlead-humates are lower than those reported for the lead in the literature (Dinu, 2013; Gilbeto and Jorg 2001). Log K values(Table 11 to 14) for magnesium-humates obtained in this study are close to those reported by (Pandey *et al*., 2015). Log K values of cadmium-humates (Table 15 to 18) obtained in this work near to the one reported by (Dinu, 2013 and Pandey *et al*., 2015).The difference between the reported values and the values obtained in this study might be probably as a result of acid hydrolysis of humic acid. The values of the overall stability constants (log β) of the copper humates complexes presented in Table 19 is high than that of other metal humate complexes, show relatively high stability of Cu-HA complexes, show the following order of stability: Cu >Pb> Cd > Mg; which are in close agreement to the findings of (Dinu, 2013 and Pandey *et al*., 2015).The high stability of Cu-humate chelate could be attributed to the existence of coordinate covalent bond between the complexing agents and the Cu^{2+} ions. Since, Cu^{2+} being a metal of the transitional series with $3d^9$ electronic configurations can accept the electrons from the complexing agents. Similarly,the low stabilities of Pb,Cd and Mg -complexes could be explained by that Pb^{2+} with $6s^2$, Cd^{2+} with $4d^{10}$ and Mg^{2+} with $2p^6$ their electronic configuration has a completely filled d,p and s orbitals. Moreover, the stabilities of metal ions with hydrolysed humic acid from peat soil were higher than those with unhydrolysed humic acid from peat soil; which is ascribed to the high content of acidity in hydrolysed humic acid than unhydrolysed humic acid.

CONCLUSION

The values of logK for Cu(II) hydrolysed humic acid complex was higher followed by Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes as compared with metal(II) unhydrolysed humic acid complexes . This indicates acid hydrolysis of humic acid can enhance the complexation behavior of humic acid with metal (II) ions. However, the higher values of logβ for Cu(II), Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes indicates more stable stepwise complexes formed as compared with Cu(II), Pb(II), Cd(II) and Mg(II) unhydrolysed humic acid complexes.

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STABILITY CONSTANTS OF COMPLEXES OF METAL IONS WITH PEATSOIL HUMIC ACIDS UNDER NON-ACID-CONDITIONS

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ABSTRACT

Stability constants of complexes of four divalent metal ions viz. Cu^{2+}, Pb^{2+},Mg^{2+} and Cd^{2+} with humic acids (HA) were determined by potentiometric titration of humic acids with the corresponding salt of the divalent metals in aqueous media under non-acid-condition. The log K (logarithm of the stability constant) ranged from 1.0942 to 2.7471 for metal-humic acid complexes were determined using point-wise computational method. The order of stability constants were obtained as follows: Cu >Pb> Cd > Mg for metal -HA complexes respectively, indicating a higher degree of complexation with Cu metal ion.

Keywords: stability constant, humic acid, potentiometric titration, divalent metals, acid hydrolysis.

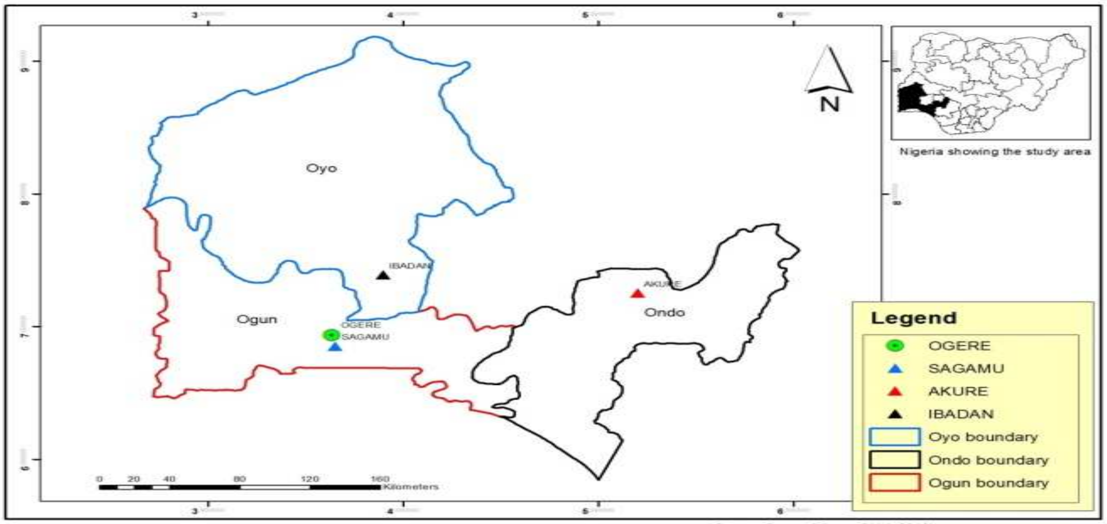
NTRODUCTION

The stability constant of a complex is the numerical expression of its stability and provides a quantitative measure of affinity of the metal ion to the complexing agent. An understanding of the relative stability of metal-complexes helps in predicting the behavior of metal ions in the soil (Ram and Raman, 1982). Extensive researches has been done to determine the stability constants of the complexes formed between humic acid (HA) with a number of metal ions. Ashok *et al.*, (2000) reported that humic acid with hydroxyl, phenoxyl and carboxyl reactive groups can form coordination compound with metal ions at pH 3.5. The stability constants(Log K) for different metal-humic acid complexes indicated the following order of the stabilities of complexes formed between humic acid and metal ion, Cu >Fe >Pb> Ni > Co > Ca > Cd > Zn >Mn> Mg. Andelkovic *et al.*, (2010) investigated the binding of Cd(II) to soil humic acid at pH 6.5 and in 0.1M KNO_3 ionic medium. The stability constant for binding indicating greater stability in the case when carboxyl groups are involved in complexation reaction. Kostic *et al.*,(2012) investigated the complexation of humic acid with certain heavy metal ions (Co(II), Ni(II),Cu(II), Zn(II), and Pb(II). The experiment was performed at 25°C, at pH 4.0 and ionic strength of 0.01M. Stability constant of complex between Pb(II) ions and humic acid is greater than stability constants of other investigated metal-humate complexes. Bogata and Sokolowska (2016) analyses the interaction between humic acids from different soils and Zn (II) ions at wide concentration ranges and at pH 5. Studies have showed significant impact of Zn concentration, pH and some properties of humic acids with zinc.But all of these studies were limited to acidic pH range. Therefore, the present study was carried out to determine and compare the stability constants of complexes of metal ions with hydrolysed peat soil humic acid and unhydrolysed peat soil humic under non-acid conditions.

MATERIALS AND METHODS

Analytical grade chemicals used includes hydrochloric acid (HCl), nitric acid (HNO_3), sodium hydroxide (NaOH), lead nitrate $Pb(NO_3)_2$, copper nitrate $Cu(NO_3)_2.3H_2O$, cadmium nitrate $Cd(NO_3)_2.4H_2O$, magnesium nitrate $Mg(NO_3)_2.6H_2O$, potassium nitrate (KNO_3), calcium chloride ($CaCl_2$), (sigma-Aldrich). Dowex 50WX8, (20-50 mesh) from Fluka.

Area of study



Source: Dept. of Geog. BUK (2016)

Figure 1: Map showing the sampling point at Sagamu Town, Ogun State.

Description of Sampling Area

Sagamu has geographical coordinates between 6°50′ north; 3° 38′ east is located in south western region of Nigeria. The region has tropical wet and dry climate with a lengthy wet season and relatively constant temperatures throughout the course of the year. Wet season runs from March to October, November to December forms the region dry season. The vegetation type of the region is savannah which is really grassland with small bushes and occasional big trees. Grassland soils have substantially higher organic matter content than forest soils (Novackova, 2011).

Sample Collection

The Peatsoil samples were collected from four different sampling points (0-10cm depth) in Sagamu into polyethylene bag with plastic spoons. Samples were taken to the laboratory, extraneous materials were removed; the samples were air-dried, crushed and ground to a fine powder in a mortar passed through a 0.20mm sieve. The samples were kept for analysis.

Isolation and purification of humic acid from peat soil sample

Peatsoil sample (100g) was mixed with 1000 cm^3 of 0.1M NaOH solution, shaken for 3hours and left to stand overnight. Dark-coloured supernatant was obtained and decanted from solid residue. The dark-coloured supernatant was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 6 hours. Yellowish brown supernatant and dark-brown precipitate were obtained. The yellowish brown supernatant was decanted followed by centrifuge and discarded. The dark-brown precipitate was mixed with $500cm^3$of 0.1M NaOH solution followed by passing through dowex resin. The dark-brown solution was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 3 hours. The dark-brown precipitate was washed several times with deionized water. The supernatant was treated with $AgNO_3$ solution until no white precipitate observed. The humic acid was transferred to weighed crucible and dried at 60°C in an oven for 12 hours. The humic acid was cooled and dried in the desiccator, weighed and recorded. The obtained humic acid was dried again at 60°C for additional 6 hours cooled and dried in the desiccator, weighed and recorded constant weight was obtained (Baruah *et al*., 2015).

FT-IR analysis

FT-IR spectra of humic acid sample was analysed using Carry 630 FT-IR Agilent Technologies.

Unhydrolysed compost humic acid

The unhydrolysed humic acid was obtained after isolation and purification of compost humic acid and kept for investigation.

Acid hydrolysis of Peatsoil acid

Peatsoil humic acid sample (1g) was refluxed for 12 hours at (160°C) with $50cm^3$ of 6M HCl. The mixture was allowed to cool, decanted, and centrifuged after hydrolysis. The insoluble residues were washed with distilled water via centrifugation several times, and the supernatant was treated with $AgNO_3$ solution until no white precipitate was observed. The residue was thoroughly dried over $CaCl_2$ in a desiccator at room temperature (Chefetz *et al*., 2002). Finally, the obtained hydrolysed humic acid was kept for investigation.

Potentiometric Titrations

Potentiometric measurements were carried out using a pH-meter Jenway (model 3510) with combine electrode, the sensitivity of the pH - meter is 0.01 units. The pH meter was switched on half an hour before starting the titration for initial warm up of the instrument. The instrument was calibrated with an aqueous standard buffer solution of pH 4.00 and 10.0 (borate buffer) prepared from a "Qualigens" buffer tablets.

The following sets of solutions were prepared in a 250cm^3 volumetric flask separately for pH metric titrations.

(i) 5 cm^3 0.1 M HCl + 40 cm^3 deionized water

(ii) 5 cm^3 0.1 M HCl + 39 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid

(iii) 5 cm^3 0.1 M HCl + 37 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid + 2 cm^3 0.01 M Cu(II)

The solutions were titrated against standardized 0.110MNaOH separately. The total volume of each mixture was adjusted to 50 cm^3 and the ionic strength of the solutions was maintained constant at by adding appropriate amount of stock solution of 1M KNO_3 (Gamal, 2015; Omar and Ali, 2015). A magnetic stirrer was used to achieve thorough mixing of the interacting solutions at 550 rpm. The same set of experimental conditions was applied for potentiometric titration of remaining samples.

Evaluation of pKa of Hydrolysed peat soil Humic Acids

The proton-ligand formation number $n_{\mathbf{A}}$ were calculated by Irving and Rossotti expression (Omar and Ali, 2015).

$$nA = Y- \frac{(V2-V1)(No-Eo)}{(Vo+V1)TcL} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 1$$

Where: Y is number of dissociable proton, (V_2-V_1) is the measure of displacement of the ligand curve relative to acid curve, N^o and E^o are the resultant concentration of alkali solution, free acid solution, $T_{cL}{}^o$ is the total ligand concentration, V^o is the total volume of titration solution,V_1 is the volume of alkali added to acid solution,V_2 is the volume of alkali added to acid solution + ligand solution, acid dissociation constants (pKa - values) of ligand were calculated by algebraic method point wise calculation (Tables 1). The dissociation constants (pKa) were calculated according to the following relation:

$$pKa = pH + \log(\frac{nA}{1-nA}) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 2$$

Where: pKa is the acid dissociation constant, $n_A$is the Proton-ligand formation number and pH is the pH-values (Omar and Ali, 2015).

Determination of metal-ligand stability constants (log K) of complexes

The potentiometric measurement for the determination of stability constant of a complex in solution is based on the fact that the redox potential of the couple $\frac{M^{+(m-n)}}{M^{+m}}$ is shifted significantly on complexation of the metal ion with the ligand. This method involves change in hydrogen ion concentration [H$^+$] due to the displacement or association of one or more protons taking place during complexation reaction. This change can be found out by titrating the solutions containing free acid, acid with ligand, and acid with ligand and metal ion, individually against a standard alkali solution at a constant ionic strength or temperature. Either ionic strength or temperature may be varied for different sets of solutions. In all the cases, the change in the pH of the solution is measured after each addition of a known amount of alkali to the reaction cell which contains the reaction mixture. The titration curves are then drawn by plotting the measured pH values against the corresponding volume of alkali added and the stability constants of the complexes are determined from the titration curves by employing pH-metric titration technique given by (Irving and Rossoti).

Metal-ligand stability constants (Log K) were determined by using the following relations:

$$\bar{n} = \frac{(V_3 - V_2)(E^0 + N^0)}{(V^0 + V_2)\bar{n}_A T_m^0} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 3$$

and

$$PL = \log_{10}\{\frac{1 + \beta_n^H \frac{1}{[anti\ \log pH]^n}}{T_L^0 - \bar{n}T_m^0} X \frac{(V^0 + V_3)}{V^0}\} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 4$$

Where $T_{L,}$ T^{o}, E°, and V^{o}havethe same significance as in equation (1) above, T_m denotes the total concentration of metal present in solution, V_3 is the volume of metal ions present in solution and β^{H} is the overall proton ligand stability constant. The metal-ligand stability constants (log K) were determined by employing point wise computational Method (eq. 5 and 6).

$$\mathrm{Log}K_1 = \log\left(\frac{n}{1-n}\right) + pL \qquad ………….5$$

$$\mathrm{Log}K_2 = \log\left(\frac{1-n}{2-n}\right) + pL……………………6$$

Where: Log K is the metal-ligand stability constant, pL is the Free ligand exponent function, **n** is the Average number of ligand attached with metal ion (Janrao*et al.*, 2014).The results obtained were analyzed by an ORIGIN 2016 program using titration data and then the proton-ligand stability constants (pKa) and Metal-ligand stability constant (LogK) calculated (Omar and Ali, 2015).

RESULTS AND DISCUSSION

Fourier transformed infrared (FT-IR) spectra of isolated humic acid from peat soils Figure 2 had distinct clear absorption bands indicating the presence of major humic acid structural elemental groups such as H bonded OH (3680cm^{-1} peak), C=O of carbonyl (1721cm^{-1} peak), functional groups of aliphatic components CH_2 (2918cm^{-1} peak) and C-O stretching of polysaccharide (1168cm^{-1} peak). The positions of the absorption bands of the spectra fell within typical major absorption bands of humic acid which is at frequencies 3680, 2918, 1721, 1168 cm^{-1}. The first peak centred in the vicinity of 3680 cm^{-1} region is attributed to phenol OH group bounded by intermolecular H bonds. The 2918cm^{-1} band usually has absorption maximum at 2918 cm^{-1} which is due to C–H stretching of alkane group (CH_2). The next major absorption band is 1721 cm^{-1}. This band has been commonly ascribed to C=O stretching of mainly carboxyl group (COOH) with trace amount of ketones. The last peak was observed at 1168 cm^{-1} due to C–O stretching of polysaccharides and this peak appeared also in the spectra of humic acid from peat soil. The FTIR spectra of the isolated humic acid contained all major characteristic absorption peaks of humic acid. These absorption peaks indicated the presence of the major structural elements of humic acid namely H bonded OH, C=C of aromatic ring, C=O of carbonyl group (both carboxyl and ketonic), CH_2 group. This strongly supports the presence of humic acid.

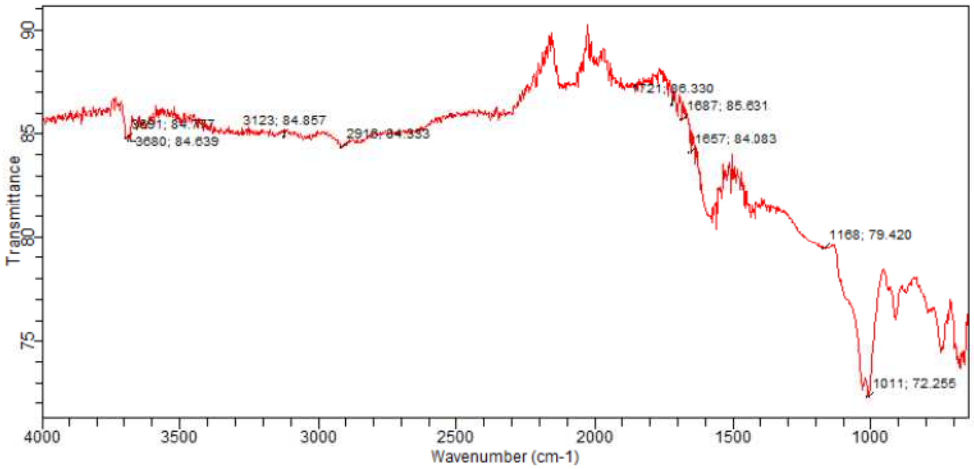


Fig. 2 : FT-IR spectraof peatsoilhumic acid (PSHA)

Evaluation of acid dissociation constant (pka) of acid hydrolysed peat soil humicacid at phenolic group

The value of the dissociation constant of the peat soil humic acid (PSHA) that underwent acidhydrolysis studied was found to be 8.9299 as shown Table 1, which is lower than the literaturevalues reported by Almeida and Szpoganics, (2015), Borges *et al.*, (2005); Badr *et al.*, (2012)and Fernandes *et al*,.(2009) of 9.73, 9.47 and 10.30. The difference between the obtained valuesand the reported values in this study might be probably as a result of acid hydrolysis of humicacid.

Table 1: PKa of (Hydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	log($\frac{nA}{1-nA}$)	pKa
8.50	5.30	6.29	0.99	0.3594	-0.2510	8.2490
8.72	5.35	6.37	1.02	0.3400	-0.2880	8.4320
9.00	5.40	6.46	1.06	0.3141	-0.3391	8.6609
9.22	5.45	6.55	1.10	0.2882	-0.3927	8.8273
9.51	5.50	6.66	1.16	0.2494	-0.4786	9.0314
9.73	5.55	6.78	1.23	0.2041	-0.5910	9.1390
10.00	5.60	6.90	1.30	0.1589	-0.7238	9.2762
10.23	5.65	7.05	1.40	0.0941	-0.9835	9.2465
10.49	5.70	7.10	1.40	0.0941	-0.9835	9.5065

Average pKa = 8.9299 ± 0.4186

Table 2: PKa of (Unhydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	Log($\frac{nA}{1-n}$)	pKa
8.50	5.30	5.81	0.51	0.6619	0.2919	8.7919
8.72	5.35	5.90	0.55	0.6357	0.2418	8.9618
9.00	5.40	6.00	0.60	0.6029	0.1813	9.1813
9.22	5.45	6.10	0.65	0.5701	0.1226	9.3426
9.51	5.50	6.20	0.70	0.5376	0.0654	9.5754
9.73	5.55	6.33	0.78	0.4851	-0.0259	9.7041
10.00	5.60	6.47	0.87	0.4262	-0.1291	9.8709
10.23	5.65	6.62	0.99	0.3609	-0.2481	9.9819
10.49	5.70	6.80	1.10	0.2759	-0.4690	10.0210

Average pKa = 9.4923± 0.4410

Metal-ligand stability constant (Log K)

The stabilityconstants require the accurate values of proton-ligand stability constants (Anil and Maroti, 2008). Metal titration curves crossed over ligand titration curve indicated the formation of complex upon proton release (Santosh, *et al*., 2011). If the values of n- are within range 0.2-0.8 and 1.2-18 this indicates the formation of 1:1 and 1:2 complexes (Sayyed and Mazahar, 2012).

The metal (II)-humate stepwise stability constants (log k) at phenolic group (Tables 3-18)

Table 3: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n}{1-n}$)	$LogK_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

$LogK_1$ (Average value) = 2.4788± 0.2203

Table 4: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	Log($\frac{n-1}{2-n}$)	$LogK_2$
9.51	5.50	6.66	6.73	0.07	1.3509	1.70	-0.2671	1.4329
9.73	5.55	6.78	6.85	0.07	1.6383	1.51	0.2467	1.7567
10.00	5.60	6.90	6.98	0.08	2.1783	1.31	-0.2158	1.0942
10.23	5.65	7.05	7.13	0.08	4.1904	1.27		
10.49	5.70	7.10	7.19	0.09	4.6920			

$LogK_2$(Average value) = 1.4280 ± 0.3312

Table 5:Point-wise method,Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$\text{Log}(\frac{n}{n-1})$	$\text{Log } K_1$
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430

LogK_1 **(Average value)** = 2.3059± 0.6153

Table 6:Point-wise method, Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$\text{Log}(\frac{n-1}{2-n})$	$\text{Log } K_2$
9.73	5.55	6.33	6.42	0.09	0.9000	1.69		
10.00	5.60	6.47	6.58	0.11	1.2578	1.44	-0.4592	0.9808
10.23	5.65	6.62	6.84	0.12	1.6137	1.26	-0.2010	1.4610
10.49	5.70	6.80	6.92	0.12	2.1052	1.03		

LogK_2 **(Average value)** = 1.2209± 0.3398

Table 7:Point-wise method,Pb (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$\log(\frac{n}{1-n})$	LogK_1
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.60	0.05	0.8333	1.96	0.6989	2.6589

$\textbf{LogK}_1$ **(Average value)** = 2.5832 ±0.1614

Table 8:Point-wise method,Pb-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$\log(\frac{n-1}{2-n})$	$\log K_2$
9.51	5.50	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.83	0.05	1.1702	1.44		
10.00	5.60	6.90	6.90	0.05	1.4864	1.22	-0.0237	1.1963
10.23	5.65	7.05	7.10	0.05	2.0190	1.09		
10.49	5.70	7.10	7.17	0.07	3.6492	1.00		

$\textbf{LogK}_2$**(Average value)** = 1.1963

Table 9:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$\text{Log} (\frac{n}{n-1})$	$\text{Log } K_1$
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.5477	2.3123
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	0.0272	2.2072
9.51	5.50	6.20	6.26	0.07	0.6417	1.89	0.2530	2.1430
9.73	5.55	6.40	6.40	0.07	0.7000	1.67	0.3680	2.0380

LogK_1 **(Average value)** = 2.2364 ± 0.1602

Table 10:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$\text{Log}(\frac{n-1}{2-n})$	$\text{Log } K_2$
10.00	5.60	6.47	6.55	0.08	1.9503	1.41		
10.23	5.65	6.62	6.72	0.11	1.4792	1.26	-0.0361	1.2239

LogK_2 **(Average value)** = 1.2239

Table 11:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$\log(\frac{n}{n-1})$	LogK_1
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4290	2.2110
8.72	5.35	6.37	6.39	0.02	0.2858	2.42	-0.3978	2.0222
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

$\textbf{LogK}_1$ **(Average value)=**2.1382**±**0.1046

Table 12:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	log($\frac{n-1}{2-n}$)	LogK$_2$
9.51	5.55	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.84	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.93	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.10		
10.49	5.70	7.10	7.18	0.07	3.6492	0.83		

LogK$_2$(Average value) = 1.5453 **±** 0.3450

Table 13:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	V$_3$-V$_2$	n	pL	Log($\frac{n}{n-1}$)	Log K$_1$
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.3477	2.3123
9.00	5.40	6.00	6.04	0.04	0.3236	2.38	-0.3202	2.0598
9.22	5.45	6.10	6.15	0.05	0.4297	2.17	-0.1230	2.0470
9.51	5.50	6.20	6.26	0.06	0.5500	1.89	0.0871	1.9771
9.73	5.55	6.33	6.40	0.07	0.7000	1.67	0.3680	2.0380

LogK$_1$ **(Average value)** = 2.1568 ± 0.2069

Table 14:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	V$_3$-V$_2$	n	pL	Log($\frac{n-1}{2-n}$)	Log K$_2$
10.00	5.60	6.47	6.55	0.08	0.9148	1.41		
10.23	5.65	6.62	6.71	0.09	1.2102	1.20	-0.5749	0.6251
10.49	5.70	6.80	6.92	0.09	1.5968	1.03	0.1703	1.2003

LogK$_2$ **(Average value)** = 0.9127± 0.4070

Table15:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	Log($\frac{n}{1-n}$)	LogK$_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4210	2.2190
8.72	5.35	6.37	6.40	0.03	0.4286	2.42	-0.1249	2.2951
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.96	0.3010	2.2610
9.51	5.55	6.66	6.70	0.04	0.7720	1.67	0.5297	2.1997

LogK$_1$ (Average value) = 2.2108± 0.0825

Table 16:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	Log($\frac{n-1}{2-n}$)	Log K$_2$
9.73	5.55	6.78	6.83	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.95	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.09		
10.49	5.70	7.10	7.16	0.06	3.1429	0.89		

LogK$_2$ **(Average value)** = 1.5453± 0.3450

Table 17:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	V$_3$-V$_2$	n	pL	Log($\frac{n}{n-1}$)	Log K$_1$
8.50	5.30	5.81	5.86	0.05	0.3717	2.88	-0.2280	2.6520
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.06	0.06	0.4853	2.38	-0.0255	2.3545
9.22	5.45	6.10	6.16	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430
9.73	5.55	6.33	6.41	0.08	0.8000	1.69	0.6020	2.2920

LogK$_1$ **(Average value)** = 2.2516± 0.5380

Table 18:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$Log(\frac{n-1}{2-n})$	Log K_2
10.00	5.60	6.47	6.57	0.10	1.1434	1.43		
10.23	5.65	6.62	6.72	0.10	1.3448	1.23	-0.2788	0.9512
10.49	5.70	6.80	6.90	0.10	1.7742	1.03	0.5351	1.5651

$LogK_2$ **(Average value)** = 1.2581± 0.4340

Table 19: Stepwise and overall Stability constants of thehydrolysed and unhydrolysed divalent metal (II) complexes

Chelates	$LogK_1$	$LogK_2$	Logβ
[Cu (Hydrolysed PSHA-1)$_2$]	2.4788	1.4280	3.9068
[Pb (Hydrolysed PSHA-1)$_2$]	2.5832	1.1963	3.7795
[Cd (Hydrolysed PSHA-1)$_2$]	2.2108	1.5453	3.7561
[Mg (Hydrolysed PSHA-1)$_2$]	2.1382	1.5453	3.6835
[Cu (Unhydrolysed PSHA-1)$_2$]	2.3059	1.2209	3.5268
[Pb (Unhydrolysed PSHA-1)$_2$]	2.2364	1.2239	3.4603
[Cd (Unhydrolysed PSHA-1)$_2$]	2.2516	1.2581	3.5097
[Mg (Unydrolysed PSHA-1)$_2$]	2.1568	0.9127	3.0695

The results obtained (Table19) shows the stepwise and overall stability constants to be not high indicating low stability of the complexes, because the solubility of most metal ions in the basic pH range is minimal due to metal hydroxide precipitation (Karimi, 2017). In general, the stepwise stability constants (K_1 and K_2) follow the order $K_1 > K_2$ for the copper, lead, magnesium and cadmium complexes respectively. The steady decrease of the values with increasing number of ligands is in agreement with the prediction made by researchers (Na'aliya, 2013). The decrease could be attributed to the fact that as the number of the ligands (Humate ions) that enters the coordination zone increases the aqua molecules available for replacement by the ligands become less. Thus, the metal ions become less electron loving with progressive intake of the ligand and this results in the decrease in the values of the constants (Na'aliya, 2013). Also the stability of the complexes is influenced by the size and number of the chelate rings(Mackay and Mackay,2002).All the complexes form rings in their structure as humate, a bidentate ligand, bond the metal ions in the ratio 1:2 (Boguta and Sokolowska, 2016) forming chelate rings. The values of the overall stability constants (logβ) obtained for humate complexes are not high indicating low stability as the values are not high. LogK values for copper-humates (Table 3 to 6) obtained in this study are lower than those reported for the complexes of humic acids (Pandey *et al.*, 2015; Dinu, 2013; Kaschl *et al.*, 2010 and Gilbeto and Jorg, 2001). The values of LogK(Table 7 to 10) forlead-humates are lower than those reported for the lead in the literature (Dinu, 2013; Gilbeto and Jorg 2001). Log K values(Table 11 to 14) for magnesium-humates obtained in this study are close to those reported by (Pandey *et al.*, 2015). Log K values of cadmium-humates (Table 15 to 18) obtained in this work near to the one reported by (Dinu, 2013 and Pandey *et al.*, 2015).The difference between the reported values and the values obtained in this study might be probably as a result of acid hydrolysis of humic acid. The values of the overall stability constants (log β) of the copper humates complexes presented in Table 19 is high than that of other metal humate complexes, show relatively high stability of Cu-HA complexes, show the following order of stability: Cu >Pb> Cd > Mg; which are in close agreement to the findings of (Dinu, 2013 and Pandey *et al.*, 2015).The high stability of Cu-humate chelate could be attributed to the existence of coordinate covalent bond between the complexing agents and the Cu^{2+} ions. Since, Cu^{2+} being a metal of the transitional series with $3d^9$ electronic configurations can accept the electrons from the complexing agents. Similarly,the low stabilities of Pb,Cd and Mg -complexes could be explained by that Pb^{2+} with $6s^2$, Cd^{2+} with $4d^{10}$ and Mg^{2+} with $2p^6$ their electronic configuration has a completely filled d,p and s orbitals. Moreover, the stabilities of metal ions with hydrolysed humic acid from peat soil were higher than those with unhydrolysed humic acid from peat soil; which is ascribed to the high content of acidity in hydrolysed humic acid than unhydrolysed humic acid.

CONCLUSION

The values of logK for Cu(II) hydrolysed humic acid complex was higher followed by Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes as compared with metal(II) unhydrolysed humic acid complexes . This indicates acid hydrolysis of humic acid can enhance the complexation behavior of humic acid with metal (II) ions. However, the higher values of logβ for Cu(II), Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes indicates more stable stepwise complexes formed as compared with Cu(II), Pb(II), Cd(II) and Mg(II) unhydrolysed humic acid complexes.

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STABILITY CONSTANTS OF COMPLEXES OF METAL IONS WITH PEATSOIL HUMIC ACIDS UNDER NON-ACID-CONDITIONS

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ABSTRACT

Stability constants of complexes of four divalent metal ions viz. Cu^{2+}, Pb^{2+},Mg^{2+} and Cd^{2+} with humic acids (HA) were determined by potentiometric titration of humic acids with the corresponding salt of the divalent metals in aqueous media under non-acid-condition. The log K (logarithm of the stability constant) ranged from 1.0942 to 2.7471 for metal-humic acid complexes were determined using point-wise computational method. The order of stability constants were obtained as follows: Cu >Pb> Cd > Mg for metal -HA complexes respectively, indicating a higher degree of complexation with Cu metal ion.

Keywords: stability constant, humic acid, potentiometric titration, divalent metals, acid hydrolysis.

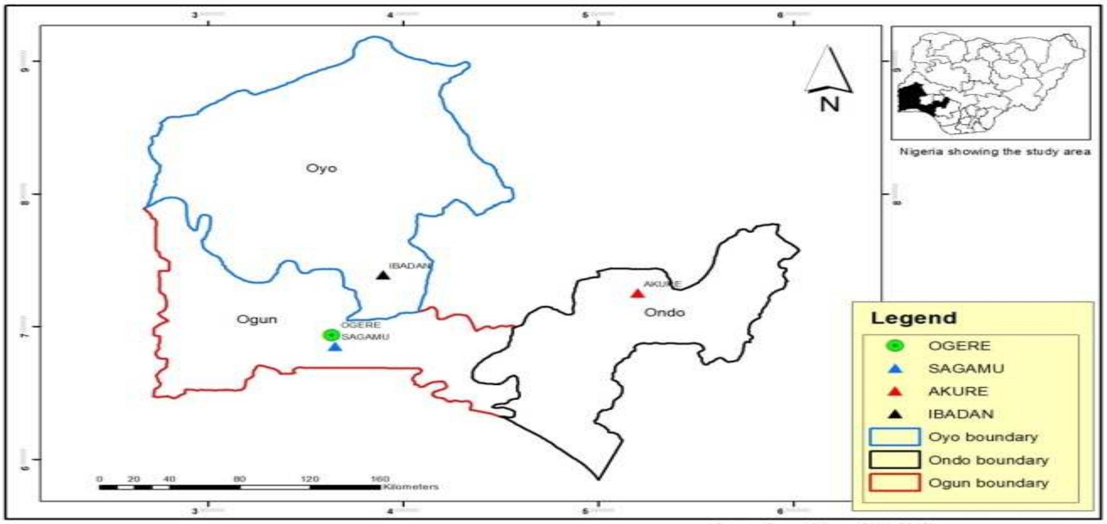
NTRODUCTION

The stability constant of a complex is the numerical expression of its stability and provides a quantitative measure of affinity of the metal ion to the complexing agent. An understanding of the relative stability of metal-complexes helps in predicting the behavior of metal ions in the soil (Ram and Raman, 1982). Extensive researches has been done to determine the stability constants of the complexes formed between humic acid (HA) with a number of metal ions. Ashok *et al.*, (2000) reported that humic acid with hydroxyl, phenoxyl and carboxyl reactive groups can form coordination compound with metal ions at pH 3.5. The stability constants(Log K) for different metal-humic acid complexes indicated the following order of the stabilities of complexes formed between humic acid and metal ion, Cu >Fe >Pb> Ni > Co > Ca > Cd > Zn >Mn> Mg. Andelkovic *et al.*, (2010) investigated the binding of Cd(II) to soil humic acid at pH 6.5 and in 0.1M KNO_3 ionic medium. The stability constant for binding indicating greater stability in the case when carboxyl groups are involved in complexation reaction. Kostic *et al.*,(2012) investigated the complexation of humic acid with certain heavy metal ions (Co(II), Ni(II),Cu(II), Zn(II), and Pb(II). The experiment was performed at 25°C, at pH 4.0 and ionic strength of 0.01M. Stability constant of complex between Pb(II) ions and humic acid is greater than stability constants of other investigated metal-humate complexes. Bogata and Sokolowska (2016) analyses the interaction between humic acids from different soils and Zn (II) ions at wide concentration ranges and at pH 5. Studies have showed significant impact of Zn concentration, pH and some properties of humic acids with zinc.But all of these studies were limited to acidic pH range. Therefore, the present study was carried out to determine and compare the stability constants of complexes of metal ions with hydrolysed peat soil humic acid and unhydrolysed peat soil humic under non-acid conditions.

MATERIALS AND METHODS

Analytical grade chemicals used includes hydrochloric acid (HCl), nitric acid (HNO_3), sodium hydroxide (NaOH), lead nitrate $Pb(NO_3)_2$, copper nitrate $Cu(NO_3)_2.3H_2O$, cadmium nitrate $Cd(NO_3)_2.4H_2O$, magnesium nitrate $Mg(NO_3)_2.6H_2O$, potassium nitrate (KNO_3), calcium chloride ($CaCl_2$), (sigma-Aldrich). Dowex 50WX8, (20-50 mesh) from Fluka.

Area of study



Source: Dept. of Geog. BUK (2016)

Figure 1: Map showing the sampling point at Sagamu Town, Ogun State.

Description of Sampling Area

Sagamu has geographical coordinates between 6°50′ north; 3° 38′ east is located in south western region of Nigeria. The region has tropical wet and dry climate with a lengthy wet season and relatively constant temperatures throughout the course of the year. Wet season runs from March to October, November to December forms the region dry season. The vegetation type of the region is savannah which is really grassland with small bushes and occasional big trees. Grassland soils have substantially higher organic matter content than forest soils (Novackova, 2011).

Sample Collection

The Peatsoil samples were collected from four different sampling points (0-10cm depth) in Sagamu into polyethylene bag with plastic spoons. Samples were taken to the laboratory, extraneous materials were removed; the samples were air-dried, crushed and ground to a fine powder in a mortar passed through a 0.20mm sieve. The samples were kept for analysis.

Isolation and purification of humic acid from peat soil sample

Peatsoil sample (100g) was mixed with 1000 cm^3 of 0.1M NaOH solution, shaken for 3hours and left to stand overnight. Dark-coloured supernatant was obtained and decanted from solid residue. The dark-coloured supernatant was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 6 hours. Yellowish brown supernatant and dark-brown precipitate were obtained. The yellowish brown supernatant was decanted followed by centrifuge and discarded. The dark-brown precipitate was mixed with $500cm^3$of 0.1M NaOH solution followed by passing through dowex resin. The dark-brown solution was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 3 hours. The dark-brown precipitate was washed several times with deionized water. The supernatant was treated with $AgNO_3$ solution until no white precipitate observed. The humic acid was transferred to weighed crucible and dried at 60°C in an oven for 12 hours. The humic acid was cooled and dried in the desiccator, weighed and recorded. The obtained humic acid was dried again at 60°C for additional 6 hours cooled and dried in the desiccator, weighed and recorded constant weight was obtained (Baruah *et al*., 2015).

FT-IR analysis

FT-IR spectra of humic acid sample was analysed using Carry 630 FT-IR Agilent Technologies.

Unhydrolysed compost humic acid

The unhydrolysed humic acid was obtained after isolation and purification of compost humic acid and kept for investigation.

Acid hydrolysis of Peatsoil acid

Peatsoil humic acid sample (1g) was refluxed for 12 hours at (160°C) with $50cm^3$ of 6M HCl. The mixture was allowed to cool, decanted, and centrifuged after hydrolysis. The insoluble residues were washed with distilled water via centrifugation several times, and the supernatant was treated with $AgNO_3$ solution until no white precipitate was observed. The residue was thoroughly dried over $CaCl_2$ in a desiccator at room temperature (Chefetz *et al*., 2002). Finally, the obtained hydrolysed humic acid was kept for investigation.

Potentiometric Titrations

Potentiometric measurements were carried out using a pH-meter Jenway (model 3510) with combine electrode, the sensitivity of the pH -meter is 0.01 units. The pH meter was switched on half an hour before starting the titration for initial warm up of the instrument. The instrument was calibrated with an aqueous standard buffer solution of pH 4.00 and 10.0 (borate buffer) prepared from a "Qualigens" buffer tablets.

The following sets of solutions were prepared in a 250cm^3 volumetric flask separately for pH metric titrations.

(i) 5 cm^3 0.1 M HCl + 40 cm^3 deionized water
(ii) 5 cm^3 0.1 M HCl + 39 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid
(iii) 5 cm^3 0.1 M HCl + 37 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid + 2 cm^3 0.01 M Cu(II)

The solutions were titrated against standardized 0.110MNaOH separately. The total volume of each mixture was adjusted to 50 cm^3 and the ionic strength of the solutions was maintained constant at by adding appropriate amount of stock solution of 1M KNO_3 (Gamal, 2015; Omar and Ali, 2015). A magnetic stirrer was used to achieve thorough mixing of the interacting solutions at 550 rpm. The same set of experimental conditions was applied for potentiometric titration of remaining samples.

Evaluation of pKa of Hydrolysed peat soil Humic Acids

The proton-ligand formation number n_A were calculated by Irving and Rossotti expression (Omar and Ali, 2015).

$$nA = Y - \frac{(V2-V1)(No-Eo)}{(Vo+V1)TcL} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 1$$

Where: Y is number of dissociable proton, (V_2-V_1) is the measure of displacement of the ligand curve relative to acid curve, N^o and E^o are the resultant concentration of alkali solution, free acid solution, $T_{cL}{}^o$ is the total ligand concentration, V^o is the total volume of titration solution,V_1 is the volume of alkali added to acid solution,V_2 is the volume of alkali added to acid solution + ligand solution, acid dissociation constants (pKa - values) of ligand were calculated by algebraic method point wise calculation (Tables 1). The dissociation constants (pKa) were calculated according to the following relation:

$$pKa = pH + \log\left(\frac{nA}{1-nA}\right) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 2$$

Where: pKa is the acid dissociation constant, $n_A$is the Proton-ligand formation number and pH is the pH-values (Omar and Ali, 2015).

Determination of metal-ligand stability constants (log K) of complexes

The potentiometric measurement for the determination of stability constant of a complex in solution is based on the fact that the redox potential of the couple $\frac{M^{+(m-n)}}{M^{+m}}$ is shifted significantly on complexation of the metal ion with the ligand. This method involves change in hydrogen ion concentration [H$^+$] due to the displacement or association of one or more protons taking place during complexation reaction. This change can be found out by titrating the solutions containing free acid, acid with ligand, and acid with ligand and metal ion, individually against a standard alkali solution at a constant ionic strength or temperature. Either ionic strength or temperature may be varied for different sets of solutions. In all the cases, the change in the pH of the solution is measured after each addition of a known amount of alkali to the reaction cell which contains the reaction mixture. The titration curves are then drawn by plotting the measured pH values against the corresponding volume of alkali added and the stability constants of the complexes are determined from the titration curves by employing pH-metric titration technique given by (Irving and Rossoti).

Metal-ligand stability constants (Log K) were determined by using the following relations:

$$\bar{n} = \frac{(V_3 - V_2)(E^0 + N^0)}{(V^0 + V_2)\bar{n}_A T_m^0} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 3$$

and

$$PL = \log_{10}\left\{\frac{1 + \beta_n^H \dfrac{1}{[anti\ \log pH]^n}}{T_L^0 - \bar{n}T_m^0} X \frac{(V^0 + V_3)}{V^0}\right\} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 4$$

Where $T_{L,}$ T^o, E°, and V^ohavethe same significance as in equation (1) above, T_m denotes the total concentration of metal present in solution, V_3 is the volume of metal ions present in solution and β^H is the overall proton ligand stability constant. The metal-ligand stability constants (log K) were determined by employing point wise computational Method (eq. 5 and 6).

$$\text{LogK}_1 = \log\left(\frac{n}{1-n}\right) + \text{pL} \qquad \text{.............}5$$

$$\text{LogK}_2 = \log\left(\frac{1-n}{2-n}\right) + \text{pL}\text{.......................}6$$

Where: Log K is the metal-ligand stability constant, pL is the Free ligand exponent function, **n** is the Average number of ligand attached with metal ion (Janrao*et al*., 2014).The results obtained were analyzed by an ORIGIN 2016 program using titration data and then the proton-ligand stability constants (pKa) and Metal-ligand stability constant (LogK) calculated (Omar and Ali, 2015).

RESULTS AND DISCUSSION

Fourier transformed infrared (FT-IR) spectra of isolated humic acid from peat soils Figure 2 had distinct clear absorption bands indicating the presence of major humic acid structural elemental groups such as H bonded OH (3680cm^{-1} peak), C=O of carbonyl (1721cm^{-1} peak), functional groups of aliphatic components CH_2 (2918cm^{-1} peak) and C-O stretching of polysaccharide (1168cm^{-1} peak). The positions of the absorption bands of the spectra fell within typical major absorption bands of humic acid which is at frequencies 3680, 2918, 1721, 1168 cm^{-1}. The first peak centred in the vicinity of 3680 cm^{-1} region is attributed to phenol OH group bounded by intermolecular H bonds. The 2918cm^{-1} band usually has absorption maximum at 2918 cm^{-1} which is due to C–H stretching of alkane group (CH_2). The next major absorption band is 1721 cm^{-1}. This band has been commonly ascribed to C=O stretching of mainly carboxyl group (COOH) with trace amount of ketones. The last peak was observed at 1168 cm^{-1} due to C–O stretching of polysaccharides and this peak appeared also in the spectra of humic acid from peat soil. The FTIR spectra of the isolated humic acid contained all major characteristic absorption peaks of humic acid. These absorption peaks indicated the presence of the major structural elements of humic acid namely H bonded OH, C=C of aromatic ring, C=O of carbonyl group (both carboxyl and ketonic), CH_2 group. This strongly supports the presence of humic acid.

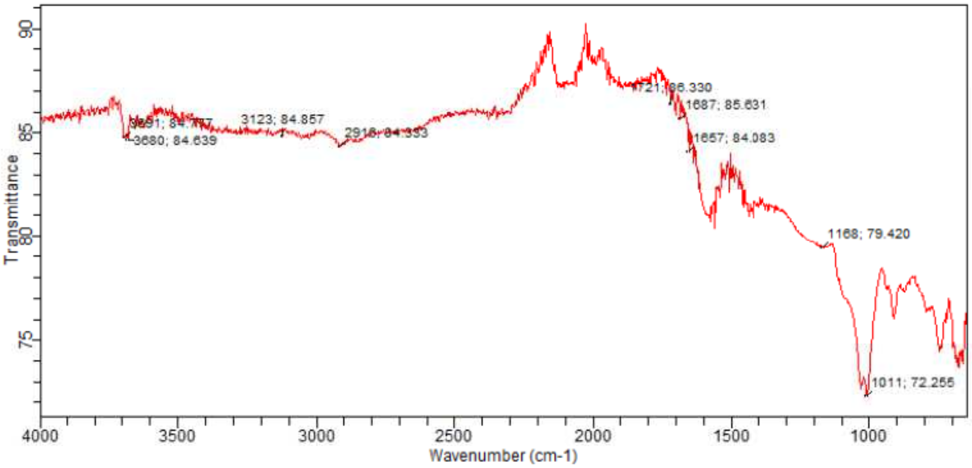


Fig. 2 : FT-IR spectraof peatsoilhumic acid (PSHA)

Evaluation of acid dissociation constant (pka) of acid hydrolysed peat soil humicacid at phenolic group

The value of the dissociation constant of the peat soil humic acid (PSHA) that underwent acidhydrolysis studied was found to be 8.9299 as shown Table 1, which is lower than the literaturevalues reported by Almeida and Szpoganics, (2015), Borges *et al*., (2005); Badr *et al*., (2012)and Fernandes *et al*,.(2009) of 9.73, 9.47 and 10.30. The difference between the obtained valuesand the reported values in this study might be probably as a result of acid hydrolysis of humicacid.

Table 1: PKa of (Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	V$_2$-V$_1$	nA	log($\frac{nA}{1-nA}$)	pKa
8.50	5.30	6.29	0.99	0.3594	-0.2510	8.2490
8.72	5.35	6.37	1.02	0.3400	-0.2880	8.4320
9.00	5.40	6.46	1.06	0.3141	-0.3391	8.6609
9.22	5.45	6.55	1.10	0.2882	-0.3927	8.8273
9.51	5.50	6.66	1.16	0.2494	-0.4786	9.0314
9.73	5.55	6.78	1.23	0.2041	-0.5910	9.1390
10.00	5.60	6.90	1.30	0.1589	-0.7238	9.2762
10.23	5.65	7.05	1.40	0.0941	-0.9835	9.2465
10.49	5.70	7.10	1.40	0.0941	-0.9835	9.5065

Average pKa = 8.9299 ± 0.4186

Table 2: PKa of (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	V$_2$-V$_1$	nA	Log($\frac{nA}{1-n}$)	pKa
8.50	5.30	5.81	0.51	0.6619	0.2919	8.7919
8.72	5.35	5.90	0.55	0.6357	0.2418	8.9618
9.00	5.40	6.00	0.60	0.6029	0.1813	9.1813
9.22	5.45	6.10	0.65	0.5701	0.1226	9.3426
9.51	5.50	6.20	0.70	0.5376	0.0654	9.5754
9.73	5.55	6.33	0.78	0.4851	-0.0259	9.7041
10.00	5.60	6.47	0.87	0.4262	-0.1291	9.8709
10.23	5.65	6.62	0.99	0.3609	-0.2481	9.9819
10.49	5.70	6.80	1.10	0.2759	-0.4690	10.0210

Average pKa = 9.4923± 0.4410

Metal-ligand stability constant (Log K)

The stabilityconstants require the accurate values of proton-ligand stability constants (Anil and Maroti, 2008). Metal titration curves crossed over ligand titration curve indicated the formation of complex upon proton release (Santosh, *et al.*, 2011). If the values of n- are within range 0.2-0.8 and 1.2-18 this indicates the formation of 1:1 and 1:2 complexes (Sayyed and Mazahar, 2012).

The metal (II)-humate stepwise stability constants (log k) at phenolic group (Tables 3-18)

Table 3: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	log($\frac{n}{1-n}$)	LogK$_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

LogK$_1$ (Average value) = 2.4788± 0.2203

Table 4: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	Log($\frac{n-1}{2-n}$)	LogK$_2$
9.51	5.50	6.66	6.73	0.07	1.3509	1.70	-0.2671	1.4329
9.73	5.55	6.78	6.85	0.07	1.6383	1.51	0.2467	1.7567
10.00	5.60	6.90	6.98	0.08	2.1783	1.31	-0.2158	1.0942
10.23	5.65	7.05	7.13	0.08	4.1904	1.27		
10.49	5.70	7.10	7.19	0.09	4.6920			

LogK$_2$(Average value) = 1.4280 ± 0.3312

Table 5:Point-wise method,Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	Log($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430

$LogK_1$ **(Average value)** = 2.3059± 0.6153

Table 6:Point-wise method, Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$V_3\text{-}V_2$	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
9.73	5.55	6.33	6.42	0.09	0.9000	1.69		
10.00	5.60	6.47	6.58	0.11	1.2578	1.44	-0.4592	0.9808
10.23	5.65	6.62	6.84	0.12	1.6137	1.26	-0.2010	1.4610
10.49	5.70	6.80	6.92	0.12	2.1052	1.03		

$LogK_2$ **(Average value)** = 1.2209± 0.3398

Table 7:Point-wise method,Pb (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	log($\frac{n}{1-n}$)	$LogK_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.60	0.05	0.8333	1.96	0.6989	2.6589

$LogK_1$ (Average value) = 2.5832 ±0.1614

Table 8:Point-wise method,Pb-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	log($\frac{n-1}{2-n}$)	$logK_2$
9.51	5.50	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.83	0.05	1.1702	1.44		
10.00	5.60	6.90	6.90	0.05	1.4864	1.22	-0.0237	1.1963
10.23	5.65	7.05	7.10	0.05	2.0190	1.09		
10.49	5.70	7.10	7.17	0.07	3.6492	1.00		

$LogK_2$(Average value) = 1.1963

Table 9:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$V_3\text{-}V_2$	n	pL	Log ($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.5477	2.3123
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	0.0272	2.2072
9.51	5.50	6.20	6.26	0.07	0.6417	1.89	0.2530	2.1430
9.73	5.55	6.40	6.40	0.07	0.7000	1.67	0.3680	2.0380

$LogK_1$ **(Average value)** = 2.2364 ± 0.1602

Table 10:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$V_3\text{-}V_2$	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
10.00	5.60	6.47	6.55	0.08	1.9503	1.41		
10.23	5.65	6.62	6.72	0.11	1.4792	1.26	-0.0361	1.2239

$LogK_2$ **(Average value)** = 1.2239

Table 11:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	log($\frac{n}{n-1}$)	$LogK_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4290	2.2110
8.72	5.35	6.37	6.39	0.02	0.2858	2.42	-0.3978	2.0222
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

$LogK_1$ (Average value)=2.1382**±**0.1046

Table 12:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	$\log(\frac{n-1}{2-n})$	LogK$_2$
9.51	5.55	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.84	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.93	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.10		
10.49	5.70	7.10	7.18	0.07	3.6492	0.83		

LogK$_2$(Average value) = 1.5453 **±** 0.3450

Table 13:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	V$_3$-V$_2$	n	pL	$\log(\frac{n}{n-1})$	Log K$_1$
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.3477	2.3123
9.00	5.40	6.00	6.04	0.04	0.3236	2.38	-0.3202	2.0598
9.22	5.45	6.10	6.15	0.05	0.4297	2.17	-0.1230	2.0470
9.51	5.50	6.20	6.26	0.06	0.5500	1.89	0.0871	1.9771
9.73	5.55	6.33	6.40	0.07	0.7000	1.67	0.3680	2.0380

LogK$_1$ **(Average value)** = 2.1568 ± 0.2069

Table 14:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	V$_3$-V$_2$	n	pL	$\log(\frac{n-1}{2-n})$	Log K$_2$
10.00	5.60	6.47	6.55	0.08	0.9148	1.41		
10.23	5.65	6.62	6.71	0.09	1.2102	1.20	-0.5749	0.6251
10.49	5.70	6.80	6.92	0.09	1.5968	1.03	0.1703	1.2003

LogK$_2$ **(Average value)** = 0.9127± 0.4070

Table15:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	$\log(\frac{n}{1-n})$	LogK$_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4210	2.2190
8.72	5.35	6.37	6.40	0.03	0.4286	2.42	-0.1249	2.2951
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.96	0.3010	2.2610
9.51	5.55	6.66	6.70	0.04	0.7720	1.67	0.5297	2.1997

LogK$_1$ (Average value) = 2.2108± 0.0825

Table 16:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	$\log(\frac{n-1}{2-n})$	Log K$_2$
9.73	5.55	6.78	6.83	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.95	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.09		
10.49	5.70	7.10	7.16	0.06	3.1429	0.89		

LogK$_2$ **(Average value)** = 1.5453± 0.3450

Table 17:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	V$_3$-V$_2$	n	pL	$\log(\frac{n}{n-1})$	Log K$_1$
8.50	5.30	5.81	5.86	0.05	0.3717	2.88	-0.2280	2.6520
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.06	0.06	0.4853	2.38	-0.0255	2.3545
9.22	5.45	6.10	6.16	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430
9.73	5.55	6.33	6.41	0.08	0.8000	1.69	0.6020	2.2920

LogK$_1$ **(Average value)** = 2.2516± 0.5380

Table 18:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
10.00	5.60	6.47	6.57	0.10	1.1434	1.43		
10.23	5.65	6.62	6.72	0.10	1.3448	1.23	-0.2788	0.9512
10.49	5.70	6.80	6.90	0.10	1.7742	1.03	0.5351	1.5651

$LogK_2$ **(Average value)** = 1.2581± 0.4340

Table 19: Stepwise and overall Stability constants of thehydrolysed and unhydrolysed divalent metal (II) complexes

Chelates	$LogK_1$	$LogK_2$	Logβ
[Cu (Hydrolysed PSHA-1)$_2$]	2.4788	1.4280	3.9068
[Pb (Hydrolysed PSHA-1)$_2$]	2.5832	1.1963	3.7795
[Cd (Hydrolysed PSHA-1)$_2$]	2.2108	1.5453	3.7561
[Mg (Hydrolysed PSHA-1)$_2$]	2.1382	1.5453	3.6835
[Cu (Unhydrolysed PSHA-1)$_2$]	2.3059	1.2209	3.5268
[Pb (Unhydrolysed PSHA-1)$_2$]	2.2364	1.2239	3.4603
[Cd (Unhydrolysed PSHA-1)$_2$]	2.2516	1.2581	3.5097
[Mg (Unydrolysed PSHA-1)$_2$]	2.1568	0.9127	3.0695

The results obtained (Table19) shows the stepwise and overall stability constants to be not high indicating low stability of the complexes, because the solubility of most metal ions in the basic pH range is minimal due to metal hydroxide precipitation (Karimi, 2017). In general, the stepwise stability constants (K_1 and K_2) follow the order $K_1 > K_2$ for the copper, lead, magnesium and cadmium complexes respectively. The steady decrease of the values with increasing number of ligands is in agreement with the prediction made by researchers (Na'aliya, 2013). The decrease could be attributed to the fact that as the number of the ligands (Humate ions) that enters the coordination zone increases the aqua molecules available for replacement by the ligands become less. Thus, the metal ions become less electron loving with progressive intake of the ligand and this results in the decrease in the values of the constants (Na'aliya, 2013). Also the stability of the complexes is influenced by the size and number of the chelate rings(Mackay and Mackay,2002).All the complexes form rings in their structure as humate, a bidentate ligand, bond the metal ions in the ratio 1:2 (Boguta and Sokolowska, 2016) forming chelate rings. The values of the overall stability constants (logβ) obtained for humate complexes are not high indicating low stability as the values are not high. LogK values for copper-humates (Table 3 to 6) obtained in this study are lower than those reported for the complexes of humic acids (Pandey *et al*., 2015; Dinu, 2013; Kaschl *et al*., 2010 and Gilbeto and Jorg, 2001). The values of LogK(Table 7 to 10) forlead-humates are lower than those reported for the lead in the literature (Dinu, 2013; Gilbeto and Jorg 2001). Log K values(Table 11 to 14) for magnesium-humates obtained in this study are close to those reported by (Pandey *et al*., 2015). Log K values of cadmium-humates (Table 15 to 18) obtained in this work near to the one reported by (Dinu, 2013 and Pandey *et al*., 2015).The difference between the reported values and the values obtained in this study might be probably as a result of acid hydrolysis of humic acid. The values of the overall stability constants (log β) of the copper humates complexes presented in Table 19 is high than that of other metal humate complexes, show relatively high stability of Cu-HA complexes, show the following order of stability: Cu >Pb> Cd > Mg; which are in close agreement to the findings of (Dinu, 2013 and Pandey *et al*., 2015).The high stability of Cu-humate chelate could be attributed to the existence of coordinate covalent bond between the complexing agents and the Cu^{2+} ions. Since, Cu^{2+} being a metal of the transitional series with $3d^9$ electronic configurations can accept the electrons from the complexing agents. Similarly,the low stabilities of Pb,Cd and Mg -complexes could be explained by that Pb^{2+} with $6s^2$, Cd^{2+} with $4d^{10}$ and Mg^{2+} with $2p^6$ their electronic configuration has a completely filled d,p and s orbitals. Moreover, the stabilities of metal ions with hydrolysed humic acid from peat soil were higher than those with unhydrolysed humic acid from peat soil; which is ascribed to the high content of acidity in hydrolysed humic acid than unhydrolysed humic acid.

CONCLUSION

The values of logK for Cu(II) hydrolysed humic acid complex was higher followed by Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes as compared with metal(II) unhydrolysed humic acid complexes . This indicates acid hydrolysis of humic acid can enhance the complexation behavior of humic acid with metal (II) ions. However, the higher values of logβ for Cu(II), Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes indicates more stable stepwise complexes formed as compared with Cu(II), Pb(II), Cd(II) and Mg(II) unhydrolysed humic acid complexes.

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STABILITY CONSTANTS OF COMPLEXES OF METAL IONS WITH PEATSOIL HUMIC ACIDS UNDER NON-ACID-CONDITIONS

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ABSTRACT

Stability constants of complexes of four divalent metal ions viz. Cu^{2+}, Pb^{2+},Mg^{2+} and Cd^{2+} with humic acids (HA) were determined by potentiometric titration of humic acids with the corresponding salt of the divalent metals in aqueous media under non-acid-condition. The log K (logarithm of the stability constant) ranged from 1.0942 to 2.7471 for metal-humic acid complexes were determined using point-wise computational method. The order of stability constants were obtained as follows: Cu >Pb> Cd > Mg for metal -HA complexes respectively, indicating a higher degree of complexation with Cu metal ion.

Keywords: stability constant, humic acid, potentiometric titration, divalent metals, acid hydrolysis.

NTRODUCTION

The stability constant of a complex is the numerical expression of its stability and provides a quantitative measure of affinity of the metal ion to the complexing agent. An understanding of the relative stability of metal-complexes helps in predicting the behavior of metal ions in the soil (Ram and Raman, 1982). Extensive researches has been done to determine the stability constants of the complexes formed between humic acid (HA) with a number of metal ions. Ashok *et al.*, (2000) reported that humic acid with hydroxyl, phenoxyl and carboxyl reactive groups can form coordination compound with metal ions at pH 3.5. The stability constants(Log K) for different metal-humic acid complexes indicated the following order of the stabilities of complexes formed between humic acid and metal ion, Cu >Fe >Pb> Ni > Co > Ca > Cd > Zn >Mn> Mg. Andelkovic *et al.*, (2010) investigated the binding of Cd(II) to soil humic acid at pH 6.5 and in 0.1M KNO_3 ionic medium. The stability constant for binding indicating greater stability in the case when carboxyl groups are involved in complexation reaction. Kostic *et al.*,(2012) investigated the complexation of humic acid with certain heavy metal ions (Co(II), Ni(II),Cu(II), Zn(II), and Pb(II). The experiment was performed at 25°C, at pH 4.0 and ionic strength of 0.01M. Stability constant of complex between Pb(II) ions and humic acid is greater than stability constants of other investigated metal-humate complexes. Bogata and Sokolowska (2016) analyses the interaction between humic acids from different soils and Zn (II) ions at wide concentration ranges and at pH 5. Studies have showed significant impact of Zn concentration, pH and some properties of humic acids with zinc.But all of these studies were limited to acidic pH range. Therefore, the present study was carried out to determine and compare the stability constants of complexes of metal ions with hydrolysed peat soil humic acid and unhydrolysed peat soil humic under non-acid conditions.

MATERIALS AND METHODS

Analytical grade chemicals used includes hydrochloric acid (HCl), nitric acid (HNO_3), sodium hydroxide (NaOH), lead nitrate $Pb(NO_3)_2$, copper nitrate $Cu(NO_3)_2.3H_2O$, cadmium nitrate $Cd(NO_3)_2.4H_2O$, magnesium nitrate $Mg(NO_3)_2.6H_2O$, potassium nitrate (KNO_3), calcium chloride ($CaCl_2$), (sigma-Aldrich). Dowex 50WX8, (20-50 mesh) from Fluka.

Area of study

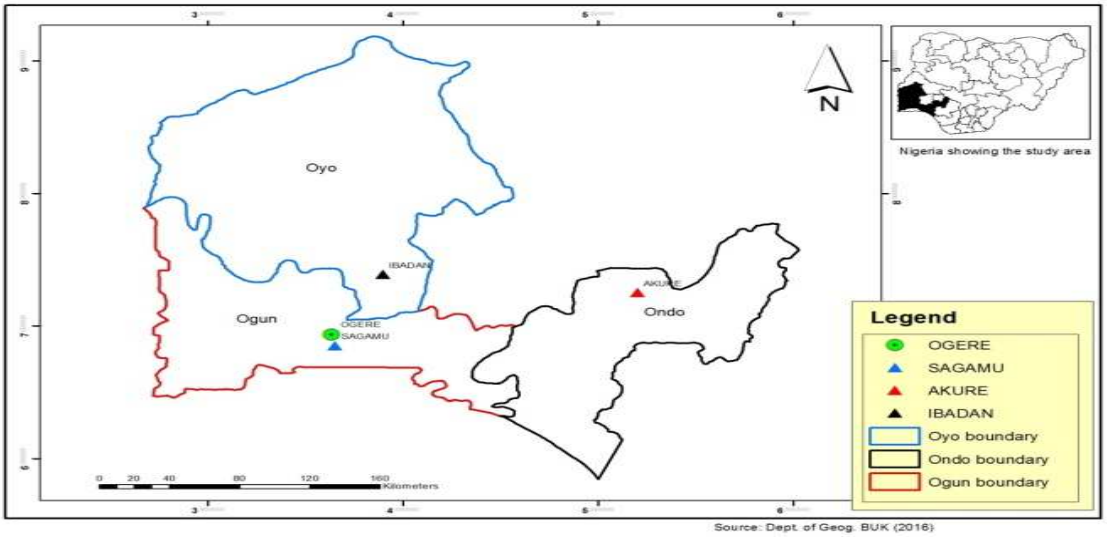

Figure 1: Map showing the sampling point at Sagamu Town, Ogun State.

Description of Sampling Area

Sagamu has geographical coordinates between 6°50′ north; 3° 38′ east is located in south western region of Nigeria. The region has tropical wet and dry climate with a lengthy wet season and relatively constant temperatures throughout the course of the year. Wet season runs from March to October, November to December forms the region dry season. The vegetation type of the region is savannah which is really grassland with small bushes and occasional big trees. Grassland soils have substantially higher organic matter content than forest soils (Novackova, 2011).

Sample Collection

The Peatsoil samples were collected from four different sampling points (0-10cm depth) in Sagamu into polyethylene bag with plastic spoons. Samples were taken to the laboratory, extraneous materials were removed; the samples were air-dried, crushed and ground to a fine powder in a mortar passed through a 0.20mm sieve. The samples were kept for analysis.

Isolation and purification of humic acid from peat soil sample

Peatsoil sample (100g) was mixed with 1000 cm^3 of 0.1M NaOH solution, shaken for 3hours and left to stand overnight. Dark-coloured supernatant was obtained and decanted from solid residue. The dark-coloured supernatant was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 6 hours. Yellowish brown supernatant and dark-brown precipitate were obtained. The yellowish brown supernatant was decanted followed by centrifuge and discarded. The dark-brown precipitate was mixed with $500cm^3$of 0.1M NaOH solution followed by passing through dowex resin. The dark-brown solution was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 3 hours. The dark-brown precipitate was washed several times with deionized water. The supernatant was treated with $AgNO_3$ solution until no white precipitate observed. The humic acid was transferred to weighed crucible and dried at 60°C in an oven for 12 hours. The humic acid was cooled and dried in the desiccator, weighed and recorded. The obtained humic acid was dried again at 60°C for additional 6 hours cooled and dried in the desiccator, weighed and recorded constant weight was obtained (Baruah *et al*., 2015).

FT-IR analysis

FT-IR spectra of humic acid sample was analysed using Carry 630 FT-IR Agilent Technologies.

Unhydrolysed compost humic acid

The unhydrolysed humic acid was obtained after isolation and purification of compost humic acid and kept for investigation.

Acid hydrolysis of Peatsoil acid

Peatsoil humic acid sample (1g) was refluxed for 12 hours at (160°C) with $50cm^3$ of 6M HCl. The mixture was allowed to cool, decanted, and centrifuged after hydrolysis. The insoluble residues were washed with distilled water via centrifugation several times, and the supernatant was treated with $AgNO_3$ solution until no white precipitate was observed. The residue was thoroughly dried over $CaCl_2$ in a desiccator at room temperature (Chefetz *et al*., 2002). Finally, the obtained hydrolysed humic acid was kept for investigation.

Potentiometric Titrations

Potentiometric measurements were carried out using a pH-meter Jenway (model 3510) with combine electrode, the sensitivity of the pH - meter is 0.01 units. The pH meter was switched on half an hour before starting the titration for initial warm up of the instrument. The instrument was calibrated with an aqueous standard buffer solution of pH 4.00 and 10.0 (borate buffer) prepared from a "Qualigens" buffer tablets.

The following sets of solutions were prepared in a 250cm^3 volumetric flask separately for pH metric titrations.

(i) 5 cm^3 0.1 M HCl + 40 cm^3 deionized water

(ii) 5 cm^3 0.1 M HCl + 39 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid

(iii) 5 cm^3 0.1 M HCl + 37 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid + 2 cm^3 0.01 M Cu(II)

The solutions were titrated against standardized 0.110MNaOH separately. The total volume of each mixture was adjusted to 50 cm^3 and the ionic strength of the solutions was maintained constant at by adding appropriate amount of stock solution of 1M KNO_3 (Gamal, 2015; Omar and Ali, 2015). A magnetic stirrer was used to achieve thorough mixing of the interacting solutions at 550 rpm. The same set of experimental conditions was applied for potentiometric titration of remaining samples.

Evaluation of pKa of Hydrolysed peat soil Humic Acids

The proton-ligand formation number n$_\mathbf{A}$ were calculated by Irving and Rossotti expression (Omar and Ali, 2015).

$$nA = Y- \frac{(V2-V1)(No-Eo)}{(Vo+V1)TcL} \quad ....1$$

Where: Y is number of dissociable proton, (V_2-V_1) is the measure of displacement of the ligand curve relative to acid curve, N^o and E^o are the resultant concentration of alkali solution, free acid solution, $T_{cL}{}^o$ is the total ligand concentration, V^o is the total volume of titration solution,V_1 is the volume of alkali added to acid solution,V_2 is the volume of alkali added to acid solution + ligand solution, acid dissociation constants (pKa - values) of ligand were calculated by algebraic method point wise calculation (Tables 1). The dissociation constants (pKa) were calculated according to the following relation:

$$pKa = pH + \log(\frac{nA}{1-nA}) \quad ....2$$

Where: pKa is the acid dissociation constant, $n_A$is the Proton-ligand formation number and pH is the pH-values (Omar and Ali, 2015).

Determination of metal-ligand stability constants (log K) of complexes

The potentiometric measurement for the determination of stability constant of a complex in solution is based on the fact that the redox potential of the couple $\frac{M^{+(m-n)}}{M^{+m}}$ is shifted significantly on complexation of the metal ion with the ligand. This method involves change in hydrogen ion concentration [H$^+$] due to the displacement or association of one or more protons taking place during complexation reaction. This change can be found out by titrating the solutions containing free acid, acid with ligand, and acid with ligand and metal ion, individually against a standard alkali solution at a constant ionic strength or temperature. Either ionic strength or temperature may be varied for different sets of solutions. In all the cases, the change in the pH of the solution is measured after each addition of a known amount of alkali to the reaction cell which contains the reaction mixture. The titration curves are then drawn by plotting the measured pH values against the corresponding volume of alkali added and the stability constants of the complexes are determined from the titration curves by employing pH-metric titration technique given by (Irving and Rossoti).

Metal-ligand stability constants (Log K) were determined by using the following relations:

$$\bar{n} = \frac{(V_3 - V_2)(E^0 + N^0)}{(V^0 + V_2)\bar{n}_A T_m^0} \quad ....3$$

and

$$PL = \log_{10}\{\frac{1+\beta_n^H \frac{1}{[anti\ \log pH]^n}}{T_L^0 - \bar{n}T_m^0} X \frac{(V^0+V_3)}{V^0}\} \quad ....4$$

Where $T_{L,}$ T^o, E°, and V^ohavethe same significance as in equation (1) above, T_m denotes the total concentration of metal present in solution, V_3 is the volume of metal ions present in solution and β^H is the overall proton ligand stability constant. The metal-ligand stability constants (log K) were determined by employing point wise computational Method (eq. 5 and 6).

$$\text{Log}K_1 = \log\left(\frac{n}{1-n}\right) + pL \quad \ldots\ldots\ldots\ldots.5$$

$$\text{Log}K_2 = \log\left(\frac{1-n}{2-n}\right) + pL\ldots\ldots\ldots\ldots\ldots\ldots\ldots.6$$

Where: Log K is the metal-ligand stability constant, pL is the Free ligand exponent function, **n** is the Average number of ligand attached with metal ion (Janrao*et al*., 2014).The results obtained were analyzed by an ORIGIN 2016 program using titration data and then the proton-ligand stability constants (pKa) and Metal-ligand stability constant (LogK) calculated (Omar and Ali, 2015).

RESULTS AND DISCUSSION

Fourier transformed infrared (FT-IR) spectra of isolated humic acid from peat soils Figure 2 had distinct clear absorption bands indicating the presence of major humic acid structural elemental groups such as H bonded OH (3680cm^{-1} peak), C=O of carbonyl (1721cm^{-1} peak), functional groups of aliphatic components CH_2 (2918cm^{-1} peak) and C-O stretching of polysaccharide (1168cm^{-1} peak). The positions of the absorption bands of the spectra fell within typical major absorption bands of humic acid which is at frequencies 3680, 2918, 1721, 1168 cm^{-1}. The first peak centred in the vicinity of 3680 cm^{-1} region is attributed to phenol OH group bounded by intermolecular H bonds. The 2918cm^{-1} band usually has absorption maximum at 2918 cm^{-1} which is due to C–H stretching of alkane group (CH_2). The next major absorption band is 1721 cm^{-1}. This band has been commonly ascribed to C=O stretching of mainly carboxyl group (COOH) with trace amount of ketones. The last peak was observed at 1168 cm^{-1} due to C–O stretching of polysaccharides and this peak appeared also in the spectra of humic acid from peat soil. The FTIR spectra of the isolated humic acid contained all major characteristic absorption peaks of humic acid. These absorption peaks indicated the presence of the major structural elements of humic acid namely H bonded OH, C=C of aromatic ring, C=O of carbonyl group (both carboxyl and ketonic), CH_2 group. This strongly supports the presence of humic acid.

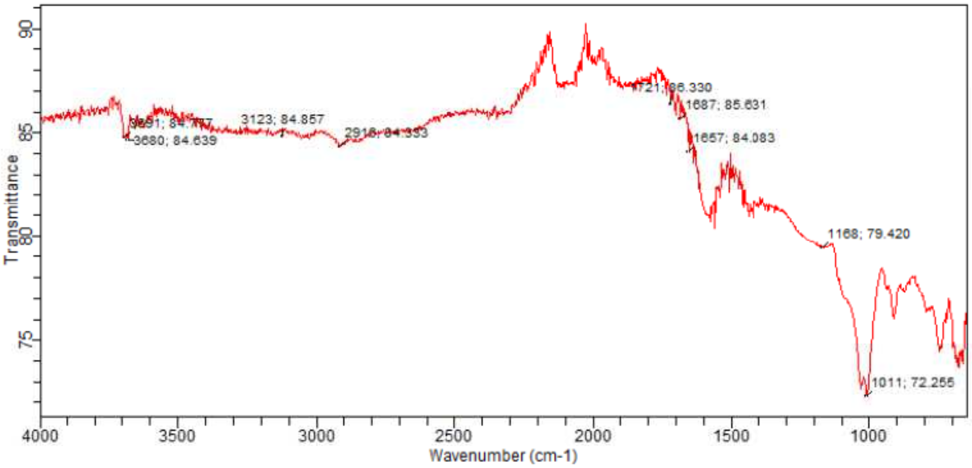

Fig. 2 : FT-IR spectraof peatsoilhumic acid (PSHA)

Evaluation of acid dissociation constant (pka) of acid hydrolysed peat soil humicacid at phenolic group

The value of the dissociation constant of the peat soil humic acid (PSHA) that underwent acidhydrolysis studied was found to be 8.9299 as shown Table 1, which is lower than the literaturevalues reported by Almeida and Szpoganics, (2015), Borges *et al*., (2005); Badr *et al*., (2012)and Fernandes *et al*,.(2009) of 9.73, 9.47 and 10.30. The difference between the obtained valuesand the reported values in this study might be probably as a result of acid hydrolysis of humicacid.

Table 1: PKa of (Hydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	$\log(\frac{nA}{1-nA})$	pKa
8.50	5.30	6.29	0.99	0.3594	-0.2510	8.2490
8.72	5.35	6.37	1.02	0.3400	-0.2880	8.4320
9.00	5.40	6.46	1.06	0.3141	-0.3391	8.6609
9.22	5.45	6.55	1.10	0.2882	-0.3927	8.8273
9.51	5.50	6.66	1.16	0.2494	-0.4786	9.0314
9.73	5.55	6.78	1.23	0.2041	-0.5910	9.1390
10.00	5.60	6.90	1.30	0.1589	-0.7238	9.2762
10.23	5.65	7.05	1.40	0.0941	-0.9835	9.2465
10.49	5.70	7.10	1.40	0.0941	-0.9835	9.5065

Average pKa = 8.9299 ± 0.4186

Table 2: PKa of (Unhydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	$\log(\frac{nA}{1-n})$	pKa
8.50	5.30	5.81	0.51	0.6619	0.2919	8.7919
8.72	5.35	5.90	0.55	0.6357	0.2418	8.9618
9.00	5.40	6.00	0.60	0.6029	0.1813	9.1813
9.22	5.45	6.10	0.65	0.5701	0.1226	9.3426
9.51	5.50	6.20	0.70	0.5376	0.0654	9.5754
9.73	5.55	6.33	0.78	0.4851	-0.0259	9.7041
10.00	5.60	6.47	0.87	0.4262	-0.1291	9.8709
10.23	5.65	6.62	0.99	0.3609	-0.2481	9.9819
10.49	5.70	6.80	1.10	0.2759	-0.4690	10.0210

Average pKa = 9.4923± 0.4410

Metal-ligand stability constant (Log K)

The stabilityconstants require the accurate values of proton-ligand stability constants (Anil and Maroti, 2008). Metal titration curves crossed over ligand titration curve indicated the formation of complex upon proton release (Santosh, *et al*., 2011). If the values of n- are within range 0.2-0.8 and 1.2-18 this indicates the formation of 1:1 and 1:2 complexes (Sayyed and Mazahar, 2012).

The metal (II)-humate stepwise stability constants (log k) at phenolic group (Tables 3-18)

Table 3: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$\log(\frac{n}{1-n})$	$LogK_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

$LogK_1$ (Average value) = 2.4788± 0.2203

Table 4: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$\log(\frac{n-1}{2-n})$	$LogK_2$
9.51	5.50	6.66	6.73	0.07	1.3509	1.70	-0.2671	1.4329
9.73	5.55	6.78	6.85	0.07	1.6383	1.51	0.2467	1.7567
10.00	5.60	6.90	6.98	0.08	2.1783	1.31	-0.2158	1.0942
10.23	5.65	7.05	7.13	0.08	4.1904	1.27		
10.49	5.70	7.10	7.19	0.09	4.6920			

$LogK_2$(Average value) = 1.4280 ± 0.3312

Table 5:Point-wise method,Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	Log($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430

$LogK_1$ **(Average value)** = 2.3059± 0.6153

Table 6:Point-wise method, Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$V_3\text{-}V_2$	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
9.73	5.55	6.33	6.42	0.09	0.9000	1.69		
10.00	5.60	6.47	6.58	0.11	1.2578	1.44	-0.4592	0.9808
10.23	5.65	6.62	6.84	0.12	1.6137	1.26	-0.2010	1.4610
10.49	5.70	6.80	6.92	0.12	2.1052	1.03		

$LogK_2$ **(Average value)** = 1.2209± 0.3398

Table 7:Point-wise method,Pb (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	log($\frac{n}{1-n}$)	$LogK_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.60	0.05	0.8333	1.96	0.6989	2.6589

$LogK_1$ (Average value) = 2.5832 ±0.1614

Table 8:Point-wise method,Pb-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	log($\frac{n-1}{2-n}$)	$logK_2$
9.51	5.50	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.83	0.05	1.1702	1.44		
10.00	5.60	6.90	6.90	0.05	1.4864	1.22	-0.0237	1.1963
10.23	5.65	7.05	7.10	0.05	2.0190	1.09		
10.49	5.70	7.10	7.17	0.07	3.6492	1.00		

$LogK_2$(Average value) = 1.1963

Table 9:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$V_3\text{-}V_2$	n	pL	Log ($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.5477	2.3123
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	0.0272	2.2072
9.51	5.50	6.20	6.26	0.07	0.6417	1.89	0.2530	2.1430
9.73	5.55	6.40	6.40	0.07	0.7000	1.67	0.3680	2.0380

$LogK_1$ **(Average value)** = 2.2364 ± 0.1602

Table 10:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$V_3\text{-}V_2$	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
10.00	5.60	6.47	6.55	0.08	1.9503	1.41		
10.23	5.65	6.62	6.72	0.11	1.4792	1.26	-0.0361	1.2239

$LogK_2$ **(Average value)** = 1.2239

Table 11:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	log($\frac{n}{n-1}$)	$LogK_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4290	2.2110
8.72	5.35	6.37	6.39	0.02	0.2858	2.42	-0.3978	2.0222
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

$LogK_1$ (Average value)=2.1382**±**0.1046

Table 12:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n-1}{2-n}$)	$LogK_2$
9.51	5.55	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.84	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.93	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.10		
10.49	5.70	7.10	7.18	0.07	3.6492	0.83		

$LogK_2$(Average value) = 1.5453 **±** 0.3450

Table 13:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.3477	2.3123
9.00	5.40	6.00	6.04	0.04	0.3236	2.38	-0.3202	2.0598
9.22	5.45	6.10	6.15	0.05	0.4297	2.17	-0.1230	2.0470
9.51	5.50	6.20	6.26	0.06	0.5500	1.89	0.0871	1.9771
9.73	5.55	6.33	6.40	0.07	0.7000	1.67	0.3680	2.0380

$LogK_1$ **(Average value)** = 2.1568 ± 0.2069

Table 14:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
10.00	5.60	6.47	6.55	0.08	0.9148	1.41		
10.23	5.65	6.62	6.71	0.09	1.2102	1.20	-0.5749	0.6251
10.49	5.70	6.80	6.92	0.09	1.5968	1.03	0.1703	1.2003

$LogK_2$ **(Average value)** = 0.9127± 0.4070

Table15:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	Log($\frac{n}{1-n}$)	$LogK_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4210	2.2190
8.72	5.35	6.37	6.40	0.03	0.4286	2.42	-0.1249	2.2951
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.96	0.3010	2.2610
9.51	5.55	6.66	6.70	0.04	0.7720	1.67	0.5297	2.1997

$LogK_1$ (Average value) = 2.2108± 0.0825

Table 16:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
9.73	5.55	6.78	6.83	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.95	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.09		
10.49	5.70	7.10	7.16	0.06	3.1429	0.89		

$LogK_2$ **(Average value)** = 1.5453± 0.3450

Table 17:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.86	0.05	0.3717	2.88	-0.2280	2.6520
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.06	0.06	0.4853	2.38	-0.0255	2.3545
9.22	5.45	6.10	6.16	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430
9.73	5.55	6.33	6.41	0.08	0.8000	1.69	0.6020	2.2920

$LogK_1$ **(Average value)** = 2.2516± 0.5380

Table 18:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$\text{Log}(\frac{n-1}{2-n})$	Log K_2
10.00	5.60	6.47	6.57	0.10	1.1434	1.43		
10.23	5.65	6.62	6.72	0.10	1.3448	1.23	-0.2788	0.9512
10.49	5.70	6.80	6.90	0.10	1.7742	1.03	0.5351	1.5651

LogK_2 **(Average value)** = 1.2581± 0.4340

Table 19: Stepwise and overall Stability constants of thehydrolysed and unhydrolysed divalent metal (II) complexes

Chelates	**LogK_1**	**LogK_2**	**Logβ**
[Cu (Hydrolysed PSHA-1)$_2$]	2.4788	1.4280	3.9068
[Pb (Hydrolysed PSHA-1)$_2$]	2.5832	1.1963	3.7795
[Cd (Hydrolysed PSHA-1)$_2$]	2.2108	1.5453	3.7561
[Mg (Hydrolysed PSHA-1)$_2$]	2.1382	1.5453	3.6835
[Cu (Unhydrolysed PSHA-1)$_2$]	2.3059	1.2209	3.5268
[Pb (Unhydrolysed PSHA-1)$_2$]	2.2364	1.2239	3.4603
[Cd (Unhydrolysed PSHA-1)$_2$]	2.2516	1.2581	3.5097
[Mg (Unydrolysed PSHA-1)$_2$]	2.1568	0.9127	3.0695

The results obtained (Table19) shows the stepwise and overall stability constants to be not high indicating low stability of the complexes, because the solubility of most metal ions in the basic pH range is minimal due to metal hydroxide precipitation (Karimi, 2017). In general, the stepwise stability constants (K_1 and K_2) follow the order $K_1 > K_2$ for the copper, lead, magnesium and cadmium complexes respectively. The steady decrease of the values with increasing number of ligands is in agreement with the prediction made by researchers (Na'aliya, 2013). The decrease could be attributed to the fact that as the number of the ligands (Humate ions) that enters the coordination zone increases the aqua molecules available for replacement by the ligands become less. Thus, the metal ions become less electron loving with progressive intake of the ligand and this results in the decrease in the values of the constants (Na'aliya, 2013). Also the stability of the complexes is influenced by the size and number of the chelate rings(Mackay and Mackay,2002).All the complexes form rings in their structure as humate, a bidentate ligand, bond the metal ions in the ratio 1:2 (Boguta and Sokolowska, 2016) forming chelate rings. The values of the overall stability constants (logβ) obtained for humate complexes are not high indicating low stability as the values are not high. LogK values for copper-humates (Table 3 to 6) obtained in this study are lower than those reported for the complexes of humic acids (Pandey *et al*., 2015; Dinu, 2013; Kaschl *et al*., 2010 and Gilbeto and Jorg, 2001). The values of LogK(Table 7 to 10) forlead-humates are lower than those reported for the lead in the literature (Dinu, 2013; Gilbeto and Jorg 2001). Log K values(Table 11 to 14) for magnesium-humates obtained in this study are close to those reported by (Pandey *et al*., 2015). Log K values of cadmium-humates (Table 15 to 18) obtained in this work near to the one reported by (Dinu, 2013 and Pandey *et al*., 2015).The difference between the reported values and the values obtained in this study might be probably as a result of acid hydrolysis of humic acid. The values of the overall stability constants (log β) of the copper humates complexes presented in Table 19 is high than that of other metal humate complexes, show relatively high stability of Cu-HA complexes, show the following order of stability: Cu >Pb> Cd > Mg; which are in close agreement to the findings of (Dinu, 2013 and Pandey *et al*., 2015).The high stability of Cu-humate chelate could be attributed to the existence of coordinate covalent bond between the complexing agents and the Cu^{2+} ions. Since, Cu^{2+} being a metal of the transitional series with $3d^9$ electronic configurations can accept the electrons from the complexing agents. Similarly,the low stabilities of Pb,Cd and Mg -complexes could be explained by that Pb^{2+} with $6s^2$, Cd^{2+} with $4d^{10}$ and Mg^{2+} with $2p^6$ their electronic configuration has a completely filled d,p and s orbitals. Moreover, the stabilities of metal ions with hydrolysed humic acid from peat soil were higher than those with unhydrolysed humic acid from peat soil; which is ascribed to the high content of acidity in hydrolysed humic acid than unhydrolysed humic acid.

CONCLUSION

The values of logK for Cu(II) hydrolysed humic acid complex was higher followed by Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes as compared with metal(II) unhydrolysed humic acid complexes . This indicates acid hydrolysis of humic acid can enhance the complexation behavior of humic acid with metal (II) ions. However, the higher values of logβ for Cu(II), Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes indicates more stable stepwise complexes formed as compared with Cu(II), Pb(II), Cd(II) and Mg(II) unhydrolysed humic acid complexes.

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STABILITY CONSTANTS OF COMPLEXES OF METAL IONS WITH PEATSOIL HUMIC ACIDS UNDER NON-ACID-CONDITIONS

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ABSTRACT

Stability constants of complexes of four divalent metal ions viz. Cu^{2+}, Pb^{2+},Mg^{2+} and Cd^{2+} with humic acids (HA) were determined by potentiometric titration of humic acids with the corresponding salt of the divalent metals in aqueous media under non-acid-condition. The log K (logarithm of the stability constant) ranged from 1.0942 to 2.7471 for metal-humic acid complexes were determined using point-wise computational method. The order of stability constants were obtained as follows: Cu >Pb> Cd > Mg for metal -HA complexes respectively, indicating a higher degree of complexation with Cu metal ion.

Keywords: stability constant, humic acid, potentiometric titration, divalent metals, acid hydrolysis.

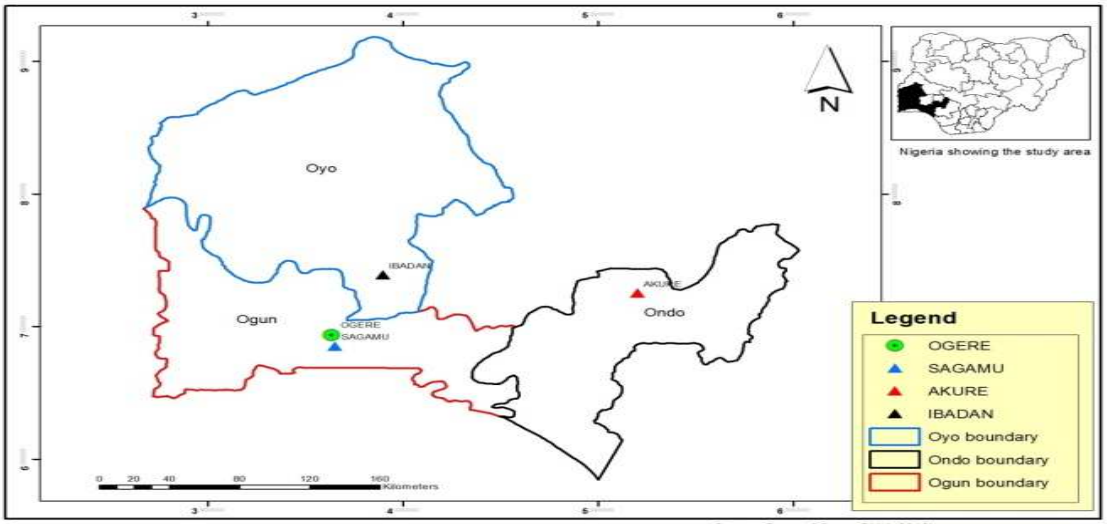
NTRODUCTION

The stability constant of a complex is the numerical expression of its stability and provides a quantitative measure of affinity of the metal ion to the complexing agent. An understanding of the relative stability of metal-complexes helps in predicting the behavior of metal ions in the soil (Ram and Raman, 1982). Extensive researches has been done to determine the stability constants of the complexes formed between humic acid (HA) with a number of metal ions. Ashok *et al.*, (2000) reported that humic acid with hydroxyl, phenoxyl and carboxyl reactive groups can form coordination compound with metal ions at pH 3.5. The stability constants(Log K) for different metal-humic acid complexes indicated the following order of the stabilities of complexes formed between humic acid and metal ion, Cu >Fe >Pb> Ni > Co > Ca > Cd > Zn >Mn> Mg. Andelkovic *et al.*, (2010) investigated the binding of Cd(II) to soil humic acid at pH 6.5 and in 0.1M KNO_3 ionic medium. The stability constant for binding indicating greater stability in the case when carboxyl groups are involved in complexation reaction. Kostic *et al.*,(2012) investigated the complexation of humic acid with certain heavy metal ions (Co(II), Ni(II),Cu(II), Zn(II), and Pb(II). The experiment was performed at 25°C, at pH 4.0 and ionic strength of 0.01M. Stability constant of complex between Pb(II) ions and humic acid is greater than stability constants of other investigated metal-humate complexes. Bogata and Sokolowska (2016) analyses the interaction between humic acids from different soils and Zn (II) ions at wide concentration ranges and at pH 5. Studies have showed significant impact of Zn concentration, pH and some properties of humic acids with zinc.But all of these studies were limited to acidic pH range. Therefore, the present study was carried out to determine and compare the stability constants of complexes of metal ions with hydrolysed peat soil humic acid and unhydrolysed peat soil humic under non-acid conditions.

MATERIALS AND METHODS

Analytical grade chemicals used includes hydrochloric acid (HCl), nitric acid (HNO_3), sodium hydroxide (NaOH), lead nitrate $Pb(NO_3)_2$, copper nitrate $Cu(NO_3)_2.3H_2O$, cadmium nitrate $Cd(NO_3)_2.4H_2O$, magnesium nitrate $Mg(NO_3)_2.6H_2O$, potassium nitrate (KNO_3), calcium chloride ($CaCl_2$), (sigma-Aldrich). Dowex 50WX8, (20-50 mesh) from Fluka.

Area of study



Source: Dept. of Geog. BUK (2016)

Figure 1: Map showing the sampling point at Sagamu Town, Ogun State.

Description of Sampling Area

Sagamu has geographical coordinates between 6°50′ north; 3° 38′ east is located in south western region of Nigeria. The region has tropical wet and dry climate with a lengthy wet season and relatively constant temperatures throughout the course of the year. Wet season runs from March to October, November to December forms the region dry season. The vegetation type of the region is savannah which is really grassland with small bushes and occasional big trees. Grassland soils have substantially higher organic matter content than forest soils (Novackova, 2011).

Sample Collection

The Peatsoil samples were collected from four different sampling points (0-10cm depth) in Sagamu into polyethylene bag with plastic spoons. Samples were taken to the laboratory, extraneous materials were removed; the samples were air-dried, crushed and ground to a fine powder in a mortar passed through a 0.20mm sieve. The samples were kept for analysis.

Isolation and purification of humic acid from peat soil sample

Peatsoil sample (100g) was mixed with 1000 cm^3 of 0.1M NaOH solution, shaken for 3hours and left to stand overnight. Dark-coloured supernatant was obtained and decanted from solid residue. The dark-coloured supernatant was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 6 hours. Yellowish brown supernatant and dark-brown precipitate were obtained. The yellowish brown supernatant was decanted followed by centrifuge and discarded. The dark-brown precipitate was mixed with $500cm^3$of 0.1M NaOH solution followed by passing through dowex resin. The dark-brown solution was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 3 hours. The dark-brown precipitate was washed several times with deionized water. The supernatant was treated with $AgNO_3$ solution until no white precipitate observed. The humic acid was transferred to weighed crucible and dried at 60°C in an oven for 12 hours. The humic acid was cooled and dried in the desiccator, weighed and recorded. The obtained humic acid was dried again at 60°C for additional 6 hours cooled and dried in the desiccator, weighed and recorded constant weight was obtained (Baruah *et al*., 2015).

FT-IR analysis

FT-IR spectra of humic acid sample was analysed using Carry 630 FT-IR Agilent Technologies.

Unhydrolysed compost humic acid

The unhydrolysed humic acid was obtained after isolation and purification of compost humic acid and kept for investigation.

Acid hydrolysis of Peatsoil acid

Peatsoil humic acid sample (1g) was refluxed for 12 hours at (160°C) with $50cm^3$ of 6M HCl. The mixture was allowed to cool, decanted, and centrifuged after hydrolysis. The insoluble residues were washed with distilled water via centrifugation several times, and the supernatant was treated with $AgNO_3$ solution until no white precipitate was observed. The residue was thoroughly dried over $CaCl_2$ in a desiccator at room temperature (Chefetz *et al*., 2002). Finally, the obtained hydrolysed humic acid was kept for investigation.

Potentiometric Titrations

Potentiometric measurements were carried out using a pH-meter Jenway (model 3510) with combine electrode, the sensitivity of the pH - meter is 0.01 units. The pH meter was switched on half an hour before starting the titration for initial warm up of the instrument. The instrument was calibrated with an aqueous standard buffer solution of pH 4.00 and 10.0 (borate buffer) prepared from a "Qualigens" buffer tablets.

The following sets of solutions were prepared in a 250cm^3 volumetric flask separately for pH metric titrations.

(i) 5 cm^3 0.1 M HCl + 40 cm^3 deionized water
(ii) 5 cm^3 0.1 M HCl + 39 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid
(iii) 5 cm^3 0.1 M HCl + 37 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid + 2 cm^3 0.01 M Cu(II)

The solutions were titrated against standardized 0.110MNaOH separately. The total volume of each mixture was adjusted to 50 cm^3 and the ionic strength of the solutions was maintained constant at by adding appropriate amount of stock solution of 1M KNO_3 (Gamal, 2015; Omar and Ali, 2015). A magnetic stirrer was used to achieve thorough mixing of the interacting solutions at 550 rpm. The same set of experimental conditions was applied for potentiometric titration of remaining samples.

Evaluation of pKa of Hydrolysed peat soil Humic Acids

The proton-ligand formation number n$_{\mathbf{A}}$ were calculated by Irving and Rossotti expression (Omar and Ali, 2015).

nA = Y- $\frac{(V2-V1)(No-Eo)}{(Vo+V1)TcL}$ ………………………………1

Where: Y is number of dissociable proton, (V_2-V_1) is the measure of displacement of the ligand curve relative to acid curve, N^o and E^o are the resultant concentration of alkali solution, free acid solution, $T_{cL}{}^o$ is the total ligand concentration, V^o is the total volume of titration solution,V_1 is the volume of alkali added to acid solution,V_2 is the volume of alkali added to acid solution + ligand solution, acid dissociation constants (pKa - values) of ligand were calculated by algebraic method point wise calculation (Tables 1). The dissociation constants (pKa) were calculated according to the following relation:

pKa = pH + log($\frac{nA}{1-nA}$) …………………………2

Where: pKa is the acid dissociation constant, $n_A$is the Proton-ligand formation number and pH is the pH-values (Omar and Ali, 2015).

Determination of metal-ligand stability constants (log K) of complexes

The potentiometric measurement for the determination of stability constant of a complex in solution is based on the fact that the redox potential of the couple $\frac{M^{+(m-n)}}{M^{+m}}$ is shifted significantly on complexation of the metal ion with the ligand. This method involves change in hydrogen ion concentration [H$^+$] due to the displacement or association of one or more protons taking place during complexation reaction. This change can be found out by titrating the solutions containing free acid, acid with ligand, and acid with ligand and metal ion, individually against a standard alkali solution at a constant ionic strength or temperature. Either ionic strength or temperature may be varied for different sets of solutions. In all the cases, the change in the pH of the solution is measured after each addition of a known amount of alkali to the reaction cell which contains the reaction mixture. The titration curves are then drawn by plotting the measured pH values against the corresponding volume of alkali added and the stability constants of the complexes are determined from the titration curves by employing pH-metric titration technique given by (Irving and Rossoti).

Metal-ligand stability constants (Log K) were determined by using the following relations:

$$\bar{n} = \frac{(V_3 - V_2)(E^0 + N^0)}{(V^0 + V_2)\bar{n}_A T_m^0} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 3$$

and

$$PL = \log_{10}\{\frac{1 + \beta_n^H \frac{1}{[anti\ \log \mathrm{pH}]^n}}{T_L^0 - \bar{n} T_m^0} \mathrm{X} \frac{(V^0 + V_3)}{V^0}\} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 4$$

Where $T_{L,}$ T^o, E°, and V^ohavethe same significance as in equation (1) above, T_m denotes the total concentration of metal present in solution, V_3 is the volume of metal ions present in solution and β^H is the overall proton ligand stability constant. The metal-ligand stability constants (log K) were determined by employing point wise computational Method (eq. 5 and 6).

$LogK_1 = \log\left(\frac{n}{1-n}\right) + pL$ 5

$LogK_2 = \log\left(\frac{1-n}{2-n}\right) + pL$.......................6

Where: Log K is the metal-ligand stability constant, pL is the Free ligand exponent function, **n** is the Average number of ligand attached with metal ion (Janrao*et al.*, 2014).The results obtained were analyzed by an ORIGIN 2016 program using titration data and then the proton-ligand stability constants (pKa) and Metal-ligand stability constant (LogK) calculated (Omar and Ali, 2015).

RESULTS AND DISCUSSION

Fourier transformed infrared (FT-IR) spectra of isolated humic acid from peat soils Figure 2 had distinct clear absorption bands indicating the presence of major humic acid structural elemental groups such as H bonded OH ($3680cm^{-1}$ peak), C=O of carbonyl ($1721cm^{-1}$ peak), functional groups of aliphatic components CH_2 ($2918cm^{-1}$ peak) and C-O stretching of polysaccharide ($1168cm^{-1}$ peak). The positions of the absorption bands of the spectra fell within typical major absorption bands of humic acid which is at frequencies 3680, 2918, 1721, 1168 cm^{-1}. The first peak centred in the vicinity of 3680 cm^{-1} region is attributed to phenol OH group bounded by intermolecular H bonds. The $2918cm^{-1}$ band usually has absorption maximum at 2918 cm^{-1} which is due to C–H stretching of alkane group (CH_2). The next major absorption band is 1721 cm^{-1}. This band has been commonly ascribed to C=O stretching of mainly carboxyl group (COOH) with trace amount of ketones. The last peak was observed at 1168 cm^{-1} due to C–O stretching of polysaccharides and this peak appeared also in the spectra of humic acid from peat soil. The FTIR spectra of the isolated humic acid contained all major characteristic absorption peaks of humic acid. These absorption peaks indicated the presence of the major structural elements of humic acid namely H bonded OH, C=C of aromatic ring, C=O of carbonyl group (both carboxyl and ketonic), CH_2 group. This strongly supports the presence of humic acid.

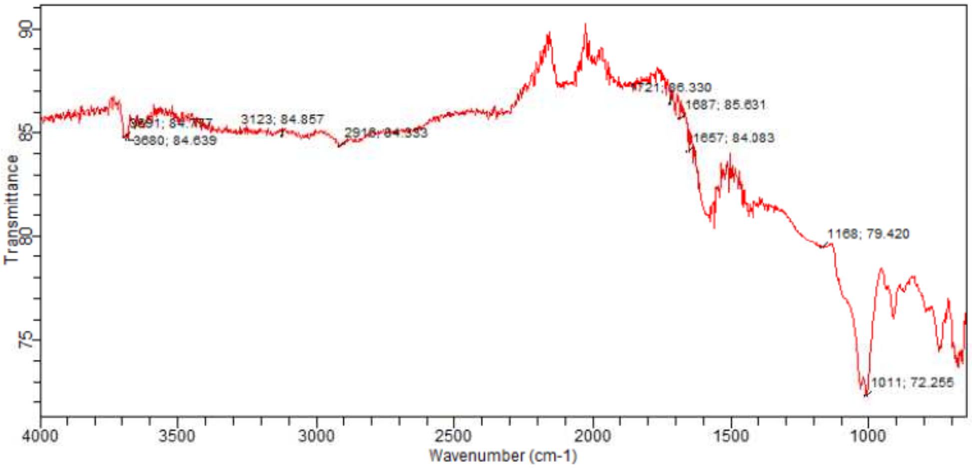


Fig. 2 : FT-IR spectraof peatsoilhumic acid (PSHA)

Evaluation of acid dissociation constant (pka) of acid hydrolysed peat soil humicacid at phenolic group

The value of the dissociation constant of the peat soil humic acid (PSHA) that underwent acidhydrolysis studied was found to be 8.9299 as shown Table 1, which is lower than the literaturevalues reported by Almeida and Szpoganics, (2015), Borges *et al.*, (2005); Badr *et al.*, (2012)and Fernandes *et al*,.(2009) of 9.73, 9.47 and 10.30. The difference between the obtained valuesand the reported values in this study might be probably as a result of acid hydrolysis of humicacid.

Table 1: PKa of (Hydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	log($\frac{nA}{1-nA}$)	pKa
8.50	5.30	6.29	0.99	0.3594	-0.2510	8.2490
8.72	5.35	6.37	1.02	0.3400	-0.2880	8.4320
9.00	5.40	6.46	1.06	0.3141	-0.3391	8.6609
9.22	5.45	6.55	1.10	0.2882	-0.3927	8.8273
9.51	5.50	6.66	1.16	0.2494	-0.4786	9.0314
9.73	5.55	6.78	1.23	0.2041	-0.5910	9.1390
10.00	5.60	6.90	1.30	0.1589	-0.7238	9.2762
10.23	5.65	7.05	1.40	0.0941	-0.9835	9.2465
10.49	5.70	7.10	1.40	0.0941	-0.9835	9.5065

Average pKa = 8.9299 ± 0.4186

Table 2: PKa of (Unhydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	Log($\frac{nA}{1-n}$)	pKa
8.50	5.30	5.81	0.51	0.6619	0.2919	8.7919
8.72	5.35	5.90	0.55	0.6357	0.2418	8.9618
9.00	5.40	6.00	0.60	0.6029	0.1813	9.1813
9.22	5.45	6.10	0.65	0.5701	0.1226	9.3426
9.51	5.50	6.20	0.70	0.5376	0.0654	9.5754
9.73	5.55	6.33	0.78	0.4851	-0.0259	9.7041
10.00	5.60	6.47	0.87	0.4262	-0.1291	9.8709
10.23	5.65	6.62	0.99	0.3609	-0.2481	9.9819
10.49	5.70	6.80	1.10	0.2759	-0.4690	10.0210

Average pKa = 9.4923± 0.4410

Metal-ligand stability constant (Log K)

The stabilityconstants require the accurate values of proton-ligand stability constants (Anil and Maroti, 2008). Metal titration curves crossed over ligand titration curve indicated the formation of complex upon proton release (Santosh, *et al.*, 2011). If the values of n- are within range 0.2-0.8 and 1.2-18 this indicates the formation of 1:1 and 1:2 complexes (Sayyed and Mazahar, 2012).

The metal (II)-humate stepwise stability constants (log k) at phenolic group (Tables 3-18)

Table 3: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n}{1-n}$)	$LogK_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

$LogK_1$ (Average value) = 2.4788± 0.2203

Table 4: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	Log($\frac{n-1}{2-n}$)	$LogK_2$
9.51	5.50	6.66	6.73	0.07	1.3509	1.70	-0.2671	1.4329
9.73	5.55	6.78	6.85	0.07	1.6383	1.51	0.2467	1.7567
10.00	5.60	6.90	6.98	0.08	2.1783	1.31	-0.2158	1.0942
10.23	5.65	7.05	7.13	0.08	4.1904	1.27		
10.49	5.70	7.10	7.19	0.09	4.6920			

$LogK_2$(Average value) = 1.4280 ± 0.3312

Table 5:Point-wise method,Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	Log($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430

LogK_1 **(Average value)** = 2.3059± 0.6153

Table 6:Point-wise method, Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$V_3\text{-}V_2$	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
9.73	5.55	6.33	6.42	0.09	0.9000	1.69		
10.00	5.60	6.47	6.58	0.11	1.2578	1.44	-0.4592	0.9808
10.23	5.65	6.62	6.84	0.12	1.6137	1.26	-0.2010	1.4610
10.49	5.70	6.80	6.92	0.12	2.1052	1.03		

LogK_2 **(Average value)** = 1.2209± 0.3398

Table 7:Point-wise method,Pb (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	log($\frac{n}{1-n}$)	LogK_1
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.60	0.05	0.8333	1.96	0.6989	2.6589

LogK_1 (Average value) = 2.5832 ±0.1614

Table 8:Point-wise method,Pb-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	log($\frac{n-1}{2-n}$)	logK_2
9.51	5.50	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.83	0.05	1.1702	1.44		
10.00	5.60	6.90	6.90	0.05	1.4864	1.22	-0.0237	1.1963
10.23	5.65	7.05	7.10	0.05	2.0190	1.09		
10.49	5.70	7.10	7.17	0.07	3.6492	1.00		

LogK_2(Average value) = 1.1963

Table 9:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$V_3\text{-}V_2$	n	pL	Log ($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.5477	2.3123
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	0.0272	2.2072
9.51	5.50	6.20	6.26	0.07	0.6417	1.89	0.2530	2.1430
9.73	5.55	6.40	6.40	0.07	0.7000	1.67	0.3680	2.0380

LogK_1 **(Average value)** = 2.2364 ± 0.1602

Table 10:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$V_3\text{-}V_2$	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
10.00	5.60	6.47	6.55	0.08	1.9503	1.41		
10.23	5.65	6.62	6.72	0.11	1.4792	1.26	-0.0361	1.2239

LogK_2 **(Average value)** = 1.2239

Table 11:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	log($\frac{n}{n-1}$)	LogK_1
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4290	2.2110
8.72	5.35	6.37	6.39	0.02	0.2858	2.42	-0.3978	2.0222
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

LogK_1 (Average value)=2.1382**±**0.1046

Table 12:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	$\log(\frac{n-1}{2-n})$	$\text{Log}K_2$
9.51	5.55	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.84	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.93	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.10		
10.49	5.70	7.10	7.18	0.07	3.6492	0.83		

$\text{Log}K_2$(Average value) = 1.5453 **±** 0.3450

Table 13:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$V_3\text{-}V_2$	n	pL	$\text{Log}(\frac{n}{n-1})$	$\text{Log } K_1$
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.3477	2.3123
9.00	5.40	6.00	6.04	0.04	0.3236	2.38	-0.3202	2.0598
9.22	5.45	6.10	6.15	0.05	0.4297	2.17	-0.1230	2.0470
9.51	5.50	6.20	6.26	0.06	0.5500	1.89	0.0871	1.9771
9.73	5.55	6.33	6.40	0.07	0.7000	1.67	0.3680	2.0380

$\text{Log}K_1$ **(Average value)** = 2.1568 ± 0.2069

Table 14:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$V_3\text{-}V_2$	n	pL	$\text{Log}(\frac{n-1}{2-n})$	$\text{Log } K_2$
10.00	5.60	6.47	6.55	0.08	0.9148	1.41		
10.23	5.65	6.62	6.71	0.09	1.2102	1.20	-0.5749	0.6251
10.49	5.70	6.80	6.92	0.09	1.5968	1.03	0.1703	1.2003

$\text{Log}K_2$ **(Average value)** = 0.9127± 0.4070

Table15:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	$\text{Log}(\frac{n}{1-n})$	$\text{Log}K_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4210	2.2190
8.72	5.35	6.37	6.40	0.03	0.4286	2.42	-0.1249	2.2951
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.96	0.3010	2.2610
9.51	5.55	6.66	6.70	0.04	0.7720	1.67	0.5297	2.1997

$\text{Log}K_1$ (Average value) = 2.2108± 0.0825

Table 16:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	$\text{Log}(\frac{n-1}{2-n})$	$\text{Log } K_2$
9.73	5.55	6.78	6.83	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.95	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.09		
10.49	5.70	7.10	7.16	0.06	3.1429	0.89		

$\text{Log}K_2$ **(Average value)** = 1.5453± 0.3450

Table 17:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$V_3\text{-}V_2$	n	pL	$\text{Log}(\frac{n}{n-1})$	$\text{Log } K_1$
8.50	5.30	5.81	5.86	0.05	0.3717	2.88	-0.2280	2.6520
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.06	0.06	0.4853	2.38	-0.0255	2.3545
9.22	5.45	6.10	6.16	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430
9.73	5.55	6.33	6.41	0.08	0.8000	1.69	0.6020	2.2920

$\text{Log}K_1$ **(Average value)** = 2.2516± 0.5380

Table 18:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$\mathrm{Log}(\frac{n-1}{2-n})$	Log K_2
10.00	5.60	6.47	6.57	0.10	1.1434	1.43		
10.23	5.65	6.62	6.72	0.10	1.3448	1.23	-0.2788	0.9512
10.49	5.70	6.80	6.90	0.10	1.7742	1.03	0.5351	1.5651

LogK_2 **(Average value)** = 1.2581± 0.4340

Table 19: Stepwise and overall Stability constants of thehydrolysed and unhydrolysed divalent metal (II) complexes

Chelates	**LogK_1**	**LogK_2**	**Logβ**
[Cu (Hydrolysed PSHA-1)$_2$]	2.4788	1.4280	3.9068
[Pb (Hydrolysed PSHA-1)$_2$]	2.5832	1.1963	3.7795
[Cd (Hydrolysed PSHA-1)$_2$]	2.2108	1.5453	3.7561
[Mg (Hydrolysed PSHA-1)$_2$]	2.1382	1.5453	3.6835
[Cu (Unhydrolysed PSHA-1)$_2$]	2.3059	1.2209	3.5268
[Pb (Unhydrolysed PSHA-1)$_2$]	2.2364	1.2239	3.4603
[Cd (Unhydrolysed PSHA-1)$_2$]	2.2516	1.2581	3.5097
[Mg (Unydrolysed PSHA-1)$_2$]	2.1568	0.9127	3.0695

The results obtained (Table19) shows the stepwise and overall stability constants to be not high indicating low stability of the complexes, because the solubility of most metal ions in the basic pH range is minimal due to metal hydroxide precipitation (Karimi, 2017). In general, the stepwise stability constants (K_1 and K_2) follow the order $K_1 > K_2$ for the copper, lead, magnesium and cadmium complexes respectively. The steady decrease of the values with increasing number of ligands is in agreement with the prediction made by researchers (Na'aliya, 2013). The decrease could be attributed to the fact that as the number of the ligands (Humate ions) that enters the coordination zone increases the aqua molecules available for replacement by the ligands become less. Thus, the metal ions become less electron loving with progressive intake of the ligand and this results in the decrease in the values of the constants (Na'aliya, 2013). Also the stability of the complexes is influenced by the size and number of the chelate rings(Mackay and Mackay,2002).All the complexes form rings in their structure as humate, a bidentate ligand, bond the metal ions in the ratio 1:2 (Boguta and Sokolowska, 2016) forming chelate rings. The values of the overall stability constants (logβ) obtained for humate complexes are not high indicating low stability as the values are not high. LogK values for copper-humates (Table 3 to 6) obtained in this study are lower than those reported for the complexes of humic acids (Pandey *et al*., 2015; Dinu, 2013; Kaschl *et al*., 2010 and Gilbeto and Jorg, 2001). The values of LogK(Table 7 to 10) forlead-humates are lower than those reported for the lead in the literature (Dinu, 2013; Gilbeto and Jorg 2001). Log K values(Table 11 to 14) for magnesium-humates obtained in this study are close to those reported by (Pandey *et al*., 2015). Log K values of cadmium-humates (Table 15 to 18) obtained in this work near to the one reported by (Dinu, 2013 and Pandey *et al*., 2015).The difference between the reported values and the values obtained in this study might be probably as a result of acid hydrolysis of humic acid. The values of the overall stability constants (log β) of the copper humates complexes presented in Table 19 is high than that of other metal humate complexes, show relatively high stability of Cu-HA complexes, show the following order of stability: Cu >Pb> Cd > Mg; which are in close agreement to the findings of (Dinu, 2013 and Pandey *et al*., 2015).The high stability of Cu-humate chelate could be attributed to the existence of coordinate covalent bond between the complexing agents and the Cu^{2+} ions. Since, Cu^{2+} being a metal of the transitional series with $3d^9$ electronic configurations can accept the electrons from the complexing agents. Similarly,the low stabilities of Pb,Cd and Mg - complexes could be explained by that Pb^{2+} with $6s^2$, Cd^{2+} with $4d^{10}$ and Mg^{2+} with $2p^6$ their electronic configuration has a completely filled d,p and s orbitals. Moreover, the stabilities of metal ions with hydrolysed humic acid from peat soil were higher than those with unhydrolysed humic acid from peat soil; which is ascribed to the high content of acidity in hydrolysed humic acid than unhydrolysed humic acid.

CONCLUSION

The values of logK for Cu(II) hydrolysed humic acid complex was higher followed by Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes as compared with metal(II) unhydrolysed humic acid complexes . This indicates acid hydrolysis of humic acid can enhance the complexation behavior of humic acid with metal (II) ions. However, the higher values of logβ for Cu(II), Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes indicates more stable stepwise complexes formed as compared with Cu(II), Pb(II), Cd(II) and Mg(II) unhydrolysed humic acid complexes.

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STABILITY CONSTANTS OF COMPLEXES OF METAL IONS WITH PEATSOIL HUMIC ACIDS UNDER NON-ACID-CONDITIONS

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ABSTRACT

Stability constants of complexes of four divalent metal ions viz. Cu^{2+}, Pb^{2+},Mg^{2+} and Cd^{2+} with humic acids (HA) were determined by potentiometric titration of humic acids with the corresponding salt of the divalent metals in aqueous media under non-acid-condition. The log K (logarithm of the stability constant) ranged from 1.0942 to 2.7471 for metal-humic acid complexes were determined using point-wise computational method. The order of stability constants were obtained as follows: Cu >Pb> Cd > Mg for metal -HA complexes respectively, indicating a higher degree of complexation with Cu metal ion.

Keywords: stability constant, humic acid, potentiometric titration, divalent metals, acid hydrolysis.

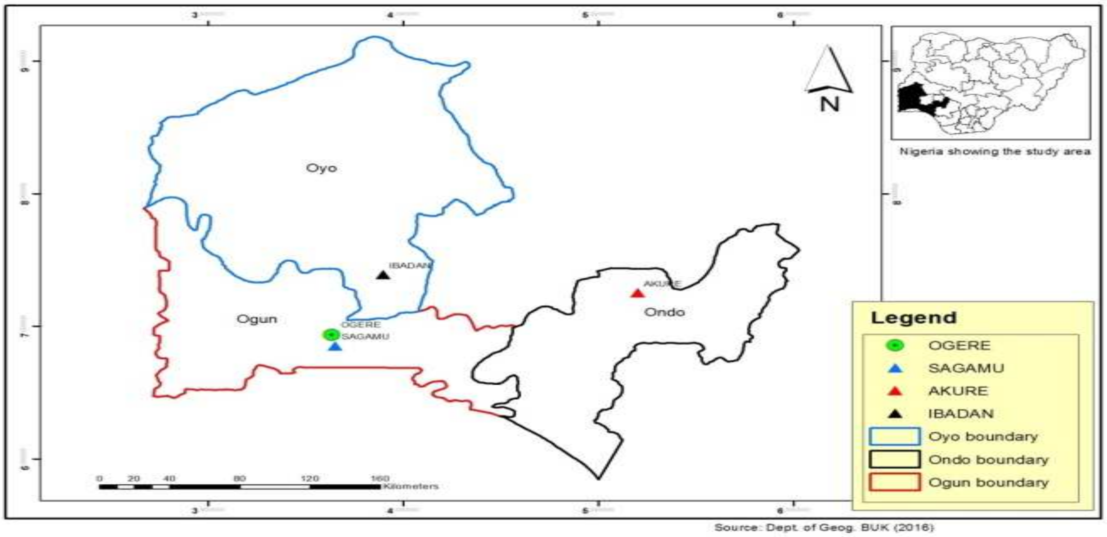
NTRODUCTION

The stability constant of a complex is the numerical expression of its stability and provides a quantitative measure of affinity of the metal ion to the complexing agent. An understanding of the relative stability of metal-complexes helps in predicting the behavior of metal ions in the soil (Ram and Raman, 1982). Extensive researches has been done to determine the stability constants of the complexes formed between humic acid (HA) with a number of metal ions. Ashok *et al*., (2000) reported that humic acid with hydroxyl, phenoxyl and carboxyl reactive groups can form coordination compound with metal ions at pH 3.5. The stability constants(Log K) for different metal-humic acid complexes indicated the following order of the stabilities of complexes formed between humic acid and metal ion, Cu >Fe >Pb> Ni > Co > Ca > Cd > Zn >Mn> Mg. Andelkovic *et al*., (2010) investigated the binding of Cd(II) to soil humic acid at pH 6.5 and in 0.1M KNO_3 ionic medium. The stability constant for binding indicating greater stability in the case when carboxyl groups are involved in complexation reaction. Kostic *et al*.,(2012) investigated the complexation of humic acid with certain heavy metal ions (Co(II), Ni(II),Cu(II), Zn(II), and Pb(II). The experiment was performed at 25°C, at pH 4.0 and ionic strength of 0.01M. Stability constant of complex between Pb(II) ions and humic acid is greater than stability constants of other investigated metal-humate complexes. Bogata and Sokolowska (2016) analyses the interaction between humic acids from different soils and Zn (II) ions at wide concentration ranges and at pH 5. Studies have showed significant impact of Zn concentration, pH and some properties of humic acids with zinc.But all of these studies were limited to acidic pH range. Therefore, the present study was carried out to determine and compare the stability constants of complexes of metal ions with hydrolysed peat soil humic acid and unhydrolysed peat soil humic under non-acid conditions.

MATERIALS AND METHODS

Analytical grade chemicals used includes hydrochloric acid (HCl), nitric acid (HNO_3), sodium hydroxide (NaOH), lead nitrate $Pb(NO_3)_2$, copper nitrate $Cu(NO_3)_2.3H_2O$, cadmium nitrate $Cd(NO_3)_2.4H_2O$, magnesium nitrate $Mg(NO_3)_2.6H_2O$, potassium nitrate (KNO_3), calcium chloride ($CaCl_2$), (sigma-Aldrich). Dowex 50WX8, (20-50 mesh) from Fluka.

Area of study



Source: Dept. of Geog. BUK (2016)

Figure 1: Map showing the sampling point at Sagamu Town, Ogun State.

Description of Sampling Area

Sagamu has geographical coordinates between 6°50′ north; 3° 38′ east is located in south western region of Nigeria. The region has tropical wet and dry climate with a lengthy wet season and relatively constant temperatures throughout the course of the year. Wet season runs from March to October, November to December forms the region dry season. The vegetation type of the region is savannah which is really grassland with small bushes and occasional big trees. Grassland soils have substantially higher organic matter content than forest soils (Novackova, 2011).

Sample Collection

The Peatsoil samples were collected from four different sampling points (0-10cm depth) in Sagamu into polyethylene bag with plastic spoons. Samples were taken to the laboratory, extraneous materials were removed; the samples were air-dried, crushed and ground to a fine powder in a mortar passed through a 0.20mm sieve. The samples were kept for analysis.

Isolation and purification of humic acid from peat soil sample

Peatsoil sample (100g) was mixed with 1000 cm^3 of 0.1M NaOH solution, shaken for 3hours and left to stand overnight. Dark-coloured supernatant was obtained and decanted from solid residue. The dark-coloured supernatant was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 6 hours. Yellowish brown supernatant and dark-brown precipitate were obtained. The yellowish brown supernatant was decanted followed by centrifuge and discarded. The dark-brown precipitate was mixed with $500cm^3$of 0.1M NaOH solution followed by passing through dowex resin. The dark-brown solution was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 3 hours. The dark-brown precipitate was washed several times with deionized water. The supernatant was treated with $AgNO_3$ solution until no white precipitate observed. The humic acid was transferred to weighed crucible and dried at 60°C in an oven for 12 hours. The humic acid was cooled and dried in the desiccator, weighed and recorded. The obtained humic acid was dried again at 60°C for additional 6 hours cooled and dried in the desiccator, weighed and recorded constant weight was obtained (Baruah *et al*., 2015).

FT-IR analysis

FT-IR spectra of humic acid sample was analysed using Carry 630 FT-IR Agilent Technologies.

Unhydrolysed compost humic acid

The unhydrolysed humic acid was obtained after isolation and purification of compost humic acid and kept for investigation.

Acid hydrolysis of Peatsoil acid

Peatsoil humic acid sample (1g) was refluxed for 12 hours at (160°C) with $50cm^3$ of 6M HCl. The mixture was allowed to cool, decanted, and centrifuged after hydrolysis. The insoluble residues were washed with distilled water via centrifugation several times, and the supernatant was treated with $AgNO_3$ solution until no white precipitate was observed. The residue was thoroughly dried over $CaCl_2$ in a desiccator at room temperature (Chefetz *et al.*, 2002). Finally, the obtained hydrolysed humic acid was kept for investigation.

Potentiometric Titrations

Potentiometric measurements were carried out using a pH-meter Jenway (model 3510) with combine electrode, the sensitivity of the pH -meter is 0.01 units. The pH meter was switched on half an hour before starting the titration for initial warm up of the instrument. The instrument was calibrated with an aqueous standard buffer solution of pH 4.00 and 10.0 (borate buffer) prepared from a "Qualigens" buffer tablets.

The following sets of solutions were prepared in a 250cm^3 volumetric flask separately for pH metric titrations.

(i) 5 cm^3 0.1 M HCl + 40 cm^3 deionized water
(ii) 5 cm^3 0.1 M HCl + 39 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid
(iii) 5 cm^3 0.1 M HCl + 37 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid + 2 cm^3 0.01 M Cu(II)

The solutions were titrated against standardized 0.110MNaOH separately. The total volume of each mixture was adjusted to 50 cm^3 and the ionic strength of the solutions was maintained constant at by adding appropriate amount of stock solution of 1M KNO$_3$ (Gamal, 2015; Omar and Ali, 2015). A magnetic stirrer was used to achieve thorough mixing of the interacting solutions at 550 rpm. The same set of experimental conditions was applied for potentiometric titration of remaining samples.

Evaluation of pKa of Hydrolysed peat soil Humic Acids

The proton-ligand formation number n$_{\mathbf{A}}$ were calculated by Irving and Rossotti expression (Omar and Ali, 2015).

$nA = Y- \frac{(V2-V1)(No-Eo)}{(Vo+V1)TcL}$ 1

Where: Y is number of dissociable proton, (V$_2$-V$_1$) is the measure of displacement of the ligand curve relative to acid curve, N^o and E^o are the resultant concentration of alkali solution, free acid solution, T$_{cL}$^{o} is the total ligand concentration, V^o is the total volume of titration solution,V$_1$ is the volume of alkali added to acid solution,V$_2$ is the volume of alkali added to acid solution + ligand solution, acid dissociation constants (pKa - values) of ligand were calculated by algebraic method point wise calculation (Tables 1). The dissociation constants (pKa) were calculated according to the following relation:

pKa = pH + log($\frac{nA}{1-nA}$) 2

Where: pKa is the acid dissociation constant, n$_A$is the Proton-ligand formation number and pH is the pH-values (Omar and Ali, 2015).

Determination of metal-ligand stability constants (log K) of complexes

The potentiometric measurement for the determination of stability constant of a complex in solution is based on the fact that the redox potential of the couple $\frac{M^{+(m-n)}}{M^{+m}}$ is shifted significantly on complexation of the metal ion with the ligand. This method involves change in hydrogen ion concentration [H$^+$] due to the displacement or association of one or more protons taking place during complexation reaction. This change can be found out by titrating the solutions containing free acid, acid with ligand, and acid with ligand and metal ion, individually against a standard alkali solution at a constant ionic strength or temperature. Either ionic strength or temperature may be varied for different sets of solutions. In all the cases, the change in the pH of the solution is measured after each addition of a known amount of alkali to the reaction cell which contains the reaction mixture. The titration curves are then drawn by plotting the measured pH values against the corresponding volume of alkali added and the stability constants of the complexes are determined from the titration curves by employing pH-metric titration technique given by (Irving and Rossoti).

Metal-ligand stability constants (Log K) were determined by using the following relations:

$$\bar{n} = \frac{(V_3 - V_2)(E^0 + N^0)}{(V^0 + V_2)\bar{n}_A T_m^0} \quad \text{...3}$$

and

$$PL = \log_{10}\{\frac{1 + \beta_n^H \frac{1}{[anti\ \log \mathrm{pH}]^n}}{\mathrm{T}_{\mathrm{L}}^0 - \bar{n} T_m^0} \mathrm{X} \frac{(V^0 + V_3)}{V^0}\} \quad \text{..4}$$

Where $T_{L,}$ T^o, E°, and V^ohavethe same significance as in equation (1) above, T_m denotes the total concentration of metal present in solution, V_3 is the volume of metal ions present in solution and β^H is the overall proton ligand stability constant. The metal-ligand stability constants (log K) were determined by employing point wise computational Method (eq. 5 and 6).

$LogK_1 = \log (\frac{n}{1-n}) + pL$ 5

$LogK_2 = \log (\frac{1-n}{2-n}) + pL$.......................6

Where: Log K is the metal-ligand stability constant, pL is the Free ligand exponent function, **n** is the Average number of ligand attached with metal ion (Janrao*et al.*, 2014).The results obtained were analyzed by an ORIGIN 2016 program using titration data and then the proton-ligand stability constants (pKa) and Metal-ligand stability constant (LogK) calculated (Omar and Ali, 2015).

RESULTS AND DISCUSSION

Fourier transformed infrared (FT-IR) spectra of isolated humic acid from peat soils Figure 2 had distinct clear absorption bands indicating the presence of major humic acid structural elemental groups such as H bonded OH ($3680cm^{-1}$ peak), C=O of carbonyl ($1721cm^{-1}$ peak), functional groups of aliphatic components CH_2 ($2918cm^{-1}$ peak) and C-O stretching of polysaccharide ($1168cm^{-1}$ peak). The positions of the absorption bands of the spectra fell within typical major absorption bands of humic acid which is at frequencies 3680, 2918, 1721, 1168 cm^{-1}. The first peak centred in the vicinity of 3680 cm^{-1} region is attributed to phenol OH group bounded by intermolecular H bonds. The $2918cm^{-1}$ band usually has absorption maximum at 2918 cm^{-1} which is due to C–H stretching of alkane group (CH_2). The next major absorption band is 1721 cm^{-1}. This band has been commonly ascribed to C=O stretching of mainly carboxyl group (COOH) with trace amount of ketones. The last peak was observed at 1168 cm^{-1} due to C–O stretching of polysaccharides and this peak appeared also in the spectra of humic acid from peat soil. The FTIR spectra of the isolated humic acid contained all major characteristic absorption peaks of humic acid. These absorption peaks indicated the presence of the major structural elements of humic acid namely H bonded OH, C=C of aromatic ring, C=O of carbonyl group (both carboxyl and ketonic), CH_2 group. This strongly supports the presence of humic acid.

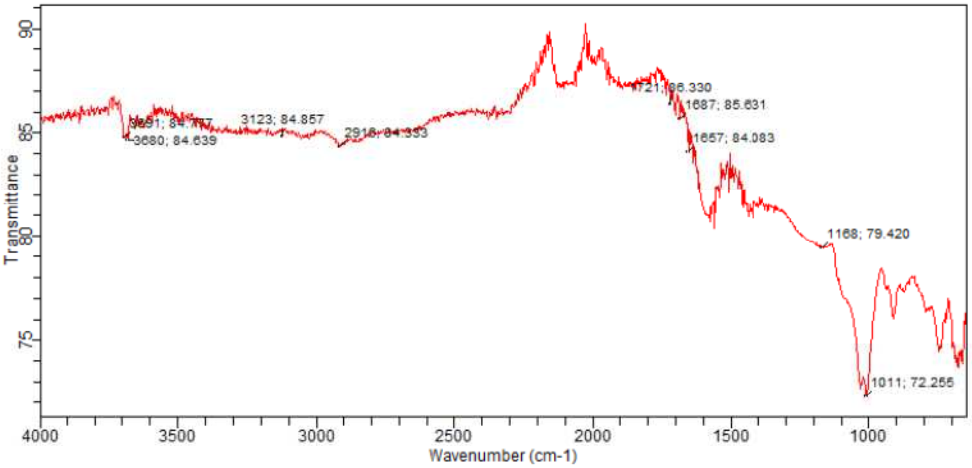


Fig. 2 : FT-IR spectraof peatsoilhumic acid (PSHA)

Evaluation of acid dissociation constant (pka) of acid hydrolysed peat soil humicacid at phenolic group

The value of the dissociation constant of the peat soil humic acid (PSHA) that underwent acidhydrolysis studied was found to be 8.9299 as shown Table 1, which is lower than the literaturevalues reported by Almeida and Szpoganics, (2015), Borges *et al.*, (2005); Badr *et al.*, (2012)and Fernandes *et al*,.(2009) of 9.73, 9.47 and 10.30. The difference between the obtained valuesand the reported values in this study might be probably as a result of acid hydrolysis of humicacid.

Table 1: PKa of (Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	V$_2$-V$_1$	nA	log($\frac{nA}{1-nA}$)	pKa
8.50	5.30	6.29	0.99	0.3594	-0.2510	8.2490
8.72	5.35	6.37	1.02	0.3400	-0.2880	8.4320
9.00	5.40	6.46	1.06	0.3141	-0.3391	8.6609
9.22	5.45	6.55	1.10	0.2882	-0.3927	8.8273
9.51	5.50	6.66	1.16	0.2494	-0.4786	9.0314
9.73	5.55	6.78	1.23	0.2041	-0.5910	9.1390
10.00	5.60	6.90	1.30	0.1589	-0.7238	9.2762
10.23	5.65	7.05	1.40	0.0941	-0.9835	9.2465
10.49	5.70	7.10	1.40	0.0941	-0.9835	9.5065

Average pKa = 8.9299 ± 0.4186

Table 2: PKa of (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	V$_2$-V$_1$	nA	Log($\frac{nA}{1-n}$)	pKa
8.50	5.30	5.81	0.51	0.6619	0.2919	8.7919
8.72	5.35	5.90	0.55	0.6357	0.2418	8.9618
9.00	5.40	6.00	0.60	0.6029	0.1813	9.1813
9.22	5.45	6.10	0.65	0.5701	0.1226	9.3426
9.51	5.50	6.20	0.70	0.5376	0.0654	9.5754
9.73	5.55	6.33	0.78	0.4851	-0.0259	9.7041
10.00	5.60	6.47	0.87	0.4262	-0.1291	9.8709
10.23	5.65	6.62	0.99	0.3609	-0.2481	9.9819
10.49	5.70	6.80	1.10	0.2759	-0.4690	10.0210

Average pKa = 9.4923± 0.4410

Metal-ligand stability constant (Log K)

The stabilityconstants require the accurate values of proton-ligand stability constants (Anil and Maroti, 2008). Metal titration curves crossed over ligand titration curve indicated the formation of complex upon proton release (Santosh, *et al.*, 2011). If the values of n- are within range 0.2-0.8 and 1.2-18 this indicates the formation of 1:1 and 1:2 complexes (Sayyed and Mazahar, 2012).

The metal (II)-humate stepwise stability constants (log k) at phenolic group (Tables 3-18)

Table 3: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	log($\frac{n}{1-n}$)	LogK$_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

LogK$_1$ (Average value) = 2.4788± 0.2203

Table 4: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	Log($\frac{n-1}{2-n}$)	LogK$_2$
9.51	5.50	6.66	6.73	0.07	1.3509	1.70	-0.2671	1.4329
9.73	5.55	6.78	6.85	0.07	1.6383	1.51	0.2467	1.7567
10.00	5.60	6.90	6.98	0.08	2.1783	1.31	-0.2158	1.0942
10.23	5.65	7.05	7.13	0.08	4.1904	1.27		
10.49	5.70	7.10	7.19	0.09	4.6920			

LogK$_2$(Average value) = 1.4280 ± 0.3312

Table 5:Point-wise method,Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	Log$(\frac{n}{n-1})$	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430

$LogK_1$ **(Average value)** = 2.3059± 0.6153

Table 6:Point-wise method, Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$V_3\text{-}V_2$	n	pL	Log$(\frac{n-1}{2-n})$	Log K_2
9.73	5.55	6.33	6.42	0.09	0.9000	1.69		
10.00	5.60	6.47	6.58	0.11	1.2578	1.44	-0.4592	0.9808
10.23	5.65	6.62	6.84	0.12	1.6137	1.26	-0.2010	1.4610
10.49	5.70	6.80	6.92	0.12	2.1052	1.03		

$LogK_2$ **(Average value)** = 1.2209± 0.3398

Table 7:Point-wise method,Pb (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	log$(\frac{n}{1-n})$	$LogK_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.60	0.05	0.8333	1.96	0.6989	2.6589

$LogK_1$ (Average value) = 2.5832 ±0.1614

Table 8:Point-wise method,Pb-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	log$(\frac{n-1}{2-n})$	$logK_2$
9.51	5.50	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.83	0.05	1.1702	1.44		
10.00	5.60	6.90	6.90	0.05	1.4864	1.22	-0.0237	1.1963
10.23	5.65	7.05	7.10	0.05	2.0190	1.09		
10.49	5.70	7.10	7.17	0.07	3.6492	1.00		

$LogK_2$(Average value) = 1.1963

Table 9:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$V_3\text{-}V_2$	n	pL	Log $(\frac{n}{n-1})$	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.5477	2.3123
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	0.0272	2.2072
9.51	5.50	6.20	6.26	0.07	0.6417	1.89	0.2530	2.1430
9.73	5.55	6.40	6.40	0.07	0.7000	1.67	0.3680	2.0380

$LogK_1$ **(Average value)** = 2.2364 ± 0.1602

Table 10:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$V_3\text{-}V_2$	n	pL	Log$(\frac{n-1}{2-n})$	Log K_2
10.00	5.60	6.47	6.55	0.08	1.9503	1.41		
10.23	5.65	6.62	6.72	0.11	1.4792	1.26	-0.0361	1.2239

$LogK_2$ **(Average value)** = 1.2239

Table 11:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	log$(\frac{n}{n-1})$	$LogK_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4290	2.2110
8.72	5.35	6.37	6.39	0.02	0.2858	2.42	-0.3978	2.0222
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

$LogK_1$ (Average value)=2.1382**±**0.1046

Table 12:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3$-$V_2)$	n	pL	$\log(\frac{n-1}{2-n})$	$LogK_2$
9.51	5.55	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.84	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.93	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.10		
10.49	5.70	7.10	7.18	0.07	3.6492	0.83		

$LogK_2$(Average value) = 1.5453 **±** 0.3450

Table 13:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$Log(\frac{n}{n-1})$	$Log\ K_1$
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.3477	2.3123
9.00	5.40	6.00	6.04	0.04	0.3236	2.38	-0.3202	2.0598
9.22	5.45	6.10	6.15	0.05	0.4297	2.17	-0.1230	2.0470
9.51	5.50	6.20	6.26	0.06	0.5500	1.89	0.0871	1.9771
9.73	5.55	6.33	6.40	0.07	0.7000	1.67	0.3680	2.0380

$LogK_1$ **(Average value)** = 2.1568 ± 0.2069

Table 14:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$Log(\frac{n-1}{2-n})$	$Log\ K_2$
10.00	5.60	6.47	6.55	0.08	0.9148	1.41		
10.23	5.65	6.62	6.71	0.09	1.2102	1.20	-0.5749	0.6251
10.49	5.70	6.80	6.92	0.09	1.5968	1.03	0.1703	1.2003

$LogK_2$ **(Average value)** = 0.9127± 0.4070

Table15:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3$-$V_2)$	n	pL	$Log(\frac{n}{1-n})$	$LogK_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4210	2.2190
8.72	5.35	6.37	6.40	0.03	0.4286	2.42	-0.1249	2.2951
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.96	0.3010	2.2610
9.51	5.55	6.66	6.70	0.04	0.7720	1.67	0.5297	2.1997

$LogK_1$ (Average value) = 2.2108± 0.0825

Table 16:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3$-$V_2)$	n	pL	$Log(\frac{n-1}{2-n})$	$Log\ K_2$
9.73	5.55	6.78	6.83	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.95	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.09		
10.49	5.70	7.10	7.16	0.06	3.1429	0.89		

$LogK_2$ **(Average value)** = 1.5453± 0.3450

Table 17:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$Log(\frac{n}{n-1})$	$Log\ K_1$
8.50	5.30	5.81	5.86	0.05	0.3717	2.88	-0.2280	2.6520
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.06	0.06	0.4853	2.38	-0.0255	2.3545
9.22	5.45	6.10	6.16	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430
9.73	5.55	6.33	6.41	0.08	0.8000	1.69	0.6020	2.2920

$LogK_1$ **(Average value)** = 2.2516± 0.5380

Table 18:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	V$_3$-V$_2$	n	pL	Log$(\frac{n-1}{2-n})$	Log K$_2$
10.00	5.60	6.47	6.57	0.10	1.1434	1.43		
10.23	5.65	6.62	6.72	0.10	1.3448	1.23	-0.2788	0.9512
10.49	5.70	6.80	6.90	0.10	1.7742	1.03	0.5351	1.5651

LogK$_2$ **(Average value)** = 1.2581± 0.4340

Table 19: Stepwise and overall Stability constants of thehydrolysed and unhydrolysed divalent metal (II) complexes

Chelates	**LogK$_1$**	**LogK$_2$**	**Logβ**
[Cu (Hydrolysed PSHA-1)$_2$]	2.4788	1.4280	3.9068
[Pb (Hydrolysed PSHA-1)$_2$]	2.5832	1.1963	3.7795
[Cd (Hydrolysed PSHA-1)$_2$]	2.2108	1.5453	3.7561
[Mg (Hydrolysed PSHA-1)$_2$]	2.1382	1.5453	3.6835
[Cu (Unhydrolysed PSHA-1)$_2$]	2.3059	1.2209	3.5268
[Pb (Unhydrolysed PSHA-1)$_2$]	2.2364	1.2239	3.4603
[Cd (Unhydrolysed PSHA-1)$_2$]	2.2516	1.2581	3.5097
[Mg (Unydrolysed PSHA-1)$_2$]	2.1568	0.9127	3.0695

The results obtained (Table19) shows the stepwise and overall stability constants to be not high indicating low stability of the complexes, because the solubility of most metal ions in the basic pH range is minimal due to metal hydroxide precipitation (Karimi, 2017). In general, the stepwise stability constants (K$_1$ and K$_2$) follow the order K$_1$> K$_2$ for the copper, lead, magnesium and cadmium complexes respectively. The steady decrease of the values with increasing number of ligands is in agreement with the prediction made by researchers (Na'aliya, 2013). The decrease could be attributed to the fact that as the number of the ligands (Humate ions) that enters the coordination zone increases the aqua molecules available for replacement by the ligands become less. Thus, the metal ions become less electron loving with progressive intake of the ligand and this results in the decrease in the values of the constants (Na'aliya, 2013). Also the stability of the complexes is influenced by the size and number of the chelate rings(Mackay and Mackay,2002).All the complexes form rings in their structure as humate, a bidentate ligand, bond the metal ions in the ratio 1:2 (Boguta and Sokolowska, 2016) forming chelate rings. The values of the overall stability constants (logβ) obtained for humate complexes are not high indicating low stability as the values are not high. LogK values for copper-humates (Table 3 to 6) obtained in this study are lower than those reported for the complexes of humic acids (Pandey *et al*., 2015; Dinu, 2013; Kaschl *et al*., 2010 and Gilbeto and Jorg, 2001). The values of LogK(Table 7 to 10) forlead-humates are lower than those reported for the lead in the literature (Dinu, 2013; Gilbeto and Jorg 2001). Log K values(Table 11 to 14) for magnesium-humates obtained in this study are close to those reported by (Pandey *et al*., 2015). Log K values of cadmium-humates (Table 15 to 18) obtained in this work near to the one reported by (Dinu, 2013 and Pandey *et al*., 2015).The difference between the reported values and the values obtained in this study might be probably as a result of acid hydrolysis of humic acid. The values of the overall stability constants (log β) of the copper humates complexes presented in Table 19 is high than that of other metal humate complexes, show relatively high stability of Cu-HA complexes, show the following order of stability: Cu >Pb> Cd > Mg; which are in close agreement to the findings of (Dinu, 2013 and Pandey *et al*., 2015).The high stability of Cu-humate chelate could be attributed to the existence of coordinate covalent bond between the complexing agents and the Cu^{2+} ions. Since, Cu^{2+} being a metal of the transitional series with 3d^9 electronic configurations can accept the electrons from the complexing agents. Similarly,the low stabilities of Pb,Cd and Mg - complexes could be explained by that Pb^{2+} with 6s^2, Cd^{2+} with 4d^{10} and Mg^{2+} with 2p^6 their electronic configuration has a completely filled d,p and s orbitals. Moreover, the stabilities of metal ions with hydrolysed humic acid from peat soil were higher than those with unhydrolysed humic acid from peat soil; which is ascribed to the high content of acidity in hydrolysed humic acid than unhydrolysed humic acid.

CONCLUSION

The values of logK for Cu(II) hydrolysed humic acid complex was higher followed by Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes as compared with metal(II) unhydrolysed humic acid complexes . This indicates acid hydrolysis of humic acid can enhance the complexation behavior of humic acid with metal (II) ions. However, the higher values of logβ for Cu(II), Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes indicates more stable stepwise complexes formed as compared with Cu(II), Pb(II), Cd(II) and Mg(II) unhydrolysed humic acid complexes.

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STABILITY CONSTANTS OF COMPLEXES OF METAL IONS WITH PEATSOIL HUMIC ACIDS UNDER NON-ACID-CONDITIONS

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ABSTRACT
Stability constants of complexes of four divalent metal ions viz. Cu^{2+}, Pb^{2+},Mg^{2+} and Cd^{2+} with humic acids (HA) were determined by potentiometric titration of humic acids with the corresponding salt of the divalent metals in aqueous media under non-acid-condition. The log K (logarithm of the stability constant) ranged from 1.0942 to 2.7471 for metal-humic acid complexes were determined using point-wise computational method. The order of stability constants were obtained as follows: Cu >Pb> Cd > Mg for metal -HA complexes respectively, indicating a higher degree of complexation with Cu metal ion.
Keywords: stability constant, humic acid, potentiometric titration, divalent metals, acid hydrolysis.

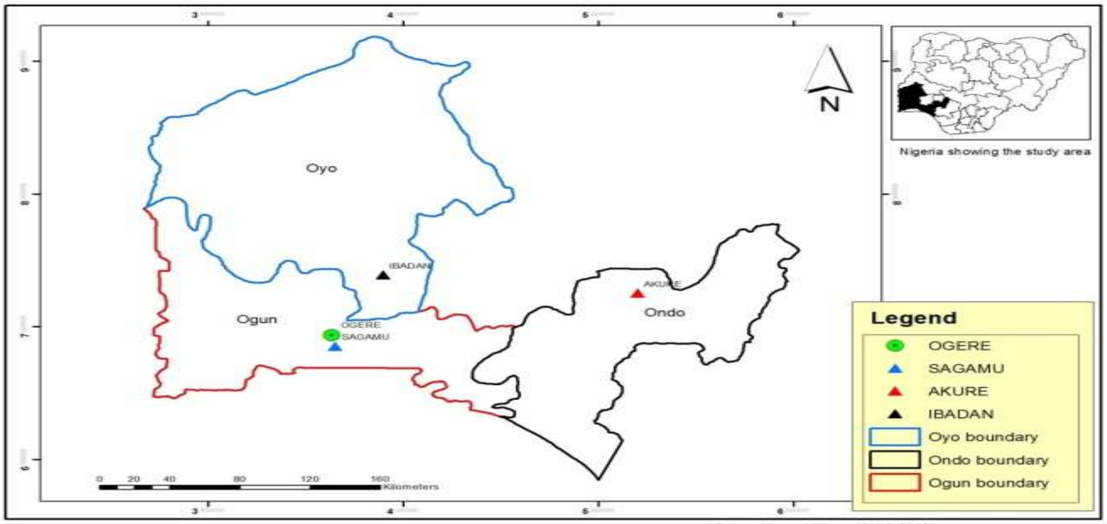
NTRODUCTION

The stability constant of a complex is the numerical expression of its stability and provides a quantitative measure of affinity of the metal ion to the complexing agent. An understanding of the relative stability of metal-complexes helps in predicting the behavior of metal ions in the soil (Ram and Raman, 1982). Extensive researches has been done to determine the stability constants of the complexes formed between humic acid (HA) with a number of metal ions. Ashok *et al*., (2000) reported that humic acid with hydroxyl, phenoxyl and carboxyl reactive groups can form coordination compound with metal ions at pH 3.5. The stability constants(Log K) for different metal-humic acid complexes indicated the following order of the stabilities of complexes formed between humic acid and metal ion, Cu >Fe >Pb> Ni > Co > Ca > Cd > Zn >Mn> Mg. Andelkovic *et al*., (2010) investigated the binding of Cd(II) to soil humic acid at pH 6.5 and in 0.1M KNO_3 ionic medium. The stability constant for binding indicating greater stability in the case when carboxyl groups are involved in complexation reaction. Kostic *et al*.,(2012) investigated the complexation of humic acid with certain heavy metal ions (Co(II), Ni(II),Cu(II), Zn(II), and Pb(II). The experiment was performed at 25°C, at pH 4.0 and ionic strength of 0.01M. Stability constant of complex between Pb(II) ions and humic acid is greater than stability constants of other investigated metal-humate complexes. Bogata and Sokolowska (2016) analyses the interaction between humic acids from different soils and Zn (II) ions at wide concentration ranges and at pH 5. Studies have showed significant impact of Zn concentration, pH and some properties of humic acids with zinc.But all of these studies were limited to acidic pH range. Therefore, the present study was carried out to determine and compare the stability constants of complexes of metal ions with hydrolysed peat soil humic acid and unhydrolysed peat soil humic under non-acid conditions.

MATERIALS AND METHODS

Analytical grade chemicals used includes hydrochloric acid (HCl), nitric acid (HNO_3), sodium hydroxide (NaOH), lead nitrate $Pb(NO_3)_2$, copper nitrate $Cu(NO_3)_2.3H_2O$, cadmium nitrate $Cd(NO_3)_2.4H_2O$, magnesium nitrate $Mg(NO_3)_2.6H_2O$, potassium nitrate (KNO_3), calcium chloride ($CaCl_2$), (sigma-Aldrich). Dowex 50WX8, (20-50 mesh) from Fluka.

Area of study



Source: Dept. of Geog. BUK (2016)

Figure 1: Map showing the sampling point at Sagamu Town, Ogun State.

Description of Sampling Area

Sagamu has geographical coordinates between 6°50′ north; 3° 38′ east is located in south western region of Nigeria. The region has tropical wet and dry climate with a lengthy wet season and relatively constant temperatures throughout the course of the year. Wet season runs from March to October, November to December forms the region dry season. The vegetation type of the region is savannah which is really grassland with small bushes and occasional big trees. Grassland soils have substantially higher organic matter content than forest soils (Novackova, 2011).

Sample Collection

The Peatsoil samples were collected from four different sampling points (0-10cm depth) in Sagamu into polyethylene bag with plastic spoons. Samples were taken to the laboratory, extraneous materials were removed; the samples were air-dried, crushed and ground to a fine powder in a mortar passed through a 0.20mm sieve. The samples were kept for analysis.

Isolation and purification of humic acid from peat soil sample

Peatsoil sample (100g) was mixed with 1000 cm^3 of 0.1M NaOH solution, shaken for 3hours and left to stand overnight. Dark-coloured supernatant was obtained and decanted from solid residue. The dark-coloured supernatant was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 6 hours. Yellowish brown supernatant and dark-brown precipitate were obtained. The yellowish brown supernatant was decanted followed by centrifuge and discarded. The dark-brown precipitate was mixed with 500$cm^3$of 0.1M NaOH solution followed by passing through dowex resin. The dark-brown solution was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 3 hours. The dark-brown precipitate was washed several times with deionized water. The supernatant was treated with $AgNO_3$ solution until no white precipitate observed. The humic acid was transferred to weighed crucible and dried at 60°C in an oven for 12 hours. The humic acid was cooled and dried in the desiccator, weighed and recorded. The obtained humic acid was dried again at 60°C for additional 6 hours cooled and dried in the desiccator, weighed and recorded constant weight was obtained (Baruah *et al.*, 2015).

FT-IR analysis

FT-IR spectra of humic acid sample was analysed using Carry 630 FT-IR Agilent Technologies.

Unhydrolysed compost humic acid

The unhydrolysed humic acid was obtained after isolation and purification of compost humic acid and kept for investigation.

Acid hydrolysis of Peatsoil acid

Peatsoil humic acid sample (1g) was refluxed for 12 hours at (160°C) with 50cm^3 of 6M HCl. The mixture was allowed to cool, decanted, and centrifuged after hydrolysis. The insoluble residues were washed with distilled water via centrifugation several times, and the supernatant was treated with $AgNO_3$ solution until no white precipitate was observed. The residue was thoroughly dried over $CaCl_2$ in a desiccator at room temperature (Chefetz *et al.*, 2002). Finally, the obtained hydrolysed humic acid was kept for investigation.

Potentiometric Titrations

Potentiometric measurements were carried out using a pH-meter Jenway (model 3510) with combine electrode, the sensitivity of the pH - meter is 0.01 units. The pH meter was switched on half an hour before starting the titration for initial warm up of the instrument. The instrument was calibrated with an aqueous standard buffer solution of pH 4.00 and 10.0 (borate buffer) prepared from a "Qualigens" buffer tablets.

The following sets of solutions were prepared in a 250cm^3 volumetric flask separately for pH metric titrations.

(i) 5 cm^3 0.1 M HCl + 40 cm^3 deionized water

(ii) 5 cm^3 0.1 M HCl + 39 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid

(iii) 5 cm^3 0.1 M HCl + 37 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid + 2 cm^3 0.01 M Cu(II)

The solutions were titrated against standardized 0.110MNaOH separately. The total volume of each mixture was adjusted to 50 cm^3 and the ionic strength of the solutions was maintained constant at by adding appropriate amount of stock solution of 1M KNO$_3$ (Gamal, 2015; Omar and Ali, 2015). A magnetic stirrer was used to achieve thorough mixing of the interacting solutions at 550 rpm. The same set of experimental conditions was applied for potentiometric titration of remaining samples.

Evaluation of pKa of Hydrolysed peat soil Humic Acids

The proton-ligand formation number n$_{\mathbf{A}}$ were calculated by Irving and Rossotti expression (Omar and Ali, 2015).

nA = Y- $\frac{(V2-V1)(No-Eo)}{(Vo+V1)TcL}$ 1

Where: Y is number of dissociable proton, (V$_2$-V$_1$) is the measure of displacement of the ligand curve relative to acid curve, N^o and E^o are the resultant concentration of alkali solution, free acid solution, T$_{cL}$^{o} is the total ligand concentration, V^o is the total volume of titration solution,V$_1$ is the volume of alkali added to acid solution,V$_2$ is the volume of alkali added to acid solution + ligand solution, acid dissociation constants (pKa - values) of ligand were calculated by algebraic method point wise calculation (Tables 1). The dissociation constants (pKa) were calculated according to the following relation:

pKa = pH + log($\frac{nA}{1-nA}$) 2

Where: pKa is the acid dissociation constant, n$_A$is the Proton-ligand formation number and pH is the pH-values (Omar and Ali, 2015).

Determination of metal-ligand stability constants (log K) of complexes

The potentiometric measurement for the determination of stability constant of a complex in solution is based on the fact that the redox potential of the couple $\frac{M^{+(m-n)}}{M^{+m}}$ is shifted significantly on complexation of the metal ion with the ligand. This method involves change in hydrogen ion concentration [H$^+$] due to the displacement or association of one or more protons taking place during complexation reaction. This change can be found out by titrating the solutions containing free acid, acid with ligand, and acid with ligand and metal ion, individually against a standard alkali solution at a constant ionic strength or temperature. Either ionic strength or temperature may be varied for different sets of solutions. In all the cases, the change in the pH of the solution is measured after each addition of a known amount of alkali to the reaction cell which contains the reaction mixture. The titration curves are then drawn by plotting the measured pH values against the corresponding volume of alkali added and the stability constants of the complexes are determined from the titration curves by employing pH-metric titration technique given by (Irving and Rossoti).

Metal-ligand stability constants (Log K) were determined by using the following relations:

$$\bar{n} = \frac{(V_3 - V_2)(E^0 + N^0)}{(V^0 + V_2)\bar{n}_A T_m^0}$$ 3

and

$$PL = \log_{10}\{\frac{1 + \beta_n^H \frac{1}{[anti\ \log pH]^n}}{T_L^0 - \bar{n}T_m^0} X \frac{(V^0 + V_3)}{V^0}\}$$ 4

Where $T_{L,}$ T^{o}, E°, and V^{o}havethe same significance as in equation (1) above, T_m denotes the total concentration of metal present in solution, V_3 is the volume of metal ions present in solution and β^H is the overall proton ligand stability constant. The metal-ligand stability constants (log K) were determined by employing point wise computational Method (eq. 5 and 6).

$$\mathrm{Log}K_1 = \log\left(\frac{n}{1-n}\right) + pL \qquad \ldots\ldots\ldots\ldots.5$$

$$\mathrm{Log}K_2 = \log\left(\frac{1-n}{2-n}\right) + pL\ldots\ldots\ldots\ldots\ldots\ldots\ldots.6$$

Where: Log K is the metal-ligand stability constant, pL is the Free ligand exponent function, **n** is the Average number of ligand attached with metal ion (Janrao*et al.*, 2014).The results obtained were analyzed by an ORIGIN 2016 program using titration data and then the proton-ligand stability constants (pKa) and Metal-ligand stability constant (LogK) calculated (Omar and Ali, 2015).

RESULTS AND DISCUSSION

Fourier transformed infrared (FT-IR) spectra of isolated humic acid from peat soils Figure 2 had distinct clear absorption bands indicating the presence of major humic acid structural elemental groups such as H bonded OH ($3680cm^{-1}$ peak), C=O of carbonyl ($1721cm^{-1}$ peak), functional groups of aliphatic components CH_2 ($2918cm^{-1}$ peak) and C-O stretching of polysaccharide ($1168cm^{-1}$ peak). The positions of the absorption bands of the spectra fell within typical major absorption bands of humic acid which is at frequencies 3680, 2918, 1721, 1168 cm^{-1}. The first peak centred in the vicinity of 3680 cm^{-1} region is attributed to phenol OH group bounded by intermolecular H bonds. The $2918cm^{-1}$ band usually has absorption maximum at 2918 cm^{-1} which is due to C–H stretching of alkane group (CH_2). The next major absorption band is 1721 cm^{-1}. This band has been commonly ascribed to C=O stretching of mainly carboxyl group (COOH) with trace amount of ketones. The last peak was observed at 1168 cm^{-1} due to C–O stretching of polysaccharides and this peak appeared also in the spectra of humic acid from peat soil. The FTIR spectra of the isolated humic acid contained all major characteristic absorption peaks of humic acid. These absorption peaks indicated the presence of the major structural elements of humic acid namely H bonded OH, C=C of aromatic ring, C=O of carbonyl group (both carboxyl and ketonic), CH_2 group. This strongly supports the presence of humic acid.

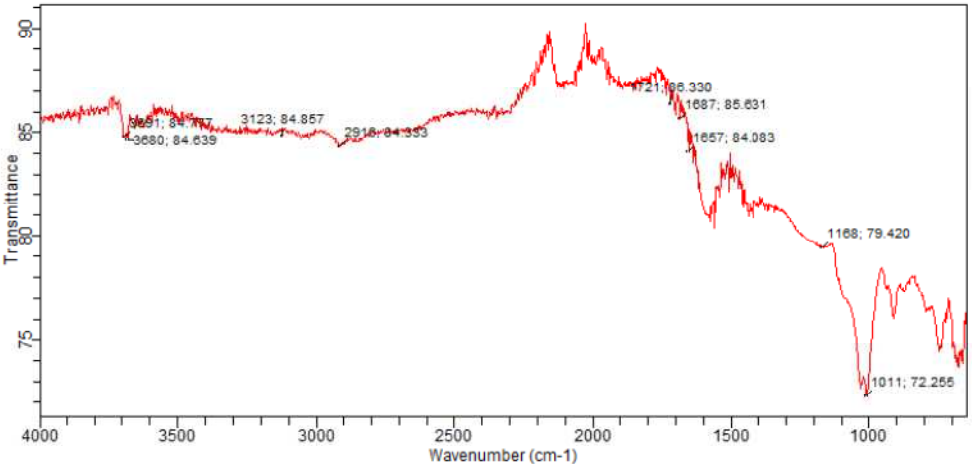


Fig. 2 : FT-IR spectraof peatsoilhumic acid (PSHA)

Evaluation of acid dissociation constant (pka) of acid hydrolysed peat soil humicacid at phenolic group

The value of the dissociation constant of the peat soil humic acid (PSHA) that underwent acidhydrolysis studied was found to be 8.9299 as shown Table 1, which is lower than the literaturevalues reported by Almeida and Szpoganics, (2015), Borges *et al.*, (2005); Badr *et al.*, (2012)and Fernandes *et al*,.(2009) of 9.73, 9.47 and 10.30. The difference between the obtained valuesand the reported values in this study might be probably as a result of acid hydrolysis of humicacid.

Table 1: PKa of (Hydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	log($\frac{nA}{1-nA}$)	pKa
8.50	5.30	6.29	0.99	0.3594	-0.2510	8.2490
8.72	5.35	6.37	1.02	0.3400	-0.2880	8.4320
9.00	5.40	6.46	1.06	0.3141	-0.3391	8.6609
9.22	5.45	6.55	1.10	0.2882	-0.3927	8.8273
9.51	5.50	6.66	1.16	0.2494	-0.4786	9.0314
9.73	5.55	6.78	1.23	0.2041	-0.5910	9.1390
10.00	5.60	6.90	1.30	0.1589	-0.7238	9.2762
10.23	5.65	7.05	1.40	0.0941	-0.9835	9.2465
10.49	5.70	7.10	1.40	0.0941	-0.9835	9.5065

Average pKa = 8.9299 ± 0.4186

Table 2: PKa of (Unhydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	Log($\frac{nA}{1-n}$)	pKa
8.50	5.30	5.81	0.51	0.6619	0.2919	8.7919
8.72	5.35	5.90	0.55	0.6357	0.2418	8.9618
9.00	5.40	6.00	0.60	0.6029	0.1813	9.1813
9.22	5.45	6.10	0.65	0.5701	0.1226	9.3426
9.51	5.50	6.20	0.70	0.5376	0.0654	9.5754
9.73	5.55	6.33	0.78	0.4851	-0.0259	9.7041
10.00	5.60	6.47	0.87	0.4262	-0.1291	9.8709
10.23	5.65	6.62	0.99	0.3609	-0.2481	9.9819
10.49	5.70	6.80	1.10	0.2759	-0.4690	10.0210

Average pKa = 9.4923± 0.4410

Metal-ligand stability constant (Log K)

The stabilityconstants require the accurate values of proton-ligand stability constants (Anil and Maroti, 2008). Metal titration curves crossed over ligand titration curve indicated the formation of complex upon proton release (Santosh, *et al.*, 2011). If the values of n- are within range 0.2-0.8 and 1.2-18 this indicates the formation of 1:1 and 1:2 complexes (Sayyed and Mazahar, 2012).

The metal (II)-humate stepwise stability constants (log k) at phenolic group (Tables 3-18)

Table 3: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n}{1-n}$)	$LogK_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

$LogK_1$ (Average value) = 2.4788± 0.2203

Table 4: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	Log($\frac{n-1}{2-n}$)	$LogK_2$
9.51	5.50	6.66	6.73	0.07	1.3509	1.70	-0.2671	1.4329
9.73	5.55	6.78	6.85	0.07	1.6383	1.51	0.2467	1.7567
10.00	5.60	6.90	6.98	0.08	2.1783	1.31	-0.2158	1.0942
10.23	5.65	7.05	7.13	0.08	4.1904	1.27		
10.49	5.70	7.10	7.19	0.09	4.6920			

$LogK_2$(Average value) = 1.4280 ± 0.3312

Table 5:Point-wise method,Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	$\text{Log}(\frac{n}{n-1})$	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430

$\text{Log}K_1$ **(Average value)** = 2.3059± 0.6153

Table 6:Point-wise method, Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$V_3\text{-}V_2$	n	pL	$\text{Log}(\frac{n-1}{2-n})$	Log K_2
9.73	5.55	6.33	6.42	0.09	0.9000	1.69		
10.00	5.60	6.47	6.58	0.11	1.2578	1.44	-0.4592	0.9808
10.23	5.65	6.62	6.84	0.12	1.6137	1.26	-0.2010	1.4610
10.49	5.70	6.80	6.92	0.12	2.1052	1.03		

$\text{Log}K_2$ **(Average value)** = 1.2209± 0.3398

Table 7:Point-wise method,Pb (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	$\log(\frac{n}{1-n})$	$\text{Log}K_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.60	0.05	0.8333	1.96	0.6989	2.6589

$\text{Log}K_1$ (Average value) = 2.5832 ±0.1614

Table 8:Point-wise method,Pb-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	$\log(\frac{n-1}{2-n})$	$\log K_2$
9.51	5.50	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.83	0.05	1.1702	1.44		
10.00	5.60	6.90	6.90	0.05	1.4864	1.22	-0.0237	1.1963
10.23	5.65	7.05	7.10	0.05	2.0190	1.09		
10.49	5.70	7.10	7.17	0.07	3.6492	1.00		

$\text{Log}K_2$(Average value) = 1.1963

Table 9:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$V_3\text{-}V_2$	n	pL	Log $(\frac{n}{n-1})$	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.5477	2.3123
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	0.0272	2.2072
9.51	5.50	6.20	6.26	0.07	0.6417	1.89	0.2530	2.1430
9.73	5.55	6.40	6.40	0.07	0.7000	1.67	0.3680	2.0380

$\text{Log}K_1$ **(Average value)** = 2.2364 ± 0.1602

Table 10:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$V_3\text{-}V_2$	n	pL	$\text{Log}(\frac{n-1}{2-n})$	Log K_2
10.00	5.60	6.47	6.55	0.08	1.9503	1.41		
10.23	5.65	6.62	6.72	0.11	1.4792	1.26	-0.0361	1.2239

$\text{Log}K_2$ **(Average value)** = 1.2239

Table 11:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	$\log(\frac{n}{n-1})$	$\text{Log}K_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4290	2.2110
8.72	5.35	6.37	6.39	0.02	0.2858	2.42	-0.3978	2.0222
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

$\text{Log}K_1$ (Average value)=2.1382**±**0.1046

Table 12:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$\log(\frac{n-1}{2-n})$	$LogK_2$
9.51	5.55	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.84	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.93	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.10		
10.49	5.70	7.10	7.18	0.07	3.6492	0.83		

$LogK_2$(Average value) = 1.5453 **±** 0.3450

Table 13:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$Log(\frac{n}{n-1})$	$Log K_1$
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.3477	2.3123
9.00	5.40	6.00	6.04	0.04	0.3236	2.38	-0.3202	2.0598
9.22	5.45	6.10	6.15	0.05	0.4297	2.17	-0.1230	2.0470
9.51	5.50	6.20	6.26	0.06	0.5500	1.89	0.0871	1.9771
9.73	5.55	6.33	6.40	0.07	0.7000	1.67	0.3680	2.0380

$LogK_1$ **(Average value)** = 2.1568 ± 0.2069

Table 14:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$Log(\frac{n-1}{2-n})$	$Log K_2$
10.00	5.60	6.47	6.55	0.08	0.9148	1.41		
10.23	5.65	6.62	6.71	0.09	1.2102	1.20	-0.5749	0.6251
10.49	5.70	6.80	6.92	0.09	1.5968	1.03	0.1703	1.2003

$LogK_2$ **(Average value)** = 0.9127± 0.4070

Table15:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$Log(\frac{n}{1-n})$	$LogK_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4210	2.2190
8.72	5.35	6.37	6.40	0.03	0.4286	2.42	-0.1249	2.2951
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.96	0.3010	2.2610
9.51	5.55	6.66	6.70	0.04	0.7720	1.67	0.5297	2.1997

$LogK_1$ (Average value) = 2.2108± 0.0825

Table 16:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$Log(\frac{n-1}{2-n})$	$Log K_2$
9.73	5.55	6.78	6.83	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.95	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.09		
10.49	5.70	7.10	7.16	0.06	3.1429	0.89		

$LogK_2$ **(Average value)** = 1.5453± 0.3450

Table 17:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$Log(\frac{n}{n-1})$	$Log K_1$
8.50	5.30	5.81	5.86	0.05	0.3717	2.88	-0.2280	2.6520
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.06	0.06	0.4853	2.38	-0.0255	2.3545
9.22	5.45	6.10	6.16	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430
9.73	5.55	6.33	6.41	0.08	0.8000	1.69	0.6020	2.2920

$LogK_1$ **(Average value)** = 2.2516± 0.5380

Table 18:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$\mathrm{Log}(\frac{n-1}{2-n})$	Log K_2
10.00	5.60	6.47	6.57	0.10	1.1434	1.43		
10.23	5.65	6.62	6.72	0.10	1.3448	1.23	-0.2788	0.9512
10.49	5.70	6.80	6.90	0.10	1.7742	1.03	0.5351	1.5651

LogK_2 **(Average value)** = 1.2581± 0.4340

Table 19: Stepwise and overall Stability constants of thehydrolysed and unhydrolysed divalent metal (II) complexes

Chelates	**LogK_1**	**LogK_2**	**Logβ**
[Cu (Hydrolysed PSHA-1)$_2$]	2.4788	1.4280	3.9068
[Pb (Hydrolysed PSHA-1)$_2$]	2.5832	1.1963	3.7795
[Cd (Hydrolysed PSHA-1)$_2$]	2.2108	1.5453	3.7561
[Mg (Hydrolysed PSHA-1)$_2$]	2.1382	1.5453	3.6835
[Cu (Unhydrolysed PSHA-1)$_2$]	2.3059	1.2209	3.5268
[Pb (Unhydrolysed PSHA-1)$_2$]	2.2364	1.2239	3.4603
[Cd (Unhydrolysed PSHA-1)$_2$]	2.2516	1.2581	3.5097
[Mg (Unydrolysed PSHA-1)$_2$]	2.1568	0.9127	3.0695

The results obtained (Table19) shows the stepwise and overall stability constants to be not high indicating low stability of the complexes, because the solubility of most metal ions in the basic pH range is minimal due to metal hydroxide precipitation (Karimi, 2017). In general, the stepwise stability constants (K_1 and K_2) follow the order $K_1 > K_2$ for the copper, lead, magnesium and cadmium complexes respectively. The steady decrease of the values with increasing number of ligands is in agreement with the prediction made by researchers (Na'aliya, 2013). The decrease could be attributed to the fact that as the number of the ligands (Humate ions) that enters the coordination zone increases the aqua molecules available for replacement by the ligands become less. Thus, the metal ions become less electron loving with progressive intake of the ligand and this results in the decrease in the values of the constants (Na'aliya, 2013). Also the stability of the complexes is influenced by the size and number of the chelate rings(Mackay and Mackay,2002).All the complexes form rings in their structure as humate, a bidentate ligand, bond the metal ions in the ratio 1:2 (Boguta and Sokolowska, 2016) forming chelate rings. The values of the overall stability constants (logβ) obtained for humate complexes are not high indicating low stability as the values are not high. LogK values for copper-humates (Table 3 to 6) obtained in this study are lower than those reported for the complexes of humic acids (Pandey *et al*., 2015; Dinu, 2013; Kaschl *et al*., 2010 and Gilbeto and Jorg, 2001). The values of LogK(Table 7 to 10) forlead-humates are lower than those reported for the lead in the literature (Dinu, 2013; Gilbeto and Jorg 2001). Log K values(Table 11 to 14) for magnesium-humates obtained in this study are close to those reported by (Pandey *et al*., 2015). Log K values of cadmium-humates (Table 15 to 18) obtained in this work near to the one reported by (Dinu, 2013 and Pandey *et al*., 2015).The difference between the reported values and the values obtained in this study might be probably as a result of acid hydrolysis of humic acid. The values of the overall stability constants (log β) of the copper humates complexes presented in Table 19 is high than that of other metal humate complexes, show relatively high stability of Cu-HA complexes, show the following order of stability: Cu >Pb> Cd > Mg; which are in close agreement to the findings of (Dinu, 2013 and Pandey *et al*., 2015).The high stability of Cu-humate chelate could be attributed to the existence of coordinate covalent bond between the complexing agents and the Cu^{2+} ions. Since, Cu^{2+} being a metal of the transitional series with $3d^9$ electronic configurations can accept the electrons from the complexing agents. Similarly,the low stabilities of Pb,Cd and Mg -complexes could be explained by that Pb^{2+} with $6s^2$, Cd^{2+} with $4d^{10}$ and Mg^{2+} with $2p^6$ their electronic configuration has a completely filled d,p and s orbitals. Moreover, the stabilities of metal ions with hydrolysed humic acid from peat soil were higher than those with unhydrolysed humic acid from peat soil; which is ascribed to the high content of acidity in hydrolysed humic acid than unhydrolysed humic acid.

CONCLUSION

The values of logK for Cu(II) hydrolysed humic acid complex was higher followed by Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes as compared with metal(II) unhydrolysed humic acid complexes . This indicates acid hydrolysis of humic acid can enhance the complexation behavior of humic acid with metal (II) ions. However, the higher values of logβ for Cu(II), Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes indicates more stable stepwise complexes formed as compared with Cu(II), Pb(II), Cd(II) and Mg(II) unhydrolysed humic acid complexes.

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STABILITY CONSTANTS OF COMPLEXES OF METAL IONS WITH PEATSOIL HUMIC ACIDS UNDER NON-ACID-CONDITIONS

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ABSTRACT

Stability constants of complexes of four divalent metal ions viz. Cu^{2+}, Pb^{2+},Mg^{2+} and Cd^{2+} with humic acids (HA) were determined by potentiometric titration of humic acids with the corresponding salt of the divalent metals in aqueous media under non-acid-condition. The log K (logarithm of the stability constant) ranged from 1.0942 to 2.7471 for metal-humic acid complexes were determined using point-wise computational method. The order of stability constants were obtained as follows: Cu >Pb> Cd > Mg for metal -HA complexes respectively, indicating a higher degree of complexation with Cu metal ion.

Keywords: stability constant, humic acid, potentiometric titration, divalent metals, acid hydrolysis.

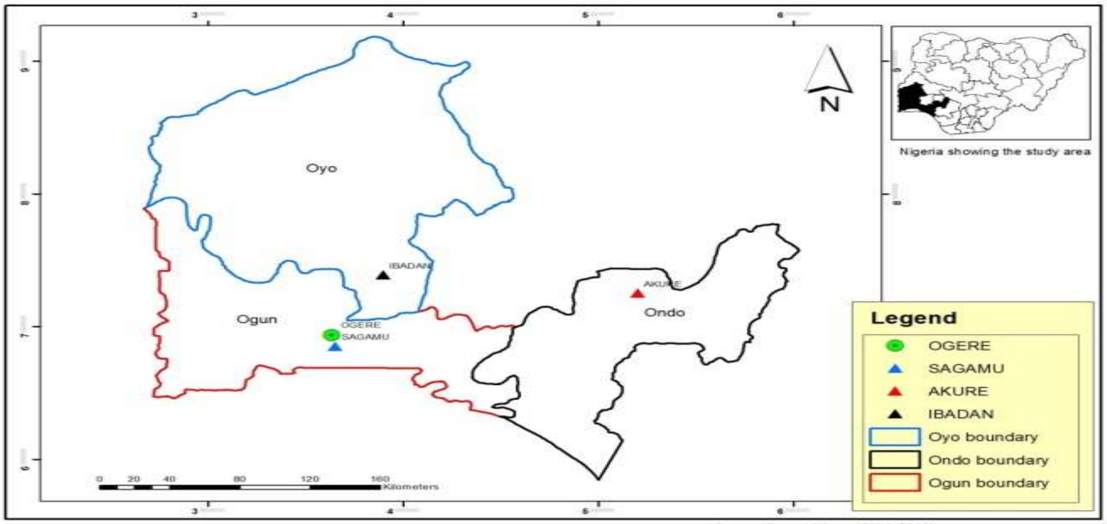
NTRODUCTION

The stability constant of a complex is the numerical expression of its stability and provides a quantitative measure of affinity of the metal ion to the complexing agent. An understanding of the relative stability of metal-complexes helps in predicting the behavior of metal ions in the soil (Ram and Raman, 1982). Extensive researches has been done to determine the stability constants of the complexes formed between humic acid (HA) with a number of metal ions. Ashok *et al.*, (2000) reported that humic acid with hydroxyl, phenoxyl and carboxyl reactive groups can form coordination compound with metal ions at pH 3.5. The stability constants(Log K) for different metal-humic acid complexes indicated the following order of the stabilities of complexes formed between humic acid and metal ion, Cu >Fe >Pb> Ni > Co > Ca > Cd > Zn >Mn> Mg. Andelkovic *et al.*, (2010) investigated the binding of Cd(II) to soil humic acid at pH 6.5 and in 0.1M KNO_3 ionic medium. The stability constant for binding indicating greater stability in the case when carboxyl groups are involved in complexation reaction. Kostic *et al.*,(2012) investigated the complexation of humic acid with certain heavy metal ions (Co(II), Ni(II),Cu(II), Zn(II), and Pb(II). The experiment was performed at 25°C, at pH 4.0 and ionic strength of 0.01M. Stability constant of complex between Pb(II) ions and humic acid is greater than stability constants of other investigated metal-humate complexes. Bogata and Sokolowska (2016) analyses the interaction between humic acids from different soils and Zn (II) ions at wide concentration ranges and at pH 5. Studies have showed significant impact of Zn concentration, pH and some properties of humic acids with zinc.But all of these studies were limited to acidic pH range. Therefore, the present study was carried out to determine and compare the stability constants of complexes of metal ions with hydrolysed peat soil humic acid and unhydrolysed peat soil humic under non-acid conditions.

MATERIALS AND METHODS

Analytical grade chemicals used includes hydrochloric acid (HCl), nitric acid (HNO_3), sodium hydroxide (NaOH), lead nitrate $Pb(NO_3)_2$, copper nitrate $Cu(NO_3)_2.3H_2O$, cadmium nitrate $Cd(NO_3)_2.4H_2O$, magnesium nitrate $Mg(NO_3)_2.6H_2O$, potassium nitrate (KNO_3), calcium chloride ($CaCl_2$), (sigma-Aldrich). Dowex 50WX8, (20-50 mesh) from Fluka.

Area of study



Source: Dept. of Geog. BUK (2016)

Figure 1: Map showing the sampling point at Sagamu Town, Ogun State.

Description of Sampling Area

Sagamu has geographical coordinates between 6°50′ north; 3° 38′ east is located in south western region of Nigeria. The region has tropical wet and dry climate with a lengthy wet season and relatively constant temperatures throughout the course of the year. Wet season runs from March to October, November to December forms the region dry season. The vegetation type of the region is savannah which is really grassland with small bushes and occasional big trees. Grassland soils have substantially higher organic matter content than forest soils (Novackova, 2011).

Sample Collection

The Peatsoil samples were collected from four different sampling points (0-10cm depth) in Sagamu into polyethylene bag with plastic spoons. Samples were taken to the laboratory, extraneous materials were removed; the samples were air-dried, crushed and ground to a fine powder in a mortar passed through a 0.20mm sieve. The samples were kept for analysis.

Isolation and purification of humic acid from peat soil sample

Peatsoil sample (100g) was mixed with 1000 cm^3 of 0.1M NaOH solution, shaken for 3hours and left to stand overnight. Dark-coloured supernatant was obtained and decanted from solid residue. The dark-coloured supernatant was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 6 hours. Yellowish brown supernatant and dark-brown precipitate were obtained. The yellowish brown supernatant was decanted followed by centrifuge and discarded. The dark-brown precipitate was mixed with $500cm^3$of 0.1M NaOH solution followed by passing through dowex resin. The dark-brown solution was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 3 hours. The dark-brown precipitate was washed several times with deionized water. The supernatant was treated with $AgNO_3$ solution until no white precipitate observed. The humic acid was transferred to weighed crucible and dried at 60^oC in an oven for 12 hours. The humic acid was cooled and dried in the desiccator, weighed and recorded. The obtained humic acid was dried again at 60^oC for additional 6 hours cooled and dried in the desiccator, weighed and recorded constant weight was obtained (Baruah *et al*., 2015).

FT-IR analysis

FT-IR spectra of humic acid sample was analysed using Carry 630 FT-IR Agilent Technologies.

Unhydrolysed compost humic acid

The unhydrolysed humic acid was obtained after isolation and purification of compost humic acid and kept for investigation.

Acid hydrolysis of Peatsoil acid

Peatsoil humic acid sample (1g) was refluxed for 12 hours at (160^oC) with $50cm^3$ of 6M HCl. The mixture was allowed to cool, decanted, and centrifuged after hydrolysis. The insoluble residues were washed with distilled water via centrifugation several times, and the supernatant was treated with $AgNO_3$ solution until no white precipitate was observed. The residue was thoroughly dried over $CaCl_2$ in a desiccator at room temperature (Chefetz *et al*., 2002). Finally, the obtained hydrolysed humic acid was kept for investigation.

Potentiometric Titrations

Potentiometric measurements were carried out using a pH-meter Jenway (model 3510) with combine electrode, the sensitivity of the pH - meter is 0.01 units. The pH meter was switched on half an hour before starting the titration for initial warm up of the instrument. The instrument was calibrated with an aqueous standard buffer solution of pH 4.00 and 10.0 (borate buffer) prepared from a "Qualigens" buffer tablets.

The following sets of solutions were prepared in a 250cm^3 volumetric flask separately for pH metric titrations.

(i) 5 cm^3 0.1 M HCl + 40 cm^3 deionized water

(ii) 5 cm^3 0.1 M HCl + 39 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid

(iii) 5 cm^3 0.1 M HCl + 37 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid + 2 cm^3 0.01 M Cu(II)

The solutions were titrated against standardized 0.110MNaOH separately. The total volume of each mixture was adjusted to 50 cm^3 and the ionic strength of the solutions was maintained constant at by adding appropriate amount of stock solution of 1M KNO_3 (Gamal, 2015; Omar and Ali, 2015). A magnetic stirrer was used to achieve thorough mixing of the interacting solutions at 550 rpm. The same set of experimental conditions was applied for potentiometric titration of remaining samples.

Evaluation of pKa of Hydrolysed peat soil Humic Acids

The proton-ligand formation number n$_{\mathbf{A}}$ were calculated by Irving and Rossotti expression (Omar and Ali, 2015).

$$nA = Y- \frac{(V2-V1)(No-Eo)}{(Vo+V1)TcL} \quad \text{.....................................}1$$

Where: Y is number of dissociable proton, (V_2-V_1) is the measure of displacement of the ligand curve relative to acid curve, N^o and E^o are the resultant concentration of alkali solution, free acid solution, $T_{cL}{}^o$ is the total ligand concentration, V^o is the total volume of titration solution,V_1 is the volume of alkali added to acid solution,V_2 is the volume of alkali added to acid solution + ligand solution, acid dissociation constants (pKa - values) of ligand were calculated by algebraic method point wise calculation (Tables 1). The dissociation constants (pKa) were calculated according to the following relation:

$$pKa = pH + \log\left(\frac{nA}{1-nA}\right) \quad \text{..............................}2$$

Where: pKa is the acid dissociation constant, $n_A$is the Proton-ligand formation number and pH is the pH-values (Omar and Ali, 2015).

Determination of metal-ligand stability constants (log K) of complexes

The potentiometric measurement for the determination of stability constant of a complex in solution is based on the fact that the redox potential of the couple $\frac{M^{+(m-n)}}{M^{+m}}$ is shifted significantly on complexation of the metal ion with the ligand. This method involves change in hydrogen ion concentration [H$^+$] due to the displacement or association of one or more protons taking place during complexation reaction. This change can be found out by titrating the solutions containing free acid, acid with ligand, and acid with ligand and metal ion, individually against a standard alkali solution at a constant ionic strength or temperature. Either ionic strength or temperature may be varied for different sets of solutions. In all the cases, the change in the pH of the solution is measured after each addition of a known amount of alkali to the reaction cell which contains the reaction mixture. The titration curves are then drawn by plotting the measured pH values against the corresponding volume of alkali added and the stability constants of the complexes are determined from the titration curves by employing pH-metric titration technique given by (Irving and Rossoti).

Metal-ligand stability constants (Log K) were determined by using the following relations:

$$\bar{n} = \frac{(V_3 - V_2)(E^0 + N^0)}{(V^0 + V_2)\bar{n}_A T_m^0} \quad \text{...}3$$

and

$$PL = \log_{10}\{\frac{1 + \beta_n^H \frac{1}{[anti\ \log pH]^n}}{T_L^0 - \bar{n}T_m^0} X \frac{(V^0 + V_3)}{V^0}\} \quad \text{..}4$$

Where $T_{L,}$ T^{o}, E°, and V^{o}havethe same significance as in equation (1) above, T_m denotes the total concentration of metal present in solution, V_3 is the volume of metal ions present in solution and β^{H} is the overall proton ligand stability constant. The metal-ligand stability constants (log K) were determined by employing point wise computational Method (eq. 5 and 6).

$\text{LogK}_1 = \log\left(\frac{n}{1-n}\right) + \text{pL}$ …………..5

$\text{LogK}_2 = \log\left(\frac{1-n}{2-n}\right) + \text{pL}$……………………6

Where: Log K is the metal-ligand stability constant, pL is the Free ligand exponent function, **n** is the Average number of ligand attached with metal ion (Janrao*et al.*, 2014).The results obtained were analyzed by an ORIGIN 2016 program using titration data and then the proton-ligand stability constants (pKa) and Metal-ligand stability constant (LogK) calculated (Omar and Ali, 2015).

RESULTS AND DISCUSSION

Fourier transformed infrared (FT-IR) spectra of isolated humic acid from peat soils Figure 2 had distinct clear absorption bands indicating the presence of major humic acid structural elemental groups such as H bonded OH ($3680cm^{-1}$ peak), C=O of carbonyl ($1721cm^{-1}$ peak), functional groups of aliphatic components CH_2 ($2918cm^{-1}$ peak) and C-O stretching of polysaccharide ($1168cm^{-1}$ peak). The positions of the absorption bands of the spectra fell within typical major absorption bands of humic acid which is at frequencies 3680, 2918, 1721, 1168 cm^{-1}. The first peak centred in the vicinity of 3680 cm^{-1} region is attributed to phenol OH group bounded by intermolecular H bonds. The $2918cm^{-1}$ band usually has absorption maximum at 2918 cm^{-1} which is due to C–H stretching of alkane group (CH_2). The next major absorption band is 1721 cm^{-1}. This band has been commonly ascribed to C=O stretching of mainly carboxyl group (COOH) with trace amount of ketones. The last peak was observed at 1168 cm^{-1} due to C–O stretching of polysaccharides and this peak appeared also in the spectra of humic acid from peat soil. The FTIR spectra of the isolated humic acid contained all major characteristic absorption peaks of humic acid. These absorption peaks indicated the presence of the major structural elements of humic acid namely H bonded OH, C=C of aromatic ring, C=O of carbonyl group (both carboxyl and ketonic), CH_2 group. This strongly supports the presence of humic acid.

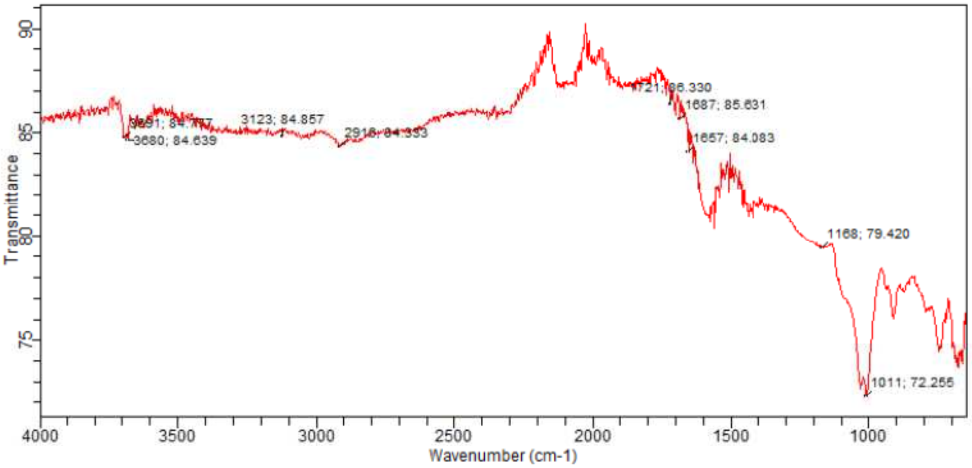


Fig. 2 : FT-IR spectraof peatsoilhumic acid (PSHA)

Evaluation of acid dissociation constant (pka) of acid hydrolysed peat soil humicacid at phenolic group

The value of the dissociation constant of the peat soil humic acid (PSHA) that underwent acidhydrolysis studied was found to be 8.9299 as shown Table 1, which is lower than the literaturevalues reported by Almeida and Szpoganics, (2015), Borges *et al.*, (2005); Badr *et al.*, (2012)and Fernandes *et al*,.(2009) of 9.73, 9.47 and 10.30. The difference between the obtained valuesand the reported values in this study might be probably as a result of acid hydrolysis of humicacid.

Table 1: PKa of (Hydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	$\log(\frac{nA}{1-nA})$	pKa
8.50	5.30	6.29	0.99	0.3594	-0.2510	8.2490
8.72	5.35	6.37	1.02	0.3400	-0.2880	8.4320
9.00	5.40	6.46	1.06	0.3141	-0.3391	8.6609
9.22	5.45	6.55	1.10	0.2882	-0.3927	8.8273
9.51	5.50	6.66	1.16	0.2494	-0.4786	9.0314
9.73	5.55	6.78	1.23	0.2041	-0.5910	9.1390
10.00	5.60	6.90	1.30	0.1589	-0.7238	9.2762
10.23	5.65	7.05	1.40	0.0941	-0.9835	9.2465
10.49	5.70	7.10	1.40	0.0941	-0.9835	9.5065

Average pKa = 8.9299 ± 0.4186

Table 2: PKa of (Unhydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	$\mathrm{Log}(\frac{nA}{1-n})$	pKa
8.50	5.30	5.81	0.51	0.6619	0.2919	8.7919
8.72	5.35	5.90	0.55	0.6357	0.2418	8.9618
9.00	5.40	6.00	0.60	0.6029	0.1813	9.1813
9.22	5.45	6.10	0.65	0.5701	0.1226	9.3426
9.51	5.50	6.20	0.70	0.5376	0.0654	9.5754
9.73	5.55	6.33	0.78	0.4851	-0.0259	9.7041
10.00	5.60	6.47	0.87	0.4262	-0.1291	9.8709
10.23	5.65	6.62	0.99	0.3609	-0.2481	9.9819
10.49	5.70	6.80	1.10	0.2759	-0.4690	10.0210

Average pKa = 9.4923± 0.4410

Metal-ligand stability constant (Log K)

The stabilityconstants require the accurate values of proton-ligand stability constants (Anil and Maroti, 2008). Metal titration curves crossed over ligand titration curve indicated the formation of complex upon proton release (Santosh, *et al.*, 2011). If the values of n- are within range 0.2-0.8 and 1.2-18 this indicates the formation of 1:1 and 1:2 complexes (Sayyed and Mazahar, 2012).

The metal (II)-humate stepwise stability constants (log k) at phenolic group (Tables 3-18)

Table 3: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$\log(\frac{n}{1-n})$	LogK_1
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

LogK_1 (Average value) = 2.4788± 0.2203

Table 4: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$\mathrm{Log}(\frac{n-1}{2-n})$	LogK_2
9.51	5.50	6.66	6.73	0.07	1.3509	1.70	-0.2671	1.4329
9.73	5.55	6.78	6.85	0.07	1.6383	1.51	0.2467	1.7567
10.00	5.60	6.90	6.98	0.08	2.1783	1.31	-0.2158	1.0942
10.23	5.65	7.05	7.13	0.08	4.1904	1.27		
10.49	5.70	7.10	7.19	0.09	4.6920			

LogK_2(Average value) = 1.4280 ± 0.3312

Table 5:Point-wise method,Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	Log($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430

$LogK_1$ **(Average value)** = 2.3059± 0.6153

Table 6:Point-wise method, Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
9.73	5.55	6.33	6.42	0.09	0.9000	1.69		
10.00	5.60	6.47	6.58	0.11	1.2578	1.44	-0.4592	0.9808
10.23	5.65	6.62	6.84	0.12	1.6137	1.26	-0.2010	1.4610
10.49	5.70	6.80	6.92	0.12	2.1052	1.03		

$LogK_2$ **(Average value)** = 1.2209± 0.3398

Table 7:Point-wise method,Pb (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n}{1-n}$)	$LogK_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.60	0.05	0.8333	1.96	0.6989	2.6589

$LogK_1$ (Average value) = 2.5832 ±0.1614

Table 8:Point-wise method,Pb-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n-1}{2-n}$)	$logK_2$
9.51	5.50	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.83	0.05	1.1702	1.44		
10.00	5.60	6.90	6.90	0.05	1.4864	1.22	-0.0237	1.1963
10.23	5.65	7.05	7.10	0.05	2.0190	1.09		
10.49	5.70	7.10	7.17	0.07	3.6492	1.00		

$LogK_2$(Average value) = 1.1963

Table 9:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log ($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.5477	2.3123
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	0.0272	2.2072
9.51	5.50	6.20	6.26	0.07	0.6417	1.89	0.2530	2.1430
9.73	5.55	6.40	6.40	0.07	0.7000	1.67	0.3680	2.0380

$LogK_1$ **(Average value)** = 2.2364 ± 0.1602

Table 10:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
10.00	5.60	6.47	6.55	0.08	1.9503	1.41		
10.23	5.65	6.62	6.72	0.11	1.4792	1.26	-0.0361	1.2239

$LogK_2$ **(Average value)** = 1.2239

Table 11:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n}{n-1}$)	$LogK_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4290	2.2110
8.72	5.35	6.37	6.39	0.02	0.2858	2.42	-0.3978	2.0222
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

$LogK_1$ (Average value)=2.1382±0.1046

Table 12:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n-1}{2-n}$)	$LogK_2$
9.51	5.55	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.84	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.93	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.10		
10.49	5.70	7.10	7.18	0.07	3.6492	0.83		

$LogK_2$(Average value) = 1.5453 **±** 0.3450

Table 13:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.3477	2.3123
9.00	5.40	6.00	6.04	0.04	0.3236	2.38	-0.3202	2.0598
9.22	5.45	6.10	6.15	0.05	0.4297	2.17	-0.1230	2.0470
9.51	5.50	6.20	6.26	0.06	0.5500	1.89	0.0871	1.9771
9.73	5.55	6.33	6.40	0.07	0.7000	1.67	0.3680	2.0380

$LogK_1$ **(Average value)** = 2.1568 ± 0.2069

Table 14:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
10.00	5.60	6.47	6.55	0.08	0.9148	1.41		
10.23	5.65	6.62	6.71	0.09	1.2102	1.20	-0.5749	0.6251
10.49	5.70	6.80	6.92	0.09	1.5968	1.03	0.1703	1.2003

$LogK_2$ **(Average value)** = 0.9127± 0.4070

Table15:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	Log($\frac{n}{1-n}$)	$LogK_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4210	2.2190
8.72	5.35	6.37	6.40	0.03	0.4286	2.42	-0.1249	2.2951
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.96	0.3010	2.2610
9.51	5.55	6.66	6.70	0.04	0.7720	1.67	0.5297	2.1997

$LogK_1$ (Average value) = 2.2108± 0.0825

Table 16:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
9.73	5.55	6.78	6.83	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.95	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.09		
10.49	5.70	7.10	7.16	0.06	3.1429	0.89		

$LogK_2$ **(Average value)** = 1.5453± 0.3450

Table 17:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.86	0.05	0.3717	2.88	-0.2280	2.6520
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.06	0.06	0.4853	2.38	-0.0255	2.3545
9.22	5.45	6.10	6.16	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430
9.73	5.55	6.33	6.41	0.08	0.8000	1.69	0.6020	2.2920

$LogK_1$ **(Average value)** = 2.2516± 0.5380

Table 18:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$\mathrm{Log}(\frac{n-1}{2-n})$	Log K_2
10.00	5.60	6.47	6.57	0.10	1.1434	1.43		
10.23	5.65	6.62	6.72	0.10	1.3448	1.23	-0.2788	0.9512
10.49	5.70	6.80	6.90	0.10	1.7742	1.03	0.5351	1.5651

LogK_2 **(Average value)** = 1.2581± 0.4340

Table 19: Stepwise and overall Stability constants of thehydrolysed and unhydrolysed divalent metal (II) complexes

Chelates	**LogK_1**	**LogK_2**	**Logβ**
[Cu (Hydrolysed PSHA-1)$_2$]	2.4788	1.4280	3.9068
[Pb (Hydrolysed PSHA-1)$_2$]	2.5832	1.1963	3.7795
[Cd (Hydrolysed PSHA-1)$_2$]	2.2108	1.5453	3.7561
[Mg (Hydrolysed PSHA-1)$_2$]	2.1382	1.5453	3.6835
[Cu (Unhydrolysed PSHA-1)$_2$]	2.3059	1.2209	3.5268
[Pb (Unhydrolysed PSHA-1)$_2$]	2.2364	1.2239	3.4603
[Cd (Unhydrolysed PSHA-1)$_2$]	2.2516	1.2581	3.5097
[Mg (Unydrolysed PSHA-1)$_2$]	2.1568	0.9127	3.0695

The results obtained (Table19) shows the stepwise and overall stability constants to be not high indicating low stability of the complexes, because the solubility of most metal ions in the basic pH range is minimal due to metal hydroxide precipitation (Karimi, 2017). In general, the stepwise stability constants (K_1 and K_2) follow the order $K_1 > K_2$ for the copper, lead, magnesium and cadmium complexes respectively. The steady decrease of the values with increasing number of ligands is in agreement with the prediction made by researchers (Na'aliya, 2013). The decrease could be attributed to the fact that as the number of the ligands (Humate ions) that enters the coordination zone increases the aqua molecules available for replacement by the ligands become less. Thus, the metal ions become less electron loving with progressive intake of the ligand and this results in the decrease in the values of the constants (Na'aliya, 2013). Also the stability of the complexes is influenced by the size and number of the chelate rings(Mackay and Mackay,2002).All the complexes form rings in their structure as humate, a bidentate ligand, bond the metal ions in the ratio 1:2 (Boguta and Sokolowska, 2016) forming chelate rings. The values of the overall stability constants (logβ) obtained for humate complexes are not high indicating low stability as the values are not high. LogK values for copper-humates (Table 3 to 6) obtained in this study are lower than those reported for the complexes of humic acids (Pandey *et al*., 2015; Dinu, 2013; Kaschl *et al*., 2010 and Gilbeto and Jorg, 2001). The values of LogK(Table 7 to 10) forlead-humates are lower than those reported for the lead in the literature (Dinu, 2013; Gilbeto and Jorg 2001). Log K values(Table 11 to 14) for magnesium-humates obtained in this study are close to those reported by (Pandey *et al*., 2015). Log K values of cadmium-humates (Table 15 to 18) obtained in this work near to the one reported by (Dinu, 2013 and Pandey *et al*., 2015).The difference between the reported values and the values obtained in this study might be probably as a result of acid hydrolysis of humic acid. The values of the overall stability constants (log β) of the copper humates complexes presented in Table 19 is high than that of other metal humate complexes, show relatively high stability of Cu-HA complexes, show the following order of stability: Cu >Pb> Cd > Mg; which are in close agreement to the findings of (Dinu, 2013 and Pandey *et al*., 2015).The high stability of Cu-humate chelate could be attributed to the existence of coordinate covalent bond between the complexing agents and the Cu^{2+} ions. Since, Cu^{2+} being a metal of the transitional series with $3d^9$ electronic configurations can accept the electrons from the complexing agents. Similarly,the low stabilities of Pb,Cd and Mg -complexes could be explained by that Pb^{2+} with $6s^2$, Cd^{2+} with $4d^{10}$ and Mg^{2+} with $2p^6$ their electronic configuration has a completely filled d,p and s orbitals. Moreover, the stabilities of metal ions with hydrolysed humic acid from peat soil were higher than those with unhydrolysed humic acid from peat soil; which is ascribed to the high content of acidity in hydrolysed humic acid than unhydrolysed humic acid.

CONCLUSION

The values of logK for Cu(II) hydrolysed humic acid complex was higher followed by Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes as compared with metal(II) unhydrolysed humic acid complexes . This indicates acid hydrolysis of humic acid can enhance the complexation behavior of humic acid with metal (II) ions. However, the higher values of logβ for Cu(II), Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes indicates more stable stepwise complexes formed as compared with Cu(II), Pb(II), Cd(II) and Mg(II) unhydrolysed humic acid complexes.

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STABILITY CONSTANTS OF COMPLEXES OF METAL IONS WITH PEATSOIL HUMIC ACIDS UNDER NON-ACID-CONDITIONS

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ABSTRACT

Stability constants of complexes of four divalent metal ions viz. Cu^{2+}, Pb^{2+},Mg^{2+} and Cd^{2+} with humic acids (HA) were determined by potentiometric titration of humic acids with the corresponding salt of the divalent metals in aqueous media under non-acid-condition. The log K (logarithm of the stability constant) ranged from 1.0942 to 2.7471 for metal-humic acid complexes were determined using point-wise computational method. The order of stability constants were obtained as follows: Cu >Pb> Cd > Mg for metal -HA complexes respectively, indicating a higher degree of complexation with Cu metal ion.

Keywords: stability constant, humic acid, potentiometric titration, divalent metals, acid hydrolysis.

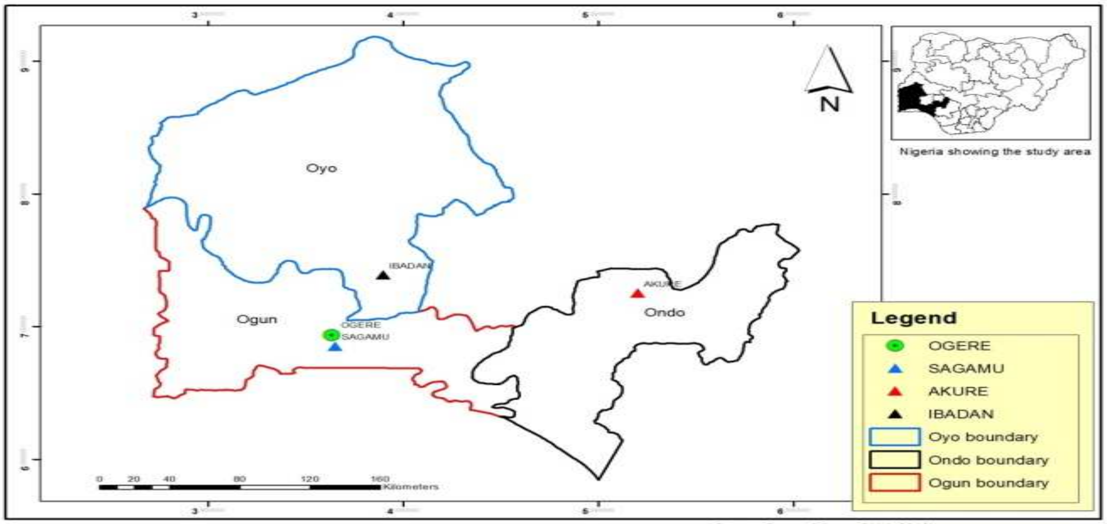
NTRODUCTION

The stability constant of a complex is the numerical expression of its stability and provides a quantitative measure of affinity of the metal ion to the complexing agent. An understanding of the relative stability of metal-complexes helps in predicting the behavior of metal ions in the soil (Ram and Raman, 1982). Extensive researches has been done to determine the stability constants of the complexes formed between humic acid (HA) with a number of metal ions. Ashok *et al*., (2000) reported that humic acid with hydroxyl, phenoxyl and carboxyl reactive groups can form coordination compound with metal ions at pH 3.5. The stability constants(Log K) for different metal-humic acid complexes indicated the following order of the stabilities of complexes formed between humic acid and metal ion, Cu >Fe >Pb> Ni > Co > Ca > Cd > Zn >Mn> Mg. Andelkovic *et al*., (2010) investigated the binding of Cd(II) to soil humic acid at pH 6.5 and in 0.1M KNO_3 ionic medium. The stability constant for binding indicating greater stability in the case when carboxyl groups are involved in complexation reaction. Kostic *et al*.,(2012) investigated the complexation of humic acid with certain heavy metal ions (Co(II), Ni(II),Cu(II), Zn(II), and Pb(II). The experiment was performed at 25°C, at pH 4.0 and ionic strength of 0.01M. Stability constant of complex between Pb(II) ions and humic acid is greater than stability constants of other investigated metal-humate complexes. Bogata and Sokolowska (2016) analyses the interaction between humic acids from different soils and Zn (II) ions at wide concentration ranges and at pH 5. Studies have showed significant impact of Zn concentration, pH and some properties of humic acids with zinc.But all of these studies were limited to acidic pH range. Therefore, the present study was carried out to determine and compare the stability constants of complexes of metal ions with hydrolysed peat soil humic acid and unhydrolysed peat soil humic under non-acid conditions.

MATERIALS AND METHODS

Analytical grade chemicals used includes hydrochloric acid (HCl), nitric acid (HNO_3), sodium hydroxide (NaOH), lead nitrate $Pb(NO_3)_2$, copper nitrate $Cu(NO_3)_2.3H_2O$, cadmium nitrate $Cd(NO_3)_2.4H_2O$, magnesium nitrate $Mg(NO_3)_2.6H_2O$, potassium nitrate (KNO_3), calcium chloride ($CaCl_2$), (sigma-Aldrich). Dowex 50WX8, (20-50 mesh) from Fluka.

Area of study



Source: Dept. of Geog. BUK (2016)

Figure 1: Map showing the sampling point at Sagamu Town, Ogun State.

Description of Sampling Area

Sagamu has geographical coordinates between 6°50′ north; 3° 38′ east is located in south western region of Nigeria. The region has tropical wet and dry climate with a lengthy wet season and relatively constant temperatures throughout the course of the year. Wet season runs from March to October, November to December forms the region dry season. The vegetation type of the region is savannah which is really grassland with small bushes and occasional big trees. Grassland soils have substantially higher organic matter content than forest soils (Novackova, 2011).

Sample Collection

The Peatsoil samples were collected from four different sampling points (0-10cm depth) in Sagamu into polyethylene bag with plastic spoons. Samples were taken to the laboratory, extraneous materials were removed; the samples were air-dried, crushed and ground to a fine powder in a mortar passed through a 0.20mm sieve. The samples were kept for analysis.

Isolation and purification of humic acid from peat soil sample

Peatsoil sample (100g) was mixed with 1000 cm^3 of 0.1M NaOH solution, shaken for 3hours and left to stand overnight. Dark-coloured supernatant was obtained and decanted from solid residue. The dark-coloured supernatant was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 6 hours. Yellowish brown supernatant and dark-brown precipitate were obtained. The yellowish brown supernatant was decanted followed by centrifuge and discarded. The dark-brown precipitate was mixed with $500cm^3$of 0.1M NaOH solution followed by passing through dowex resin. The dark-brown solution was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 3 hours. The dark-brown precipitate was washed several times with deionized water. The supernatant was treated with $AgNO_3$ solution until no white precipitate observed. The humic acid was transferred to weighed crucible and dried at 60^oC in an oven for 12 hours. The humic acid was cooled and dried in the desiccator, weighed and recorded. The obtained humic acid was dried again at 60^oC for additional 6 hours cooled and dried in the desiccator, weighed and recorded constant weight was obtained (Baruah *et al.*, 2015).

FT-IR analysis

FT-IR spectra of humic acid sample was analysed using Carry 630 FT-IR Agilent Technologies.

Unhydrolysed compost humic acid

The unhydrolysed humic acid was obtained after isolation and purification of compost humic acid and kept for investigation.

Acid hydrolysis of Peatsoil acid

Peatsoil humic acid sample (1g) was refluxed for 12 hours at (160^oC) with $50cm^3$ of 6M HCl. The mixture was allowed to cool, decanted, and centrifuged after hydrolysis. The insoluble residues were washed with distilled water via centrifugation several times, and the supernatant was treated with $AgNO_3$ solution until no white precipitate was observed. The residue was thoroughly dried over $CaCl_2$ in a desiccator at room temperature (Chefetz *et al.*, 2002). Finally, the obtained hydrolysed humic acid was kept for investigation.

Potentiometric Titrations

Potentiometric measurements were carried out using a pH-meter Jenway (model 3510) with combine electrode, the sensitivity of the pH - meter is 0.01 units. The pH meter was switched on half an hour before starting the titration for initial warm up of the instrument. The instrument was calibrated with an aqueous standard buffer solution of pH 4.00 and 10.0 (borate buffer) prepared from a "Qualigens" buffer tablets.

The following sets of solutions were prepared in a 250cm^3 volumetric flask separately for pH metric titrations.

(i) 5 cm^3 0.1 M HCl + 40 cm^3 deionized water
(ii) 5 cm^3 0.1 M HCl + 39 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid
(iii) 5 cm^3 0.1 M HCl + 37 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid + 2 cm^3 0.01 M Cu(II)

The solutions were titrated against standardized 0.110MNaOH separately. The total volume of each mixture was adjusted to 50 cm^3 and the ionic strength of the solutions was maintained constant at by adding appropriate amount of stock solution of 1M KNO$_3$ (Gamal, 2015; Omar and Ali, 2015). A magnetic stirrer was used to achieve thorough mixing of the interacting solutions at 550 rpm. The same set of experimental conditions was applied for potentiometric titration of remaining samples.

Evaluation of pKa of Hydrolysed peat soil Humic Acids

The proton-ligand formation number n$_{\mathbf{A}}$ were calculated by Irving and Rossotti expression (Omar and Ali, 2015).

$nA = Y- \frac{(V2-V1)(No-Eo)}{(Vo+V1)TcL}$ 1

Where: Y is number of dissociable proton, (V_2-V_1) is the measure of displacement of the ligand curve relative to acid curve, N^o and E^o are the resultant concentration of alkali solution, free acid solution, $T_{cL}{}^o$ is the total ligand concentration, V^o is the total volume of titration solution,V_1 is the volume of alkali added to acid solution,V_2 is the volume of alkali added to acid solution + ligand solution, acid dissociation constants (pKa - values) of ligand were calculated by algebraic method point wise calculation (Tables 1). The dissociation constants (pKa) were calculated according to the following relation:

$pKa = pH + \log(\frac{nA}{1-nA})$ 2

Where: pKa is the acid dissociation constant, $n_A$is the Proton-ligand formation number and pH is the pH-values (Omar and Ali, 2015).

Determination of metal-ligand stability constants (log K) of complexes

The potentiometric measurement for the determination of stability constant of a complex in solution is based on the fact that the redox potential of the couple $\frac{M^{+(m-n)}}{M^{+m}}$ is shifted significantly on complexation of the metal ion with the ligand. This method involves change in hydrogen ion concentration [H$^+$] due to the displacement or association of one or more protons taking place during complexation reaction. This change can be found out by titrating the solutions containing free acid, acid with ligand, and acid with ligand and metal ion, individually against a standard alkali solution at a constant ionic strength or temperature. Either ionic strength or temperature may be varied for different sets of solutions. In all the cases, the change in the pH of the solution is measured after each addition of a known amount of alkali to the reaction cell which contains the reaction mixture. The titration curves are then drawn by plotting the measured pH values against the corresponding volume of alkali added and the stability constants of the complexes are determined from the titration curves by employing pH-metric titration technique given by (Irving and Rossoti).

Metal-ligand stability constants (Log K) were determined by using the following relations:

$$\bar{n} = \frac{(V_3 - V_2)(E^0 + N^0)}{(V^0 + V_2)\bar{n}_A T_m^0} \qquad \text{...3}$$

and

$$PL = \log_{10}\{\frac{1 + \beta_n^H \frac{1}{[anti\ \log pH]^n}}{T_L^0 - \bar{n}T_m^0} X \frac{(V^0 + V_3)}{V^0}\} \qquad \text{..4}$$

Where $T_{L,}$ T^{o}, E°, and V^{o}havethe same significance as in equation (1) above, T_m denotes the total concentration of metal present in solution, V_3 is the volume of metal ions present in solution and β^H is the overall proton ligand stability constant. The metal-ligand stability constants (log K) were determined by employing point wise computational Method (eq. 5 and 6).

$\text{LogK}_1 = \log\left(\frac{n}{1-n}\right) + \text{pL}$ 5

$\text{LogK}_2 = \log\left(\frac{1-n}{2-n}\right) + \text{pL}$......................6

Where: Log K is the metal-ligand stability constant, pL is the Free ligand exponent function, **n** is the Average number of ligand attached with metal ion (Janrao*et al*., 2014).The results obtained were analyzed by an ORIGIN 2016 program using titration data and then the proton-ligand stability constants (pKa) and Metal-ligand stability constant (LogK) calculated (Omar and Ali, 2015).

RESULTS AND DISCUSSION

Fourier transformed infrared (FT-IR) spectra of isolated humic acid from peat soils Figure 2 had distinct clear absorption bands indicating the presence of major humic acid structural elemental groups such as H bonded OH (3680cm^{-1} peak), C=O of carbonyl (1721cm^{-1} peak), functional groups of aliphatic components CH_2 (2918cm^{-1} peak) and C-O stretching of polysaccharide (1168cm^{-1} peak). The positions of the absorption bands of the spectra fell within typical major absorption bands of humic acid which is at frequencies 3680, 2918, 1721, 1168 cm^{-1}. The first peak centred in the vicinity of 3680 cm^{-1} region is attributed to phenol OH group bounded by intermolecular H bonds. The 2918cm^{-1} band usually has absorption maximum at 2918 cm^{-1} which is due to C–H stretching of alkane group (CH_2). The next major absorption band is 1721 cm^{-1}. This band has been commonly ascribed to C=O stretching of mainly carboxyl group (COOH) with trace amount of ketones. The last peak was observed at 1168 cm^{-1} due to C–O stretching of polysaccharides and this peak appeared also in the spectra of humic acid from peat soil. The FTIR spectra of the isolated humic acid contained all major characteristic absorption peaks of humic acid. These absorption peaks indicated the presence of the major structural elements of humic acid namely H bonded OH, C=C of aromatic ring, C=O of carbonyl group (both carboxyl and ketonic), CH_2 group. This strongly supports the presence of humic acid.

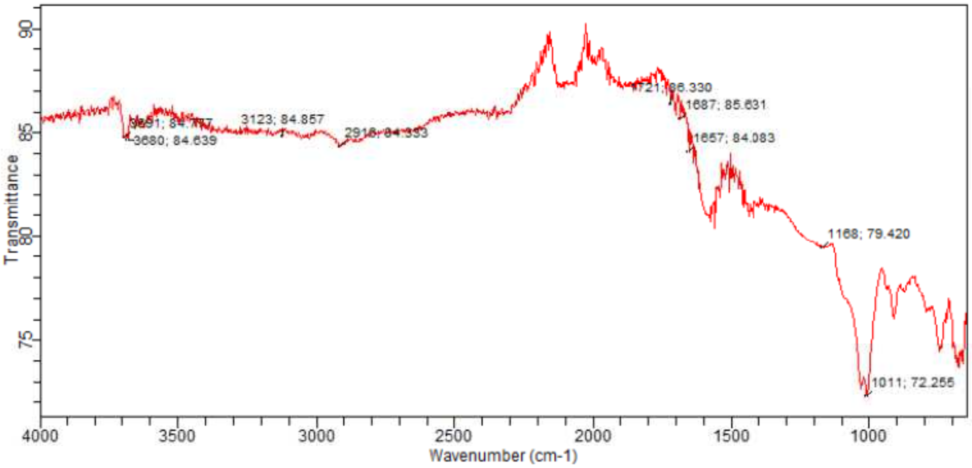


Fig. 2 : FT-IR spectraof peatsoilhumic acid (PSHA)

Evaluation of acid dissociation constant (pka) of acid hydrolysed peat soil humicacid at phenolic group

The value of the dissociation constant of the peat soil humic acid (PSHA) that underwent acidhydrolysis studied was found to be 8.9299 as shown Table 1, which is lower than the literaturevalues reported by Almeida and Szpoganics, (2015), Borges *et al*., (2005); Badr *et al*., (2012)and Fernandes *et al*,.(2009) of 9.73, 9.47 and 10.30. The difference between the obtained valuesand the reported values in this study might be probably as a result of acid hydrolysis of humicacid.

Table 1: PKa of (Hydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	log($\frac{nA}{1-nA}$)	pKa
8.50	5.30	6.29	0.99	0.3594	-0.2510	8.2490
8.72	5.35	6.37	1.02	0.3400	-0.2880	8.4320
9.00	5.40	6.46	1.06	0.3141	-0.3391	8.6609
9.22	5.45	6.55	1.10	0.2882	-0.3927	8.8273
9.51	5.50	6.66	1.16	0.2494	-0.4786	9.0314
9.73	5.55	6.78	1.23	0.2041	-0.5910	9.1390
10.00	5.60	6.90	1.30	0.1589	-0.7238	9.2762
10.23	5.65	7.05	1.40	0.0941	-0.9835	9.2465
10.49	5.70	7.10	1.40	0.0941	-0.9835	9.5065

Average pKa = 8.9299 ± 0.4186

Table 2: PKa of (Unhydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	Log($\frac{nA}{1-n}$)	pKa
8.50	5.30	5.81	0.51	0.6619	0.2919	8.7919
8.72	5.35	5.90	0.55	0.6357	0.2418	8.9618
9.00	5.40	6.00	0.60	0.6029	0.1813	9.1813
9.22	5.45	6.10	0.65	0.5701	0.1226	9.3426
9.51	5.50	6.20	0.70	0.5376	0.0654	9.5754
9.73	5.55	6.33	0.78	0.4851	-0.0259	9.7041
10.00	5.60	6.47	0.87	0.4262	-0.1291	9.8709
10.23	5.65	6.62	0.99	0.3609	-0.2481	9.9819
10.49	5.70	6.80	1.10	0.2759	-0.4690	10.0210

Average pKa = 9.4923± 0.4410

Metal-ligand stability constant (Log K)

The stabilityconstants require the accurate values of proton-ligand stability constants (Anil and Maroti, 2008). Metal titration curves crossed over ligand titration curve indicated the formation of complex upon proton release (Santosh, *et al.*, 2011). If the values of n- are within range 0.2-0.8 and 1.2-18 this indicates the formation of 1:1 and 1:2 complexes (Sayyed and Mazahar, 2012).

The metal (II)-humate stepwise stability constants (log k) at phenolic group (Tables 3-18)

Table 3: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n}{1-n}$)	$LogK_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

$LogK_1$ (Average value) = 2.4788± 0.2203

Table 4: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	Log($\frac{n-1}{2-n}$)	$LogK_2$
9.51	5.50	6.66	6.73	0.07	1.3509	1.70	-0.2671	1.4329
9.73	5.55	6.78	6.85	0.07	1.6383	1.51	0.2467	1.7567
10.00	5.60	6.90	6.98	0.08	2.1783	1.31	-0.2158	1.0942
10.23	5.65	7.05	7.13	0.08	4.1904	1.27		
10.49	5.70	7.10	7.19	0.09	4.6920			

$LogK_2$(Average value) = 1.4280 ± 0.3312

Table 5:Point-wise method,Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	Log$(\frac{n}{n-1})$	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430

$LogK_1$ **(Average value)** = 2.3059± 0.6153

Table 6:Point-wise method, Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log$(\frac{n-1}{2-n})$	Log K_2
9.73	5.55	6.33	6.42	0.09	0.9000	1.69		
10.00	5.60	6.47	6.58	0.11	1.2578	1.44	-0.4592	0.9808
10.23	5.65	6.62	6.84	0.12	1.6137	1.26	-0.2010	1.4610
10.49	5.70	6.80	6.92	0.12	2.1052	1.03		

$LogK_2$ **(Average value)** = 1.2209± 0.3398

Table 7:Point-wise method,Pb (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log$(\frac{n}{1-n})$	$LogK_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.60	0.05	0.8333	1.96	0.6989	2.6589

$LogK_1$ (Average value) = 2.5832 ±0.1614

Table 8:Point-wise method,Pb-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log$(\frac{n-1}{2-n})$	$logK_2$
9.51	5.50	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.83	0.05	1.1702	1.44		
10.00	5.60	6.90	6.90	0.05	1.4864	1.22	-0.0237	1.1963
10.23	5.65	7.05	7.10	0.05	2.0190	1.09		
10.49	5.70	7.10	7.17	0.07	3.6492	1.00		

$LogK_2$(Average value) = 1.1963

Table 9:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log $(\frac{n}{n-1})$	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.5477	2.3123
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	0.0272	2.2072
9.51	5.50	6.20	6.26	0.07	0.6417	1.89	0.2530	2.1430
9.73	5.55	6.40	6.40	0.07	0.7000	1.67	0.3680	2.0380

$LogK_1$ **(Average value)** = 2.2364 ± 0.1602

Table 10:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log$(\frac{n-1}{2-n})$	Log K_2
10.00	5.60	6.47	6.55	0.08	1.9503	1.41		
10.23	5.65	6.62	6.72	0.11	1.4792	1.26	-0.0361	1.2239

$LogK_2$ **(Average value)** = 1.2239

Table 11:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log$(\frac{n}{n-1})$	$LogK_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4290	2.2110
8.72	5.35	6.37	6.39	0.02	0.2858	2.42	-0.3978	2.0222
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

$LogK_1$ (Average value)=2.1382±0.1046

Table 12:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	log$(\frac{n-1}{2-n})$	$LogK_2$
9.51	5.55	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.84	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.93	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.10		
10.49	5.70	7.10	7.18	0.07	3.6492	0.83		

$LogK_2$(Average value) = 1.5453 **±** 0.3450

Table 13:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$V_3\text{-}V_2$	n	pL	Log$(\frac{n}{n-1})$	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.3477	2.3123
9.00	5.40	6.00	6.04	0.04	0.3236	2.38	-0.3202	2.0598
9.22	5.45	6.10	6.15	0.05	0.4297	2.17	-0.1230	2.0470
9.51	5.50	6.20	6.26	0.06	0.5500	1.89	0.0871	1.9771
9.73	5.55	6.33	6.40	0.07	0.7000	1.67	0.3680	2.0380

$LogK_1$ **(Average value)** = 2.1568 ± 0.2069

Table 14:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$V_3\text{-}V_2$	n	pL	Log$(\frac{n-1}{2-n})$	Log K_2
10.00	5.60	6.47	6.55	0.08	0.9148	1.41		
10.23	5.65	6.62	6.71	0.09	1.2102	1.20	-0.5749	0.6251
10.49	5.70	6.80	6.92	0.09	1.5968	1.03	0.1703	1.2003

$LogK_2$ **(Average value)** = 0.9127± 0.4070

Table15:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	Log$(\frac{n}{1-n})$	$LogK_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4210	2.2190
8.72	5.35	6.37	6.40	0.03	0.4286	2.42	-0.1249	2.2951
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.96	0.3010	2.2610
9.51	5.55	6.66	6.70	0.04	0.7720	1.67	0.5297	2.1997

$LogK_1$ (Average value) = 2.2108± 0.0825

Table 16:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	Log$(\frac{n-1}{2-n})$	Log K_2
9.73	5.55	6.78	6.83	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.95	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.09		
10.49	5.70	7.10	7.16	0.06	3.1429	0.89		

$LogK_2$ **(Average value)** = 1.5453± 0.3450

Table 17:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$V_3\text{-}V_2$	n	pL	Log$(\frac{n}{n-1})$	Log K_1
8.50	5.30	5.81	5.86	0.05	0.3717	2.88	-0.2280	2.6520
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.06	0.06	0.4853	2.38	-0.0255	2.3545
9.22	5.45	6.10	6.16	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430
9.73	5.55	6.33	6.41	0.08	0.8000	1.69	0.6020	2.2920

$LogK_1$ **(Average value)** = 2.2516± 0.5380

Table 18:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$\text{Log}(\frac{n-1}{2-n})$	Log K_2
10.00	5.60	6.47	6.57	0.10	1.1434	1.43		
10.23	5.65	6.62	6.72	0.10	1.3448	1.23	-0.2788	0.9512
10.49	5.70	6.80	6.90	0.10	1.7742	1.03	0.5351	1.5651

LogK_2 **(Average value)** = 1.2581± 0.4340

Table 19: Stepwise and overall Stability constants of thehydrolysed and unhydrolysed divalent metal (II) complexes

Chelates	**LogK_1**	**LogK_2**	**Logβ**
[Cu (Hydrolysed PSHA-1)$_2$]	2.4788	1.4280	3.9068
[Pb (Hydrolysed PSHA-1)$_2$]	2.5832	1.1963	3.7795
[Cd (Hydrolysed PSHA-1)$_2$]	2.2108	1.5453	3.7561
[Mg (Hydrolysed PSHA-1)$_2$]	2.1382	1.5453	3.6835
[Cu (Unhydrolysed PSHA-1)$_2$]	2.3059	1.2209	3.5268
[Pb (Unhydrolysed PSHA-1)$_2$]	2.2364	1.2239	3.4603
[Cd (Unhydrolysed PSHA-1)$_2$]	2.2516	1.2581	3.5097
[Mg (Unydrolysed PSHA-1)$_2$]	2.1568	0.9127	3.0695

The results obtained (Table19) shows the stepwise and overall stability constants to be not high indicating low stability of the complexes, because the solubility of most metal ions in the basic pH range is minimal due to metal hydroxide precipitation (Karimi, 2017). In general, the stepwise stability constants (K_1 and K_2) follow the order $K_1 > K_2$ for the copper, lead, magnesium and cadmium complexes respectively. The steady decrease of the values with increasing number of ligands is in agreement with the prediction made by researchers (Na'aliya, 2013). The decrease could be attributed to the fact that as the number of the ligands (Humate ions) that enters the coordination zone increases the aqua molecules available for replacement by the ligands become less. Thus, the metal ions become less electron loving with progressive intake of the ligand and this results in the decrease in the values of the constants (Na'aliya, 2013). Also the stability of the complexes is influenced by the size and number of the chelate rings(Mackay and Mackay,2002).All the complexes form rings in their structure as humate, a bidentate ligand, bond the metal ions in the ratio 1:2 (Boguta and Sokolowska, 2016) forming chelate rings. The values of the overall stability constants (logβ) obtained for humate complexes are not high indicating low stability as the values are not high. LogK values for copper-humates (Table 3 to 6) obtained in this study are lower than those reported for the complexes of humic acids (Pandey *et al.*, 2015; Dinu, 2013; Kaschl *et al.*, 2010 and Gilbeto and Jorg, 2001). The values of LogK(Table 7 to 10) forlead-humates are lower than those reported for the lead in the literature (Dinu, 2013; Gilbeto and Jorg 2001). Log K values(Table 11 to 14) for magnesium-humates obtained in this study are close to those reported by (Pandey *et al.*, 2015). Log K values of cadmium-humates (Table 15 to 18) obtained in this work near to the one reported by (Dinu, 2013 and Pandey *et al.*, 2015).The difference between the reported values and the values obtained in this study might be probably as a result of acid hydrolysis of humic acid. The values of the overall stability constants (log β) of the copper humates complexes presented in Table 19 is high than that of other metal humate complexes, show relatively high stability of Cu-HA complexes, show the following order of stability: Cu >Pb> Cd > Mg; which are in close agreement to the findings of (Dinu, 2013 and Pandey *et al.*, 2015).The high stability of Cu-humate chelate could be attributed to the existence of coordinate covalent bond between the complexing agents and the Cu^{2+} ions. Since, Cu^{2+} being a metal of the transitional series with $3d^9$ electronic configurations can accept the electrons from the complexing agents. Similarly,the low stabilities of Pb,Cd and Mg -complexes could be explained by that Pb^{2+} with $6s^2$, Cd^{2+} with $4d^{10}$ and Mg^{2+} with $2p^6$ their electronic configuration has a completely filled d,p and s orbitals. Moreover, the stabilities of metal ions with hydrolysed humic acid from peat soil were higher than those with unhydrolysed humic acid from peat soil; which is ascribed to the high content of acidity in hydrolysed humic acid than unhydrolysed humic acid.

CONCLUSION

The values of logK for Cu(II) hydrolysed humic acid complex was higher followed by Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes as compared with metal(II) unhydrolysed humic acid complexes . This indicates acid hydrolysis of humic acid can enhance the complexation behavior of humic acid with metal (II) ions. However, the higher values of logβ for Cu(II), Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes indicates more stable stepwise complexes formed as compared with Cu(II), Pb(II), Cd(II) and Mg(II) unhydrolysed humic acid complexes.

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STABILITY CONSTANTS OF COMPLEXES OF METAL IONS WITH PEATSOIL HUMIC ACIDS UNDER NON-ACID-CONDITIONS

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ABSTRACT

Stability constants of complexes of four divalent metal ions viz. Cu^{2+}, Pb^{2+},Mg^{2+} and Cd^{2+} with humic acids (HA) were determined by potentiometric titration of humic acids with the corresponding salt of the divalent metals in aqueous media under non-acid-condition. The log K (logarithm of the stability constant) ranged from 1.0942 to 2.7471 for metal-humic acid complexes were determined using point-wise computational method. The order of stability constants were obtained as follows: Cu >Pb> Cd > Mg for metal -HA complexes respectively, indicating a higher degree of complexation with Cu metal ion.

Keywords: stability constant, humic acid, potentiometric titration, divalent metals, acid hydrolysis.

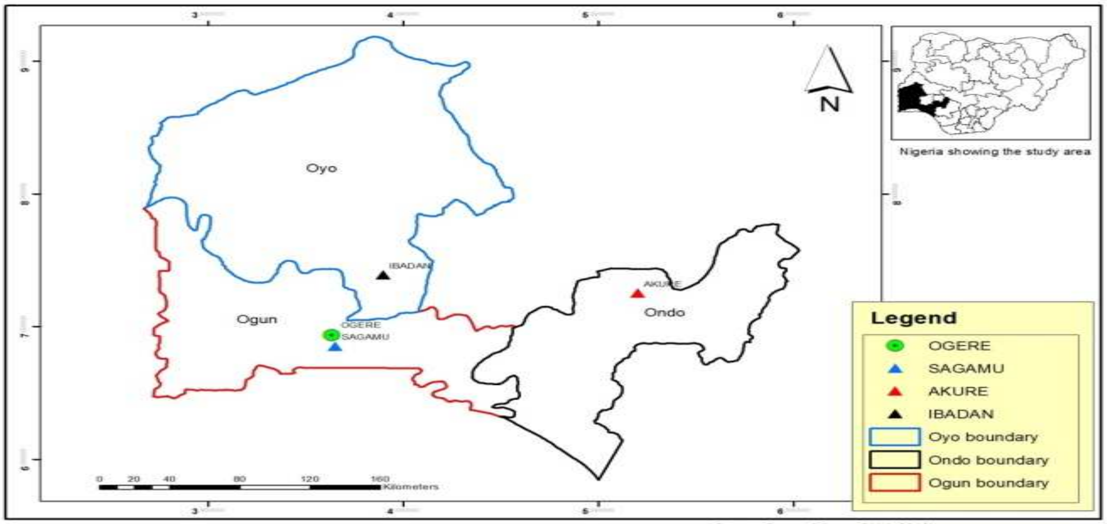
NTRODUCTION

The stability constant of a complex is the numerical expression of its stability and provides a quantitative measure of affinity of the metal ion to the complexing agent. An understanding of the relative stability of metal-complexes helps in predicting the behavior of metal ions in the soil (Ram and Raman, 1982). Extensive researches has been done to determine the stability constants of the complexes formed between humic acid (HA) with a number of metal ions. Ashok *et al*., (2000) reported that humic acid with hydroxyl, phenoxyl and carboxyl reactive groups can form coordination compound with metal ions at pH 3.5. The stability constants(Log K) for different metal-humic acid complexes indicated the following order of the stabilities of complexes formed between humic acid and metal ion, Cu >Fe >Pb> Ni > Co > Ca > Cd > Zn >Mn> Mg. Andelkovic *et al*., (2010) investigated the binding of Cd(II) to soil humic acid at pH 6.5 and in 0.1M KNO_3 ionic medium. The stability constant for binding indicating greater stability in the case when carboxyl groups are involved in complexation reaction. Kostic *et al*.,(2012) investigated the complexation of humic acid with certain heavy metal ions (Co(II), Ni(II),Cu(II), Zn(II), and Pb(II). The experiment was performed at 25°C, at pH 4.0 and ionic strength of 0.01M. Stability constant of complex between Pb(II) ions and humic acid is greater than stability constants of other investigated metal-humate complexes. Bogata and Sokolowska (2016) analyses the interaction between humic acids from different soils and Zn (II) ions at wide concentration ranges and at pH 5. Studies have showed significant impact of Zn concentration, pH and some properties of humic acids with zinc.But all of these studies were limited to acidic pH range. Therefore, the present study was carried out to determine and compare the stability constants of complexes of metal ions with hydrolysed peat soil humic acid and unhydrolysed peat soil humic under non-acid conditions.

MATERIALS AND METHODS

Analytical grade chemicals used includes hydrochloric acid (HCl), nitric acid (HNO_3), sodium hydroxide (NaOH), lead nitrate $Pb(NO_3)_2$, copper nitrate $Cu(NO_3)_2.3H_2O$, cadmium nitrate $Cd(NO_3)_2.4H_2O$, magnesium nitrate $Mg(NO_3)_2.6H_2O$, potassium nitrate (KNO_3), calcium chloride ($CaCl_2$), (sigma-Aldrich). Dowex 50WX8, (20-50 mesh) from Fluka.

Area of study



Source: Dept. of Geog. BUK (2016)

Figure 1: Map showing the sampling point at Sagamu Town, Ogun State.

Description of Sampling Area

Sagamu has geographical coordinates between 6°50′ north; 3° 38′ east is located in south western region of Nigeria. The region has tropical wet and dry climate with a lengthy wet season and relatively constant temperatures throughout the course of the year. Wet season runs from March to October, November to December forms the region dry season. The vegetation type of the region is savannah which is really grassland with small bushes and occasional big trees. Grassland soils have substantially higher organic matter content than forest soils (Novackova, 2011).

Sample Collection

The Peatsoil samples were collected from four different sampling points (0-10cm depth) in Sagamu into polyethylene bag with plastic spoons. Samples were taken to the laboratory, extraneous materials were removed; the samples were air-dried, crushed and ground to a fine powder in a mortar passed through a 0.20mm sieve. The samples were kept for analysis.

Isolation and purification of humic acid from peat soil sample

Peatsoil sample (100g) was mixed with 1000 cm^3 of 0.1M NaOH solution, shaken for 3hours and left to stand overnight. Dark-coloured supernatant was obtained and decanted from solid residue. The dark-coloured supernatant was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 6 hours. Yellowish brown supernatant and dark-brown precipitate were obtained. The yellowish brown supernatant was decanted followed by centrifuge and discarded. The dark-brown precipitate was mixed with 500cm^{3}of 0.1M NaOH solution followed by passing through dowex resin. The dark-brown solution was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 3 hours. The dark-brown precipitate was washed several times with deionized water. The supernatant was treated with $AgNO_3$ solution until no white precipitate observed. The humic acid was transferred to weighed crucible and dried at 60^{o}C in an oven for 12 hours. The humic acid was cooled and dried in the desiccator, weighed and recorded. The obtained humic acid was dried again at 60^{o}C for additional 6 hours cooled and dried in the desiccator, weighed and recorded constant weight was obtained (Baruah *et al.*, 2015).

FT-IR analysis

FT-IR spectra of humic acid sample was analysed using Carry 630 FT-IR Agilent Technologies.

Unhydrolysed compost humic acid

The unhydrolysed humic acid was obtained after isolation and purification of compost humic acid and kept for investigation.

Acid hydrolysis of Peatsoil acid

Peatsoil humic acid sample (1g) was refluxed for 12 hours at (160^{o}C) with 50cm^3 of 6M HCl. The mixture was allowed to cool, decanted, and centrifuged after hydrolysis. The insoluble residues were washed with distilled water via centrifugation several times, and the supernatant was treated with $AgNO_3$ solution until no white precipitate was observed. The residue was thoroughly dried over $CaCl_2$ in a desiccator at room temperature (Chefetz *et al.*, 2002). Finally, the obtained hydrolysed humic acid was kept for investigation.

Potentiometric Titrations

Potentiometric measurements were carried out using a pH-meter Jenway (model 3510) with combine electrode, the sensitivity of the pH - meter is 0.01 units. The pH meter was switched on half an hour before starting the titration for initial warm up of the instrument. The instrument was calibrated with an aqueous standard buffer solution of pH 4.00 and 10.0 (borate buffer) prepared from a "Qualigens" buffer tablets.

The following sets of solutions were prepared in a 250cm^3 volumetric flask separately for pH metric titrations.

(i) 5 cm^3 0.1 M HCl + 40 cm^3 deionized water
(ii) 5 cm^3 0.1 M HCl + 39 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid
(iii) 5 cm^3 0.1 M HCl + 37 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid + 2 cm^3 0.01 M Cu(II)

The solutions were titrated against standardized 0.110MNaOH separately. The total volume of each mixture was adjusted to 50 cm^3 and the ionic strength of the solutions was maintained constant at by adding appropriate amount of stock solution of 1M KNO$_3$ (Gamal, 2015; Omar and Ali, 2015). A magnetic stirrer was used to achieve thorough mixing of the interacting solutions at 550 rpm. The same set of experimental conditions was applied for potentiometric titration of remaining samples.

Evaluation of pKa of Hydrolysed peat soil Humic Acids

The proton-ligand formation number n$_\mathbf{A}$ were calculated by Irving and Rossotti expression (Omar and Ali, 2015).

$$nA = Y - \frac{(V2-V1)(No-Eo)}{(Vo+V1)TcL} \quad \text{....................................1}$$

Where: Y is number of dissociable proton, (V$_2$-V$_1$) is the measure of displacement of the ligand curve relative to acid curve, N^o and E^o are the resultant concentration of alkali solution, free acid solution, T$_{cL}$^{o} is the total ligand concentration, V^o is the total volume of titration solution,V$_1$ is the volume of alkali added to acid solution,V$_2$ is the volume of alkali added to acid solution + ligand solution, acid dissociation constants (pKa - values) of ligand were calculated by algebraic method point wise calculation (Tables 1). The dissociation constants (pKa) were calculated according to the following relation:

$$pKa = pH + \log\left(\frac{nA}{1-nA}\right) \quad \text{..............................2}$$

Where: pKa is the acid dissociation constant, n$_A$is the Proton-ligand formation number and pH is the pH-values (Omar and Ali, 2015).

Determination of metal-ligand stability constants (log K) of complexes

The potentiometric measurement for the determination of stability constant of a complex in solution is based on the fact that the redox potential of the couple $\frac{M^{+(m-n)}}{M^{+m}}$ is shifted significantly on complexation of the metal ion with the ligand. This method involves change in hydrogen ion concentration [H$^+$] due to the displacement or association of one or more protons taking place during complexation reaction. This change can be found out by titrating the solutions containing free acid, acid with ligand, and acid with ligand and metal ion, individually against a standard alkali solution at a constant ionic strength or temperature. Either ionic strength or temperature may be varied for different sets of solutions. In all the cases, the change in the pH of the solution is measured after each addition of a known amount of alkali to the reaction cell which contains the reaction mixture. The titration curves are then drawn by plotting the measured pH values against the corresponding volume of alkali added and the stability constants of the complexes are determined from the titration curves by employing pH-metric titration technique given by (Irving and Rossoti).

Metal-ligand stability constants (Log K) were determined by using the following relations:

$$\bar{n} = \frac{(V_3 - V_2)(E^0 + N^0)}{(V^0 + V_2)\bar{n}_A T_m^0} \quad \text{..3}$$

and

$$PL = \log_{10}\left\{\frac{1 + \beta_n^H \dfrac{1}{[anti\ \log \mathrm{pH}]^n}}{\mathrm{T}_\mathrm{L}^0 - \bar{n}T_m^0} \mathrm{X} \frac{(V^0 + V_3)}{V^0}\right\} \quad \text{..4}$$

Where $T_{L,}$ T^o, $E°$, and V^ohavethe same significance as in equation (1) above, T_m denotes the total concentration of metal present in solution, V_3 is the volume of metal ions present in solution and β^H is the overall proton ligand stability constant. The metal-ligand stability constants (log K) were determined by employing point wise computational Method (eq. 5 and 6).

$$\text{LogK}_1 = \log\left(\frac{n}{1-n}\right) + \text{pL} \qquad \ldots\ldots\ldots\ldots.5$$

$$\text{LogK}_2 = \log\left(\frac{1-n}{2-n}\right) + \text{pL}\ldots\ldots\ldots\ldots\ldots\ldots\ldots.6$$

Where: Log K is the metal-ligand stability constant, pL is the Free ligand exponent function, **n** is the Average number of ligand attached with metal ion (Janrao*et al.*, 2014).The results obtained were analyzed by an ORIGIN 2016 program using titration data and then the proton-ligand stability constants (pKa) and Metal-ligand stability constant (LogK) calculated (Omar and Ali, 2015).

RESULTS AND DISCUSSION

Fourier transformed infrared (FT-IR) spectra of isolated humic acid from peat soils Figure 2 had distinct clear absorption bands indicating the presence of major humic acid structural elemental groups such as H bonded OH (3680cm^{-1} peak), C=O of carbonyl (1721cm^{-1} peak), functional groups of aliphatic components CH_2 (2918cm^{-1} peak) and C-O stretching of polysaccharide (1168cm^{-1} peak). The positions of the absorption bands of the spectra fell within typical major absorption bands of humic acid which is at frequencies 3680, 2918, 1721, 1168 cm^{-1}. The first peak centred in the vicinity of 3680 cm^{-1} region is attributed to phenol OH group bounded by intermolecular H bonds. The 2918cm^{-1} band usually has absorption maximum at 2918 cm^{-1} which is due to C–H stretching of alkane group (CH_2). The next major absorption band is 1721 cm^{-1}. This band has been commonly ascribed to C=O stretching of mainly carboxyl group (COOH) with trace amount of ketones. The last peak was observed at 1168 cm^{-1} due to C–O stretching of polysaccharides and this peak appeared also in the spectra of humic acid from peat soil. The FTIR spectra of the isolated humic acid contained all major characteristic absorption peaks of humic acid. These absorption peaks indicated the presence of the major structural elements of humic acid namely H bonded OH, C=C of aromatic ring, C=O of carbonyl group (both carboxyl and ketonic), CH_2 group. This strongly supports the presence of humic acid.

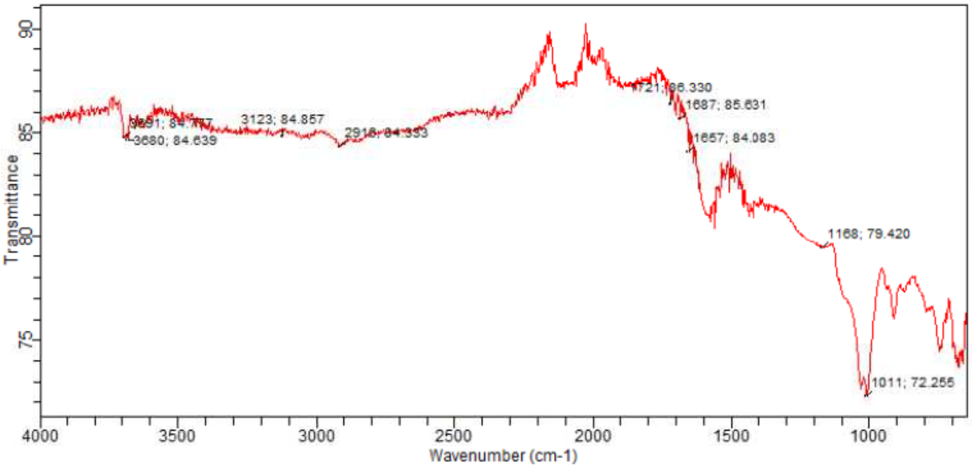


Fig. 2 : FT-IR spectraof peatsoilhumic acid (PSHA)

Evaluation of acid dissociation constant (pka) of acid hydrolysed peat soil humicacid at phenolic group

The value of the dissociation constant of the peat soil humic acid (PSHA) that underwent acidhydrolysis studied was found to be 8.9299 as shown Table 1, which is lower than the literaturevalues reported by Almeida and Szpoganics, (2015), Borges *et al.*, (2005); Badr *et al.*, (2012)and Fernandes *et al*,.(2009) of 9.73, 9.47 and 10.30. The difference between the obtained valuesand the reported values in this study might be probably as a result of acid hydrolysis of humicacid.

Table 1: PKa of (Hydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	log($\frac{nA}{1-nA}$)	pKa
8.50	5.30	6.29	0.99	0.3594	-0.2510	8.2490
8.72	5.35	6.37	1.02	0.3400	-0.2880	8.4320
9.00	5.40	6.46	1.06	0.3141	-0.3391	8.6609
9.22	5.45	6.55	1.10	0.2882	-0.3927	8.8273
9.51	5.50	6.66	1.16	0.2494	-0.4786	9.0314
9.73	5.55	6.78	1.23	0.2041	-0.5910	9.1390
10.00	5.60	6.90	1.30	0.1589	-0.7238	9.2762
10.23	5.65	7.05	1.40	0.0941	-0.9835	9.2465
10.49	5.70	7.10	1.40	0.0941	-0.9835	9.5065

Average pKa = 8.9299 ± 0.4186

Table 2: PKa of (Unhydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	Log($\frac{nA}{1-n}$)	pKa
8.50	5.30	5.81	0.51	0.6619	0.2919	8.7919
8.72	5.35	5.90	0.55	0.6357	0.2418	8.9618
9.00	5.40	6.00	0.60	0.6029	0.1813	9.1813
9.22	5.45	6.10	0.65	0.5701	0.1226	9.3426
9.51	5.50	6.20	0.70	0.5376	0.0654	9.5754
9.73	5.55	6.33	0.78	0.4851	-0.0259	9.7041
10.00	5.60	6.47	0.87	0.4262	-0.1291	9.8709
10.23	5.65	6.62	0.99	0.3609	-0.2481	9.9819
10.49	5.70	6.80	1.10	0.2759	-0.4690	10.0210

Average pKa = 9.4923± 0.4410

Metal-ligand stability constant (Log K)

The stabilityconstants require the accurate values of proton-ligand stability constants (Anil and Maroti, 2008). Metal titration curves crossed over ligand titration curve indicated the formation of complex upon proton release (Santosh, *et al.*, 2011). If the values of n- are within range 0.2-0.8 and 1.2-18 this indicates the formation of 1:1 and 1:2 complexes (Sayyed and Mazahar, 2012).

The metal (II)-humate stepwise stability constants (log k) at phenolic group (Tables 3-18)

Table 3: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n}{1-n}$)	$LogK_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

$LogK_1$ (Average value) = 2.4788± 0.2203

Table 4: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	Log($\frac{n-1}{2-n}$)	$LogK_2$
9.51	5.50	6.66	6.73	0.07	1.3509	1.70	-0.2671	1.4329
9.73	5.55	6.78	6.85	0.07	1.6383	1.51	0.2467	1.7567
10.00	5.60	6.90	6.98	0.08	2.1783	1.31	-0.2158	1.0942
10.23	5.65	7.05	7.13	0.08	4.1904	1.27		
10.49	5.70	7.10	7.19	0.09	4.6920			

$LogK_2$(Average value) = 1.4280 ± 0.3312

Table 5:Point-wise method,Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	Log($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430

$LogK_1$ **(Average value)** = 2.3059± 0.6153

Table 6:Point-wise method, Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$V_3\text{-}V_2$	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
9.73	5.55	6.33	6.42	0.09	0.9000	1.69		
10.00	5.60	6.47	6.58	0.11	1.2578	1.44	-0.4592	0.9808
10.23	5.65	6.62	6.84	0.12	1.6137	1.26	-0.2010	1.4610
10.49	5.70	6.80	6.92	0.12	2.1052	1.03		

$LogK_2$ **(Average value)** = 1.2209± 0.3398

Table 7:Point-wise method,Pb (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	log($\frac{n}{1-n}$)	$LogK_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.60	0.05	0.8333	1.96	0.6989	2.6589

$LogK_1$ (Average value) = 2.5832 ±0.1614

Table 8:Point-wise method,Pb-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	log($\frac{n-1}{2-n}$)	$logK_2$
9.51	5.50	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.83	0.05	1.1702	1.44		
10.00	5.60	6.90	6.90	0.05	1.4864	1.22	-0.0237	1.1963
10.23	5.65	7.05	7.10	0.05	2.0190	1.09		
10.49	5.70	7.10	7.17	0.07	3.6492	1.00		

$LogK_2$(Average value) = 1.1963

Table 9:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$V_3\text{-}V_2$	n	pL	Log ($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.5477	2.3123
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	0.0272	2.2072
9.51	5.50	6.20	6.26	0.07	0.6417	1.89	0.2530	2.1430
9.73	5.55	6.40	6.40	0.07	0.7000	1.67	0.3680	2.0380

$LogK_1$ **(Average value)** = 2.2364 ± 0.1602

Table 10:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$V_3\text{-}V_2$	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
10.00	5.60	6.47	6.55	0.08	1.9503	1.41		
10.23	5.65	6.62	6.72	0.11	1.4792	1.26	-0.0361	1.2239

$LogK_2$ **(Average value)** = 1.2239

Table 11:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	log($\frac{n}{n-1}$)	$LogK_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4290	2.2110
8.72	5.35	6.37	6.39	0.02	0.2858	2.42	-0.3978	2.0222
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

$LogK_1$ (Average value)=2.1382**±**0.1046

Table 12:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	$\log(\frac{n-1}{2-n})$	LogK$_2$
9.51	5.55	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.84	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.93	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.10		
10.49	5.70	7.10	7.18	0.07	3.6492	0.83		

LogK$_2$(Average value) = 1.5453 **±** 0.3450

Table 13:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	V$_3$-V$_2$	n	pL	$\text{Log}(\frac{n}{n-1})$	Log K$_1$
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.3477	2.3123
9.00	5.40	6.00	6.04	0.04	0.3236	2.38	-0.3202	2.0598
9.22	5.45	6.10	6.15	0.05	0.4297	2.17	-0.1230	2.0470
9.51	5.50	6.20	6.26	0.06	0.5500	1.89	0.0871	1.9771
9.73	5.55	6.33	6.40	0.07	0.7000	1.67	0.3680	2.0380

LogK$_1$ **(Average value)** = 2.1568 ± 0.2069

Table 14:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	V$_3$-V$_2$	n	pL	$\text{Log}(\frac{n-1}{2-n})$	Log K$_2$
10.00	5.60	6.47	6.55	0.08	0.9148	1.41		
10.23	5.65	6.62	6.71	0.09	1.2102	1.20	-0.5749	0.6251
10.49	5.70	6.80	6.92	0.09	1.5968	1.03	0.1703	1.2003

LogK$_2$ **(Average value)** = 0.9127± 0.4070

Table15:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	$\text{Log}(\frac{n}{1-n})$	LogK$_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4210	2.2190
8.72	5.35	6.37	6.40	0.03	0.4286	2.42	-0.1249	2.2951
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.96	0.3010	2.2610
9.51	5.55	6.66	6.70	0.04	0.7720	1.67	0.5297	2.1997

LogK$_1$ (Average value) = 2.2108± 0.0825

Table 16:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	$\text{Log}(\frac{n-1}{2-n})$	Log K$_2$
9.73	5.55	6.78	6.83	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.95	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.09		
10.49	5.70	7.10	7.16	0.06	3.1429	0.89		

LogK$_2$ **(Average value)** = 1.5453± 0.3450

Table 17:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	V$_3$-V$_2$	n	pL	$\text{Log}(\frac{n}{n-1})$	Log K$_1$
8.50	5.30	5.81	5.86	0.05	0.3717	2.88	-0.2280	2.6520
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.06	0.06	0.4853	2.38	-0.0255	2.3545
9.22	5.45	6.10	6.16	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430
9.73	5.55	6.33	6.41	0.08	0.8000	1.69	0.6020	2.2920

LogK$_1$ **(Average value)** = 2.2516± 0.5380

Table 18:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$\mathrm{Log}(\frac{n-1}{2-n})$	Log K_2
10.00	5.60	6.47	6.57	0.10	1.1434	1.43		
10.23	5.65	6.62	6.72	0.10	1.3448	1.23	-0.2788	0.9512
10.49	5.70	6.80	6.90	0.10	1.7742	1.03	0.5351	1.5651

LogK_2 **(Average value)** = 1.2581± 0.4340

Table 19: Stepwise and overall Stability constants of thehydrolysed and unhydrolysed divalent metal (II) complexes

Chelates	LogK_1	LogK_2	Logβ
[Cu (Hydrolysed PSHA-1)$_2$]	2.4788	1.4280	3.9068
[Pb (Hydrolysed PSHA-1)$_2$]	2.5832	1.1963	3.7795
[Cd (Hydrolysed PSHA-1)$_2$]	2.2108	1.5453	3.7561
[Mg (Hydrolysed PSHA-1)$_2$]	2.1382	1.5453	3.6835
[Cu (Unhydrolysed PSHA-1)$_2$]	2.3059	1.2209	3.5268
[Pb (Unhydrolysed PSHA-1)$_2$]	2.2364	1.2239	3.4603
[Cd (Unhydrolysed PSHA-1)$_2$]	2.2516	1.2581	3.5097
[Mg (Unydrolysed PSHA-1)$_2$]	2.1568	0.9127	3.0695

The results obtained (Table19) shows the stepwise and overall stability constants to be not high indicating low stability of the complexes, because the solubility of most metal ions in the basic pH range is minimal due to metal hydroxide precipitation (Karimi, 2017). In general, the stepwise stability constants (K_1 and K_2) follow the order $K_1 > K_2$ for the copper, lead, magnesium and cadmium complexes respectively. The steady decrease of the values with increasing number of ligands is in agreement with the prediction made by researchers (Na'aliya, 2013). The decrease could be attributed to the fact that as the number of the ligands (Humate ions) that enters the coordination zone increases the aqua molecules available for replacement by the ligands become less. Thus, the metal ions become less electron loving with progressive intake of the ligand and this results in the decrease in the values of the constants (Na'aliya, 2013). Also the stability of the complexes is influenced by the size and number of the chelate rings(Mackay and Mackay,2002).All the complexes form rings in their structure as humate, a bidentate ligand, bond the metal ions in the ratio 1:2 (Boguta and Sokolowska, 2016) forming chelate rings. The values of the overall stability constants (logβ) obtained for humate complexes are not high indicating low stability as the values are not high. LogK values for copper-humates (Table 3 to 6) obtained in this study are lower than those reported for the complexes of humic acids (Pandey *et al.*, 2015; Dinu, 2013; Kaschl *et al.*, 2010 and Gilbeto and Jorg, 2001). The values of LogK(Table 7 to 10) forlead-humates are lower than those reported for the lead in the literature (Dinu, 2013; Gilbeto and Jorg 2001). Log K values(Table 11 to 14) for magnesium-humates obtained in this study are close to those reported by (Pandey *et al.*, 2015). Log K values of cadmium-humates (Table 15 to 18) obtained in this work near to the one reported by (Dinu, 2013 and Pandey *et al.*, 2015).The difference between the reported values and the values obtained in this study might be probably as a result of acid hydrolysis of humic acid. The values of the overall stability constants (log β) of the copper humates complexes presented in Table 19 is high than that of other metal humate complexes, show relatively high stability of Cu-HA complexes, show the following order of stability: Cu >Pb> Cd > Mg; which are in close agreement to the findings of (Dinu, 2013 and Pandey *et al.*, 2015).The high stability of Cu-humate chelate could be attributed to the existence of coordinate covalent bond between the complexing agents and the Cu^{2+} ions. Since, Cu^{2+} being a metal of the transitional series with $3d^9$ electronic configurations can accept the electrons from the complexing agents. Similarly,the low stabilities of Pb,Cd and Mg -complexes could be explained by that Pb^{2+} with $6s^2$, Cd^{2+} with $4d^{10}$ and Mg^{2+} with $2p^6$ their electronic configuration has a completely filled d,p and s orbitals. Moreover, the stabilities of metal ions with hydrolysed humic acid from peat soil were higher than those with unhydrolysed humic acid from peat soil; which is ascribed to the high content of acidity in hydrolysed humic acid than unhydrolysed humic acid.

CONCLUSION

The values of logK for Cu(II) hydrolysed humic acid complex was higher followed by Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes as compared with metal(II) unhydrolysed humic acid complexes . This indicates acid hydrolysis of humic acid can enhance the complexation behavior of humic acid with metal (II) ions. However, the higher values of logβ for Cu(II), Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes indicates more stable stepwise complexes formed as compared with Cu(II), Pb(II), Cd(II) and Mg(II) unhydrolysed humic acid complexes.

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STABILITY CONSTANTS OF COMPLEXES OF METAL IONS WITH PEATSOIL HUMIC ACIDS UNDER NON-ACID-CONDITIONS

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ABSTRACT

Stability constants of complexes of four divalent metal ions viz. Cu^{2+}, Pb^{2+},Mg^{2+} and Cd^{2+} with humic acids (HA) were determined by potentiometric titration of humic acids with the corresponding salt of the divalent metals in aqueous media under non-acid-condition. The log K (logarithm of the stability constant) ranged from 1.0942 to 2.7471 for metal-humic acid complexes were determined using point-wise computational method. The order of stability constants were obtained as follows: Cu >Pb> Cd > Mg for metal -HA complexes respectively, indicating a higher degree of complexation with Cu metal ion.

Keywords: stability constant, humic acid, potentiometric titration, divalent metals, acid hydrolysis.

NTRODUCTION

The stability constant of a complex is the numerical expression of its stability and provides a quantitative measure of affinity of the metal ion to the complexing agent. An understanding of the relative stability of metal-complexes helps in predicting the behavior of metal ions in the soil (Ram and Raman, 1982). Extensive researches has been done to determine the stability constants of the complexes formed between humic acid (HA) with a number of metal ions. Ashok *et al*., (2000) reported that humic acid with hydroxyl, phenoxyl and carboxyl reactive groups can form coordination compound with metal ions at pH 3.5. The stability constants(Log K) for different metal-humic acid complexes indicated the following order of the stabilities of complexes formed between humic acid and metal ion, Cu >Fe >Pb> Ni > Co > Ca > Cd > Zn >Mn> Mg. Andelkovic *et al*., (2010) investigated the binding of Cd(II) to soil humic acid at pH 6.5 and in 0.1M KNO_3 ionic medium. The stability constant for binding indicating greater stability in the case when carboxyl groups are involved in complexation reaction. Kostic *et al*.,(2012) investigated the complexation of humic acid with certain heavy metal ions (Co(II), Ni(II),Cu(II), Zn(II), and Pb(II). The experiment was performed at 25°C, at pH 4.0 and ionic strength of 0.01M. Stability constant of complex between Pb(II) ions and humic acid is greater than stability constants of other investigated metal-humate complexes. Bogata and Sokolowska (2016) analyses the interaction between humic acids from different soils and Zn (II) ions at wide concentration ranges and at pH 5. Studies have showed significant impact of Zn concentration, pH and some properties of humic acids with zinc.But all of these studies were limited to acidic pH range. Therefore, the present study was carried out to determine and compare the stability constants of complexes of metal ions with hydrolysed peat soil humic acid and unhydrolysed peat soil humic under non-acid conditions.

MATERIALS AND METHODS

Analytical grade chemicals used includes hydrochloric acid (HCl), nitric acid (HNO_3), sodium hydroxide (NaOH), lead nitrate $Pb(NO_3)_2$, copper nitrate $Cu(NO_3)_2.3H_2O$, cadmium nitrate $Cd(NO_3)_2.4H_2O$, magnesium nitrate $Mg(NO_3)_2.6H_2O$, potassium nitrate (KNO_3), calcium chloride ($CaCl_2$), (sigma-Aldrich). Dowex 50WX8, (20-50 mesh) from Fluka.

Area of study

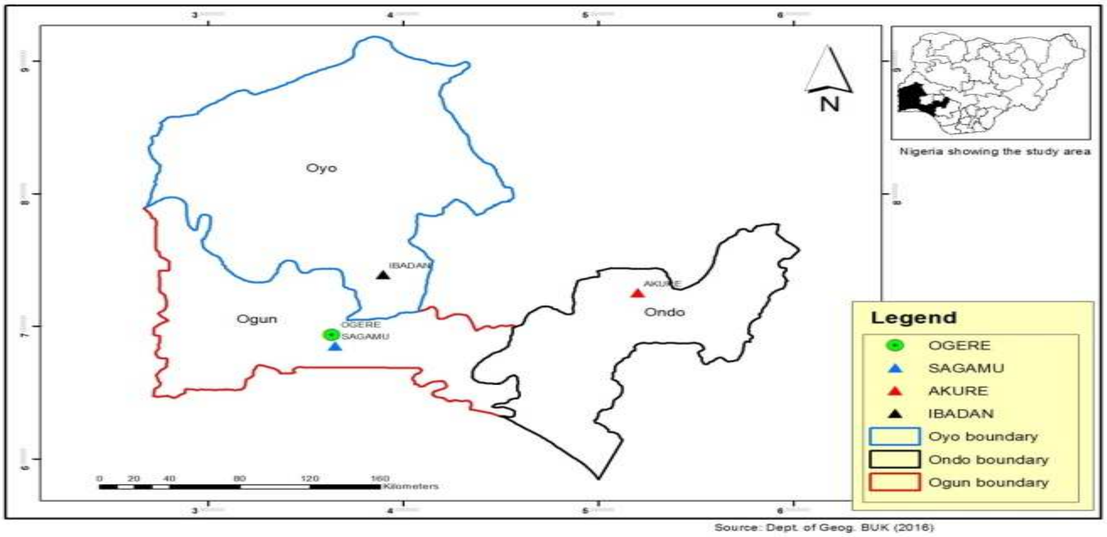

Figure 1: Map showing the sampling point at Sagamu Town, Ogun State.

Description of Sampling Area

Sagamu has geographical coordinates between 6°50′ north; 3° 38′ east is located in south western region of Nigeria. The region has tropical wet and dry climate with a lengthy wet season and relatively constant temperatures throughout the course of the year. Wet season runs from March to October, November to December forms the region dry season. The vegetation type of the region is savannah which is really grassland with small bushes and occasional big trees. Grassland soils have substantially higher organic matter content than forest soils (Novackova, 2011).

Sample Collection

The Peatsoil samples were collected from four different sampling points (0-10cm depth) in Sagamu into polyethylene bag with plastic spoons. Samples were taken to the laboratory, extraneous materials were removed; the samples were air-dried, crushed and ground to a fine powder in a mortar passed through a 0.20mm sieve. The samples were kept for analysis.

Isolation and purification of humic acid from peat soil sample

Peatsoil sample (100g) was mixed with 1000 cm^3 of 0.1M NaOH solution, shaken for 3hours and left to stand overnight. Dark-coloured supernatant was obtained and decanted from solid residue. The dark-coloured supernatant was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 6 hours. Yellowish brown supernatant and dark-brown precipitate were obtained. The yellowish brown supernatant was decanted followed by centrifuge and discarded. The dark-brown precipitate was mixed with 500$cm^3$of 0.1M NaOH solution followed by passing through dowex resin. The dark-brown solution was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 3 hours. The dark-brown precipitate was washed several times with deionized water. The supernatant was treated with $AgNO_3$ solution until no white precipitate observed. The humic acid was transferred to weighed crucible and dried at 60°C in an oven for 12 hours. The humic acid was cooled and dried in the desiccator, weighed and recorded. The obtained humic acid was dried again at 60°C for additional 6 hours cooled and dried in the desiccator, weighed and recorded constant weight was obtained (Baruah *et al.*, 2015).

FT-IR analysis

FT-IR spectra of humic acid sample was analysed using Carry 630 FT-IR Agilent Technologies.

Unhydrolysed compost humic acid

The unhydrolysed humic acid was obtained after isolation and purification of compost humic acid and kept for investigation.

Acid hydrolysis of Peatsoil acid

Peatsoil humic acid sample (1g) was refluxed for 12 hours at (160°C) with 50cm^3 of 6M HCl. The mixture was allowed to cool, decanted, and centrifuged after hydrolysis. The insoluble residues were washed with distilled water via centrifugation several times, and the supernatant was treated with $AgNO_3$ solution until no white precipitate was observed. The residue was thoroughly dried over $CaCl_2$ in a desiccator at room temperature (Chefetz *et al.*, 2002). Finally, the obtained hydrolysed humic acid was kept for investigation.

Potentiometric Titrations

Potentiometric measurements were carried out using a pH-meter Jenway (model 3510) with combine electrode, the sensitivity of the pH - meter is 0.01 units. The pH meter was switched on half an hour before starting the titration for initial warm up of the instrument. The instrument was calibrated with an aqueous standard buffer solution of pH 4.00 and 10.0 (borate buffer) prepared from a "Qualigens" buffer tablets.

The following sets of solutions were prepared in a 250cm^3 volumetric flask separately for pH metric titrations.

(i) 5 cm^3 0.1 M HCl + 40 cm^3 deionized water
(ii) 5 cm^3 0.1 M HCl + 39 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid
(iii) 5 cm^3 0.1 M HCl + 37 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid + 2 cm^3 0.01 M Cu(II)

The solutions were titrated against standardized 0.110MNaOH separately. The total volume of each mixture was adjusted to 50 cm^3 and the ionic strength of the solutions was maintained constant at by adding appropriate amount of stock solution of 1M KNO_3 (Gamal, 2015; Omar and Ali, 2015). A magnetic stirrer was used to achieve thorough mixing of the interacting solutions at 550 rpm. The same set of experimental conditions was applied for potentiometric titration of remaining samples.

Evaluation of pKa of Hydrolysed peat soil Humic Acids

The proton-ligand formation number $n_{\mathbf{A}}$ were calculated by Irving and Rossotti expression (Omar and Ali, 2015).

$$nA = Y - \frac{(V2-V1)(No-Eo)}{(Vo+V1)TcL} \quad \text{....................................1}$$

Where: Y is number of dissociable proton, (V_2-V_1) is the measure of displacement of the ligand curve relative to acid curve, N^o and E^o are the resultant concentration of alkali solution, free acid solution, $T_{cL}{}^o$ is the total ligand concentration, V^o is the total volume of titration solution,V_1 is the volume of alkali added to acid solution,V_2 is the volume of alkali added to acid solution + ligand solution, acid dissociation constants (pKa - values) of ligand were calculated by algebraic method point wise calculation (Tables 1). The dissociation constants (pKa) were calculated according to the following relation:

$$pKa = pH + \log\left(\frac{nA}{1-nA}\right) \quad \text{..............................2}$$

Where: pKa is the acid dissociation constant, $n_A$is the Proton-ligand formation number and pH is the pH-values (Omar and Ali, 2015).

Determination of metal-ligand stability constants (log K) of complexes

The potentiometric measurement for the determination of stability constant of a complex in solution is based on the fact that the redox potential of the couple $\frac{M^{+(m-n)}}{M^{+m}}$ is shifted significantly on complexation of the metal ion with the ligand. This method involves change in hydrogen ion concentration [H^+] due to the displacement or association of one or more protons taking place during complexation reaction. This change can be found out by titrating the solutions containing free acid, acid with ligand, and acid with ligand and metal ion, individually against a standard alkali solution at a constant ionic strength or temperature. Either ionic strength or temperature may be varied for different sets of solutions. In all the cases, the change in the pH of the solution is measured after each addition of a known amount of alkali to the reaction cell which contains the reaction mixture. The titration curves are then drawn by plotting the measured pH values against the corresponding volume of alkali added and the stability constants of the complexes are determined from the titration curves by employing pH-metric titration technique given by (Irving and Rossoti).

Metal-ligand stability constants (Log K) were determined by using the following relations:

$$\bar{n} = \frac{(V_3 - V_2)(E^0 + N^0)}{(V^0 + V_2)\bar{n}_A T_m^0} \quad \text{...3}$$

and

$$PL = \log_{10}\left\{\frac{1 + \beta_n^H \dfrac{1}{[anti\ \log pH]^n}}{T_L^0 - \bar{n} T_m^0} \text{X} \frac{(V^0 + V_3)}{V^0}\right\} \quad \text{...4}$$

Where $T_{L,}$ T^o, E°, and V^ohavethe same significance as in equation (1) above, T_m denotes the total concentration of metal present in solution, V_3 is the volume of metal ions present in solution and β^H is the overall proton ligand stability constant. The metal-ligand stability constants (log K) were determined by employing point wise computational Method (eq. 5 and 6).

$$\text{Log}K_1 = \log\left(\frac{n}{1-n}\right) + pL \qquad \ldots\ldots\ldots\ldots.5$$

$$\text{Log}K_2 = \log\left(\frac{1-n}{2-n}\right) + pL\ldots\ldots\ldots\ldots\ldots\ldots\ldots.6$$

Where: Log K is the metal-ligand stability constant, pL is the Free ligand exponent function, **n** is the Average number of ligand attached with metal ion (Janrao*et al*., 2014).The results obtained were analyzed by an ORIGIN 2016 program using titration data and then the proton-ligand stability constants (pKa) and Metal-ligand stability constant (LogK) calculated (Omar and Ali, 2015).

RESULTS AND DISCUSSION

Fourier transformed infrared (FT-IR) spectra of isolated humic acid from peat soils Figure 2 had distinct clear absorption bands indicating the presence of major humic acid structural elemental groups such as H bonded OH ($3680cm^{-1}$ peak), C=O of carbonyl ($1721cm^{-1}$ peak), functional groups of aliphatic components CH_2 ($2918cm^{-1}$ peak) and C-O stretching of polysaccharide ($1168cm^{-1}$ peak). The positions of the absorption bands of the spectra fell within typical major absorption bands of humic acid which is at frequencies 3680, 2918, 1721, 1168 cm^{-1}. The first peak centred in the vicinity of 3680 cm^{-1} region is attributed to phenol OH group bounded by intermolecular H bonds. The $2918cm^{-1}$ band usually has absorption maximum at 2918 cm^{-1} which is due to C–H stretching of alkane group (CH_2). The next major absorption band is 1721 cm^{-1}. This band has been commonly ascribed to C=O stretching of mainly carboxyl group (COOH) with trace amount of ketones. The last peak was observed at 1168 cm^{-1} due to C–O stretching of polysaccharides and this peak appeared also in the spectra of humic acid from peat soil. The FTIR spectra of the isolated humic acid contained all major characteristic absorption peaks of humic acid. These absorption peaks indicated the presence of the major structural elements of humic acid namely H bonded OH, C=C of aromatic ring, C=O of carbonyl group (both carboxyl and ketonic), CH_2 group. This strongly supports the presence of humic acid.

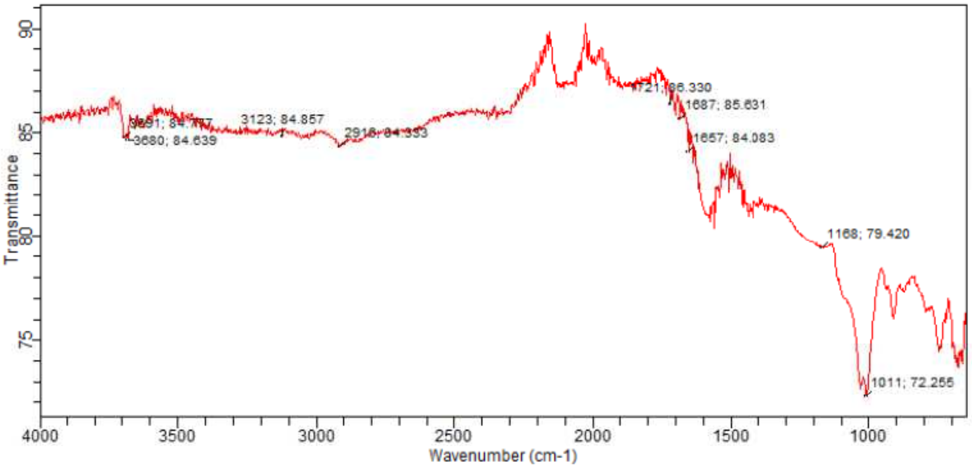

Fig. 2 : FT-IR spectraof peatsoilhumic acid (PSHA)

Evaluation of acid dissociation constant (pka) of acid hydrolysed peat soil humicacid at phenolic group

The value of the dissociation constant of the peat soil humic acid (PSHA) that underwent acidhydrolysis studied was found to be 8.9299 as shown Table 1, which is lower than the literaturevalues reported by Almeida and Szpoganics, (2015), Borges *et al*., (2005); Badr *et al*., (2012)and Fernandes *et al*,.(2009) of 9.73, 9.47 and 10.30. The difference between the obtained valuesand the reported values in this study might be probably as a result of acid hydrolysis of humicacid.

Table 1: PKa of (Hydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	$\log(\frac{nA}{1-nA})$	pKa
8.50	5.30	6.29	0.99	0.3594	-0.2510	8.2490
8.72	5.35	6.37	1.02	0.3400	-0.2880	8.4320
9.00	5.40	6.46	1.06	0.3141	-0.3391	8.6609
9.22	5.45	6.55	1.10	0.2882	-0.3927	8.8273
9.51	5.50	6.66	1.16	0.2494	-0.4786	9.0314
9.73	5.55	6.78	1.23	0.2041	-0.5910	9.1390
10.00	5.60	6.90	1.30	0.1589	-0.7238	9.2762
10.23	5.65	7.05	1.40	0.0941	-0.9835	9.2465
10.49	5.70	7.10	1.40	0.0941	-0.9835	9.5065

Average pKa = 8.9299 ± 0.4186

Table 2: PKa of (Unhydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	$\text{Log}(\frac{nA}{1-n})$	pKa
8.50	5.30	5.81	0.51	0.6619	0.2919	8.7919
8.72	5.35	5.90	0.55	0.6357	0.2418	8.9618
9.00	5.40	6.00	0.60	0.6029	0.1813	9.1813
9.22	5.45	6.10	0.65	0.5701	0.1226	9.3426
9.51	5.50	6.20	0.70	0.5376	0.0654	9.5754
9.73	5.55	6.33	0.78	0.4851	-0.0259	9.7041
10.00	5.60	6.47	0.87	0.4262	-0.1291	9.8709
10.23	5.65	6.62	0.99	0.3609	-0.2481	9.9819
10.49	5.70	6.80	1.10	0.2759	-0.4690	10.0210

Average pKa = 9.4923± 0.4410

Metal-ligand stability constant (Log K)

The stabilityconstants require the accurate values of proton-ligand stability constants (Anil and Maroti, 2008). Metal titration curves crossed over ligand titration curve indicated the formation of complex upon proton release (Santosh, *et al.*, 2011). If the values of n- are within range 0.2-0.8 and 1.2-18 this indicates the formation of 1:1 and 1:2 complexes (Sayyed and Mazahar, 2012).

The metal (II)-humate stepwise stability constants (log k) at phenolic group (Tables 3-18)

Table 3: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$\log(\frac{n}{1-n})$	LogK_1
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

LogK_1 (Average value) = 2.4788± 0.2203

Table 4: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$\text{Log}(\frac{n-1}{2-n})$	LogK_2
9.51	5.50	6.66	6.73	0.07	1.3509	1.70	-0.2671	1.4329
9.73	5.55	6.78	6.85	0.07	1.6383	1.51	0.2467	1.7567
10.00	5.60	6.90	6.98	0.08	2.1783	1.31	-0.2158	1.0942
10.23	5.65	7.05	7.13	0.08	4.1904	1.27		
10.49	5.70	7.10	7.19	0.09	4.6920			

LogK_2(Average value) = 1.4280 ± 0.3312

Table 5:Point-wise method,Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	Log($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430

$LogK_1$ **(Average value)** = 2.3059± 0.6153

Table 6:Point-wise method, Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$V_3\text{-}V_2$	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
9.73	5.55	6.33	6.42	0.09	0.9000	1.69		
10.00	5.60	6.47	6.58	0.11	1.2578	1.44	-0.4592	0.9808
10.23	5.65	6.62	6.84	0.12	1.6137	1.26	-0.2010	1.4610
10.49	5.70	6.80	6.92	0.12	2.1052	1.03		

$LogK_2$ **(Average value)** = 1.2209± 0.3398

Table 7:Point-wise method,Pb (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	log($\frac{n}{1-n}$)	$LogK_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.60	0.05	0.8333	1.96	0.6989	2.6589

$\mathbf{LogK_1}$ **(Average value)** = 2.5832 ±0.1614

Table 8:Point-wise method,Pb-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	log($\frac{n-1}{2-n}$)	$logK_2$
9.51	5.50	6.66	6.71	0.05	0.9650	1.67	-0.0237	1.1963
9.73	5.55	6.78	6.83	0.05	1.1702	1.44		
10.00	5.60	6.90	6.90	0.05	1.4864	1.22		
10.23	5.65	7.05	7.10	0.05	2.0190	1.09		
10.49	5.70	7.10	7.17	0.07	3.6492	1.00		

$\mathbf{LogK_2}$**(Average value)** = 1.1963

Table 9:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$V_3\text{-}V_2$	n	pL	Log ($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.5477	2.3123
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	0.0272	2.2072
9.51	5.50	6.20	6.26	0.07	0.6417	1.89	0.2530	2.1430
9.73	5.55	6.40	6.40	0.07	0.7000	1.67	0.3680	2.0380

$LogK_1$ **(Average value)** = 2.2364 ± 0.1602

Table 10:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$V_3\text{-}V_2$	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
10.00	5.60	6.47	6.55	0.08	1.9503	1.41	-0.0361	1.2239
10.23	5.65	6.62	6.72	0.11	1.4792	1.26		

$LogK_2$ **(Average value)** = 1.2239

Table 11:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	log($\frac{n}{n-1}$)	$LogK_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4290	2.2110
8.72	5.35	6.37	6.39	0.02	0.2858	2.42	-0.3978	2.0222
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

$\mathbf{LogK_1}$ **(Average value)=**2.1382**±**0.1046

Table 12:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	log($\frac{n-1}{2-n}$)	LogK$_2$
9.51	5.55	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.84	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.93	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.10		
10.49	5.70	7.10	7.18	0.07	3.6492	0.83		

LogK$_2$(Average value) = 1.5453 **±** 0.3450

Table 13:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	V$_3$-V$_2$	n	pL	Log($\frac{n}{n-1}$)	Log K$_1$
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.3477	2.3123
9.00	5.40	6.00	6.04	0.04	0.3236	2.38	-0.3202	2.0598
9.22	5.45	6.10	6.15	0.05	0.4297	2.17	-0.1230	2.0470
9.51	5.50	6.20	6.26	0.06	0.5500	1.89	0.0871	1.9771
9.73	5.55	6.33	6.40	0.07	0.7000	1.67	0.3680	2.0380

LogK$_1$ **(Average value)** = 2.1568 ± 0.2069

Table 14:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	V$_3$-V$_2$	n	pL	Log($\frac{n-1}{2-n}$)	Log K$_2$
10.00	5.60	6.47	6.55	0.08	0.9148	1.41		
10.23	5.65	6.62	6.71	0.09	1.2102	1.20	-0.5749	0.6251
10.49	5.70	6.80	6.92	0.09	1.5968	1.03	0.1703	1.2003

LogK$_2$ **(Average value)** = 0.9127± 0.4070

Table15:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	Log($\frac{n}{1-n}$)	LogK$_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4210	2.2190
8.72	5.35	6.37	6.40	0.03	0.4286	2.42	-0.1249	2.2951
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.96	0.3010	2.2610
9.51	5.55	6.66	6.70	0.04	0.7720	1.67	0.5297	2.1997

LogK$_1$ (Average value) = 2.2108± 0.0825

Table 16:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	Log($\frac{n-1}{2-n}$)	Log K$_2$
9.73	5.55	6.78	6.83	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.95	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.09		
10.49	5.70	7.10	7.16	0.06	3.1429	0.89		

LogK$_2$ **(Average value)** = 1.5453± 0.3450

Table 17:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	V$_3$-V$_2$	n	pL	Log($\frac{n}{n-1}$)	Log K$_1$
8.50	5.30	5.81	5.86	0.05	0.3717	2.88	-0.2280	2.6520
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.06	0.06	0.4853	2.38	-0.0255	2.3545
9.22	5.45	6.10	6.16	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430
9.73	5.55	6.33	6.41	0.08	0.8000	1.69	0.6020	2.2920

LogK$_1$ **(Average value)** = 2.2516± 0.5380

Table 18:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
10.00	5.60	6.47	6.57	0.10	1.1434	1.43		
10.23	5.65	6.62	6.72	0.10	1.3448	1.23	-0.2788	0.9512
10.49	5.70	6.80	6.90	0.10	1.7742	1.03	0.5351	1.5651

$LogK_2$ **(Average value)** = 1.2581± 0.4340

Table 19: Stepwise and overall Stability constants of thehydrolysed and unhydrolysed divalent metal (II) complexes

Chelates	**$LogK_1$**	**$LogK_2$**	**Logβ**
[Cu (Hydrolysed PSHA-1$)_2$]	2.4788	1.4280	3.9068
[Pb (Hydrolysed PSHA-1$)_2$]	2.5832	1.1963	3.7795
[Cd (Hydrolysed PSHA-1$)_2$]	2.2108	1.5453	3.7561
[Mg (Hydrolysed PSHA-1$)_2$]	2.1382	1.5453	3.6835
[Cu (Unhydrolysed PSHA-1$)_2$]	2.3059	1.2209	3.5268
[Pb (Unhydrolysed PSHA-1$)_2$]	2.2364	1.2239	3.4603
[Cd (Unhydrolysed PSHA-1$)_2$]	2.2516	1.2581	3.5097
[Mg (Unydrolysed PSHA-1$)_2$]	2.1568	0.9127	3.0695

The results obtained (Table19) shows the stepwise and overall stability constants to be not high indicating low stability of the complexes, because the solubility of most metal ions in the basic pH range is minimal due to metal hydroxide precipitation (Karimi, 2017). In general, the stepwise stability constants (K_1 and K_2) follow the order $K_1 > K_2$ for the copper, lead, magnesium and cadmium complexes respectively. The steady decrease of the values with increasing number of ligands is in agreement with the prediction made by researchers (Na'aliya, 2013). The decrease could be attributed to the fact that as the number of the ligands (Humate ions) that enters the coordination zone increases the aqua molecules available for replacement by the ligands become less. Thus, the metal ions become less electron loving with progressive intake of the ligand and this results in the decrease in the values of the constants (Na'aliya, 2013). Also the stability of the complexes is influenced by the size and number of the chelate rings(Mackay and Mackay,2002).All the complexes form rings in their structure as humate, a bidentate ligand, bond the metal ions in the ratio 1:2 (Boguta and Sokolowska, 2016) forming chelate rings. The values of the overall stability constants (logβ) obtained for humate complexes are not high indicating low stability as the values are not high. LogK values for copper-humates (Table 3 to 6) obtained in this study are lower than those reported for the complexes of humic acids (Pandey *et al*., 2015; Dinu, 2013; Kaschl *et al*., 2010 and Gilbeto and Jorg, 2001). The values of LogK(Table 7 to 10) forlead-humates are lower than those reported for the lead in the literature (Dinu, 2013; Gilbeto and Jorg 2001). Log K values(Table 11 to 14) for magnesium-humates obtained in this study are close to those reported by (Pandey *et al*., 2015). Log K values of cadmium-humates (Table 15 to 18) obtained in this work near to the one reported by (Dinu, 2013 and Pandey *et al*., 2015).The difference between the reported values and the values obtained in this study might be probably as a result of acid hydrolysis of humic acid. The values of the overall stability constants (log β) of the copper humates complexes presented in Table 19 is high than that of other metal humate complexes, show relatively high stability of Cu-HA complexes, show the following order of stability: Cu >Pb> Cd > Mg; which are in close agreement to the findings of (Dinu, 2013 and Pandey *et al*., 2015).The high stability of Cu-humate chelate could be attributed to the existence of coordinate covalent bond between the complexing agents and the Cu^{2+} ions. Since, Cu^{2+} being a metal of the transitional series with $3d^9$ electronic configurations can accept the electrons from the complexing agents. Similarly,the low stabilities of Pb,Cd and Mg -complexes could be explained by that Pb^{2+} with $6s^2$, Cd^{2+} with $4d^{10}$ and Mg^{2+} with $2p^6$ their electronic configuration has a completely filled d,p and s orbitals. Moreover, the stabilities of metal ions with hydrolysed humic acid from peat soil were higher than those with unhydrolysed humic acid from peat soil; which is ascribed to the high content of acidity in hydrolysed humic acid than unhydrolysed humic acid.

CONCLUSION

The values of logK for Cu(II) hydrolysed humic acid complex was higher followed by Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes as compared with metal(II) unhydrolysed humic acid complexes . This indicates acid hydrolysis of humic acid can enhance the complexation behavior of humic acid with metal (II) ions. However, the higher values of logβ for Cu(II), Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes indicates more stable stepwise complexes formed as compared with Cu(II), Pb(II), Cd(II) and Mg(II) unhydrolysed humic acid complexes.

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STABILITY CONSTANTS OF COMPLEXES OF METAL IONS WITH PEATSOIL HUMIC ACIDS UNDER NON-ACID-CONDITIONS

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ABSTRACT

Stability constants of complexes of four divalent metal ions viz. Cu^{2+}, Pb^{2+},Mg^{2+} and Cd^{2+} with humic acids (HA) were determined by potentiometric titration of humic acids with the corresponding salt of the divalent metals in aqueous media under non-acid-condition. The log K (logarithm of the stability constant) ranged from 1.0942 to 2.7471 for metal-humic acid complexes were determined using point-wise computational method. The order of stability constants were obtained as follows: Cu >Pb> Cd > Mg for metal -HA complexes respectively, indicating a higher degree of complexation with Cu metal ion.

Keywords: stability constant, humic acid, potentiometric titration, divalent metals, acid hydrolysis.

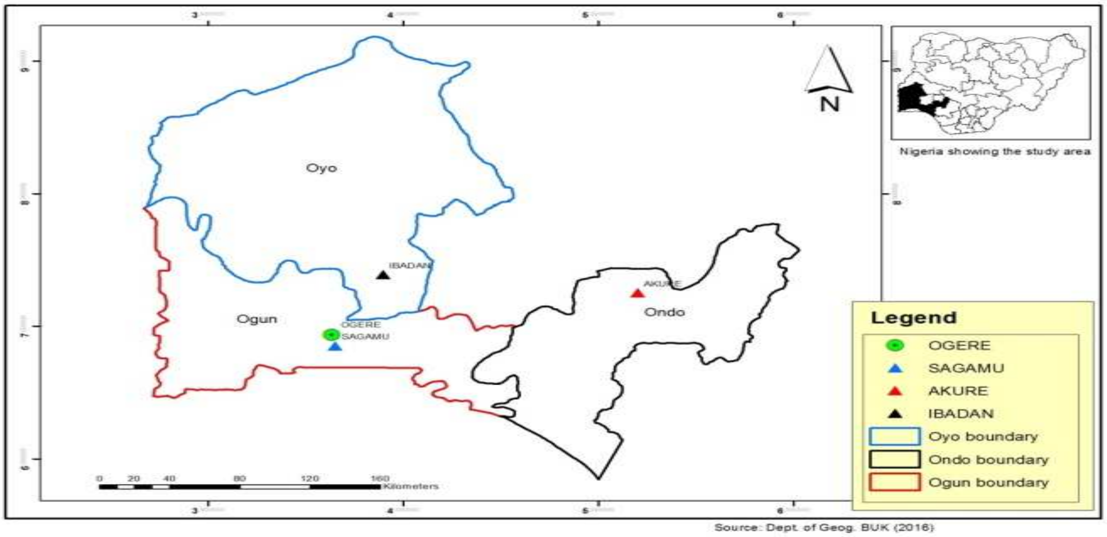
NTRODUCTION

The stability constant of a complex is the numerical expression of its stability and provides a quantitative measure of affinity of the metal ion to the complexing agent. An understanding of the relative stability of metal-complexes helps in predicting the behavior of metal ions in the soil (Ram and Raman, 1982). Extensive researches has been done to determine the stability constants of the complexes formed between humic acid (HA) with a number of metal ions. Ashok *et al*., (2000) reported that humic acid with hydroxyl, phenoxyl and carboxyl reactive groups can form coordination compound with metal ions at pH 3.5. The stability constants(Log K) for different metal-humic acid complexes indicated the following order of the stabilities of complexes formed between humic acid and metal ion, Cu >Fe >Pb> Ni > Co > Ca > Cd > Zn >Mn> Mg. Andelkovic *et al*., (2010) investigated the binding of Cd(II) to soil humic acid at pH 6.5 and in 0.1M KNO_3 ionic medium. The stability constant for binding indicating greater stability in the case when carboxyl groups are involved in complexation reaction. Kostic *et al*.,(2012) investigated the complexation of humic acid with certain heavy metal ions (Co(II), Ni(II),Cu(II), Zn(II), and Pb(II). The experiment was performed at 25°C, at pH 4.0 and ionic strength of 0.01M. Stability constant of complex between Pb(II) ions and humic acid is greater than stability constants of other investigated metal-humate complexes. Bogata and Sokolowska (2016) analyses the interaction between humic acids from different soils and Zn (II) ions at wide concentration ranges and at pH 5. Studies have showed significant impact of Zn concentration, pH and some properties of humic acids with zinc.But all of these studies were limited to acidic pH range. Therefore, the present study was carried out to determine and compare the stability constants of complexes of metal ions with hydrolysed peat soil humic acid and unhydrolysed peat soil humic under non-acid conditions.

MATERIALS AND METHODS

Analytical grade chemicals used includes hydrochloric acid (HCl), nitric acid (HNO_3), sodium hydroxide (NaOH), lead nitrate $Pb(NO_3)_2$, copper nitrate $Cu(NO_3)_2.3H_2O$, cadmium nitrate $Cd(NO_3)_2.4H_2O$, magnesium nitrate $Mg(NO_3)_2.6H_2O$, potassium nitrate (KNO_3), calcium chloride ($CaCl_2$), (sigma-Aldrich). Dowex 50WX8, (20-50 mesh) from Fluka.

Area of study



Source: Dept. of Geog. BUK (2016)

Figure 1: Map showing the sampling point at Sagamu Town, Ogun State.

Description of Sampling Area

Sagamu has geographical coordinates between 6°50′ north; 3° 38′ east is located in south western region of Nigeria. The region has tropical wet and dry climate with a lengthy wet season and relatively constant temperatures throughout the course of the year. Wet season runs from March to October, November to December forms the region dry season. The vegetation type of the region is savannah which is really grassland with small bushes and occasional big trees. Grassland soils have substantially higher organic matter content than forest soils (Novackova, 2011).

Sample Collection

The Peatsoil samples were collected from four different sampling points (0-10cm depth) in Sagamu into polyethylene bag with plastic spoons. Samples were taken to the laboratory, extraneous materials were removed; the samples were air-dried, crushed and ground to a fine powder in a mortar passed through a 0.20mm sieve. The samples were kept for analysis.

Isolation and purification of humic acid from peat soil sample

Peatsoil sample (100g) was mixed with 1000 cm^3 of 0.1M NaOH solution, shaken for 3hours and left to stand overnight. Dark-coloured supernatant was obtained and decanted from solid residue. The dark-coloured supernatant was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 6 hours. Yellowish brown supernatant and dark-brown precipitate were obtained. The yellowish brown supernatant was decanted followed by centrifuge and discarded. The dark-brown precipitate was mixed with 500$cm^3$of 0.1M NaOH solution followed by passing through dowex resin. The dark-brown solution was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 3 hours. The dark-brown precipitate was washed several times with deionized water. The supernatant was treated with $AgNO_3$ solution until no white precipitate observed. The humic acid was transferred to weighed crucible and dried at 60°C in an oven for 12 hours. The humic acid was cooled and dried in the desiccator, weighed and recorded. The obtained humic acid was dried again at 60°C for additional 6 hours cooled and dried in the desiccator, weighed and recorded constant weight was obtained (Baruah *et al.*, 2015).

FT-IR analysis

FT-IR spectra of humic acid sample was analysed using Carry 630 FT-IR Agilent Technologies.

Unhydrolysed compost humic acid

The unhydrolysed humic acid was obtained after isolation and purification of compost humic acid and kept for investigation.

Acid hydrolysis of Peatsoil acid

Peatsoil humic acid sample (1g) was refluxed for 12 hours at (160°C) with 50cm^3 of 6M HCl. The mixture was allowed to cool, decanted, and centrifuged after hydrolysis. The insoluble residues were washed with distilled water via centrifugation several times, and the supernatant was treated with $AgNO_3$ solution until no white precipitate was observed. The residue was thoroughly dried over $CaCl_2$ in a desiccator at room temperature (Chefetz *et al.*, 2002). Finally, the obtained hydrolysed humic acid was kept for investigation.

Potentiometric Titrations

Potentiometric measurements were carried out using a pH-meter Jenway (model 3510) with combine electrode, the sensitivity of the pH - meter is 0.01 units. The pH meter was switched on half an hour before starting the titration for initial warm up of the instrument. The instrument was calibrated with an aqueous standard buffer solution of pH 4.00 and 10.0 (borate buffer) prepared from a "Qualigens" buffer tablets.

The following sets of solutions were prepared in a 250cm^3 volumetric flask separately for pH metric titrations.

(i) 5 cm^3 0.1 M HCl + 40 cm^3 deionized water

(ii) 5 cm^3 0.1 M HCl + 39 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid

(iii) 5 cm^3 0.1 M HCl + 37 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid + 2 cm^3 0.01 M Cu(II)

The solutions were titrated against standardized 0.110MNaOH separately. The total volume of each mixture was adjusted to 50 cm^3 and the ionic strength of the solutions was maintained constant at by adding appropriate amount of stock solution of 1M KNO$_3$ (Gamal, 2015; Omar and Ali, 2015). A magnetic stirrer was used to achieve thorough mixing of the interacting solutions at 550 rpm. The same set of experimental conditions was applied for potentiometric titration of remaining samples.

Evaluation of pKa of Hydrolysed peat soil Humic Acids

The proton-ligand formation number n$_{\mathbf{A}}$ were calculated by Irving and Rossotti expression (Omar and Ali, 2015).

$$nA = Y - \frac{(V2-V1)(No-Eo)}{(Vo+V1)TcL} \quad \text{......................................1}$$

Where: Y is number of dissociable proton, (V$_2$-V$_1$) is the measure of displacement of the ligand curve relative to acid curve, N^o and E^o are the resultant concentration of alkali solution, free acid solution, T$_{cL}$^{o} is the total ligand concentration, V^o is the total volume of titration solution,V$_1$ is the volume of alkali added to acid solution,V$_2$ is the volume of alkali added to acid solution + ligand solution, acid dissociation constants (pKa - values) of ligand were calculated by algebraic method point wise calculation (Tables 1). The dissociation constants (pKa) were calculated according to the following relation:

$$pKa = pH + \log(\frac{nA}{1-nA}) \quad \text{.............................2}$$

Where: pKa is the acid dissociation constant, n$_A$is the Proton-ligand formation number and pH is the pH-values (Omar and Ali, 2015).

Determination of metal-ligand stability constants (log K) of complexes

The potentiometric measurement for the determination of stability constant of a complex in solution is based on the fact that the redox potential of the couple $\frac{M^{+(m-n)}}{M^{+m}}$ is shifted significantly on complexation of the metal ion with the ligand. This method involves change in hydrogen ion concentration [H$^+$] due to the displacement or association of one or more protons taking place during complexation reaction. This change can be found out by titrating the solutions containing free acid, acid with ligand, and acid with ligand and metal ion, individually against a standard alkali solution at a constant ionic strength or temperature. Either ionic strength or temperature may be varied for different sets of solutions. In all the cases, the change in the pH of the solution is measured after each addition of a known amount of alkali to the reaction cell which contains the reaction mixture. The titration curves are then drawn by plotting the measured pH values against the corresponding volume of alkali added and the stability constants of the complexes are determined from the titration curves by employing pH-metric titration technique given by (Irving and Rossoti).

Metal-ligand stability constants (Log K) were determined by using the following relations:

$$\bar{n} = \frac{(V_3 - V_2)(E^0 + N^0)}{(V^0 + V_2)\bar{n}_A T_m^0} \quad \text{...3}$$

and

$$PL = \log_{10}\{\frac{1+\beta_n^H \frac{1}{[anti\ \log pH]^n}}{T_L^0 - \bar{n}T_m^0} X \frac{(V^0+V_3)}{V^0}\} \quad \text{...4}$$

Where $T_{L,}$ T^o, E°, and V^ohavethe same significance as in equation (1) above, T_m denotes the total concentration of metal present in solution, V_3 is the volume of metal ions present in solution and β^H is the overall proton ligand stability constant. The metal-ligand stability constants (log K) were determined by employing point wise computational Method (eq. 5 and 6).

$$\mathrm{Log}K_1 = \log\left(\frac{n}{1-n}\right) + pL \quad \ldots\ldots\ldots\ldots.5$$

$$\mathrm{Log}K_2 = \log\left(\frac{1-n}{2-n}\right) + pL\ldots\ldots\ldots\ldots\ldots\ldots\ldots.6$$

Where: Log K is the metal-ligand stability constant, pL is the Free ligand exponent function, **n** is the Average number of ligand attached with metal ion (Janrao*et al.*, 2014).The results obtained were analyzed by an ORIGIN 2016 program using titration data and then the proton-ligand stability constants (pKa) and Metal-ligand stability constant (LogK) calculated (Omar and Ali, 2015).

RESULTS AND DISCUSSION

Fourier transformed infrared (FT-IR) spectra of isolated humic acid from peat soils Figure 2 had distinct clear absorption bands indicating the presence of major humic acid structural elemental groups such as H bonded OH (3680cm^{-1} peak), C=O of carbonyl (1721cm^{-1} peak), functional groups of aliphatic components CH_2 (2918cm^{-1} peak) and C-O stretching of polysaccharide (1168cm^{-1} peak). The positions of the absorption bands of the spectra fell within typical major absorption bands of humic acid which is at frequencies 3680, 2918, 1721, 1168 cm^{-1}. The first peak centred in the vicinity of 3680 cm^{-1} region is attributed to phenol OH group bounded by intermolecular H bonds. The 2918cm^{-1} band usually has absorption maximum at 2918 cm^{-1} which is due to C–H stretching of alkane group (CH_2). The next major absorption band is 1721 cm^{-1}. This band has been commonly ascribed to C=O stretching of mainly carboxyl group (COOH) with trace amount of ketones. The last peak was observed at 1168 cm^{-1} due to C–O stretching of polysaccharides and this peak appeared also in the spectra of humic acid from peat soil. The FTIR spectra of the isolated humic acid contained all major characteristic absorption peaks of humic acid. These absorption peaks indicated the presence of the major structural elements of humic acid namely H bonded OH, C=C of aromatic ring, C=O of carbonyl group (both carboxyl and ketonic), CH_2 group. This strongly supports the presence of humic acid.

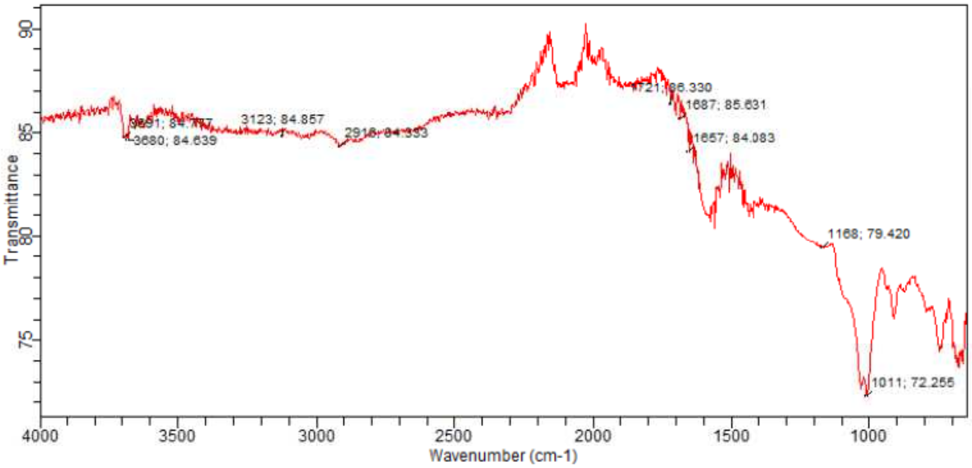


Fig. 2 : FT-IR spectraof peatsoilhumic acid (PSHA)

Evaluation of acid dissociation constant (pka) of acid hydrolysed peat soil humicacid at phenolic group

The value of the dissociation constant of the peat soil humic acid (PSHA) that underwent acidhydrolysis studied was found to be 8.9299 as shown Table 1, which is lower than the literaturevalues reported by Almeida and Szpoganics, (2015), Borges *et al.*, (2005); Badr *et al.*, (2012)and Fernandes *et al*,.(2009) of 9.73, 9.47 and 10.30. The difference between the obtained valuesand the reported values in this study might be probably as a result of acid hydrolysis of humicacid.

Table 1: PKa of (Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	V$_2$-V$_1$	nA	$\log(\frac{nA}{1-nA})$	pKa
8.50	5.30	6.29	0.99	0.3594	-0.2510	8.2490
8.72	5.35	6.37	1.02	0.3400	-0.2880	8.4320
9.00	5.40	6.46	1.06	0.3141	-0.3391	8.6609
9.22	5.45	6.55	1.10	0.2882	-0.3927	8.8273
9.51	5.50	6.66	1.16	0.2494	-0.4786	9.0314
9.73	5.55	6.78	1.23	0.2041	-0.5910	9.1390
10.00	5.60	6.90	1.30	0.1589	-0.7238	9.2762
10.23	5.65	7.05	1.40	0.0941	-0.9835	9.2465
10.49	5.70	7.10	1.40	0.0941	-0.9835	9.5065

Average pKa = 8.9299 ± 0.4186

Table 2: PKa of (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	V$_2$-V$_1$	nA	$\mathrm{Log}(\frac{nA}{1-n})$	pKa
8.50	5.30	5.81	0.51	0.6619	0.2919	8.7919
8.72	5.35	5.90	0.55	0.6357	0.2418	8.9618
9.00	5.40	6.00	0.60	0.6029	0.1813	9.1813
9.22	5.45	6.10	0.65	0.5701	0.1226	9.3426
9.51	5.50	6.20	0.70	0.5376	0.0654	9.5754
9.73	5.55	6.33	0.78	0.4851	-0.0259	9.7041
10.00	5.60	6.47	0.87	0.4262	-0.1291	9.8709
10.23	5.65	6.62	0.99	0.3609	-0.2481	9.9819
10.49	5.70	6.80	1.10	0.2759	-0.4690	10.0210

Average pKa = 9.4923± 0.4410

Metal-ligand stability constant (Log K)

The stabilityconstants require the accurate values of proton-ligand stability constants (Anil and Maroti, 2008). Metal titration curves crossed over ligand titration curve indicated the formation of complex upon proton release (Santosh, *et al.*, 2011). If the values of n- are within range 0.2-0.8 and 1.2-18 this indicates the formation of 1:1 and 1:2 complexes (Sayyed and Mazahar, 2012).

The metal (II)-humate stepwise stability constants (log k) at phenolic group (Tables 3-18)

Table 3: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	$\log(\frac{n}{1-n})$	LogK$_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

LogK$_1$ (Average value) = 2.4788± 0.2203

Table 4: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	$\mathrm{Log}(\frac{n-1}{2-n})$	LogK$_2$
9.51	5.50	6.66	6.73	0.07	1.3509	1.70	-0.2671	1.4329
9.73	5.55	6.78	6.85	0.07	1.6383	1.51	0.2467	1.7567
10.00	5.60	6.90	6.98	0.08	2.1783	1.31	-0.2158	1.0942
10.23	5.65	7.05	7.13	0.08	4.1904	1.27		
10.49	5.70	7.10	7.19	0.09	4.6920			

LogK$_2$(Average value) = 1.4280 ± 0.3312

Table 5:Point-wise method,Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	Log($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430

$LogK_1$ **(Average value)** = 2.3059± 0.6153

Table 6:Point-wise method, Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$V_3\text{-}V_2$	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
9.73	5.55	6.33	6.42	0.09	0.9000	1.69		
10.00	5.60	6.47	6.58	0.11	1.2578	1.44	-0.4592	0.9808
10.23	5.65	6.62	6.84	0.12	1.6137	1.26	-0.2010	1.4610
10.49	5.70	6.80	6.92	0.12	2.1052	1.03		

$LogK_2$ **(Average value)** = 1.2209± 0.3398

Table 7:Point-wise method,Pb (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	log($\frac{n}{1-n}$)	$LogK_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.60	0.05	0.8333	1.96	0.6989	2.6589

$LogK_1$ (Average value) = 2.5832 ±0.1614

Table 8:Point-wise method,Pb-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	log($\frac{n-1}{2-n}$)	$logK_2$
9.51	5.50	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.83	0.05	1.1702	1.44		
10.00	5.60	6.90	6.90	0.05	1.4864	1.22	-0.0237	1.1963
10.23	5.65	7.05	7.10	0.05	2.0190	1.09		
10.49	5.70	7.10	7.17	0.07	3.6492	1.00		

$LogK_2$(Average value) = 1.1963

Table 9:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$V_3\text{-}V_2$	n	pL	Log ($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.5477	2.3123
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	0.0272	2.2072
9.51	5.50	6.20	6.26	0.07	0.6417	1.89	0.2530	2.1430
9.73	5.55	6.40	6.40	0.07	0.7000	1.67	0.3680	2.0380

$LogK_1$ **(Average value)** = 2.2364 ± 0.1602

Table 10:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$V_3\text{-}V_2$	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
10.00	5.60	6.47	6.55	0.08	1.9503	1.41		
10.23	5.65	6.62	6.72	0.11	1.4792	1.26	-0.0361	1.2239

$LogK_2$ **(Average value)** = 1.2239

Table 11:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	log($\frac{n}{n-1}$)	$LogK_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4290	2.2110
8.72	5.35	6.37	6.39	0.02	0.2858	2.42	-0.3978	2.0222
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

$LogK_1$ (Average value)=2.1382±0.1046

Table 12:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	log($\frac{n-1}{2-n}$)	LogK$_2$
9.51	5.55	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.84	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.93	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.10		
10.49	5.70	7.10	7.18	0.07	3.6492	0.83		

LogK$_2$(Average value) = 1.5453 **±** 0.3450

Table 13:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	V$_3$-V$_2$	n	pL	Log($\frac{n}{n-1}$)	Log K$_1$
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.3477	2.3123
9.00	5.40	6.00	6.04	0.04	0.3236	2.38	-0.3202	2.0598
9.22	5.45	6.10	6.15	0.05	0.4297	2.17	-0.1230	2.0470
9.51	5.50	6.20	6.26	0.06	0.5500	1.89	0.0871	1.9771
9.73	5.55	6.33	6.40	0.07	0.7000	1.67	0.3680	2.0380

LogK$_1$ **(Average value)** = 2.1568 ± 0.2069

Table 14:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	V$_3$-V$_2$	n	pL	Log($\frac{n-1}{2-n}$)	Log K$_2$
10.00	5.60	6.47	6.55	0.08	0.9148	1.41		
10.23	5.65	6.62	6.71	0.09	1.2102	1.20	-0.5749	0.6251
10.49	5.70	6.80	6.92	0.09	1.5968	1.03	0.1703	1.2003

LogK$_2$ **(Average value)** = 0.9127± 0.4070

Table15:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	Log($\frac{n}{1-n}$)	LogK$_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4210	2.2190
8.72	5.35	6.37	6.40	0.03	0.4286	2.42	-0.1249	2.2951
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.96	0.3010	2.2610
9.51	5.55	6.66	6.70	0.04	0.7720	1.67	0.5297	2.1997

LogK$_1$ (Average value) = 2.2108± 0.0825

Table 16:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	Log($\frac{n-1}{2-n}$)	Log K$_2$
9.73	5.55	6.78	6.83	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.95	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.09		
10.49	5.70	7.10	7.16	0.06	3.1429	0.89		

LogK$_2$ **(Average value)** = 1.5453± 0.3450

Table 17:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	V$_3$-V$_2$	n	pL	Log($\frac{n}{n-1}$)	Log K$_1$
8.50	5.30	5.81	5.86	0.05	0.3717	2.88	-0.2280	2.6520
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.06	0.06	0.4853	2.38	-0.0255	2.3545
9.22	5.45	6.10	6.16	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430
9.73	5.55	6.33	6.41	0.08	0.8000	1.69	0.6020	2.2920

LogK$_1$ **(Average value)** = 2.2516± 0.5380

Table 18:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$\text{Log}(\frac{n-1}{2-n})$	Log K_2
10.00	5.60	6.47	6.57	0.10	1.1434	1.43		
10.23	5.65	6.62	6.72	0.10	1.3448	1.23	-0.2788	0.9512
10.49	5.70	6.80	6.90	0.10	1.7742	1.03	0.5351	1.5651

LogK_2 **(Average value)** = 1.2581± 0.4340

Table 19: Stepwise and overall Stability constants of thehydrolysed and unhydrolysed divalent metal (II) complexes

Chelates	**LogK_1**	**LogK_2**	**Logβ**
[Cu (Hydrolysed PSHA-1)$_2$]	2.4788	1.4280	3.9068
[Pb (Hydrolysed PSHA-1)$_2$]	2.5832	1.1963	3.7795
[Cd (Hydrolysed PSHA-1)$_2$]	2.2108	1.5453	3.7561
[Mg (Hydrolysed PSHA-1)$_2$]	2.1382	1.5453	3.6835
[Cu (Unhydrolysed PSHA-1)$_2$]	2.3059	1.2209	3.5268
[Pb (Unhydrolysed PSHA-1)$_2$]	2.2364	1.2239	3.4603
[Cd (Unhydrolysed PSHA-1)$_2$]	2.2516	1.2581	3.5097
[Mg (Unydrolysed PSHA-1)$_2$]	2.1568	0.9127	3.0695

The results obtained (Table19) shows the stepwise and overall stability constants to be not high indicating low stability of the complexes, because the solubility of most metal ions in the basic pH range is minimal due to metal hydroxide precipitation (Karimi, 2017). In general, the stepwise stability constants (K_1 and K_2) follow the order $K_1 > K_2$ for the copper, lead, magnesium and cadmium complexes respectively. The steady decrease of the values with increasing number of ligands is in agreement with the prediction made by researchers (Na'aliya, 2013). The decrease could be attributed to the fact that as the number of the ligands (Humate ions) that enters the coordination zone increases the aqua molecules available for replacement by the ligands become less. Thus, the metal ions become less electron loving with progressive intake of the ligand and this results in the decrease in the values of the constants (Na'aliya, 2013). Also the stability of the complexes is influenced by the size and number of the chelate rings(Mackay and Mackay,2002).All the complexes form rings in their structure as humate, a bidentate ligand, bond the metal ions in the ratio 1:2 (Boguta and Sokolowska, 2016) forming chelate rings. The values of the overall stability constants (logβ) obtained for humate complexes are not high indicating low stability as the values are not high. LogK values for copper-humates (Table 3 to 6) obtained in this study are lower than those reported for the complexes of humic acids (Pandey *et al*., 2015; Dinu, 2013; Kaschl *et al*., 2010 and Gilbeto and Jorg, 2001). The values of LogK(Table 7 to 10) forlead-humates are lower than those reported for the lead in the literature (Dinu, 2013; Gilbeto and Jorg 2001). Log K values(Table 11 to 14) for magnesium-humates obtained in this study are close to those reported by (Pandey *et al*., 2015). Log K values of cadmium-humates (Table 15 to 18) obtained in this work near to the one reported by (Dinu, 2013 and Pandey *et al*., 2015).The difference between the reported values and the values obtained in this study might be probably as a result of acid hydrolysis of humic acid. The values of the overall stability constants (log β) of the copper humates complexes presented in Table 19 is high than that of other metal humate complexes, show relatively high stability of Cu-HA complexes, show the following order of stability: Cu >Pb> Cd > Mg; which are in close agreement to the findings of (Dinu, 2013 and Pandey *et al*., 2015).The high stability of Cu-humate chelate could be attributed to the existence of coordinate covalent bond between the complexing agents and the Cu^{2+} ions. Since, Cu^{2+} being a metal of the transitional series with $3d^9$ electronic configurations can accept the electrons from the complexing agents. Similarly,the low stabilities of Pb,Cd and Mg -complexes could be explained by that Pb^{2+} with $6s^2$, Cd^{2+} with $4d^{10}$ and Mg^{2+} with $2p^6$ their electronic configuration has a completely filled d,p and s orbitals. Moreover, the stabilities of metal ions with hydrolysed humic acid from peat soil were higher than those with unhydrolysed humic acid from peat soil; which is ascribed to the high content of acidity in hydrolysed humic acid than unhydrolysed humic acid.

CONCLUSION

The values of logK for Cu(II) hydrolysed humic acid complex was higher followed by Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes as compared with metal(II) unhydrolysed humic acid complexes . This indicates acid hydrolysis of humic acid can enhance the complexation behavior of humic acid with metal (II) ions. However, the higher values of logβ for Cu(II), Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes indicates more stable stepwise complexes formed as compared with Cu(II), Pb(II), Cd(II) and Mg(II) unhydrolysed humic acid complexes.

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STABILITY CONSTANTS OF COMPLEXES OF METAL IONS WITH PEATSOIL HUMIC ACIDS UNDER NON-ACID-CONDITIONS

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ABSTRACT

Stability constants of complexes of four divalent metal ions viz. Cu^{2+}, Pb^{2+},Mg^{2+} and Cd^{2+} with humic acids (HA) were determined by potentiometric titration of humic acids with the corresponding salt of the divalent metals in aqueous media under non-acid-condition. The log K (logarithm of the stability constant) ranged from 1.0942 to 2.7471 for metal-humic acid complexes were determined using point-wise computational method. The order of stability constants were obtained as follows: Cu >Pb> Cd > Mg for metal -HA complexes respectively, indicating a higher degree of complexation with Cu metal ion.

Keywords: stability constant, humic acid, potentiometric titration, divalent metals, acid hydrolysis.

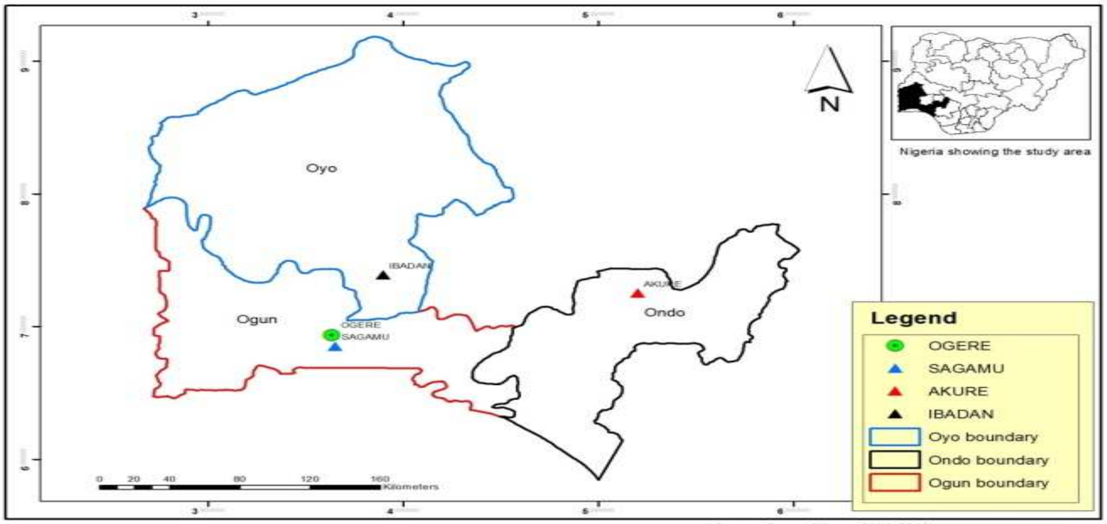
NTRODUCTION

The stability constant of a complex is the numerical expression of its stability and provides a quantitative measure of affinity of the metal ion to the complexing agent. An understanding of the relative stability of metal-complexes helps in predicting the behavior of metal ions in the soil (Ram and Raman, 1982). Extensive researches has been done to determine the stability constants of the complexes formed between humic acid (HA) with a number of metal ions. Ashok *et al.*, (2000) reported that humic acid with hydroxyl, phenoxyl and carboxyl reactive groups can form coordination compound with metal ions at pH 3.5. The stability constants(Log K) for different metal-humic acid complexes indicated the following order of the stabilities of complexes formed between humic acid and metal ion, Cu >Fe >Pb> Ni > Co > Ca > Cd > Zn >Mn> Mg. Andelkovic *et al.*, (2010) investigated the binding of Cd(II) to soil humic acid at pH 6.5 and in 0.1M KNO_3 ionic medium. The stability constant for binding indicating greater stability in the case when carboxyl groups are involved in complexation reaction. Kostic *et al.*,(2012) investigated the complexation of humic acid with certain heavy metal ions (Co(II), Ni(II),Cu(II), Zn(II), and Pb(II). The experiment was performed at 25°C, at pH 4.0 and ionic strength of 0.01M. Stability constant of complex between Pb(II) ions and humic acid is greater than stability constants of other investigated metal-humate complexes. Bogata and Sokolowska (2016) analyses the interaction between humic acids from different soils and Zn (II) ions at wide concentration ranges and at pH 5. Studies have showed significant impact of Zn concentration, pH and some properties of humic acids with zinc.But all of these studies were limited to acidic pH range. Therefore, the present study was carried out to determine and compare the stability constants of complexes of metal ions with hydrolysed peat soil humic acid and unhydrolysed peat soil humic under non-acid conditions.

MATERIALS AND METHODS

Analytical grade chemicals used includes hydrochloric acid (HCl), nitric acid (HNO_3), sodium hydroxide (NaOH), lead nitrate $Pb(NO_3)_2$, copper nitrate $Cu(NO_3)_2.3H_2O$, cadmium nitrate $Cd(NO_3)_2.4H_2O$, magnesium nitrate $Mg(NO_3)_2.6H_2O$, potassium nitrate (KNO_3), calcium chloride ($CaCl_2$), (sigma-Aldrich). Dowex 50WX8, (20-50 mesh) from Fluka.

Area of study



Source: Dept. of Geog. BUK (2016)

Figure 1: Map showing the sampling point at Sagamu Town, Ogun State.

Description of Sampling Area

Sagamu has geographical coordinates between 6°50′ north; 3° 38′ east is located in south western region of Nigeria. The region has tropical wet and dry climate with a lengthy wet season and relatively constant temperatures throughout the course of the year. Wet season runs from March to October, November to December forms the region dry season. The vegetation type of the region is savannah which is really grassland with small bushes and occasional big trees. Grassland soils have substantially higher organic matter content than forest soils (Novackova, 2011).

Sample Collection

The Peatsoil samples were collected from four different sampling points (0-10cm depth) in Sagamu into polyethylene bag with plastic spoons. Samples were taken to the laboratory, extraneous materials were removed; the samples were air-dried, crushed and ground to a fine powder in a mortar passed through a 0.20mm sieve. The samples were kept for analysis.

Isolation and purification of humic acid from peat soil sample

Peatsoil sample (100g) was mixed with 1000 cm^3 of 0.1M NaOH solution, shaken for 3hours and left to stand overnight. Dark-coloured supernatant was obtained and decanted from solid residue. The dark-coloured supernatant was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 6 hours. Yellowish brown supernatant and dark-brown precipitate were obtained. The yellowish brown supernatant was decanted followed by centrifuge and discarded. The dark-brown precipitate was mixed with $500cm^3$of 0.1M NaOH solution followed by passing through dowex resin. The dark-brown solution was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 3 hours. The dark-brown precipitate was washed several times with deionized water. The supernatant was treated with $AgNO_3$ solution until no white precipitate observed. The humic acid was transferred to weighed crucible and dried at 60°C in an oven for 12 hours. The humic acid was cooled and dried in the desiccator, weighed and recorded. The obtained humic acid was dried again at 60°C for additional 6 hours cooled and dried in the desiccator, weighed and recorded constant weight was obtained (Baruah *et al.*, 2015).

FT-IR analysis

FT-IR spectra of humic acid sample was analysed using Carry 630 FT-IR Agilent Technologies.

Unhydrolysed compost humic acid

The unhydrolysed humic acid was obtained after isolation and purification of compost humic acid and kept for investigation.

Acid hydrolysis of Peatsoil acid

Peatsoil humic acid sample (1g) was refluxed for 12 hours at (160°C) with $50cm^3$ of 6M HCl. The mixture was allowed to cool, decanted, and centrifuged after hydrolysis. The insoluble residues were washed with distilled water via centrifugation several times, and the supernatant was treated with $AgNO_3$ solution until no white precipitate was observed. The residue was thoroughly dried over $CaCl_2$ in a desiccator at room temperature (Chefetz *et al.*, 2002). Finally, the obtained hydrolysed humic acid was kept for investigation.

Potentiometric Titrations

Potentiometric measurements were carried out using a pH-meter Jenway (model 3510) with combine electrode, the sensitivity of the pH - meter is 0.01 units. The pH meter was switched on half an hour before starting the titration for initial warm up of the instrument. The instrument was calibrated with an aqueous standard buffer solution of pH 4.00 and 10.0 (borate buffer) prepared from a "Qualigens" buffer tablets.

The following sets of solutions were prepared in a 250cm^3 volumetric flask separately for pH metric titrations.

(i) 5 cm^3 0.1 M HCl + 40 cm^3 deionized water
(ii) 5 cm^3 0.1 M HCl + 39 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid
(iii) 5 cm^3 0.1 M HCl + 37 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid + 2 cm^3 0.01 M Cu(II)

The solutions were titrated against standardized 0.110MNaOH separately. The total volume of each mixture was adjusted to 50 cm^3 and the ionic strength of the solutions was maintained constant at by adding appropriate amount of stock solution of 1M KNO$_3$ (Gamal, 2015; Omar and Ali, 2015). A magnetic stirrer was used to achieve thorough mixing of the interacting solutions at 550 rpm. The same set of experimental conditions was applied for potentiometric titration of remaining samples.

Evaluation of pKa of Hydrolysed peat soil Humic Acids

The proton-ligand formation number n$_{\mathbf{A}}$ were calculated by Irving and Rossotti expression (Omar and Ali, 2015).

$$nA = Y - \frac{(V2-V1)(No-Eo)}{(Vo+V1)TcL} \text{ ....1}$$

Where: Y is number of dissociable proton, (V$_2$-V$_1$) is the measure of displacement of the ligand curve relative to acid curve, N^o and E^o are the resultant concentration of alkali solution, free acid solution, T$_{cL}$^{o} is the total ligand concentration, V^o is the total volume of titration solution,V$_1$ is the volume of alkali added to acid solution,V$_2$ is the volume of alkali added to acid solution + ligand solution, acid dissociation constants (pKa - values) of ligand were calculated by algebraic method point wise calculation (Tables 1). The dissociation constants (pKa) were calculated according to the following relation:

$$pKa = pH + \log\left(\frac{nA}{1-nA}\right) \text{ ....2}$$

Where: pKa is the acid dissociation constant, n$_A$is the Proton-ligand formation number and pH is the pH-values (Omar and Ali, 2015).

Determination of metal-ligand stability constants (log K) of complexes

The potentiometric measurement for the determination of stability constant of a complex in solution is based on the fact that the redox potential of the couple $\frac{M^{+(m-n)}}{M^{+m}}$ is shifted significantly on complexation of the metal ion with the ligand. This method involves change in hydrogen ion concentration [H$^+$] due to the displacement or association of one or more protons taking place during complexation reaction. This change can be found out by titrating the solutions containing free acid, acid with ligand, and acid with ligand and metal ion, individually against a standard alkali solution at a constant ionic strength or temperature. Either ionic strength or temperature may be varied for different sets of solutions. In all the cases, the change in the pH of the solution is measured after each addition of a known amount of alkali to the reaction cell which contains the reaction mixture. The titration curves are then drawn by plotting the measured pH values against the corresponding volume of alkali added and the stability constants of the complexes are determined from the titration curves by employing pH-metric titration technique given by (Irving and Rossoti).

Metal-ligand stability constants (Log K) were determined by using the following relations:

$$\bar{n} = \frac{(V_3 - V_2)(E^0 + N^0)}{(V^0 + V_2)\bar{n}_A T_m^0} \text{ ....3}$$

and

$$PL = \log_{10}\left\{\frac{1 + \beta_n^H \dfrac{1}{[anti\ \log pH]^n}}{T_L^0 - \bar{n}T_m^0} \text{X} \frac{(V^0 + V_3)}{V^0}\right\} \text{ ....4}$$

Where $T_{L,}$ T^{o}, E°, and V^{o}havethe same significance as in equation (1) above, T_m denotes the total concentration of metal present in solution, V_3 is the volume of metal ions present in solution and β^H is the overall proton ligand stability constant. The metal-ligand stability constants (log K) were determined by employing point wise computational Method (eq. 5 and 6).

$LogK_1 = \log\left(\frac{n}{1-n}\right) + pL$ 5

$LogK_2 = \log\left(\frac{1-n}{2-n}\right) + pL$.......................6

Where: Log K is the metal-ligand stability constant, pL is the Free ligand exponent function, **n** is the Average number of ligand attached with metal ion (Janrao*et al.*, 2014).The results obtained were analyzed by an ORIGIN 2016 program using titration data and then the proton-ligand stability constants (pKa) and Metal-ligand stability constant (LogK) calculated (Omar and Ali, 2015).

RESULTS AND DISCUSSION

Fourier transformed infrared (FT-IR) spectra of isolated humic acid from peat soils Figure 2 had distinct clear absorption bands indicating the presence of major humic acid structural elemental groups such as H bonded OH (3680cm^{-1} peak), C=O of carbonyl (1721cm^{-1} peak), functional groups of aliphatic components CH_2 (2918cm^{-1} peak) and C-O stretching of polysaccharide (1168cm^{-1} peak). The positions of the absorption bands of the spectra fell within typical major absorption bands of humic acid which is at frequencies 3680, 2918, 1721, 1168 cm^{-1}. The first peak centred in the vicinity of 3680 cm^{-1} region is attributed to phenol OH group bounded by intermolecular H bonds. The 2918cm^{-1} band usually has absorption maximum at 2918 cm^{-1} which is due to C–H stretching of alkane group (CH_2). The next major absorption band is 1721 cm^{-1}. This band has been commonly ascribed to C=O stretching of mainly carboxyl group (COOH) with trace amount of ketones. The last peak was observed at 1168 cm^{-1} due to C–O stretching of polysaccharides and this peak appeared also in the spectra of humic acid from peat soil. The FTIR spectra of the isolated humic acid contained all major characteristic absorption peaks of humic acid. These absorption peaks indicated the presence of the major structural elements of humic acid namely H bonded OH, C=C of aromatic ring, C=O of carbonyl group (both carboxyl and ketonic), CH_2 group. This strongly supports the presence of humic acid.

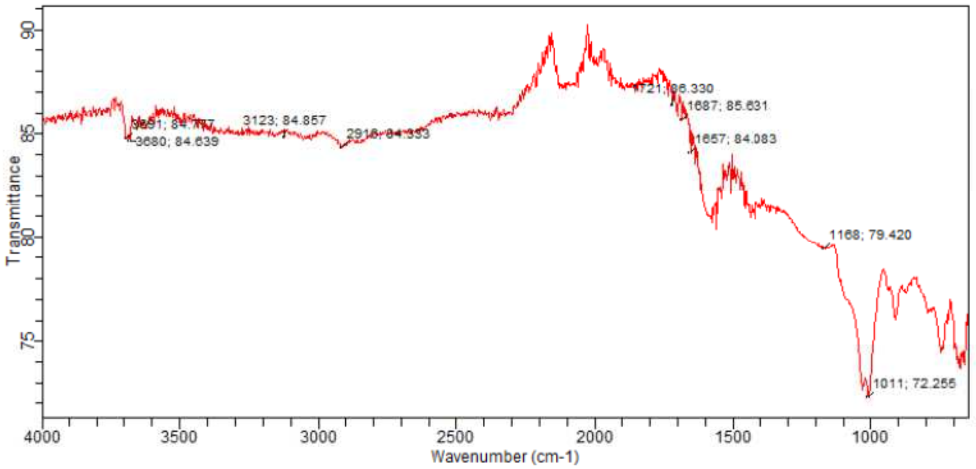


Fig. 2 : FT-IR spectraof peatsoilhumic acid (PSHA)

Evaluation of acid dissociation constant (pka) of acid hydrolysed peat soil humicacid at phenolic group

The value of the dissociation constant of the peat soil humic acid (PSHA) that underwent acidhydrolysis studied was found to be 8.9299 as shown Table 1, which is lower than the literaturevalues reported by Almeida and Szpoganics, (2015), Borges *et al.*, (2005); Badr *et al.*, (2012)and Fernandes *et al*,.(2009) of 9.73, 9.47 and 10.30. The difference between the obtained valuesand the reported values in this study might be probably as a result of acid hydrolysis of humicacid.

Table 1: PKa of (Hydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	log($\frac{nA}{1-nA}$)	pKa
8.50	5.30	6.29	0.99	0.3594	-0.2510	8.2490
8.72	5.35	6.37	1.02	0.3400	-0.2880	8.4320
9.00	5.40	6.46	1.06	0.3141	-0.3391	8.6609
9.22	5.45	6.55	1.10	0.2882	-0.3927	8.8273
9.51	5.50	6.66	1.16	0.2494	-0.4786	9.0314
9.73	5.55	6.78	1.23	0.2041	-0.5910	9.1390
10.00	5.60	6.90	1.30	0.1589	-0.7238	9.2762
10.23	5.65	7.05	1.40	0.0941	-0.9835	9.2465
10.49	5.70	7.10	1.40	0.0941	-0.9835	9.5065

Average pKa = 8.9299 ± 0.4186

Table 2: PKa of (Unhydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	Log($\frac{nA}{1-n}$)	pKa
8.50	5.30	5.81	0.51	0.6619	0.2919	8.7919
8.72	5.35	5.90	0.55	0.6357	0.2418	8.9618
9.00	5.40	6.00	0.60	0.6029	0.1813	9.1813
9.22	5.45	6.10	0.65	0.5701	0.1226	9.3426
9.51	5.50	6.20	0.70	0.5376	0.0654	9.5754
9.73	5.55	6.33	0.78	0.4851	-0.0259	9.7041
10.00	5.60	6.47	0.87	0.4262	-0.1291	9.8709
10.23	5.65	6.62	0.99	0.3609	-0.2481	9.9819
10.49	5.70	6.80	1.10	0.2759	-0.4690	10.0210

Average pKa = 9.4923± 0.4410

Metal-ligand stability constant (Log K)

The stabilityconstants require the accurate values of proton-ligand stability constants (Anil and Maroti, 2008). Metal titration curves crossed over ligand titration curve indicated the formation of complex upon proton release (Santosh, *et al.*, 2011). If the values of n- are within range 0.2-0.8 and 1.2-18 this indicates the formation of 1:1 and 1:2 complexes (Sayyed and Mazahar, 2012).

The metal (II)-humate stepwise stability constants (log k) at phenolic group (Tables 3-18)

Table 3: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n}{1-n}$)	$LogK_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

$LogK_1$ (Average value) = 2.4788± 0.2203

Table 4: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	Log($\frac{n-1}{2-n}$)	$LogK_2$
9.51	5.50	6.66	6.73	0.07	1.3509	1.70	-0.2671	1.4329
9.73	5.55	6.78	6.85	0.07	1.6383	1.51	0.2467	1.7567
10.00	5.60	6.90	6.98	0.08	2.1783	1.31	-0.2158	1.0942
10.23	5.65	7.05	7.13	0.08	4.1904	1.27		
10.49	5.70	7.10	7.19	0.09	4.6920			

$LogK_2$(Average value) = 1.4280 ± 0.3312

Table 5:Point-wise method,Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	$\mathrm{Log}(\frac{n}{n-1})$	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430

$\mathrm{Log}K_1$ **(Average value)** = 2.3059± 0.6153

Table 6:Point-wise method, Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$V_3\text{-}V_2$	n	pL	$\mathrm{Log}(\frac{n-1}{2-n})$	Log K_2
9.73	5.55	6.33	6.42	0.09	0.9000	1.69		
10.00	5.60	6.47	6.58	0.11	1.2578	1.44	-0.4592	0.9808
10.23	5.65	6.62	6.84	0.12	1.6137	1.26	-0.2010	1.4610
10.49	5.70	6.80	6.92	0.12	2.1052	1.03		

$\mathrm{Log}K_2$ **(Average value)** = 1.2209± 0.3398

Table 7:Point-wise method,Pb (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	$\log(\frac{n}{1-n})$	$\mathrm{Log}K_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.60	0.05	0.8333	1.96	0.6989	2.6589

$\mathrm{Log}K_1$ (Average value) = 2.5832 ±0.1614

Table 8:Point-wise method,Pb-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	$\log(\frac{n-1}{2-n})$	$\log K_2$
9.51	5.50	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.83	0.05	1.1702	1.44		
10.00	5.60	6.90	6.90	0.05	1.4864	1.22	-0.0237	1.1963
10.23	5.65	7.05	7.10	0.05	2.0190	1.09		
10.49	5.70	7.10	7.17	0.07	3.6492	1.00		

$\mathrm{Log}K_2$(Average value) = 1.1963

Table 9:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$V_3\text{-}V_2$	n	pL	$\mathrm{Log}(\frac{n}{n-1})$	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.5477	2.3123
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	0.0272	2.2072
9.51	5.50	6.20	6.26	0.07	0.6417	1.89	0.2530	2.1430
9.73	5.55	6.40	6.40	0.07	0.7000	1.67	0.3680	2.0380

$\mathrm{Log}K_1$ **(Average value)** = 2.2364 ± 0.1602

Table 10:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$V_3\text{-}V_2$	n	pL	$\mathrm{Log}(\frac{n-1}{2-n})$	Log K_2
10.00	5.60	6.47	6.55	0.08	1.9503	1.41		
10.23	5.65	6.62	6.72	0.11	1.4792	1.26	-0.0361	1.2239

$\mathrm{Log}K_2$ **(Average value)** = 1.2239

Table 11:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	$\log(\frac{n}{n-1})$	$\mathrm{Log}K_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4290	2.2110
8.72	5.35	6.37	6.39	0.02	0.2858	2.42	-0.3978	2.0222
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

$\mathrm{Log}K_1$ (Average value)=2.1382±0.1046

Table 12:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	log($\frac{n-1}{2-n}$)	LogK$_2$
9.51	5.55	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.84	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.93	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.10		
10.49	5.70	7.10	7.18	0.07	3.6492	0.83		

LogK$_2$(Average value) = 1.5453 **±** 0.3450

Table 13:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	V$_3$-V$_2$	n	pL	Log($\frac{n}{n-1}$)	Log K$_1$
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.3477	2.3123
9.00	5.40	6.00	6.04	0.04	0.3236	2.38	-0.3202	2.0598
9.22	5.45	6.10	6.15	0.05	0.4297	2.17	-0.1230	2.0470
9.51	5.50	6.20	6.26	0.06	0.5500	1.89	0.0871	1.9771
9.73	5.55	6.33	6.40	0.07	0.7000	1.67	0.3680	2.0380

LogK$_1$ **(Average value)** = 2.1568 ± 0.2069

Table 14:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	V$_3$-V$_2$	n	pL	Log($\frac{n-1}{2-n}$)	Log K$_2$
10.00	5.60	6.47	6.55	0.08	0.9148	1.41		
10.23	5.65	6.62	6.71	0.09	1.2102	1.20	-0.5749	0.6251
10.49	5.70	6.80	6.92	0.09	1.5968	1.03	0.1703	1.2003

LogK$_2$ **(Average value)** = 0.9127± 0.4070

Table15:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	Log($\frac{n}{1-n}$)	LogK$_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4210	2.2190
8.72	5.35	6.37	6.40	0.03	0.4286	2.42	-0.1249	2.2951
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.96	0.3010	2.2610
9.51	5.55	6.66	6.70	0.04	0.7720	1.67	0.5297	2.1997

LogK$_1$ (Average value) = 2.2108± 0.0825

Table 16:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	Log($\frac{n-1}{2-n}$)	Log K$_2$
9.73	5.55	6.78	6.83	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.95	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.09		
10.49	5.70	7.10	7.16	0.06	3.1429	0.89		

LogK$_2$ **(Average value)** = 1.5453± 0.3450

Table 17:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	V$_3$-V$_2$	n	pL	Log($\frac{n}{n-1}$)	Log K$_1$
8.50	5.30	5.81	5.86	0.05	0.3717	2.88	-0.2280	2.6520
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.06	0.06	0.4853	2.38	-0.0255	2.3545
9.22	5.45	6.10	6.16	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430
9.73	5.55	6.33	6.41	0.08	0.8000	1.69	0.6020	2.2920

LogK$_1$ **(Average value)** = 2.2516± 0.5380

Table 18:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$\mathrm{Log}(\frac{n-1}{2-n})$	Log K_2
10.00	5.60	6.47	6.57	0.10	1.1434	1.43		
10.23	5.65	6.62	6.72	0.10	1.3448	1.23	-0.2788	0.9512
10.49	5.70	6.80	6.90	0.10	1.7742	1.03	0.5351	1.5651

LogK_2 **(Average value)** = 1.2581± 0.4340

Table 19: Stepwise and overall Stability constants of thehydrolysed and unhydrolysed divalent metal (II) complexes

Chelates	**LogK_1**	**LogK_2**	**Logβ**
[Cu (Hydrolysed PSHA-1)$_2$]	2.4788	1.4280	3.9068
[Pb (Hydrolysed PSHA-1)$_2$]	2.5832	1.1963	3.7795
[Cd (Hydrolysed PSHA-1)$_2$]	2.2108	1.5453	3.7561
[Mg (Hydrolysed PSHA-1)$_2$]	2.1382	1.5453	3.6835
[Cu (Unhydrolysed PSHA-1)$_2$]	2.3059	1.2209	3.5268
[Pb (Unhydrolysed PSHA-1)$_2$]	2.2364	1.2239	3.4603
[Cd (Unhydrolysed PSHA-1)$_2$]	2.2516	1.2581	3.5097
[Mg (Unydrolysed PSHA-1)$_2$]	2.1568	0.9127	3.0695

The results obtained (Table19) shows the stepwise and overall stability constants to be not high indicating low stability of the complexes, because the solubility of most metal ions in the basic pH range is minimal due to metal hydroxide precipitation (Karimi, 2017). In general, the stepwise stability constants (K_1 and K_2) follow the order $K_1 > K_2$ for the copper, lead, magnesium and cadmium complexes respectively. The steady decrease of the values with increasing number of ligands is in agreement with the prediction made by researchers (Na'aliya, 2013). The decrease could be attributed to the fact that as the number of the ligands (Humate ions) that enters the coordination zone increases the aqua molecules available for replacement by the ligands become less. Thus, the metal ions become less electron loving with progressive intake of the ligand and this results in the decrease in the values of the constants (Na'aliya, 2013). Also the stability of the complexes is influenced by the size and number of the chelate rings(Mackay and Mackay,2002).All the complexes form rings in their structure as humate, a bidentate ligand, bond the metal ions in the ratio 1:2 (Boguta and Sokolowska, 2016) forming chelate rings. The values of the overall stability constants (logβ) obtained for humate complexes are not high indicating low stability as the values are not high. LogK values for copper-humates (Table 3 to 6) obtained in this study are lower than those reported for the complexes of humic acids (Pandey *et al*., 2015; Dinu, 2013; Kaschl *et al*., 2010 and Gilbeto and Jorg, 2001). The values of LogK(Table 7 to 10) forlead-humates are lower than those reported for the lead in the literature (Dinu, 2013; Gilbeto and Jorg 2001). Log K values(Table 11 to 14) for magnesium-humates obtained in this study are close to those reported by (Pandey *et al*., 2015). Log K values of cadmium-humates (Table 15 to 18) obtained in this work near to the one reported by (Dinu, 2013 and Pandey *et al*., 2015).The difference between the reported values and the values obtained in this study might be probably as a result of acid hydrolysis of humic acid. The values of the overall stability constants (log β) of the copper humates complexes presented in Table 19 is high than that of other metal humate complexes, show relatively high stability of Cu-HA complexes, show the following order of stability: Cu >Pb> Cd > Mg; which are in close agreement to the findings of (Dinu, 2013 and Pandey *et al*., 2015).The high stability of Cu-humate chelate could be attributed to the existence of coordinate covalent bond between the complexing agents and the Cu^{2+} ions. Since, Cu^{2+} being a metal of the transitional series with $3d^9$ electronic configurations can accept the electrons from the complexing agents. Similarly,the low stabilities of Pb,Cd and Mg -complexes could be explained by that Pb^{2+} with $6s^2$, Cd^{2+} with $4d^{10}$ and Mg^{2+} with $2p^6$ their electronic configuration has a completely filled d,p and s orbitals. Moreover, the stabilities of metal ions with hydrolysed humic acid from peat soil were higher than those with unhydrolysed humic acid from peat soil; which is ascribed to the high content of acidity in hydrolysed humic acid than unhydrolysed humic acid.

CONCLUSION

The values of logK for Cu(II) hydrolysed humic acid complex was higher followed by Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes as compared with metal(II) unhydrolysed humic acid complexes . This indicates acid hydrolysis of humic acid can enhance the complexation behavior of humic acid with metal (II) ions. However, the higher values of logβ for Cu(II), Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes indicates more stable stepwise complexes formed as compared with Cu(II), Pb(II), Cd(II) and Mg(II) unhydrolysed humic acid complexes.

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STABILITY CONSTANTS OF COMPLEXES OF METAL IONS WITH PEATSOIL HUMIC ACIDS UNDER NON-ACID-CONDITIONS

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ABSTRACT

Stability constants of complexes of four divalent metal ions viz. Cu^{2+}, Pb^{2+},Mg^{2+} and Cd^{2+} with humic acids (HA) were determined by potentiometric titration of humic acids with the corresponding salt of the divalent metals in aqueous media under non-acid-condition. The log K (logarithm of the stability constant) ranged from 1.0942 to 2.7471 for metal-humic acid complexes were determined using point-wise computational method. The order of stability constants were obtained as follows: Cu >Pb> Cd > Mg for metal -HA complexes respectively, indicating a higher degree of complexation with Cu metal ion.

Keywords: stability constant, humic acid, potentiometric titration, divalent metals, acid hydrolysis.

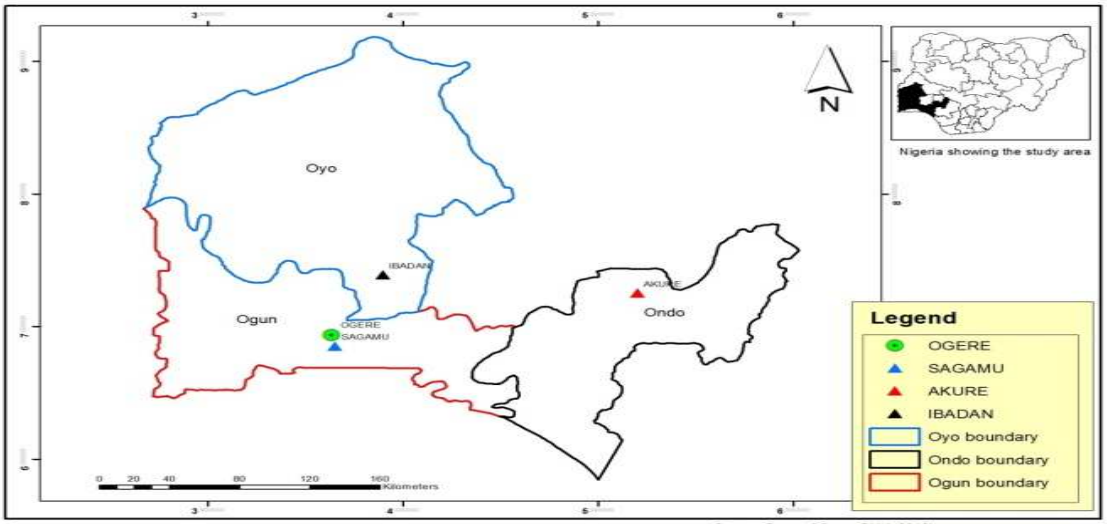
NTRODUCTION

The stability constant of a complex is the numerical expression of its stability and provides a quantitative measure of affinity of the metal ion to the complexing agent. An understanding of the relative stability of metal-complexes helps in predicting the behavior of metal ions in the soil (Ram and Raman, 1982). Extensive researches has been done to determine the stability constants of the complexes formed between humic acid (HA) with a number of metal ions. Ashok *et al*., (2000) reported that humic acid with hydroxyl, phenoxyl and carboxyl reactive groups can form coordination compound with metal ions at pH 3.5. The stability constants(Log K) for different metal-humic acid complexes indicated the following order of the stabilities of complexes formed between humic acid and metal ion, Cu >Fe >Pb> Ni > Co > Ca > Cd > Zn >Mn> Mg. Andelkovic *et al*., (2010) investigated the binding of Cd(II) to soil humic acid at pH 6.5 and in 0.1M KNO_3 ionic medium. The stability constant for binding indicating greater stability in the case when carboxyl groups are involved in complexation reaction. Kostic *et al*.,(2012) investigated the complexation of humic acid with certain heavy metal ions (Co(II), Ni(II),Cu(II), Zn(II), and Pb(II). The experiment was performed at 25°C, at pH 4.0 and ionic strength of 0.01M. Stability constant of complex between Pb(II) ions and humic acid is greater than stability constants of other investigated metal-humate complexes. Bogata and Sokolowska (2016) analyses the interaction between humic acids from different soils and Zn (II) ions at wide concentration ranges and at pH 5. Studies have showed significant impact of Zn concentration, pH and some properties of humic acids with zinc.But all of these studies were limited to acidic pH range. Therefore, the present study was carried out to determine and compare the stability constants of complexes of metal ions with hydrolysed peat soil humic acid and unhydrolysed peat soil humic under non-acid conditions.

MATERIALS AND METHODS

Analytical grade chemicals used includes hydrochloric acid (HCl), nitric acid (HNO_3), sodium hydroxide (NaOH), lead nitrate $Pb(NO_3)_2$, copper nitrate $Cu(NO_3)_2.3H_2O$, cadmium nitrate $Cd(NO_3)_2.4H_2O$, magnesium nitrate $Mg(NO_3)_2.6H_2O$, potassium nitrate (KNO_3), calcium chloride ($CaCl_2$), (sigma-Aldrich). Dowex 50WX8, (20-50 mesh) from Fluka.

Area of study



Source: Dept. of Geog. BUK (2016)

Figure 1: Map showing the sampling point at Sagamu Town, Ogun State.

Description of Sampling Area

Sagamu has geographical coordinates between 6°50′ north; 3° 38′ east is located in south western region of Nigeria. The region has tropical wet and dry climate with a lengthy wet season and relatively constant temperatures throughout the course of the year. Wet season runs from March to October, November to December forms the region dry season. The vegetation type of the region is savannah which is really grassland with small bushes and occasional big trees. Grassland soils have substantially higher organic matter content than forest soils (Novackova, 2011).

Sample Collection

The Peatsoil samples were collected from four different sampling points (0-10cm depth) in Sagamu into polyethylene bag with plastic spoons. Samples were taken to the laboratory, extraneous materials were removed; the samples were air-dried, crushed and ground to a fine powder in a mortar passed through a 0.20mm sieve. The samples were kept for analysis.

Isolation and purification of humic acid from peat soil sample

Peatsoil sample (100g) was mixed with 1000 cm^3 of 0.1M NaOH solution, shaken for 3hours and left to stand overnight. Dark-coloured supernatant was obtained and decanted from solid residue. The dark-coloured supernatant was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 6 hours. Yellowish brown supernatant and dark-brown precipitate were obtained. The yellowish brown supernatant was decanted followed by centrifuge and discarded. The dark-brown precipitate was mixed with 500$cm^3$of 0.1M NaOH solution followed by passing through dowex resin. The dark-brown solution was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 3 hours. The dark-brown precipitate was washed several times with deionized water. The supernatant was treated with $AgNO_3$ solution until no white precipitate observed. The humic acid was transferred to weighed crucible and dried at 60°C in an oven for 12 hours. The humic acid was cooled and dried in the desiccator, weighed and recorded. The obtained humic acid was dried again at 60°C for additional 6 hours cooled and dried in the desiccator, weighed and recorded constant weight was obtained (Baruah *et al*., 2015).

FT-IR analysis

FT-IR spectra of humic acid sample was analysed using Carry 630 FT-IR Agilent Technologies.

Unhydrolysed compost humic acid

The unhydrolysed humic acid was obtained after isolation and purification of compost humic acid and kept for investigation.

Acid hydrolysis of Peatsoil acid

Peatsoil humic acid sample (1g) was refluxed for 12 hours at (160°C) with 50cm^3 of 6M HCl. The mixture was allowed to cool, decanted, and centrifuged after hydrolysis. The insoluble residues were washed with distilled water via centrifugation several times, and the supernatant was treated with $AgNO_3$ solution until no white precipitate was observed. The residue was thoroughly dried over $CaCl_2$ in a desiccator at room temperature (Chefetz *et al*., 2002). Finally, the obtained hydrolysed humic acid was kept for investigation.

Potentiometric Titrations

Potentiometric measurements were carried out using a pH-meter Jenway (model 3510) with combine electrode, the sensitivity of the pH - meter is 0.01 units. The pH meter was switched on half an hour before starting the titration for initial warm up of the instrument. The instrument was calibrated with an aqueous standard buffer solution of pH 4.00 and 10.0 (borate buffer) prepared from a "Qualigens" buffer tablets.

The following sets of solutions were prepared in a 250cm^3 volumetric flask separately for pH metric titrations.

(i) 5 cm^3 0.1 M HCl + 40 cm^3 deionized water

(ii) 5 cm^3 0.1 M HCl + 39 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid

(iii) 5 cm^3 0.1 M HCl + 37 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid + 2 cm^3 0.01 M Cu(II)

The solutions were titrated against standardized 0.110MNaOH separately. The total volume of each mixture was adjusted to 50 cm^3 and the ionic strength of the solutions was maintained constant at by adding appropriate amount of stock solution of 1M KNO_3 (Gamal, 2015; Omar and Ali, 2015). A magnetic stirrer was used to achieve thorough mixing of the interacting solutions at 550 rpm. The same set of experimental conditions was applied for potentiometric titration of remaining samples.

Evaluation of pKa of Hydrolysed peat soil Humic Acids

The proton-ligand formation number n_A were calculated by Irving and Rossotti expression (Omar and Ali, 2015).

$$nA = Y- \frac{(V2-V1)(No-Eo)}{(Vo+V1)TcL} \quad \text{...................................1}$$

Where: Y is number of dissociable proton, (V_2-V_1) is the measure of displacement of the ligand curve relative to acid curve, N^o and E^o are the resultant concentration of alkali solution, free acid solution, $T_{cL}{}^o$ is the total ligand concentration, V^o is the total volume of titration solution,V_1 is the volume of alkali added to acid solution,V_2 is the volume of alkali added to acid solution + ligand solution, acid dissociation constants (pKa - values) of ligand were calculated by algebraic method point wise calculation (Tables 1). The dissociation constants (pKa) were calculated according to the following relation:

$$pKa = pH + \log(\frac{nA}{1-nA}) \quad \text{.............................2}$$

Where: pKa is the acid dissociation constant, $n_A$is the Proton-ligand formation number and pH is the pH-values (Omar and Ali, 2015).

Determination of metal-ligand stability constants (log K) of complexes

The potentiometric measurement for the determination of stability constant of a complex in solution is based on the fact that the redox potential of the couple $\frac{M^{+(m-n)}}{M^{+m}}$ is shifted significantly on complexation of the metal ion with the ligand. This method involves change in hydrogen ion concentration [H$^+$] due to the displacement or association of one or more protons taking place during complexation reaction. This change can be found out by titrating the solutions containing free acid, acid with ligand, and acid with ligand and metal ion, individually against a standard alkali solution at a constant ionic strength or temperature. Either ionic strength or temperature may be varied for different sets of solutions. In all the cases, the change in the pH of the solution is measured after each addition of a known amount of alkali to the reaction cell which contains the reaction mixture. The titration curves are then drawn by plotting the measured pH values against the corresponding volume of alkali added and the stability constants of the complexes are determined from the titration curves by employing pH-metric titration technique given by (Irving and Rossoti).

Metal-ligand stability constants (Log K) were determined by using the following relations:

$$\bar{n} = \frac{(V_3 - V_2)(E^0 + N^0)}{(V^0 + V_2)\bar{n}_A T_m^0} \quad \text{...3}$$

and

$$PL = \log_{10}\{\frac{1 + \beta_n^H \frac{1}{[anti\ \log pH]^n}}{T_L^0 - \bar{n} T_m^0} X \frac{(V^0 + V_3)}{V^0}\} \quad \text{...4}$$

Where $T_{L,}$ T^{o}, E°, and V^{o}havethe same significance as in equation (1) above, T_m denotes the total concentration of metal present in solution, V_3 is the volume of metal ions present in solution and β^H is the overall proton ligand stability constant. The metal-ligand stability constants (log K) were determined by employing point wise computational Method (eq. 5 and 6).

$$\mathrm{LogK}_1 = \log\left(\frac{n}{1-n}\right) + \mathrm{pL} \qquad \ldots\ldots\ldots\ldots.5$$

$$\mathrm{LogK}_2 = \log\left(\frac{1-n}{2-n}\right) + \mathrm{pL}\ldots\ldots\ldots\ldots\ldots\ldots\ldots6$$

Where: Log K is the metal-ligand stability constant, pL is the Free ligand exponent function, **n** is the Average number of ligand attached with metal ion (Janrao*et al.*, 2014).The results obtained were analyzed by an ORIGIN 2016 program using titration data and then the proton-ligand stability constants (pKa) and Metal-ligand stability constant (LogK) calculated (Omar and Ali, 2015).

RESULTS AND DISCUSSION

Fourier transformed infrared (FT-IR) spectra of isolated humic acid from peat soils Figure 2 had distinct clear absorption bands indicating the presence of major humic acid structural elemental groups such as H bonded OH ($3680cm^{-1}$ peak), C=O of carbonyl ($1721cm^{-1}$ peak), functional groups of aliphatic components CH_2 ($2918cm^{-1}$ peak) and C-O stretching of polysaccharide ($1168cm^{-1}$ peak). The positions of the absorption bands of the spectra fell within typical major absorption bands of humic acid which is at frequencies 3680, 2918, 1721, 1168 cm^{-1}. The first peak centred in the vicinity of 3680 cm^{-1} region is attributed to phenol OH group bounded by intermolecular H bonds. The $2918cm^{-1}$ band usually has absorption maximum at 2918 cm^{-1} which is due to C–H stretching of alkane group (CH_2). The next major absorption band is 1721 cm^{-1}. This band has been commonly ascribed to C=O stretching of mainly carboxyl group (COOH) with trace amount of ketones. The last peak was observed at 1168 cm^{-1} due to C–O stretching of polysaccharides and this peak appeared also in the spectra of humic acid from peat soil. The FTIR spectra of the isolated humic acid contained all major characteristic absorption peaks of humic acid. These absorption peaks indicated the presence of the major structural elements of humic acid namely H bonded OH, C=C of aromatic ring, C=O of carbonyl group (both carboxyl and ketonic), CH_2 group. This strongly supports the presence of humic acid.

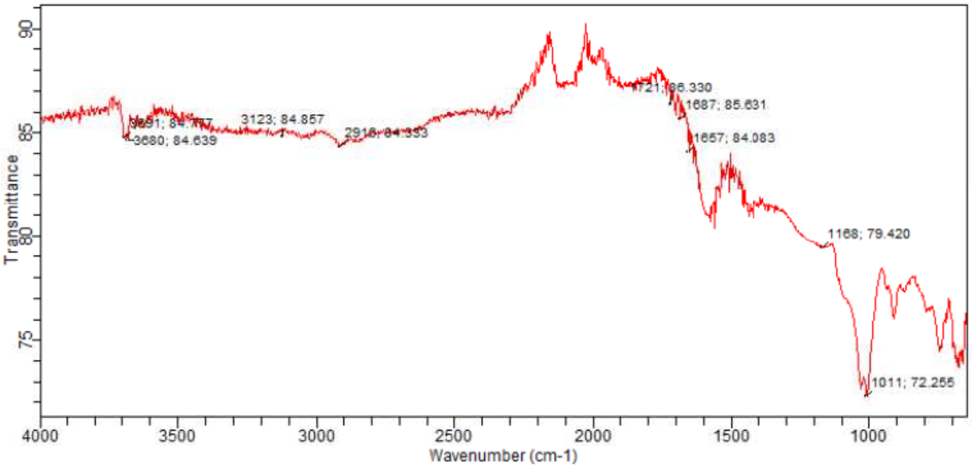


Fig. 2 : FT-IR spectraof peatsoilhumic acid (PSHA)

Evaluation of acid dissociation constant (pka) of acid hydrolysed peat soil humicacid at phenolic group

The value of the dissociation constant of the peat soil humic acid (PSHA) that underwent acidhydrolysis studied was found to be 8.9299 as shown Table 1, which is lower than the literaturevalues reported by Almeida and Szpoganics, (2015), Borges *et al.*, (2005); Badr *et al.*, (2012)and Fernandes *et al*,.(2009) of 9.73, 9.47 and 10.30. The difference between the obtained valuesand the reported values in this study might be probably as a result of acid hydrolysis of humicacid.

Table 1: PKa of (Hydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	$\log(\frac{nA}{1-nA})$	pKa
8.50	5.30	6.29	0.99	0.3594	-0.2510	8.2490
8.72	5.35	6.37	1.02	0.3400	-0.2880	8.4320
9.00	5.40	6.46	1.06	0.3141	-0.3391	8.6609
9.22	5.45	6.55	1.10	0.2882	-0.3927	8.8273
9.51	5.50	6.66	1.16	0.2494	-0.4786	9.0314
9.73	5.55	6.78	1.23	0.2041	-0.5910	9.1390
10.00	5.60	6.90	1.30	0.1589	-0.7238	9.2762
10.23	5.65	7.05	1.40	0.0941	-0.9835	9.2465
10.49	5.70	7.10	1.40	0.0941	-0.9835	9.5065

Average pKa = 8.9299 ± 0.4186

Table 2: PKa of (Unhydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	$\mathrm{Log}(\frac{nA}{1-n})$	pKa
8.50	5.30	5.81	0.51	0.6619	0.2919	8.7919
8.72	5.35	5.90	0.55	0.6357	0.2418	8.9618
9.00	5.40	6.00	0.60	0.6029	0.1813	9.1813
9.22	5.45	6.10	0.65	0.5701	0.1226	9.3426
9.51	5.50	6.20	0.70	0.5376	0.0654	9.5754
9.73	5.55	6.33	0.78	0.4851	-0.0259	9.7041
10.00	5.60	6.47	0.87	0.4262	-0.1291	9.8709
10.23	5.65	6.62	0.99	0.3609	-0.2481	9.9819
10.49	5.70	6.80	1.10	0.2759	-0.4690	10.0210

Average pKa = 9.4923± 0.4410

Metal-ligand stability constant (Log K)

The stabilityconstants require the accurate values of proton-ligand stability constants (Anil and Maroti, 2008). Metal titration curves crossed over ligand titration curve indicated the formation of complex upon proton release (Santosh, *et al.*, 2011). If the values of n- are within range 0.2-0.8 and 1.2-18 this indicates the formation of 1:1 and 1:2 complexes (Sayyed and Mazahar, 2012).

The metal (II)-humate stepwise stability constants (log k) at phenolic group (Tables 3-18)

Table 3: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$\log(\frac{n}{1-n})$	$\mathrm{Log}K_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

LogK_1 (Average value) = 2.4788± 0.2203

Table 4: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$\mathrm{Log}(\frac{n-1}{2-n})$	$\mathrm{Log}K_2$
9.51	5.50	6.66	6.73	0.07	1.3509	1.70	-0.2671	1.4329
9.73	5.55	6.78	6.85	0.07	1.6383	1.51	0.2467	1.7567
10.00	5.60	6.90	6.98	0.08	2.1783	1.31	-0.2158	1.0942
10.23	5.65	7.05	7.13	0.08	4.1904	1.27		
10.49	5.70	7.10	7.19	0.09	4.6920			

LogK_2(Average value) = 1.4280 ± 0.3312

Table 5:Point-wise method,Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	Log$(\frac{n}{n-1})$	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430

$LogK_1$ **(Average value)** = 2.3059± 0.6153

Table 6:Point-wise method, Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log$(\frac{n-1}{2-n})$	Log K_2
9.73	5.55	6.33	6.42	0.09	0.9000	1.69		
10.00	5.60	6.47	6.58	0.11	1.2578	1.44	-0.4592	0.9808
10.23	5.65	6.62	6.84	0.12	1.6137	1.26	-0.2010	1.4610
10.49	5.70	6.80	6.92	0.12	2.1052	1.03		

$LogK_2$ **(Average value)** = 1.2209± 0.3398

Table 7:Point-wise method,Pb (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log$(\frac{n}{1-n})$	$LogK_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.60	0.05	0.8333	1.96	0.6989	2.6589

$LogK_1$ (Average value) = 2.5832 ±0.1614

Table 8:Point-wise method,Pb-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log$(\frac{n-1}{2-n})$	$logK_2$
9.51	5.50	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.83	0.05	1.1702	1.44		
10.00	5.60	6.90	6.90	0.05	1.4864	1.22	-0.0237	1.1963
10.23	5.65	7.05	7.10	0.05	2.0190	1.09		
10.49	5.70	7.10	7.17	0.07	3.6492	1.00		

$LogK_2$(Average value) = 1.1963

Table 9:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log $(\frac{n}{n-1})$	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.5477	2.3123
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	0.0272	2.2072
9.51	5.50	6.20	6.26	0.07	0.6417	1.89	0.2530	2.1430
9.73	5.55	6.40	6.40	0.07	0.7000	1.67	0.3680	2.0380

$LogK_1$ **(Average value)** = 2.2364 ± 0.1602

Table 10:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log$(\frac{n-1}{2-n})$	Log K_2
10.00	5.60	6.47	6.55	0.08	1.9503	1.41		
10.23	5.65	6.62	6.72	0.11	1.4792	1.26	-0.0361	1.2239

$LogK_2$ **(Average value)** = 1.2239

Table 11:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log$(\frac{n}{n-1})$	$LogK_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4290	2.2110
8.72	5.35	6.37	6.39	0.02	0.2858	2.42	-0.3978	2.0222
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

$LogK_1$ (Average value)=2.1382**±**0.1046

Table 12:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	$\log(\frac{n-1}{2-n})$	$LogK_2$
9.51	5.55	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.84	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.93	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.10		
10.49	5.70	7.10	7.18	0.07	3.6492	0.83		

$LogK_2$(Average value) = 1.5453 **±** 0.3450

Table 13:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$V_3\text{-}V_2$	n	pL	$Log(\frac{n}{n-1})$	$Log\ K_1$
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.3477	2.3123
9.00	5.40	6.00	6.04	0.04	0.3236	2.38	-0.3202	2.0598
9.22	5.45	6.10	6.15	0.05	0.4297	2.17	-0.1230	2.0470
9.51	5.50	6.20	6.26	0.06	0.5500	1.89	0.0871	1.9771
9.73	5.55	6.33	6.40	0.07	0.7000	1.67	0.3680	2.0380

$LogK_1$ **(Average value)** = 2.1568 ± 0.2069

Table 14:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$V_3\text{-}V_2$	n	pL	$Log(\frac{n-1}{2-n})$	$Log\ K_2$
10.00	5.60	6.47	6.55	0.08	0.9148	1.41		
10.23	5.65	6.62	6.71	0.09	1.2102	1.20	-0.5749	0.6251
10.49	5.70	6.80	6.92	0.09	1.5968	1.03	0.1703	1.2003

$LogK_2$ **(Average value)** = 0.9127± 0.4070

Table15:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	$Log(\frac{n}{1-n})$	$LogK_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4210	2.2190
8.72	5.35	6.37	6.40	0.03	0.4286	2.42	-0.1249	2.2951
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.96	0.3010	2.2610
9.51	5.55	6.66	6.70	0.04	0.7720	1.67	0.5297	2.1997

$LogK_1$ (Average value) = 2.2108± 0.0825

Table 16:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	$Log(\frac{n-1}{2-n})$	$Log\ K_2$
9.73	5.55	6.78	6.83	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.95	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.09		
10.49	5.70	7.10	7.16	0.06	3.1429	0.89		

$LogK_2$ **(Average value)** = 1.5453± 0.3450

Table 17:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$V_3\text{-}V_2$	n	pL	$Log(\frac{n}{n-1})$	$Log\ K_1$
8.50	5.30	5.81	5.86	0.05	0.3717	2.88	-0.2280	2.6520
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.06	0.06	0.4853	2.38	-0.0255	2.3545
9.22	5.45	6.10	6.16	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430
9.73	5.55	6.33	6.41	0.08	0.8000	1.69	0.6020	2.2920

$LogK_1$ **(Average value)** = 2.2516± 0.5380

Table 18:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
10.00	5.60	6.47	6.57	0.10	1.1434	1.43		
10.23	5.65	6.62	6.72	0.10	1.3448	1.23	-0.2788	0.9512
10.49	5.70	6.80	6.90	0.10	1.7742	1.03	0.5351	1.5651

LogK_2 **(Average value)** = 1.2581± 0.4340

Table 19: Stepwise and overall Stability constants of thehydrolysed and unhydrolysed divalent metal (II) complexes

Chelates	**LogK_1**	**LogK_2**	**Logβ**
[Cu (Hydrolysed PSHA-1)$_2$]	2.4788	1.4280	3.9068
[Pb (Hydrolysed PSHA-1)$_2$]	2.5832	1.1963	3.7795
[Cd (Hydrolysed PSHA-1)$_2$]	2.2108	1.5453	3.7561
[Mg (Hydrolysed PSHA-1)$_2$]	2.1382	1.5453	3.6835
[Cu (Unhydrolysed PSHA-1)$_2$]	2.3059	1.2209	3.5268
[Pb (Unhydrolysed PSHA-1)$_2$]	2.2364	1.2239	3.4603
[Cd (Unhydrolysed PSHA-1)$_2$]	2.2516	1.2581	3.5097
[Mg (Unydrolysed PSHA-1)$_2$]	2.1568	0.9127	3.0695

The results obtained (Table19) shows the stepwise and overall stability constants to be not high indicating low stability of the complexes, because the solubility of most metal ions in the basic pH range is minimal due to metal hydroxide precipitation (Karimi, 2017). In general, the stepwise stability constants (K_1 and K_2) follow the order $K_1 > K_2$ for the copper, lead, magnesium and cadmium complexes respectively. The steady decrease of the values with increasing number of ligands is in agreement with the prediction made by researchers (Na'aliya, 2013). The decrease could be attributed to the fact that as the number of the ligands (Humate ions) that enters the coordination zone increases the aqua molecules available for replacement by the ligands become less. Thus, the metal ions become less electron loving with progressive intake of the ligand and this results in the decrease in the values of the constants (Na'aliya, 2013). Also the stability of the complexes is influenced by the size and number of the chelate rings(Mackay and Mackay,2002).All the complexes form rings in their structure as humate, a bidentate ligand, bond the metal ions in the ratio 1:2 (Boguta and Sokolowska, 2016) forming chelate rings. The values of the overall stability constants (logβ) obtained for humate complexes are not high indicating low stability as the values are not high. LogK values for copper-humates (Table 3 to 6) obtained in this study are lower than those reported for the complexes of humic acids (Pandey *et al.*, 2015; Dinu, 2013; Kaschl *et al.*, 2010 and Gilbeto and Jorg, 2001). The values of LogK(Table 7 to 10) forlead-humates are lower than those reported for the lead in the literature (Dinu, 2013; Gilbeto and Jorg 2001). Log K values(Table 11 to 14) for magnesium-humates obtained in this study are close to those reported by (Pandey *et al.*, 2015). Log K values of cadmium-humates (Table 15 to 18) obtained in this work near to the one reported by (Dinu, 2013 and Pandey *et al.*, 2015).The difference between the reported values and the values obtained in this study might be probably as a result of acid hydrolysis of humic acid. The values of the overall stability constants (log β) of the copper humates complexes presented in Table 19 is high than that of other metal humate complexes, show relatively high stability of Cu-HA complexes, show the following order of stability: Cu >Pb> Cd > Mg; which are in close agreement to the findings of (Dinu, 2013 and Pandey *et al.*, 2015).The high stability of Cu-humate chelate could be attributed to the existence of coordinate covalent bond between the complexing agents and the Cu^{2+} ions. Since, Cu^{2+} being a metal of the transitional series with $3d^9$ electronic configurations can accept the electrons from the complexing agents. Similarly,the low stabilities of Pb,Cd and Mg - complexes could be explained by that Pb^{2+} with $6s^2$, Cd^{2+} with $4d^{10}$ and Mg^{2+} with $2p^6$ their electronic configuration has a completely filled d,p and s orbitals. Moreover, the stabilities of metal ions with hydrolysed humic acid from peat soil were higher than those with unhydrolysed humic acid from peat soil; which is ascribed to the high content of acidity in hydrolysed humic acid than unhydrolysed humic acid.

CONCLUSION

The values of logK for Cu(II) hydrolysed humic acid complex was higher followed by Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes as compared with metal(II) unhydrolysed humic acid complexes . This indicates acid hydrolysis of humic acid can enhance the complexation behavior of humic acid with metal (II) ions. However, the higher values of logβ for Cu(II), Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes indicates more stable stepwise complexes formed as compared with Cu(II), Pb(II), Cd(II) and Mg(II) unhydrolysed humic acid complexes.

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STABILITY CONSTANTS OF COMPLEXES OF METAL IONS WITH PEATSOIL HUMIC ACIDS UNDER NON-ACID-CONDITIONS

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ABSTRACT

Stability constants of complexes of four divalent metal ions viz. Cu^{2+}, Pb^{2+},Mg^{2+} and Cd^{2+} with humic acids (HA) were determined by potentiometric titration of humic acids with the corresponding salt of the divalent metals in aqueous media under non-acid-condition. The log K (logarithm of the stability constant) ranged from 1.0942 to 2.7471 for metal-humic acid complexes were determined using point-wise computational method. The order of stability constants were obtained as follows: Cu >Pb> Cd > Mg for metal -HA complexes respectively, indicating a higher degree of complexation with Cu metal ion.

Keywords: stability constant, humic acid, potentiometric titration, divalent metals, acid hydrolysis.

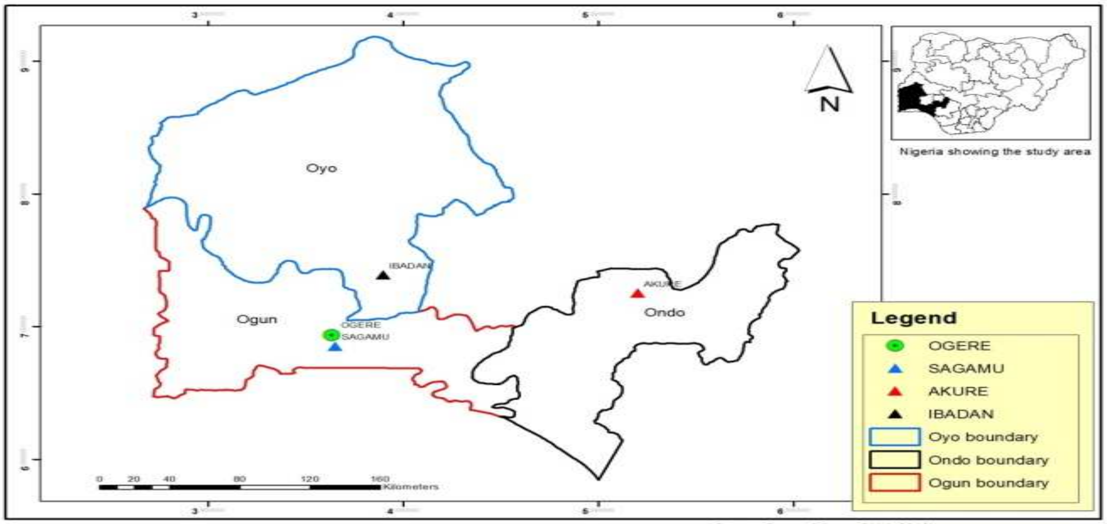
NTRODUCTION

The stability constant of a complex is the numerical expression of its stability and provides a quantitative measure of affinity of the metal ion to the complexing agent. An understanding of the relative stability of metal-complexes helps in predicting the behavior of metal ions in the soil (Ram and Raman, 1982). Extensive researches has been done to determine the stability constants of the complexes formed between humic acid (HA) with a number of metal ions. Ashok *et al.*, (2000) reported that humic acid with hydroxyl, phenoxyl and carboxyl reactive groups can form coordination compound with metal ions at pH 3.5. The stability constants(Log K) for different metal-humic acid complexes indicated the following order of the stabilities of complexes formed between humic acid and metal ion, Cu >Fe >Pb> Ni > Co > Ca > Cd > Zn >Mn> Mg. Andelkovic *et al.*, (2010) investigated the binding of Cd(II) to soil humic acid at pH 6.5 and in 0.1M KNO_3 ionic medium. The stability constant for binding indicating greater stability in the case when carboxyl groups are involved in complexation reaction. Kostic *et al.*,(2012) investigated the complexation of humic acid with certain heavy metal ions (Co(II), Ni(II),Cu(II), Zn(II), and Pb(II). The experiment was performed at 25°C, at pH 4.0 and ionic strength of 0.01M. Stability constant of complex between Pb(II) ions and humic acid is greater than stability constants of other investigated metal-humate complexes. Bogata and Sokolowska (2016) analyses the interaction between humic acids from different soils and Zn (II) ions at wide concentration ranges and at pH 5. Studies have showed significant impact of Zn concentration, pH and some properties of humic acids with zinc.But all of these studies were limited to acidic pH range. Therefore, the present study was carried out to determine and compare the stability constants of complexes of metal ions with hydrolysed peat soil humic acid and unhydrolysed peat soil humic under non-acid conditions.

MATERIALS AND METHODS

Analytical grade chemicals used includes hydrochloric acid (HCl), nitric acid (HNO_3), sodium hydroxide (NaOH), lead nitrate $Pb(NO_3)_2$, copper nitrate $Cu(NO_3)_2.3H_2O$, cadmium nitrate $Cd(NO_3)_2.4H_2O$, magnesium nitrate $Mg(NO_3)_2.6H_2O$, potassium nitrate (KNO_3), calcium chloride ($CaCl_2$), (sigma-Aldrich). Dowex 50WX8, (20-50 mesh) from Fluka.

Area of study



Source: Dept. of Geog. BUK (2016)

Figure 1: Map showing the sampling point at Sagamu Town, Ogun State.

Description of Sampling Area

Sagamu has geographical coordinates between 6°50′ north; 3° 38′ east is located in south western region of Nigeria. The region has tropical wet and dry climate with a lengthy wet season and relatively constant temperatures throughout the course of the year. Wet season runs from March to October, November to December forms the region dry season. The vegetation type of the region is savannah which is really grassland with small bushes and occasional big trees. Grassland soils have substantially higher organic matter content than forest soils (Novackova, 2011).

Sample Collection

The Peatsoil samples were collected from four different sampling points (0-10cm depth) in Sagamu into polyethylene bag with plastic spoons. Samples were taken to the laboratory, extraneous materials were removed; the samples were air-dried, crushed and ground to a fine powder in a mortar passed through a 0.20mm sieve. The samples were kept for analysis.

Isolation and purification of humic acid from peat soil sample

Peatsoil sample (100g) was mixed with 1000 cm^3 of 0.1M NaOH solution, shaken for 3hours and left to stand overnight. Dark-coloured supernatant was obtained and decanted from solid residue. The dark-coloured supernatant was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 6 hours. Yellowish brown supernatant and dark-brown precipitate were obtained. The yellowish brown supernatant was decanted followed by centrifuge and discarded. The dark-brown precipitate was mixed with 500$cm^3$of 0.1M NaOH solution followed by passing through dowex resin. The dark-brown solution was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 3 hours. The dark-brown precipitate was washed several times with deionized water. The supernatant was treated with $AgNO_3$ solution until no white precipitate observed. The humic acid was transferred to weighed crucible and dried at 60°C in an oven for 12 hours. The humic acid was cooled and dried in the desiccator, weighed and recorded. The obtained humic acid was dried again at 60°C for additional 6 hours cooled and dried in the desiccator, weighed and recorded constant weight was obtained (Baruah *et al*., 2015).

FT-IR analysis

FT-IR spectra of humic acid sample was analysed using Carry 630 FT-IR Agilent Technologies.

Unhydrolysed compost humic acid

The unhydrolysed humic acid was obtained after isolation and purification of compost humic acid and kept for investigation.

Acid hydrolysis of Peatsoil acid

Peatsoil humic acid sample (1g) was refluxed for 12 hours at (160°C) with 50cm^3 of 6M HCl. The mixture was allowed to cool, decanted, and centrifuged after hydrolysis. The insoluble residues were washed with distilled water via centrifugation several times, and the supernatant was treated with $AgNO_3$ solution until no white precipitate was observed. The residue was thoroughly dried over $CaCl_2$ in a desiccator at room temperature (Chefetz *et al*., 2002). Finally, the obtained hydrolysed humic acid was kept for investigation.

Potentiometric Titrations

Potentiometric measurements were carried out using a pH-meter Jenway (model 3510) with combine electrode, the sensitivity of the pH - meter is 0.01 units. The pH meter was switched on half an hour before starting the titration for initial warm up of the instrument. The instrument was calibrated with an aqueous standard buffer solution of pH 4.00 and 10.0 (borate buffer) prepared from a "Qualigens" buffer tablets.

The following sets of solutions were prepared in a 250cm^3 volumetric flask separately for pH metric titrations.

(i) 5 cm^3 0.1 M HCl + 40 cm^3 deionized water
(ii) 5 cm^3 0.1 M HCl + 39 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid
(iii) 5 cm^3 0.1 M HCl + 37 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid + 2 cm^3 0.01 M Cu(II)

The solutions were titrated against standardized 0.110MNaOH separately. The total volume of each mixture was adjusted to 50 cm^3 and the ionic strength of the solutions was maintained constant at by adding appropriate amount of stock solution of 1M KNO$_3$ (Gamal, 2015; Omar and Ali, 2015). A magnetic stirrer was used to achieve thorough mixing of the interacting solutions at 550 rpm. The same set of experimental conditions was applied for potentiometric titration of remaining samples.

Evaluation of pKa of Hydrolysed peat soil Humic Acids

The proton-ligand formation number n$_{\mathbf{A}}$ were calculated by Irving and Rossotti expression (Omar and Ali, 2015).

$$nA = Y - \frac{(V2-V1)(No-Eo)}{(Vo+V1)TcL} \quad \text{....................................1}$$

Where: Y is number of dissociable proton, (V$_2$-V$_1$) is the measure of displacement of the ligand curve relative to acid curve, N^o and E^o are the resultant concentration of alkali solution, free acid solution, T$_{cL}$^{o} is the total ligand concentration, V^o is the total volume of titration solution,V$_1$ is the volume of alkali added to acid solution,V$_2$ is the volume of alkali added to acid solution + ligand solution, acid dissociation constants (pKa - values) of ligand were calculated by algebraic method point wise calculation (Tables 1). The dissociation constants (pKa) were calculated according to the following relation:

$$pKa = pH + \log\left(\frac{nA}{1-nA}\right) \quad \text{..............................2}$$

Where: pKa is the acid dissociation constant, n$_A$is the Proton-ligand formation number and pH is the pH-values (Omar and Ali, 2015).

Determination of metal-ligand stability constants (log K) of complexes

The potentiometric measurement for the determination of stability constant of a complex in solution is based on the fact that the redox potential of the couple $\frac{M^{+(m-n)}}{M^{+m}}$ is shifted significantly on complexation of the metal ion with the ligand. This method involves change in hydrogen ion concentration [H$^+$] due to the displacement or association of one or more protons taking place during complexation reaction. This change can be found out by titrating the solutions containing free acid, acid with ligand, and acid with ligand and metal ion, individually against a standard alkali solution at a constant ionic strength or temperature. Either ionic strength or temperature may be varied for different sets of solutions. In all the cases, the change in the pH of the solution is measured after each addition of a known amount of alkali to the reaction cell which contains the reaction mixture. The titration curves are then drawn by plotting the measured pH values against the corresponding volume of alkali added and the stability constants of the complexes are determined from the titration curves by employing pH-metric titration technique given by (Irving and Rossoti).

Metal-ligand stability constants (Log K) were determined by using the following relations:

$$\bar{n} = \frac{(V_3 - V_2)(E^0 + N^0)}{(V^0 + V_2)\bar{n}_A T_m^0} \quad \text{...3}$$

and

$$PL = \log_{10}\left\{\frac{1 + \beta_n^H \dfrac{1}{[anti\ \log pH]^n}}{T_L^0 - \bar{n}T_m^0} X \frac{(V^0 + V_3)}{V^0}\right\} \quad \text{..4}$$

Where $T_{L,}$ T^o, E°, and V^ohavethe same significance as in equation (1) above, T_m denotes the total concentration of metal present in solution, V_3 is the volume of metal ions present in solution and β^H is the overall proton ligand stability constant. The metal-ligand stability constants (log K) were determined by employing point wise computational Method (eq. 5 and 6).

$$\text{Log}K_1 = \log\left(\frac{n}{1-n}\right) + pL \qquad \text{.............}5$$

$$\text{Log}K_2 = \log\left(\frac{1-n}{2-n}\right) + pL\text{.......................}6$$

Where: Log K is the metal-ligand stability constant, pL is the Free ligand exponent function, **n** is the Average number of ligand attached with metal ion (Janrao*et al*., 2014).The results obtained were analyzed by an ORIGIN 2016 program using titration data and then the proton-ligand stability constants (pKa) and Metal-ligand stability constant (LogK) calculated (Omar and Ali, 2015).

RESULTS AND DISCUSSION

Fourier transformed infrared (FT-IR) spectra of isolated humic acid from peat soils Figure 2 had distinct clear absorption bands indicating the presence of major humic acid structural elemental groups such as H bonded OH ($3680cm^{-1}$ peak), C=O of carbonyl ($1721cm^{-1}$ peak), functional groups of aliphatic components CH_2 ($2918cm^{-1}$ peak) and C-O stretching of polysaccharide ($1168cm^{-1}$ peak). The positions of the absorption bands of the spectra fell within typical major absorption bands of humic acid which is at frequencies 3680, 2918, 1721, 1168 cm^{-1}. The first peak centred in the vicinity of 3680 cm^{-1} region is attributed to phenol OH group bounded by intermolecular H bonds. The $2918cm^{-1}$ band usually has absorption maximum at 2918 cm^{-1} which is due to C–H stretching of alkane group (CH_2). The next major absorption band is 1721 cm^{-1}. This band has been commonly ascribed to C=O stretching of mainly carboxyl group (COOH) with trace amount of ketones. The last peak was observed at 1168 cm^{-1} due to C–O stretching of polysaccharides and this peak appeared also in the spectra of humic acid from peat soil. The FTIR spectra of the isolated humic acid contained all major characteristic absorption peaks of humic acid. These absorption peaks indicated the presence of the major structural elements of humic acid namely H bonded OH, C=C of aromatic ring, C=O of carbonyl group (both carboxyl and ketonic), CH_2 group. This strongly supports the presence of humic acid.

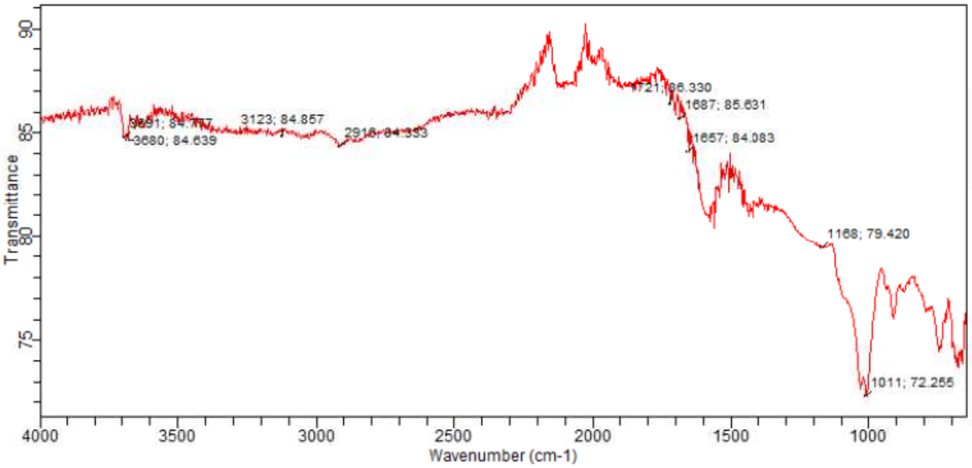


Fig. 2 : FT-IR spectraof peatsoilhumic acid (PSHA)

Evaluation of acid dissociation constant (pka) of acid hydrolysed peat soil humicacid at phenolic group

The value of the dissociation constant of the peat soil humic acid (PSHA) that underwent acidhydrolysis studied was found to be 8.9299 as shown Table 1, which is lower than the literaturevalues reported by Almeida and Szpoganics, (2015), Borges *et al*., (2005); Badr *et al*., (2012)and Fernandes *et al*,.(2009) of 9.73, 9.47 and 10.30. The difference between the obtained valuesand the reported values in this study might be probably as a result of acid hydrolysis of humicacid.

Table 1: PKa of (Hydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	log($\frac{nA}{1-nA}$)	pKa
8.50	5.30	6.29	0.99	0.3594	-0.2510	8.2490
8.72	5.35	6.37	1.02	0.3400	-0.2880	8.4320
9.00	5.40	6.46	1.06	0.3141	-0.3391	8.6609
9.22	5.45	6.55	1.10	0.2882	-0.3927	8.8273
9.51	5.50	6.66	1.16	0.2494	-0.4786	9.0314
9.73	5.55	6.78	1.23	0.2041	-0.5910	9.1390
10.00	5.60	6.90	1.30	0.1589	-0.7238	9.2762
10.23	5.65	7.05	1.40	0.0941	-0.9835	9.2465
10.49	5.70	7.10	1.40	0.0941	-0.9835	9.5065

Average pKa = 8.9299 ± 0.4186

Table 2: PKa of (Unhydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	Log($\frac{nA}{1-n}$)	pKa
8.50	5.30	5.81	0.51	0.6619	0.2919	8.7919
8.72	5.35	5.90	0.55	0.6357	0.2418	8.9618
9.00	5.40	6.00	0.60	0.6029	0.1813	9.1813
9.22	5.45	6.10	0.65	0.5701	0.1226	9.3426
9.51	5.50	6.20	0.70	0.5376	0.0654	9.5754
9.73	5.55	6.33	0.78	0.4851	-0.0259	9.7041
10.00	5.60	6.47	0.87	0.4262	-0.1291	9.8709
10.23	5.65	6.62	0.99	0.3609	-0.2481	9.9819
10.49	5.70	6.80	1.10	0.2759	-0.4690	10.0210

Average pKa = 9.4923± 0.4410

Metal-ligand stability constant (Log K)

The stabilityconstants require the accurate values of proton-ligand stability constants (Anil and Maroti, 2008). Metal titration curves crossed over ligand titration curve indicated the formation of complex upon proton release (Santosh, *et al.*, 2011). If the values of n- are within range 0.2-0.8 and 1.2-18 this indicates the formation of 1:1 and 1:2 complexes (Sayyed and Mazahar, 2012).

The metal (II)-humate stepwise stability constants (log k) at phenolic group (Tables 3-18)

Table 3: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n}{1-n}$)	$LogK_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

$LogK_1$ (Average value) = 2.4788± 0.2203

Table 4: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	Log($\frac{n-1}{2-n}$)	$LogK_2$
9.51	5.50	6.66	6.73	0.07	1.3509	1.70	-0.2671	1.4329
9.73	5.55	6.78	6.85	0.07	1.6383	1.51	0.2467	1.7567
10.00	5.60	6.90	6.98	0.08	2.1783	1.31	-0.2158	1.0942
10.23	5.65	7.05	7.13	0.08	4.1904	1.27		
10.49	5.70	7.10	7.19	0.09	4.6920			

$LogK_2$(Average value) = 1.4280 ± 0.3312

Table 5:Point-wise method,Cu (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	Log($\frac{n}{n-1}$)	Log K$_1$
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430

LogK$_1$ **(Average value)** = 2.3059± 0.6153

Table 6:Point-wise method, Cu (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	V$_3$-V$_2$	n	pL	Log($\frac{n-1}{2-n}$)	Log K$_2$
9.73	5.55	6.33	6.42	0.09	0.9000	1.69		
10.00	5.60	6.47	6.58	0.11	1.2578	1.44	-0.4592	0.9808
10.23	5.65	6.62	6.84	0.12	1.6137	1.26	-0.2010	1.4610
10.49	5.70	6.80	6.92	0.12	2.1052	1.03		

LogK$_2$ **(Average value)** = 1.2209± 0.3398

Table 7:Point-wise method,Pb (Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	log($\frac{n}{1-n}$)	LogK$_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.60	0.05	0.8333	1.96	0.6989	2.6589

LogK$_1$ (Average value) = 2.5832 ±0.1614

Table 8:Point-wise method,Pb-(Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	log($\frac{n-1}{2-n}$)	logK$_2$
9.51	5.50	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.83	0.05	1.1702	1.44		
10.00	5.60	6.90	6.90	0.05	1.4864	1.22	-0.0237	1.1963
10.23	5.65	7.05	7.10	0.05	2.0190	1.09		
10.49	5.70	7.10	7.17	0.07	3.6492	1.00		

LogK$_2$(Average value) = 1.1963

Table 9:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	V$_3$-V$_2$	n	pL	Log ($\frac{n}{n-1}$)	Log K$_1$
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.5477	2.3123
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	0.0272	2.2072
9.51	5.50	6.20	6.26	0.07	0.6417	1.89	0.2530	2.1430
9.73	5.55	6.40	6.40	0.07	0.7000	1.67	0.3680	2.0380

LogK$_1$ **(Average value)** = 2.2364 ± 0.1602

Table 10:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	V$_3$-V$_2$	n	pL	Log($\frac{n-1}{2-n}$)	Log K$_2$
10.00	5.60	6.47	6.55	0.08	1.9503	1.41		
10.23	5.65	6.62	6.72	0.11	1.4792	1.26	-0.0361	1.2239

LogK$_2$ **(Average value)** = 1.2239

Table 11:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	log($\frac{n}{n-1}$)	LogK$_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4290	2.2110
8.72	5.35	6.37	6.39	0.02	0.2858	2.42	-0.3978	2.0222
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

LogK$_1$ (Average value)=2.1382**±**0.1046

Table 12:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	log($\frac{n-1}{2-n}$)	LogK$_2$
9.51	5.55	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.84	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.93	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.10		
10.49	5.70	7.10	7.18	0.07	3.6492	0.83		

LogK$_2$(Average value) = 1.5453 **±** 0.3450

Table 13:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	V$_3$-V$_2$	n	pL	Log($\frac{n}{n-1}$)	Log K$_1$
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.3477	2.3123
9.00	5.40	6.00	6.04	0.04	0.3236	2.38	-0.3202	2.0598
9.22	5.45	6.10	6.15	0.05	0.4297	2.17	-0.1230	2.0470
9.51	5.50	6.20	6.26	0.06	0.5500	1.89	0.0871	1.9771
9.73	5.55	6.33	6.40	0.07	0.7000	1.67	0.3680	2.0380

LogK$_1$ **(Average value)** = 2.1568 ± 0.2069

Table 14:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	V$_3$-V$_2$	n	pL	Log($\frac{n-1}{2-n}$)	Log K$_2$
10.00	5.60	6.47	6.55	0.08	0.9148	1.41		
10.23	5.65	6.62	6.71	0.09	1.2102	1.20	-0.5749	0.6251
10.49	5.70	6.80	6.92	0.09	1.5968	1.03	0.1703	1.2003

LogK$_2$ **(Average value)** = 0.9127± 0.4070

Table15:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	Log($\frac{n}{1-n}$)	LogK$_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4210	2.2190
8.72	5.35	6.37	6.40	0.03	0.4286	2.42	-0.1249	2.2951
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.96	0.3010	2.2610
9.51	5.55	6.66	6.70	0.04	0.7720	1.67	0.5297	2.1997

LogK$_1$ (Average value) = 2.2108± 0.0825

Table 16:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	Log($\frac{n-1}{2-n}$)	Log K$_2$
9.73	5.55	6.78	6.83	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.95	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.09		
10.49	5.70	7.10	7.16	0.06	3.1429	0.89		

LogK$_2$ **(Average value)** = 1.5453± 0.3450

Table 17:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	V$_3$-V$_2$	n	pL	Log($\frac{n}{n-1}$)	Log K$_1$
8.50	5.30	5.81	5.86	0.05	0.3717	2.88	-0.2280	2.6520
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.06	0.06	0.4853	2.38	-0.0255	2.3545
9.22	5.45	6.10	6.16	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430
9.73	5.55	6.33	6.41	0.08	0.8000	1.69	0.6020	2.2920

LogK$_1$ **(Average value)** = 2.2516± 0.5380

Table 18:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$\text{Log}(\frac{n-1}{2-n})$	Log K_2
10.00	5.60	6.47	6.57	0.10	1.1434	1.43		
10.23	5.65	6.62	6.72	0.10	1.3448	1.23	-0.2788	0.9512
10.49	5.70	6.80	6.90	0.10	1.7742	1.03	0.5351	1.5651

LogK_2 **(Average value)** = 1.2581± 0.4340

Table 19: Stepwise and overall Stability constants of thehydrolysed and unhydrolysed divalent metal (II) complexes

Chelates	**LogK_1**	**LogK_2**	**Logβ**
[Cu (Hydrolysed PSHA-1)$_2$]	2.4788	1.4280	3.9068
[Pb (Hydrolysed PSHA-1)$_2$]	2.5832	1.1963	3.7795
[Cd (Hydrolysed PSHA-1)$_2$]	2.2108	1.5453	3.7561
[Mg (Hydrolysed PSHA-1)$_2$]	2.1382	1.5453	3.6835
[Cu (Unhydrolysed PSHA-1)$_2$]	2.3059	1.2209	3.5268
[Pb (Unhydrolysed PSHA-1)$_2$]	2.2364	1.2239	3.4603
[Cd (Unhydrolysed PSHA-1)$_2$]	2.2516	1.2581	3.5097
[Mg (Unydrolysed PSHA-1)$_2$]	2.1568	0.9127	3.0695

The results obtained (Table19) shows the stepwise and overall stability constants to be not high indicating low stability of the complexes, because the solubility of most metal ions in the basic pH range is minimal due to metal hydroxide precipitation (Karimi, 2017). In general, the stepwise stability constants (K_1 and K_2) follow the order $K_1 > K_2$ for the copper, lead, magnesium and cadmium complexes respectively. The steady decrease of the values with increasing number of ligands is in agreement with the prediction made by researchers (Na'aliya, 2013). The decrease could be attributed to the fact that as the number of the ligands (Humate ions) that enters the coordination zone increases the aqua molecules available for replacement by the ligands become less. Thus, the metal ions become less electron loving with progressive intake of the ligand and this results in the decrease in the values of the constants (Na'aliya, 2013). Also the stability of the complexes is influenced by the size and number of the chelate rings(Mackay and Mackay,2002).All the complexes form rings in their structure as humate, a bidentate ligand, bond the metal ions in the ratio 1:2 (Boguta and Sokolowska, 2016) forming chelate rings. The values of the overall stability constants (logβ) obtained for humate complexes are not high indicating low stability as the values are not high. LogK values for copper-humates (Table 3 to 6) obtained in this study are lower than those reported for the complexes of humic acids (Pandey *et al.*, 2015; Dinu, 2013; Kaschl *et al.*, 2010 and Gilbeto and Jorg, 2001). The values of LogK(Table 7 to 10) forlead-humates are lower than those reported for the lead in the literature (Dinu, 2013; Gilbeto and Jorg 2001). Log K values(Table 11 to 14) for magnesium-humates obtained in this study are close to those reported by (Pandey *et al.*, 2015). Log K values of cadmium-humates (Table 15 to 18) obtained in this work near to the one reported by (Dinu, 2013 and Pandey *et al.*, 2015).The difference between the reported values and the values obtained in this study might be probably as a result of acid hydrolysis of humic acid. The values of the overall stability constants (log β) of the copper humates complexes presented in Table 19 is high than that of other metal humate complexes, show relatively high stability of Cu-HA complexes, show the following order of stability: Cu >Pb> Cd > Mg; which are in close agreement to the findings of (Dinu, 2013 and Pandey *et al.*, 2015).The high stability of Cu-humate chelate could be attributed to the existence of coordinate covalent bond between the complexing agents and the Cu^{2+} ions. Since, Cu^{2+} being a metal of the transitional series with $3d^9$ electronic configurations can accept the electrons from the complexing agents. Similarly,the low stabilities of Pb,Cd and Mg -complexes could be explained by that Pb^{2+} with $6s^2$, Cd^{2+} with $4d^{10}$ and Mg^{2+} with $2p^6$ their electronic configuration has a completely filled d,p and s orbitals. Moreover, the stabilities of metal ions with hydrolysed humic acid from peat soil were higher than those with unhydrolysed humic acid from peat soil; which is ascribed to the high content of acidity in hydrolysed humic acid than unhydrolysed humic acid.

CONCLUSION

The values of logK for Cu(II) hydrolysed humic acid complex was higher followed by Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes as compared with metal(II) unhydrolysed humic acid complexes . This indicates acid hydrolysis of humic acid can enhance the complexation behavior of humic acid with metal (II) ions. However, the higher values of logβ for Cu(II), Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes indicates more stable stepwise complexes formed as compared with Cu(II), Pb(II), Cd(II) and Mg(II) unhydrolysed humic acid complexes.

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STABILITY CONSTANTS OF COMPLEXES OF METAL IONS WITH PEATSOIL HUMIC ACIDS UNDER NON-ACID-CONDITIONS

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ABSTRACT

Stability constants of complexes of four divalent metal ions viz. Cu^{2+}, Pb^{2+},Mg^{2+} and Cd^{2+} with humic acids (HA) were determined by potentiometric titration of humic acids with the corresponding salt of the divalent metals in aqueous media under non-acid-condition. The log K (logarithm of the stability constant) ranged from 1.0942 to 2.7471 for metal-humic acid complexes were determined using point-wise computational method. The order of stability constants were obtained as follows: Cu >Pb> Cd > Mg for metal -HA complexes respectively, indicating a higher degree of complexation with Cu metal ion.

Keywords: stability constant, humic acid, potentiometric titration, divalent metals, acid hydrolysis.

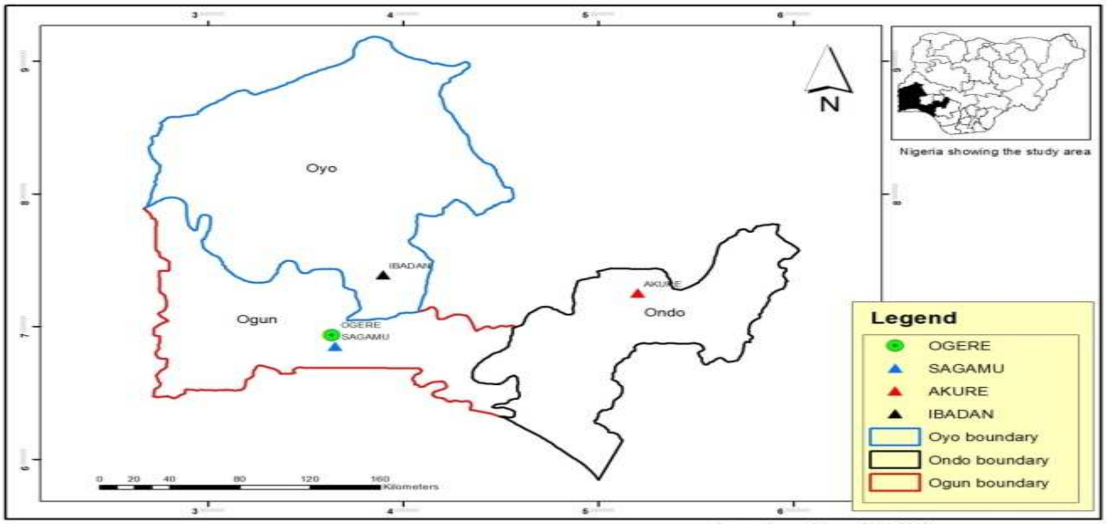
NTRODUCTION

The stability constant of a complex is the numerical expression of its stability and provides a quantitative measure of affinity of the metal ion to the complexing agent. An understanding of the relative stability of metal-complexes helps in predicting the behavior of metal ions in the soil (Ram and Raman, 1982). Extensive researches has been done to determine the stability constants of the complexes formed between humic acid (HA) with a number of metal ions. Ashok *et al*., (2000) reported that humic acid with hydroxyl, phenoxyl and carboxyl reactive groups can form coordination compound with metal ions at pH 3.5. The stability constants(Log K) for different metal-humic acid complexes indicated the following order of the stabilities of complexes formed between humic acid and metal ion, Cu >Fe >Pb> Ni > Co > Ca > Cd > Zn >Mn> Mg. Andelkovic *et al*., (2010) investigated the binding of Cd(II) to soil humic acid at pH 6.5 and in 0.1M KNO_3 ionic medium. The stability constant for binding indicating greater stability in the case when carboxyl groups are involved in complexation reaction. Kostic *et al*.,(2012) investigated the complexation of humic acid with certain heavy metal ions (Co(II), Ni(II),Cu(II), Zn(II), and Pb(II). The experiment was performed at 25°C, at pH 4.0 and ionic strength of 0.01M. Stability constant of complex between Pb(II) ions and humic acid is greater than stability constants of other investigated metal-humate complexes. Bogata and Sokolowska (2016) analyses the interaction between humic acids from different soils and Zn (II) ions at wide concentration ranges and at pH 5. Studies have showed significant impact of Zn concentration, pH and some properties of humic acids with zinc.But all of these studies were limited to acidic pH range. Therefore, the present study was carried out to determine and compare the stability constants of complexes of metal ions with hydrolysed peat soil humic acid and unhydrolysed peat soil humic under non-acid conditions.

MATERIALS AND METHODS

Analytical grade chemicals used includes hydrochloric acid (HCl), nitric acid (HNO_3), sodium hydroxide (NaOH), lead nitrate $Pb(NO_3)_2$, copper nitrate $Cu(NO_3)_2.3H_2O$, cadmium nitrate $Cd(NO_3)_2.4H_2O$, magnesium nitrate $Mg(NO_3)_2.6H_2O$, potassium nitrate (KNO_3), calcium chloride ($CaCl_2$), (sigma-Aldrich). Dowex 50WX8, (20-50 mesh) from Fluka.

Area of study



Source: Dept. of Geog. BUK (2016)

Figure 1: Map showing the sampling point at Sagamu Town, Ogun State.

Description of Sampling Area

Sagamu has geographical coordinates between 6°50′ north; 3° 38′ east is located in south western region of Nigeria. The region has tropical wet and dry climate with a lengthy wet season and relatively constant temperatures throughout the course of the year. Wet season runs from March to October, November to December forms the region dry season. The vegetation type of the region is savannah which is really grassland with small bushes and occasional big trees. Grassland soils have substantially higher organic matter content than forest soils (Novackova, 2011).

Sample Collection

The Peatsoil samples were collected from four different sampling points (0-10cm depth) in Sagamu into polyethylene bag with plastic spoons. Samples were taken to the laboratory, extraneous materials were removed; the samples were air-dried, crushed and ground to a fine powder in a mortar passed through a 0.20mm sieve. The samples were kept for analysis.

Isolation and purification of humic acid from peat soil sample

Peatsoil sample (100g) was mixed with 1000 cm^3 of 0.1M NaOH solution, shaken for 3hours and left to stand overnight. Dark-coloured supernatant was obtained and decanted from solid residue. The dark-coloured supernatant was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 6 hours. Yellowish brown supernatant and dark-brown precipitate were obtained. The yellowish brown supernatant was decanted followed by centrifuge and discarded. The dark-brown precipitate was mixed with $500cm^3$of 0.1M NaOH solution followed by passing through dowex resin. The dark-brown solution was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 3 hours. The dark-brown precipitate was washed several times with deionized water. The supernatant was treated with $AgNO_3$ solution until no white precipitate observed. The humic acid was transferred to weighed crucible and dried at 60°C in an oven for 12 hours. The humic acid was cooled and dried in the desiccator, weighed and recorded. The obtained humic acid was dried again at 60°C for additional 6 hours cooled and dried in the desiccator, weighed and recorded constant weight was obtained (Baruah *et al*., 2015).

FT-IR analysis

FT-IR spectra of humic acid sample was analysed using Carry 630 FT-IR Agilent Technologies.

Unhydrolysed compost humic acid

The unhydrolysed humic acid was obtained after isolation and purification of compost humic acid and kept for investigation.

Acid hydrolysis of Peatsoil acid

Peatsoil humic acid sample (1g) was refluxed for 12 hours at (160°C) with $50cm^3$ of 6M HCl. The mixture was allowed to cool, decanted, and centrifuged after hydrolysis. The insoluble residues were washed with distilled water via centrifugation several times, and the supernatant was treated with $AgNO_3$ solution until no white precipitate was observed. The residue was thoroughly dried over $CaCl_2$ in a desiccator at room temperature (Chefetz *et al*., 2002). Finally, the obtained hydrolysed humic acid was kept for investigation.

Potentiometric Titrations

Potentiometric measurements were carried out using a pH-meter Jenway (model 3510) with combine electrode, the sensitivity of the pH - meter is 0.01 units. The pH meter was switched on half an hour before starting the titration for initial warm up of the instrument. The instrument was calibrated with an aqueous standard buffer solution of pH 4.00 and 10.0 (borate buffer) prepared from a "Qualigens" buffer tablets.

The following sets of solutions were prepared in a 250cm^3 volumetric flask separately for pH metric titrations.

(i) 5 cm^3 0.1 M HCl + 40 cm^3 deionized water
(ii) 5 cm^3 0.1 M HCl + 39 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid
(iii) 5 cm^3 0.1 M HCl + 37 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid + 2 cm^3 0.01 M Cu(II)

The solutions were titrated against standardized 0.110MNaOH separately. The total volume of each mixture was adjusted to 50 cm^3 and the ionic strength of the solutions was maintained constant at by adding appropriate amount of stock solution of 1M KNO$_3$ (Gamal, 2015; Omar and Ali, 2015). A magnetic stirrer was used to achieve thorough mixing of the interacting solutions at 550 rpm. The same set of experimental conditions was applied for potentiometric titration of remaining samples.

Evaluation of pKa of Hydrolysed peat soil Humic Acids

The proton-ligand formation number $n_{\mathbf{A}}$ were calculated by Irving and Rossotti expression (Omar and Ali, 2015).

$$nA = Y- \frac{(V2-V1)(No-Eo)}{(Vo+V1)TcL} \quad \text{……………………………}1$$

Where: Y is number of dissociable proton, (V_2-V_1) is the measure of displacement of the ligand curve relative to acid curve, N^o and E^o are the resultant concentration of alkali solution, free acid solution, $T_{cL}{}^o$ is the total ligand concentration, V^o is the total volume of titration solution,V_1 is the volume of alkali added to acid solution,V_2 is the volume of alkali added to acid solution + ligand solution, acid dissociation constants (pKa - values) of ligand were calculated by algebraic method point wise calculation (Tables 1). The dissociation constants (pKa) were calculated according to the following relation:

$$pKa = pH + \log\left(\frac{nA}{1-nA}\right) \quad \text{………………………}2$$

Where: pKa is the acid dissociation constant, $n_A$is the Proton-ligand formation number and pH is the pH-values (Omar and Ali, 2015).

Determination of metal-ligand stability constants (log K) of complexes

The potentiometric measurement for the determination of stability constant of a complex in solution is based on the fact that the redox potential of the couple $\frac{M^{+(m-n)}}{M^{+m}}$ is shifted significantly on complexation of the metal ion with the ligand. This method involves change in hydrogen ion concentration [H$^+$] due to the displacement or association of one or more protons taking place during complexation reaction. This change can be found out by titrating the solutions containing free acid, acid with ligand, and acid with ligand and metal ion, individually against a standard alkali solution at a constant ionic strength or temperature. Either ionic strength or temperature may be varied for different sets of solutions. In all the cases, the change in the pH of the solution is measured after each addition of a known amount of alkali to the reaction cell which contains the reaction mixture. The titration curves are then drawn by plotting the measured pH values against the corresponding volume of alkali added and the stability constants of the complexes are determined from the titration curves by employing pH-metric titration technique given by (Irving and Rossoti).

Metal-ligand stability constants (Log K) were determined by using the following relations:

$$\bar{n} = \frac{(V_3 - V_2)(E^0 + N^0)}{(V^0 + V_2)\bar{n}_A T_m^0} \quad \text{……………………………………………………………………}3$$

and

$$PL = \log_{10}\{\frac{1+\beta_n^H \frac{1}{[anti\ \log pH]^n}}{T_L^0 - \bar{n}T_m^0} X \frac{(V^0+V_3)}{V^0}\} \quad \text{…………………………………………………}4$$

Where $T_{L,}$ T^o, E°, and V^ohavethe same significance as in equation (1) above, T_m denotes the total concentration of metal present in solution, V_3 is the volume of metal ions present in solution and β^H is the overall proton ligand stability constant. The metal-ligand stability constants (log K) were determined by employing point wise computational Method (eq. 5 and 6).

$$\text{Log}K_1 = \log\left(\frac{n}{1-n}\right) + pL \quad \ldots\ldots\ldots\ldots.5$$

$$\text{Log}K_2 = \log\left(\frac{1-n}{2-n}\right) + pL \ldots\ldots\ldots\ldots\ldots\ldots\ldots.6$$

Where: Log K is the metal-ligand stability constant, pL is the Free ligand exponent function, **n** is the Average number of ligand attached with metal ion (Janrao*et al*., 2014).The results obtained were analyzed by an ORIGIN 2016 program using titration data and then the proton-ligand stability constants (pKa) and Metal-ligand stability constant (LogK) calculated (Omar and Ali, 2015).

RESULTS AND DISCUSSION

Fourier transformed infrared (FT-IR) spectra of isolated humic acid from peat soils Figure 2 had distinct clear absorption bands indicating the presence of major humic acid structural elemental groups such as H bonded OH ($3680cm^{-1}$ peak), C=O of carbonyl ($1721cm^{-1}$ peak), functional groups of aliphatic components CH_2 ($2918cm^{-1}$ peak) and C-O stretching of polysaccharide ($1168cm^{-1}$ peak). The positions of the absorption bands of the spectra fell within typical major absorption bands of humic acid which is at frequencies 3680, 2918, 1721, 1168 cm^{-1}. The first peak centred in the vicinity of 3680 cm^{-1} region is attributed to phenol OH group bounded by intermolecular H bonds. The $2918cm^{-1}$ band usually has absorption maximum at 2918 cm^{-1} which is due to C–H stretching of alkane group (CH_2). The next major absorption band is 1721 cm^{-1}. This band has been commonly ascribed to C=O stretching of mainly carboxyl group (COOH) with trace amount of ketones. The last peak was observed at 1168 cm^{-1} due to C–O stretching of polysaccharides and this peak appeared also in the spectra of humic acid from peat soil. The FTIR spectra of the isolated humic acid contained all major characteristic absorption peaks of humic acid. These absorption peaks indicated the presence of the major structural elements of humic acid namely H bonded OH, C=C of aromatic ring, C=O of carbonyl group (both carboxyl and ketonic), CH_2 group. This strongly supports the presence of humic acid.

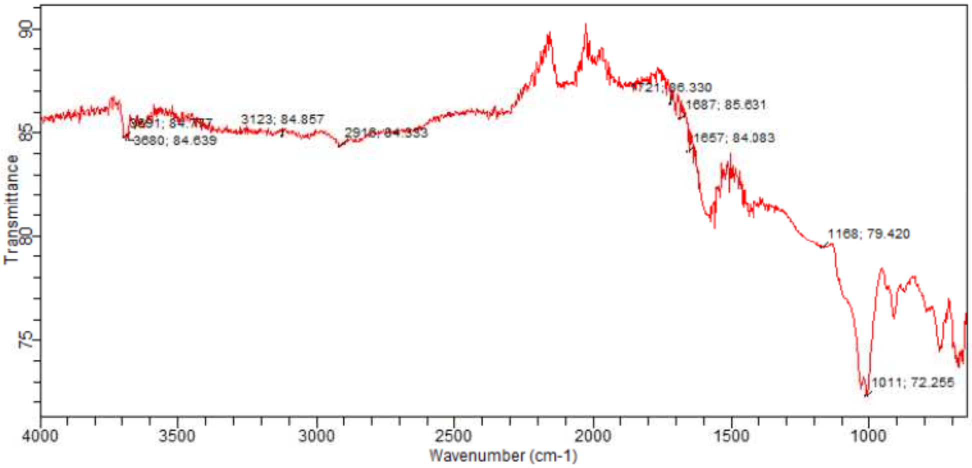


Fig. 2 : FT-IR spectraof peatsoilhumic acid (PSHA)

Evaluation of acid dissociation constant (pka) of acid hydrolysed peat soil humicacid at phenolic group

The value of the dissociation constant of the peat soil humic acid (PSHA) that underwent acidhydrolysis studied was found to be 8.9299 as shown Table 1, which is lower than the literaturevalues reported by Almeida and Szpoganics, (2015), Borges *et al*., (2005); Badr *et al*., (2012)and Fernandes *et al*,.(2009) of 9.73, 9.47 and 10.30. The difference between the obtained valuesand the reported values in this study might be probably as a result of acid hydrolysis of humicacid.

Table 1: PKa of (Hydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	$\log(\frac{nA}{1-nA})$	pKa
8.50	5.30	6.29	0.99	0.3594	-0.2510	8.2490
8.72	5.35	6.37	1.02	0.3400	-0.2880	8.4320
9.00	5.40	6.46	1.06	0.3141	-0.3391	8.6609
9.22	5.45	6.55	1.10	0.2882	-0.3927	8.8273
9.51	5.50	6.66	1.16	0.2494	-0.4786	9.0314
9.73	5.55	6.78	1.23	0.2041	-0.5910	9.1390
10.00	5.60	6.90	1.30	0.1589	-0.7238	9.2762
10.23	5.65	7.05	1.40	0.0941	-0.9835	9.2465
10.49	5.70	7.10	1.40	0.0941	-0.9835	9.5065

Average pKa = 8.9299 ± 0.4186

Table 2: PKa of (Unhydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	$\mathrm{Log}(\frac{nA}{1-n})$	pKa
8.50	5.30	5.81	0.51	0.6619	0.2919	8.7919
8.72	5.35	5.90	0.55	0.6357	0.2418	8.9618
9.00	5.40	6.00	0.60	0.6029	0.1813	9.1813
9.22	5.45	6.10	0.65	0.5701	0.1226	9.3426
9.51	5.50	6.20	0.70	0.5376	0.0654	9.5754
9.73	5.55	6.33	0.78	0.4851	-0.0259	9.7041
10.00	5.60	6.47	0.87	0.4262	-0.1291	9.8709
10.23	5.65	6.62	0.99	0.3609	-0.2481	9.9819
10.49	5.70	6.80	1.10	0.2759	-0.4690	10.0210

Average pKa = 9.4923± 0.4410

Metal-ligand stability constant (Log K)

The stabilityconstants require the accurate values of proton-ligand stability constants (Anil and Maroti, 2008). Metal titration curves crossed over ligand titration curve indicated the formation of complex upon proton release (Santosh, *et al.*, 2011). If the values of n- are within range 0.2-0.8 and 1.2-18 this indicates the formation of 1:1 and 1:2 complexes (Sayyed and Mazahar, 2012).

The metal (II)-humate stepwise stability constants (log k) at phenolic group (Tables 3-18)

Table 3: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3$-$V_2)$	n	pL	$\log(\frac{n}{1-n})$	LogK_1
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

LogK_1 (Average value) = 2.4788± 0.2203

Table 4: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3$-$V_2)$	n	pL	$\mathrm{Log}(\frac{n-1}{2-n})$	LogK_2
9.51	5.50	6.66	6.73	0.07	1.3509	1.70	-0.2671	1.4329
9.73	5.55	6.78	6.85	0.07	1.6383	1.51	0.2467	1.7567
10.00	5.60	6.90	6.98	0.08	2.1783	1.31	-0.2158	1.0942
10.23	5.65	7.05	7.13	0.08	4.1904	1.27		
10.49	5.70	7.10	7.19	0.09	4.6920			

LogK_2(Average value) = 1.4280 ± 0.3312

Table 5:Point-wise method,Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	Log($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430

$LogK_1$ **(Average value)** = 2.3059± 0.6153

Table 6:Point-wise method, Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$V_3\text{-}V_2$	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
9.73	5.55	6.33	6.42	0.09	0.9000	1.69		
10.00	5.60	6.47	6.58	0.11	1.2578	1.44	-0.4592	0.9808
10.23	5.65	6.62	6.84	0.12	1.6137	1.26	-0.2010	1.4610
10.49	5.70	6.80	6.92	0.12	2.1052	1.03		

$LogK_2$ **(Average value)** = 1.2209± 0.3398

Table 7:Point-wise method,Pb (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	log($\frac{n}{1-n}$)	$LogK_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.60	0.05	0.8333	1.96	0.6989	2.6589

$LogK_1$ (Average value) = 2.5832 ±0.1614

Table 8:Point-wise method,Pb-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	log($\frac{n-1}{2-n}$)	$logK_2$
9.51	5.50	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.83	0.05	1.1702	1.44		
10.00	5.60	6.90	6.90	0.05	1.4864	1.22	-0.0237	1.1963
10.23	5.65	7.05	7.10	0.05	2.0190	1.09		
10.49	5.70	7.10	7.17	0.07	3.6492	1.00		

$LogK_2$(Average value) = 1.1963

Table 9:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$V_3\text{-}V_2$	n	pL	Log ($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.5477	2.3123
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	0.0272	2.2072
9.51	5.50	6.20	6.26	0.07	0.6417	1.89	0.2530	2.1430
9.73	5.55	6.40	6.40	0.07	0.7000	1.67	0.3680	2.0380

$LogK_1$ **(Average value)** = 2.2364 ± 0.1602

Table 10:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$V_3\text{-}V_2$	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
10.00	5.60	6.47	6.55	0.08	1.9503	1.41		
10.23	5.65	6.62	6.72	0.11	1.4792	1.26	-0.0361	1.2239

$LogK_2$ **(Average value)** = 1.2239

Table 11:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	log($\frac{n}{n-1}$)	$LogK_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4290	2.2110
8.72	5.35	6.37	6.39	0.02	0.2858	2.42	-0.3978	2.0222
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

$LogK_1$ (Average value)=2.1382**±**0.1046

Table 12:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$\log(\frac{n-1}{2-n})$	$LogK_2$
9.51	5.55	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.84	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.93	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.10		
10.49	5.70	7.10	7.18	0.07	3.6492	0.83		

$LogK_2$(Average value) = 1.5453 **±** 0.3450

Table 13:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$Log(\frac{n}{n-1})$	$Log K_1$
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.3477	2.3123
9.00	5.40	6.00	6.04	0.04	0.3236	2.38	-0.3202	2.0598
9.22	5.45	6.10	6.15	0.05	0.4297	2.17	-0.1230	2.0470
9.51	5.50	6.20	6.26	0.06	0.5500	1.89	0.0871	1.9771
9.73	5.55	6.33	6.40	0.07	0.7000	1.67	0.3680	2.0380

$LogK_1$ **(Average value)** = 2.1568 ± 0.2069

Table 14:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$Log(\frac{n-1}{2-n})$	$Log K_2$
10.00	5.60	6.47	6.55	0.08	0.9148	1.41		
10.23	5.65	6.62	6.71	0.09	1.2102	1.20	-0.5749	0.6251
10.49	5.70	6.80	6.92	0.09	1.5968	1.03	0.1703	1.2003

$LogK_2$ **(Average value)** = 0.9127± 0.4070

Table15:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$Log(\frac{n}{1-n})$	$LogK_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4210	2.2190
8.72	5.35	6.37	6.40	0.03	0.4286	2.42	-0.1249	2.2951
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.96	0.3010	2.2610
9.51	5.55	6.66	6.70	0.04	0.7720	1.67	0.5297	2.1997

$LogK_1$ (Average value) = 2.2108± 0.0825

Table 16:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$Log(\frac{n-1}{2-n})$	$Log K_2$
9.73	5.55	6.78	6.83	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.95	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.09		
10.49	5.70	7.10	7.16	0.06	3.1429	0.89		

$LogK_2$ **(Average value)** = 1.5453± 0.3450

Table 17:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$Log(\frac{n}{n-1})$	$Log K_1$
8.50	5.30	5.81	5.86	0.05	0.3717	2.88	-0.2280	2.6520
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.06	0.06	0.4853	2.38	-0.0255	2.3545
9.22	5.45	6.10	6.16	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430
9.73	5.55	6.33	6.41	0.08	0.8000	1.69	0.6020	2.2920

$LogK_1$ **(Average value)** = 2.2516± 0.5380

Table 18:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$\mathrm{Log}(\frac{n-1}{2-n})$	Log K_2
10.00	5.60	6.47	6.57	0.10	1.1434	1.43		
10.23	5.65	6.62	6.72	0.10	1.3448	1.23	-0.2788	0.9512
10.49	5.70	6.80	6.90	0.10	1.7742	1.03	0.5351	1.5651

LogK_2 **(Average value)** = 1.2581± 0.4340

Table 19: Stepwise and overall Stability constants of thehydrolysed and unhydrolysed divalent metal (II) complexes

Chelates	**LogK₁**	**LogK₂**	**Logβ**
[Cu (Hydrolysed PSHA-1)$_2$]	2.4788	1.4280	3.9068
[Pb (Hydrolysed PSHA-1)$_2$]	2.5832	1.1963	3.7795
[Cd (Hydrolysed PSHA-1)$_2$]	2.2108	1.5453	3.7561
[Mg (Hydrolysed PSHA-1)$_2$]	2.1382	1.5453	3.6835
[Cu (Unhydrolysed PSHA-1)$_2$]	2.3059	1.2209	3.5268
[Pb (Unhydrolysed PSHA-1)$_2$]	2.2364	1.2239	3.4603
[Cd (Unhydrolysed PSHA-1)$_2$]	2.2516	1.2581	3.5097
[Mg (Unydrolysed PSHA-1)$_2$]	2.1568	0.9127	3.0695

The results obtained (Table19) shows the stepwise and overall stability constants to be not high indicating low stability of the complexes, because the solubility of most metal ions in the basic pH range is minimal due to metal hydroxide precipitation (Karimi, 2017). In general, the stepwise stability constants (K_1 and K_2) follow the order $K_1 > K_2$ for the copper, lead, magnesium and cadmium complexes respectively. The steady decrease of the values with increasing number of ligands is in agreement with the prediction made by researchers (Na'aliya, 2013). The decrease could be attributed to the fact that as the number of the ligands (Humate ions) that enters the coordination zone increases the aqua molecules available for replacement by the ligands become less. Thus, the metal ions become less electron loving with progressive intake of the ligand and this results in the decrease in the values of the constants (Na'aliya, 2013). Also the stability of the complexes is influenced by the size and number of the chelate rings(Mackay and Mackay,2002).All the complexes form rings in their structure as humate, a bidentate ligand, bond the metal ions in the ratio 1:2 (Boguta and Sokolowska, 2016) forming chelate rings. The values of the overall stability constants (logβ) obtained for humate complexes are not high indicating low stability as the values are not high. LogK values for copper-humates (Table 3 to 6) obtained in this study are lower than those reported for the complexes of humic acids (Pandey *et al*., 2015; Dinu, 2013; Kaschl *et al*., 2010 and Gilbeto and Jorg, 2001). The values of LogK(Table 7 to 10) forlead-humates are lower than those reported for the lead in the literature (Dinu, 2013; Gilbeto and Jorg 2001). Log K values(Table 11 to 14) for magnesium-humates obtained in this study are close to those reported by (Pandey *et al*., 2015). Log K values of cadmium-humates (Table 15 to 18) obtained in this work near to the one reported by (Dinu, 2013 and Pandey *et al*., 2015).The difference between the reported values and the values obtained in this study might be probably as a result of acid hydrolysis of humic acid. The values of the overall stability constants (log β) of the copper humates complexes presented in Table 19 is high than that of other metal humate complexes, show relatively high stability of Cu-HA complexes, show the following order of stability: Cu >Pb> Cd > Mg; which are in close agreement to the findings of (Dinu, 2013 and Pandey *et al*., 2015).The high stability of Cu-humate chelate could be attributed to the existence of coordinate covalent bond between the complexing agents and the Cu^{2+} ions. Since, Cu^{2+} being a metal of the transitional series with $3d^9$ electronic configurations can accept the electrons from the complexing agents. Similarly,the low stabilities of Pb,Cd and Mg -complexes could be explained by that Pb^{2+} with $6s^2$, Cd^{2+} with $4d^{10}$ and Mg^{2+} with $2p^6$ their electronic configuration has a completely filled d,p and s orbitals. Moreover, the stabilities of metal ions with hydrolysed humic acid from peat soil were higher than those with unhydrolysed humic acid from peat soil; which is ascribed to the high content of acidity in hydrolysed humic acid than unhydrolysed humic acid.

CONCLUSION

The values of logK for Cu(II) hydrolysed humic acid complex was higher followed by Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes as compared with metal(II) unhydrolysed humic acid complexes . This indicates acid hydrolysis of humic acid can enhance the complexation behavior of humic acid with metal (II) ions. However, the higher values of logβ for Cu(II), Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes indicates more stable stepwise complexes formed as compared with Cu(II), Pb(II), Cd(II) and Mg(II) unhydrolysed humic acid complexes.

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STABILITY CONSTANTS OF COMPLEXES OF METAL IONS WITH PEATSOIL HUMIC ACIDS UNDER NON-ACID-CONDITIONS

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ABSTRACT

Stability constants of complexes of four divalent metal ions viz. Cu^{2+}, Pb^{2+},Mg^{2+} and Cd^{2+} with humic acids (HA) were determined by potentiometric titration of humic acids with the corresponding salt of the divalent metals in aqueous media under non-acid-condition. The log K (logarithm of the stability constant) ranged from 1.0942 to 2.7471 for metal-humic acid complexes were determined using point-wise computational method. The order of stability constants were obtained as follows: Cu >Pb> Cd > Mg for metal -HA complexes respectively, indicating a higher degree of complexation with Cu metal ion.

Keywords: stability constant, humic acid, potentiometric titration, divalent metals, acid hydrolysis.

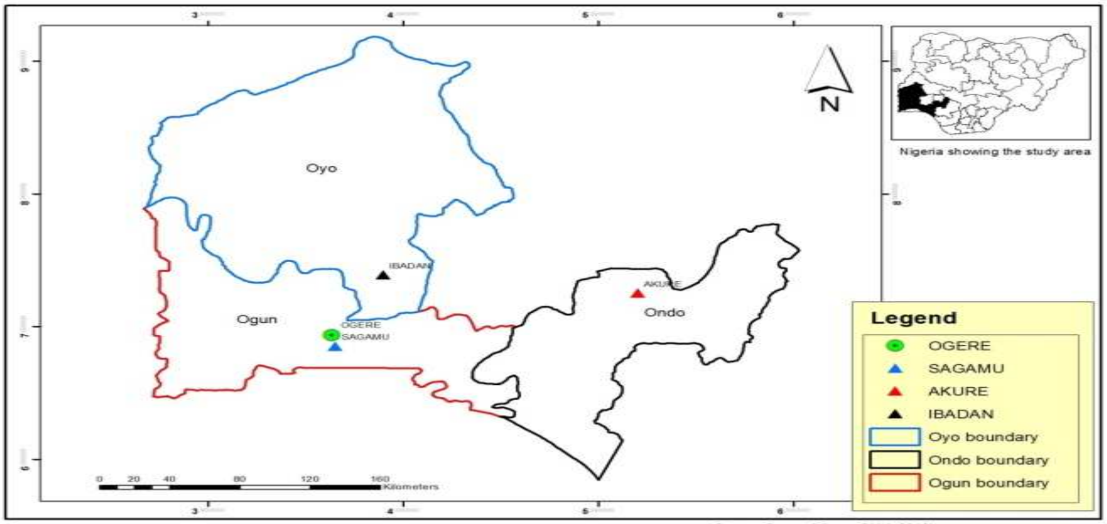
NTRODUCTION

The stability constant of a complex is the numerical expression of its stability and provides a quantitative measure of affinity of the metal ion to the complexing agent. An understanding of the relative stability of metal-complexes helps in predicting the behavior of metal ions in the soil (Ram and Raman, 1982). Extensive researches has been done to determine the stability constants of the complexes formed between humic acid (HA) with a number of metal ions. Ashok *et al*., (2000) reported that humic acid with hydroxyl, phenoxyl and carboxyl reactive groups can form coordination compound with metal ions at pH 3.5. The stability constants(Log K) for different metal-humic acid complexes indicated the following order of the stabilities of complexes formed between humic acid and metal ion, Cu >Fe >Pb> Ni > Co > Ca > Cd > Zn >Mn> Mg. Andelkovic *et al*., (2010) investigated the binding of Cd(II) to soil humic acid at pH 6.5 and in 0.1M KNO_3 ionic medium. The stability constant for binding indicating greater stability in the case when carboxyl groups are involved in complexation reaction. Kostic *et al*.,(2012) investigated the complexation of humic acid with certain heavy metal ions (Co(II), Ni(II),Cu(II), Zn(II), and Pb(II). The experiment was performed at 25°C, at pH 4.0 and ionic strength of 0.01M. Stability constant of complex between Pb(II) ions and humic acid is greater than stability constants of other investigated metal-humate complexes. Bogata and Sokolowska (2016) analyses the interaction between humic acids from different soils and Zn (II) ions at wide concentration ranges and at pH 5. Studies have showed significant impact of Zn concentration, pH and some properties of humic acids with zinc.But all of these studies were limited to acidic pH range. Therefore, the present study was carried out to determine and compare the stability constants of complexes of metal ions with hydrolysed peat soil humic acid and unhydrolysed peat soil humic under non-acid conditions.

MATERIALS AND METHODS

Analytical grade chemicals used includes hydrochloric acid (HCl), nitric acid (HNO_3), sodium hydroxide (NaOH), lead nitrate $Pb(NO_3)_2$, copper nitrate $Cu(NO_3)_2.3H_2O$, cadmium nitrate $Cd(NO_3)_2.4H_2O$, magnesium nitrate $Mg(NO_3)_2.6H_2O$, potassium nitrate (KNO_3), calcium chloride ($CaCl_2$), (sigma-Aldrich). Dowex 50WX8, (20-50 mesh) from Fluka.

Area of study



Source: Dept. of Geog. BUK (2016)

Figure 1: Map showing the sampling point at Sagamu Town, Ogun State.

Description of Sampling Area

Sagamu has geographical coordinates between 6°50′ north; 3° 38′ east is located in south western region of Nigeria. The region has tropical wet and dry climate with a lengthy wet season and relatively constant temperatures throughout the course of the year. Wet season runs from March to October, November to December forms the region dry season. The vegetation type of the region is savannah which is really grassland with small bushes and occasional big trees. Grassland soils have substantially higher organic matter content than forest soils (Novackova, 2011).

Sample Collection

The Peatsoil samples were collected from four different sampling points (0-10cm depth) in Sagamu into polyethylene bag with plastic spoons. Samples were taken to the laboratory, extraneous materials were removed; the samples were air-dried, crushed and ground to a fine powder in a mortar passed through a 0.20mm sieve. The samples were kept for analysis.

Isolation and purification of humic acid from peat soil sample

Peatsoil sample (100g) was mixed with 1000 cm^3 of 0.1M NaOH solution, shaken for 3hours and left to stand overnight. Dark-coloured supernatant was obtained and decanted from solid residue. The dark-coloured supernatant was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 6 hours. Yellowish brown supernatant and dark-brown precipitate were obtained. The yellowish brown supernatant was decanted followed by centrifuge and discarded. The dark-brown precipitate was mixed with $500cm^3$of 0.1M NaOH solution followed by passing through dowex resin. The dark-brown solution was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 3 hours. The dark-brown precipitate was washed several times with deionized water. The supernatant was treated with $AgNO_3$ solution until no white precipitate observed. The humic acid was transferred to weighed crucible and dried at 60°C in an oven for 12 hours. The humic acid was cooled and dried in the desiccator, weighed and recorded. The obtained humic acid was dried again at 60°C for additional 6 hours cooled and dried in the desiccator, weighed and recorded constant weight was obtained (Baruah *et al*., 2015).

FT-IR analysis

FT-IR spectra of humic acid sample was analysed using Carry 630 FT-IR Agilent Technologies.

Unhydrolysed compost humic acid

The unhydrolysed humic acid was obtained after isolation and purification of compost humic acid and kept for investigation.

Acid hydrolysis of Peatsoil acid

Peatsoil humic acid sample (1g) was refluxed for 12 hours at (160°C) with $50cm^3$ of 6M HCl. The mixture was allowed to cool, decanted, and centrifuged after hydrolysis. The insoluble residues were washed with distilled water via centrifugation several times, and the supernatant was treated with $AgNO_3$ solution until no white precipitate was observed. The residue was thoroughly dried over $CaCl_2$ in a desiccator at room temperature (Chefetz *et al*., 2002). Finally, the obtained hydrolysed humic acid was kept for investigation.

Potentiometric Titrations

Potentiometric measurements were carried out using a pH-meter Jenway (model 3510) with combine electrode, the sensitivity of the pH - meter is 0.01 units. The pH meter was switched on half an hour before starting the titration for initial warm up of the instrument. The instrument was calibrated with an aqueous standard buffer solution of pH 4.00 and 10.0 (borate buffer) prepared from a "Qualigens" buffer tablets.

The following sets of solutions were prepared in a 250cm^3 volumetric flask separately for pH metric titrations.

(i) 5 cm^3 0.1 M HCl + 40 cm^3 deionized water

(ii) 5 cm^3 0.1 M HCl + 39 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid

(iii) 5 cm^3 0.1 M HCl + 37 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid + 2 cm^3 0.01 M Cu(II)

The solutions were titrated against standardized 0.110MNaOH separately. The total volume of each mixture was adjusted to 50 cm^3 and the ionic strength of the solutions was maintained constant at by adding appropriate amount of stock solution of 1M KNO$_3$ (Gamal, 2015; Omar and Ali, 2015). A magnetic stirrer was used to achieve thorough mixing of the interacting solutions at 550 rpm. The same set of experimental conditions was applied for potentiometric titration of remaining samples.

Evaluation of pKa of Hydrolysed peat soil Humic Acids

The proton-ligand formation number n$_{\mathbf{A}}$ were calculated by Irving and Rossotti expression (Omar and Ali, 2015).

$$nA = Y- \frac{(V2-V1)(No-Eo)}{(Vo+V1)TcL} \text{ ....1}$$

Where: Y is number of dissociable proton, (V$_2$-V$_1$) is the measure of displacement of the ligand curve relative to acid curve, N^o and E^o are the resultant concentration of alkali solution, free acid solution, T$_{cL}{}^o$ is the total ligand concentration, V^o is the total volume of titration solution,V$_1$ is the volume of alkali added to acid solution,V$_2$ is the volume of alkali added to acid solution + ligand solution, acid dissociation constants (pKa - values) of ligand were calculated by algebraic method point wise calculation (Tables 1). The dissociation constants (pKa) were calculated according to the following relation:

$$pKa = pH + \log(\frac{nA}{1-nA}) \text{ ....2}$$

Where: pKa is the acid dissociation constant, n$_A$is the Proton-ligand formation number and pH is the pH-values (Omar and Ali, 2015).

Determination of metal-ligand stability constants (log K) of complexes

The potentiometric measurement for the determination of stability constant of a complex in solution is based on the fact that the redox potential of the couple $\frac{M^{+(m-n)}}{M^{+m}}$ is shifted significantly on complexation of the metal ion with the ligand. This method involves change in hydrogen ion concentration [H$^+$] due to the displacement or association of one or more protons taking place during complexation reaction. This change can be found out by titrating the solutions containing free acid, acid with ligand, and acid with ligand and metal ion, individually against a standard alkali solution at a constant ionic strength or temperature. Either ionic strength or temperature may be varied for different sets of solutions. In all the cases, the change in the pH of the solution is measured after each addition of a known amount of alkali to the reaction cell which contains the reaction mixture. The titration curves are then drawn by plotting the measured pH values against the corresponding volume of alkali added and the stability constants of the complexes are determined from the titration curves by employing pH-metric titration technique given by (Irving and Rossoti).

Metal-ligand stability constants (Log K) were determined by using the following relations:

$$\bar{n} = \frac{(V_3 - V_2)(E^0 + N^0)}{(V^0 + V_2)\bar{n}_A T_m^0} \text{ ....3}$$

and

$$PL = \log_{10}\{\frac{1+\beta_n^H \frac{1}{[anti\ \log pH]^n}}{T_L^0 - \bar{n}T_m^0} X \frac{(V^0 + V_3)}{V^0}\} \text{ ....4}$$

Where $T_{L,}$ T^{o}, E°, and V^{o}havethe same significance as in equation (1) above, T_m denotes the total concentration of metal present in solution, V_3 is the volume of metal ions present in solution and β^H is the overall proton ligand stability constant. The metal-ligand stability constants (log K) were determined by employing point wise computational Method (eq. 5 and 6).

$$\text{LogK}_1 = \log \left(\frac{n}{1-n}\right) + \text{pL} \qquad ....5$$

$$\text{LogK}_2 = \log \left(\frac{1-n}{2-n}\right) + \text{pL}.......................6$$

Where: Log K is the metal-ligand stability constant, pL is the Free ligand exponent function, **n** is the Average number of ligand attached with metal ion (Janrao*et al*., 2014).The results obtained were analyzed by an ORIGIN 2016 program using titration data and then the proton-ligand stability constants (pKa) and Metal-ligand stability constant (LogK) calculated (Omar and Ali, 2015).

RESULTS AND DISCUSSION

Fourier transformed infrared (FT-IR) spectra of isolated humic acid from peat soils Figure 2 had distinct clear absorption bands indicating the presence of major humic acid structural elemental groups such as H bonded OH ($3680cm^{-1}$ peak), C=O of carbonyl ($1721cm^{-1}$ peak), functional groups of aliphatic components CH_2 ($2918cm^{-1}$ peak) and C-O stretching of polysaccharide ($1168cm^{-1}$ peak). The positions of the absorption bands of the spectra fell within typical major absorption bands of humic acid which is at frequencies 3680, 2918, 1721, 1168 cm^{-1}. The first peak centred in the vicinity of 3680 cm^{-1} region is attributed to phenol OH group bounded by intermolecular H bonds. The $2918cm^{-1}$ band usually has absorption maximum at 2918 cm^{-1} which is due to C–H stretching of alkane group (CH_2). The next major absorption band is 1721 cm^{-1}. This band has been commonly ascribed to C=O stretching of mainly carboxyl group (COOH) with trace amount of ketones. The last peak was observed at 1168 cm^{-1} due to C–O stretching of polysaccharides and this peak appeared also in the spectra of humic acid from peat soil. The FTIR spectra of the isolated humic acid contained all major characteristic absorption peaks of humic acid. These absorption peaks indicated the presence of the major structural elements of humic acid namely H bonded OH, C=C of aromatic ring, C=O of carbonyl group (both carboxyl and ketonic), CH_2 group. This strongly supports the presence of humic acid.

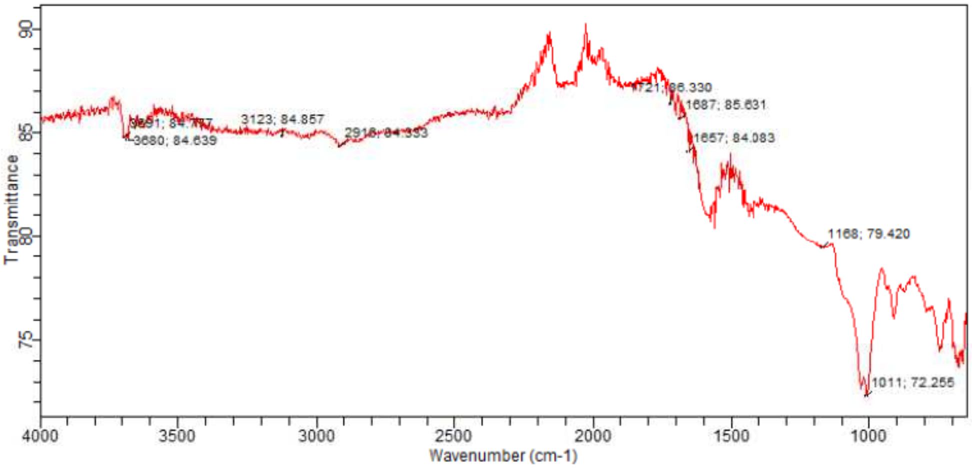


Fig. 2 : FT-IR spectraof peatsoilhumic acid (PSHA)

Evaluation of acid dissociation constant (pka) of acid hydrolysed peat soil humicacid at phenolic group

The value of the dissociation constant of the peat soil humic acid (PSHA) that underwent acidhydrolysis studied was found to be 8.9299 as shown Table 1, which is lower than the literaturevalues reported by Almeida and Szpoganics, (2015), Borges *et al*., (2005); Badr *et al*., (2012)and Fernandes *et al*,.(2009) of 9.73, 9.47 and 10.30. The difference between the obtained valuesand the reported values in this study might be probably as a result of acid hydrolysis of humicacid.

Table 1: PKa of (Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	V$_2$-V$_1$	nA	log($\frac{nA}{1-nA}$)	pKa
8.50	5.30	6.29	0.99	0.3594	-0.2510	8.2490
8.72	5.35	6.37	1.02	0.3400	-0.2880	8.4320
9.00	5.40	6.46	1.06	0.3141	-0.3391	8.6609
9.22	5.45	6.55	1.10	0.2882	-0.3927	8.8273
9.51	5.50	6.66	1.16	0.2494	-0.4786	9.0314
9.73	5.55	6.78	1.23	0.2041	-0.5910	9.1390
10.00	5.60	6.90	1.30	0.1589	-0.7238	9.2762
10.23	5.65	7.05	1.40	0.0941	-0.9835	9.2465
10.49	5.70	7.10	1.40	0.0941	-0.9835	9.5065

Average pKa = 8.9299 ± 0.4186

Table 2: PKa of (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	V$_2$-V$_1$	nA	Log($\frac{nA}{1-n}$)	pKa
8.50	5.30	5.81	0.51	0.6619	0.2919	8.7919
8.72	5.35	5.90	0.55	0.6357	0.2418	8.9618
9.00	5.40	6.00	0.60	0.6029	0.1813	9.1813
9.22	5.45	6.10	0.65	0.5701	0.1226	9.3426
9.51	5.50	6.20	0.70	0.5376	0.0654	9.5754
9.73	5.55	6.33	0.78	0.4851	-0.0259	9.7041
10.00	5.60	6.47	0.87	0.4262	-0.1291	9.8709
10.23	5.65	6.62	0.99	0.3609	-0.2481	9.9819
10.49	5.70	6.80	1.10	0.2759	-0.4690	10.0210

Average pKa = 9.4923± 0.4410

Metal-ligand stability constant (Log K)

The stabilityconstants require the accurate values of proton-ligand stability constants (Anil and Maroti, 2008). Metal titration curves crossed over ligand titration curve indicated the formation of complex upon proton release (Santosh, *et al.*, 2011). If the values of n- are within range 0.2-0.8 and 1.2-18 this indicates the formation of 1:1 and 1:2 complexes (Sayyed and Mazahar, 2012).

The metal (II)-humate stepwise stability constants (log k) at phenolic group (Tables 3-18)

Table 3: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	log($\frac{n}{1-n}$)	LogK$_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

LogK$_1$ (Average value) = 2.4788± 0.2203

Table 4: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	Log($\frac{n-1}{2-n}$)	LogK$_2$
9.51	5.50	6.66	6.73	0.07	1.3509	1.70	-0.2671	1.4329
9.73	5.55	6.78	6.85	0.07	1.6383	1.51	0.2467	1.7567
10.00	5.60	6.90	6.98	0.08	2.1783	1.31	-0.2158	1.0942
10.23	5.65	7.05	7.13	0.08	4.1904	1.27		
10.49	5.70	7.10	7.19	0.09	4.6920			

LogK$_2$(Average value) = 1.4280 ± 0.3312

Table 5:Point-wise method,Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	Log($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430

LogK_1 **(Average value)** = 2.3059± 0.6153

Table 6:Point-wise method, Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
9.73	5.55	6.33	6.42	0.09	0.9000	1.69		
10.00	5.60	6.47	6.58	0.11	1.2578	1.44	-0.4592	0.9808
10.23	5.65	6.62	6.84	0.12	1.6137	1.26	-0.2010	1.4610
10.49	5.70	6.80	6.92	0.12	2.1052	1.03		

LogK_2 **(Average value)** = 1.2209± 0.3398

Table 7:Point-wise method,Pb (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n}{1-n}$)	LogK_1
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.60	0.05	0.8333	1.96	0.6989	2.6589

LogK_1 (Average value) = 2.5832 ±0.1614

Table 8:Point-wise method,Pb-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n-1}{2-n}$)	logK_2
9.51	5.50	6.66	6.71	0.05	0.9650	1.67	-0.0237	1.1963
9.73	5.55	6.78	6.83	0.05	1.1702	1.44		
10.00	5.60	6.90	6.90	0.05	1.4864	1.22		
10.23	5.65	7.05	7.10	0.05	2.0190	1.09		
10.49	5.70	7.10	7.17	0.07	3.6492	1.00		

LogK_2(Average value) = 1.1963

Table 9:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log ($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.5477	2.3123
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	0.0272	2.2072
9.51	5.50	6.20	6.26	0.07	0.6417	1.89	0.2530	2.1430
9.73	5.55	6.40	6.40	0.07	0.7000	1.67	0.3680	2.0380

LogK_1 **(Average value)** = 2.2364 ± 0.1602

Table 10:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
10.00	5.60	6.47	6.55	0.08	1.9503	1.41		
10.23	5.65	6.62	6.72	0.11	1.4792	1.26	-0.0361	1.2239

LogK_2 **(Average value)** = 1.2239

Table 11:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n}{n-1}$)	LogK_1
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4290	2.2110
8.72	5.35	6.37	6.39	0.02	0.2858	2.42	-0.3978	2.0222
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

LogK_1 (Average value)=2.1382**±**0.1046

Table 12:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n-1}{2-n}$)	$LogK_2$
9.51	5.55	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.84	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.93	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.10		
10.49	5.70	7.10	7.18	0.07	3.6492	0.83		

$LogK_2$(Average value) = 1.5453 **±** 0.3450

Table 13:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.3477	2.3123
9.00	5.40	6.00	6.04	0.04	0.3236	2.38	-0.3202	2.0598
9.22	5.45	6.10	6.15	0.05	0.4297	2.17	-0.1230	2.0470
9.51	5.50	6.20	6.26	0.06	0.5500	1.89	0.0871	1.9771
9.73	5.55	6.33	6.40	0.07	0.7000	1.67	0.3680	2.0380

$LogK_1$ **(Average value)** = 2.1568 ± 0.2069

Table 14:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
10.00	5.60	6.47	6.55	0.08	0.9148	1.41		
10.23	5.65	6.62	6.71	0.09	1.2102	1.20	-0.5749	0.6251
10.49	5.70	6.80	6.92	0.09	1.5968	1.03	0.1703	1.2003

$LogK_2$ **(Average value)** = 0.9127± 0.4070

Table15:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	Log($\frac{n}{1-n}$)	$LogK_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4210	2.2190
8.72	5.35	6.37	6.40	0.03	0.4286	2.42	-0.1249	2.2951
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.96	0.3010	2.2610
9.51	5.55	6.66	6.70	0.04	0.7720	1.67	0.5297	2.1997

$LogK_1$ (Average value) = 2.2108± 0.0825

Table 16:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
9.73	5.55	6.78	6.83	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.95	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.09		
10.49	5.70	7.10	7.16	0.06	3.1429	0.89		

$LogK_2$ **(Average value)** = 1.5453± 0.3450

Table 17:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.86	0.05	0.3717	2.88	-0.2280	2.6520
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.06	0.06	0.4853	2.38	-0.0255	2.3545
9.22	5.45	6.10	6.16	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430
9.73	5.55	6.33	6.41	0.08	0.8000	1.69	0.6020	2.2920

$LogK_1$ **(Average value)** = 2.2516± 0.5380

Table 18:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$\text{Log}(\frac{n-1}{2-n})$	Log K_2
10.00	5.60	6.47	6.57	0.10	1.1434	1.43		
10.23	5.65	6.62	6.72	0.10	1.3448	1.23	-0.2788	0.9512
10.49	5.70	6.80	6.90	0.10	1.7742	1.03	0.5351	1.5651

LogK_2 **(Average value)** = 1.2581± 0.4340

Table 19: Stepwise and overall Stability constants of thehydrolysed and unhydrolysed divalent metal (II) complexes

Chelates	**LogK_1**	**LogK_2**	**Logβ**
[Cu (Hydrolysed PSHA-1)$_2$]	2.4788	1.4280	3.9068
[Pb (Hydrolysed PSHA-1)$_2$]	2.5832	1.1963	3.7795
[Cd (Hydrolysed PSHA-1)$_2$]	2.2108	1.5453	3.7561
[Mg (Hydrolysed PSHA-1)$_2$]	2.1382	1.5453	3.6835
[Cu (Unhydrolysed PSHA-1)$_2$]	2.3059	1.2209	3.5268
[Pb (Unhydrolysed PSHA-1)$_2$]	2.2364	1.2239	3.4603
[Cd (Unhydrolysed PSHA-1)$_2$]	2.2516	1.2581	3.5097
[Mg (Unydrolysed PSHA-1)$_2$]	2.1568	0.9127	3.0695

The results obtained (Table19) shows the stepwise and overall stability constants to be not high indicating low stability of the complexes, because the solubility of most metal ions in the basic pH range is minimal due to metal hydroxide precipitation (Karimi, 2017). In general, the stepwise stability constants (K_1 and K_2) follow the order $K_1 > K_2$ for the copper, lead, magnesium and cadmium complexes respectively. The steady decrease of the values with increasing number of ligands is in agreement with the prediction made by researchers (Na'aliya, 2013). The decrease could be attributed to the fact that as the number of the ligands (Humate ions) that enters the coordination zone increases the aqua molecules available for replacement by the ligands become less. Thus, the metal ions become less electron loving with progressive intake of the ligand and this results in the decrease in the values of the constants (Na'aliya, 2013). Also the stability of the complexes is influenced by the size and number of the chelate rings(Mackay and Mackay,2002).All the complexes form rings in their structure as humate, a bidentate ligand, bond the metal ions in the ratio 1:2 (Boguta and Sokolowska, 2016) forming chelate rings. The values of the overall stability constants (logβ) obtained for humate complexes are not high indicating low stability as the values are not high. LogK values for copper-humates (Table 3 to 6) obtained in this study are lower than those reported for the complexes of humic acids (Pandey *et al.*, 2015; Dinu, 2013; Kaschl *et al.*, 2010 and Gilbeto and Jorg, 2001). The values of LogK(Table 7 to 10) forlead-humates are lower than those reported for the lead in the literature (Dinu, 2013; Gilbeto and Jorg 2001). Log K values(Table 11 to 14) for magnesium-humates obtained in this study are close to those reported by (Pandey *et al.*, 2015). Log K values of cadmium-humates (Table 15 to 18) obtained in this work near to the one reported by (Dinu, 2013 and Pandey *et al.*, 2015).The difference between the reported values and the values obtained in this study might be probably as a result of acid hydrolysis of humic acid. The values of the overall stability constants (log β) of the copper humates complexes presented in Table 19 is high than that of other metal humate complexes, show relatively high stability of Cu-HA complexes, show the following order of stability: Cu >Pb> Cd > Mg; which are in close agreement to the findings of (Dinu, 2013 and Pandey *et al.*, 2015).The high stability of Cu-humate chelate could be attributed to the existence of coordinate covalent bond between the complexing agents and the Cu^{2+} ions. Since, Cu^{2+} being a metal of the transitional series with $3d^9$ electronic configurations can accept the electrons from the complexing agents. Similarly,the low stabilities of Pb,Cd and Mg -complexes could be explained by that Pb^{2+} with $6s^2$, Cd^{2+} with $4d^{10}$ and Mg^{2+} with $2p^6$ their electronic configuration has a completely filled d,p and s orbitals. Moreover, the stabilities of metal ions with hydrolysed humic acid from peat soil were higher than those with unhydrolysed humic acid from peat soil; which is ascribed to the high content of acidity in hydrolysed humic acid than unhydrolysed humic acid.

CONCLUSION

The values of logK for Cu(II) hydrolysed humic acid complex was higher followed by Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes as compared with metal(II) unhydrolysed humic acid complexes . This indicates acid hydrolysis of humic acid can enhance the complexation behavior of humic acid with metal (II) ions. However, the higher values of logβ for Cu(II), Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes indicates more stable stepwise complexes formed as compared with Cu(II), Pb(II), Cd(II) and Mg(II) unhydrolysed humic acid complexes.

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STABILITY CONSTANTS OF COMPLEXES OF METAL IONS WITH PEATSOIL HUMIC ACIDS UNDER NON-ACID-CONDITIONS

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ABSTRACT

Stability constants of complexes of four divalent metal ions viz. Cu^{2+}, Pb^{2+},Mg^{2+} and Cd^{2+} with humic acids (HA) were determined by potentiometric titration of humic acids with the corresponding salt of the divalent metals in aqueous media under non-acid-condition. The log K (logarithm of the stability constant) ranged from 1.0942 to 2.7471 for metal-humic acid complexes were determined using point-wise computational method. The order of stability constants were obtained as follows: Cu >Pb> Cd > Mg for metal -HA complexes respectively, indicating a higher degree of complexation with Cu metal ion.

Keywords: stability constant, humic acid, potentiometric titration, divalent metals, acid hydrolysis.

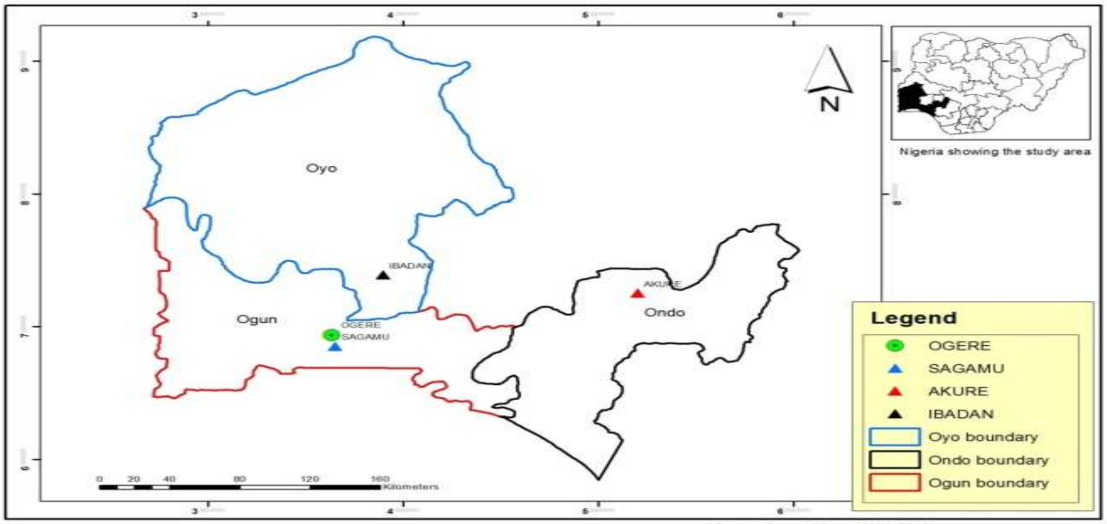
NTRODUCTION

The stability constant of a complex is the numerical expression of its stability and provides a quantitative measure of affinity of the metal ion to the complexing agent. An understanding of the relative stability of metal-complexes helps in predicting the behavior of metal ions in the soil (Ram and Raman, 1982). Extensive researches has been done to determine the stability constants of the complexes formed between humic acid (HA) with a number of metal ions. Ashok *et al*., (2000) reported that humic acid with hydroxyl, phenoxyl and carboxyl reactive groups can form coordination compound with metal ions at pH 3.5. The stability constants(Log K) for different metal-humic acid complexes indicated the following order of the stabilities of complexes formed between humic acid and metal ion, Cu >Fe >Pb> Ni > Co > Ca > Cd > Zn >Mn> Mg. Andelkovic *et al*., (2010) investigated the binding of Cd(II) to soil humic acid at pH 6.5 and in 0.1M KNO_3 ionic medium. The stability constant for binding indicating greater stability in the case when carboxyl groups are involved in complexation reaction. Kostic *et al*.,(2012) investigated the complexation of humic acid with certain heavy metal ions (Co(II), Ni(II),Cu(II), Zn(II), and Pb(II). The experiment was performed at 25°C, at pH 4.0 and ionic strength of 0.01M. Stability constant of complex between Pb(II) ions and humic acid is greater than stability constants of other investigated metal-humate complexes. Bogata and Sokolowska (2016) analyses the interaction between humic acids from different soils and Zn (II) ions at wide concentration ranges and at pH 5. Studies have showed significant impact of Zn concentration, pH and some properties of humic acids with zinc.But all of these studies were limited to acidic pH range. Therefore, the present study was carried out to determine and compare the stability constants of complexes of metal ions with hydrolysed peat soil humic acid and unhydrolysed peat soil humic under non-acid conditions.

MATERIALS AND METHODS

Analytical grade chemicals used includes hydrochloric acid (HCl), nitric acid (HNO_3), sodium hydroxide (NaOH), lead nitrate $Pb(NO_3)_2$, copper nitrate $Cu(NO_3)_2.3H_2O$, cadmium nitrate $Cd(NO_3)_2.4H_2O$, magnesium nitrate $Mg(NO_3)_2.6H_2O$, potassium nitrate (KNO_3), calcium chloride ($CaCl_2$), (sigma-Aldrich). Dowex 50WX8, (20-50 mesh) from Fluka.

Area of study



Source: Dept. of Geog. BUK (2016)

Figure 1: Map showing the sampling point at Sagamu Town, Ogun State.

Description of Sampling Area

Sagamu has geographical coordinates between 6°50′ north; 3° 38′ east is located in south western region of Nigeria. The region has tropical wet and dry climate with a lengthy wet season and relatively constant temperatures throughout the course of the year. Wet season runs from March to October, November to December forms the region dry season. The vegetation type of the region is savannah which is really grassland with small bushes and occasional big trees. Grassland soils have substantially higher organic matter content than forest soils (Novackova, 2011).

Sample Collection

The Peatsoil samples were collected from four different sampling points (0-10cm depth) in Sagamu into polyethylene bag with plastic spoons. Samples were taken to the laboratory, extraneous materials were removed; the samples were air-dried, crushed and ground to a fine powder in a mortar passed through a 0.20mm sieve. The samples were kept for analysis.

Isolation and purification of humic acid from peat soil sample

Peatsoil sample (100g) was mixed with 1000 cm^3 of 0.1M NaOH solution, shaken for 3hours and left to stand overnight. Dark-coloured supernatant was obtained and decanted from solid residue. The dark-coloured supernatant was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 6 hours. Yellowish brown supernatant and dark-brown precipitate were obtained. The yellowish brown supernatant was decanted followed by centrifuge and discarded. The dark-brown precipitate was mixed with $500cm^3$of 0.1M NaOH solution followed by passing through dowex resin. The dark-brown solution was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 3 hours. The dark-brown precipitate was washed several times with deionized water. The supernatant was treated with $AgNO_3$ solution until no white precipitate observed. The humic acid was transferred to weighed crucible and dried at 60°C in an oven for 12 hours. The humic acid was cooled and dried in the desiccator, weighed and recorded. The obtained humic acid was dried again at 60°C for additional 6 hours cooled and dried in the desiccator, weighed and recorded constant weight was obtained (Baruah *et al*., 2015).

FT-IR analysis

FT-IR spectra of humic acid sample was analysed using Carry 630 FT-IR Agilent Technologies.

Unhydrolysed compost humic acid

The unhydrolysed humic acid was obtained after isolation and purification of compost humic acid and kept for investigation.

Acid hydrolysis of Peatsoil acid

Peatsoil humic acid sample (1g) was refluxed for 12 hours at (160°C) with $50cm^3$ of 6M HCl. The mixture was allowed to cool, decanted, and centrifuged after hydrolysis. The insoluble residues were washed with distilled water via centrifugation several times, and the supernatant was treated with $AgNO_3$ solution until no white precipitate was observed. The residue was thoroughly dried over $CaCl_2$ in a desiccator at room temperature (Chefetz *et al*., 2002). Finally, the obtained hydrolysed humic acid was kept for investigation.

Potentiometric Titrations

Potentiometric measurements were carried out using a pH-meter Jenway (model 3510) with combine electrode, the sensitivity of the pH - meter is 0.01 units. The pH meter was switched on half an hour before starting the titration for initial warm up of the instrument. The instrument was calibrated with an aqueous standard buffer solution of pH 4.00 and 10.0 (borate buffer) prepared from a "Qualigens" buffer tablets.

The following sets of solutions were prepared in a 250cm^3 volumetric flask separately for pH metric titrations.

(i) 5 cm^3 0.1 M HCl + 40 cm^3 deionized water

(ii) 5 cm^3 0.1 M HCl + 39 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid

(iii) 5 cm^3 0.1 M HCl + 37 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid + 2 cm^3 0.01 M Cu(II)

The solutions were titrated against standardized 0.110MNaOH separately. The total volume of each mixture was adjusted to 50 cm^3 and the ionic strength of the solutions was maintained constant at by adding appropriate amount of stock solution of 1M KNO$_3$ (Gamal, 2015; Omar and Ali, 2015). A magnetic stirrer was used to achieve thorough mixing of the interacting solutions at 550 rpm. The same set of experimental conditions was applied for potentiometric titration of remaining samples.

Evaluation of pKa of Hydrolysed peat soil Humic Acids

The proton-ligand formation number n$_{\mathbf{A}}$ were calculated by Irving and Rossotti expression (Omar and Ali, 2015).

$$nA = Y - \frac{(V2-V1)(No-Eo)}{(Vo+V1)TcL} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 1$$

Where: Y is number of dissociable proton, (V$_2$-V$_1$) is the measure of displacement of the ligand curve relative to acid curve, N^o and E^o are the resultant concentration of alkali solution, free acid solution, T$_{cL}$^{o} is the total ligand concentration, V^o is the total volume of titration solution,V$_1$ is the volume of alkali added to acid solution,V$_2$ is the volume of alkali added to acid solution + ligand solution, acid dissociation constants (pKa - values) of ligand were calculated by algebraic method point wise calculation (Tables 1). The dissociation constants (pKa) were calculated according to the following relation:

$$pKa = pH + \log\left(\frac{nA}{1-nA}\right) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 2$$

Where: pKa is the acid dissociation constant, n$_A$is the Proton-ligand formation number and pH is the pH-values (Omar and Ali, 2015).

Determination of metal-ligand stability constants (log K) of complexes

The potentiometric measurement for the determination of stability constant of a complex in solution is based on the fact that the redox potential of the couple $\frac{M^{+(m-n)}}{M^{+m}}$ is shifted significantly on complexation of the metal ion with the ligand. This method involves change in hydrogen ion concentration [H$^+$] due to the displacement or association of one or more protons taking place during complexation reaction. This change can be found out by titrating the solutions containing free acid, acid with ligand, and acid with ligand and metal ion, individually against a standard alkali solution at a constant ionic strength or temperature. Either ionic strength or temperature may be varied for different sets of solutions. In all the cases, the change in the pH of the solution is measured after each addition of a known amount of alkali to the reaction cell which contains the reaction mixture. The titration curves are then drawn by plotting the measured pH values against the corresponding volume of alkali added and the stability constants of the complexes are determined from the titration curves by employing pH-metric titration technique given by (Irving and Rossoti).

Metal-ligand stability constants (Log K) were determined by using the following relations:

$$\bar{n} = \frac{(V_3 - V_2)(E^0 + N^0)}{(V^0 + V_2)\bar{n}_A T_m^0} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 3$$

and

$$PL = \log_{10}\left\{\frac{1 + \beta_n^H \dfrac{1}{[anti\ \log \mathrm{pH}]^n}}{T_L^0 - \bar{n} T_m^0} X \frac{(V^0 + V_3)}{V^0}\right\} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 4$$

Where $T_{L,}$ T^{o}, E°, and V^{o}havethe same significance as in equation (1) above, T_m denotes the total concentration of metal present in solution, V_3 is the volume of metal ions present in solution and β^H is the overall proton ligand stability constant. The metal-ligand stability constants (log K) were determined by employing point wise computational Method (eq. 5 and 6).

$$\mathrm{Log}K_1 = \log\left(\frac{n}{1-n}\right) + pL \qquad ....5$$

$$\mathrm{Log}K_2 = \log\left(\frac{1-n}{2-n}\right) + pL.......................6$$

Where: Log K is the metal-ligand stability constant, pL is the Free ligand exponent function, **n** is the Average number of ligand attached with metal ion (Janrao*et al*., 2014).The results obtained were analyzed by an ORIGIN 2016 program using titration data and then the proton-ligand stability constants (pKa) and Metal-ligand stability constant (LogK) calculated (Omar and Ali, 2015).

RESULTS AND DISCUSSION

Fourier transformed infrared (FT-IR) spectra of isolated humic acid from peat soils Figure 2 had distinct clear absorption bands indicating the presence of major humic acid structural elemental groups such as H bonded OH (3680cm^{-1} peak), C=O of carbonyl (1721cm^{-1} peak), functional groups of aliphatic components CH_2 (2918cm^{-1} peak) and C-O stretching of polysaccharide (1168cm^{-1} peak). The positions of the absorption bands of the spectra fell within typical major absorption bands of humic acid which is at frequencies 3680, 2918, 1721, 1168 cm^{-1}. The first peak centred in the vicinity of 3680 cm^{-1} region is attributed to phenol OH group bounded by intermolecular H bonds. The 2918cm^{-1} band usually has absorption maximum at 2918 cm^{-1} which is due to C–H stretching of alkane group (CH_2). The next major absorption band is 1721 cm^{-1}. This band has been commonly ascribed to C=O stretching of mainly carboxyl group (COOH) with trace amount of ketones. The last peak was observed at 1168 cm^{-1} due to C–O stretching of polysaccharides and this peak appeared also in the spectra of humic acid from peat soil. The FTIR spectra of the isolated humic acid contained all major characteristic absorption peaks of humic acid. These absorption peaks indicated the presence of the major structural elements of humic acid namely H bonded OH, C=C of aromatic ring, C=O of carbonyl group (both carboxyl and ketonic), CH_2 group. This strongly supports the presence of humic acid.

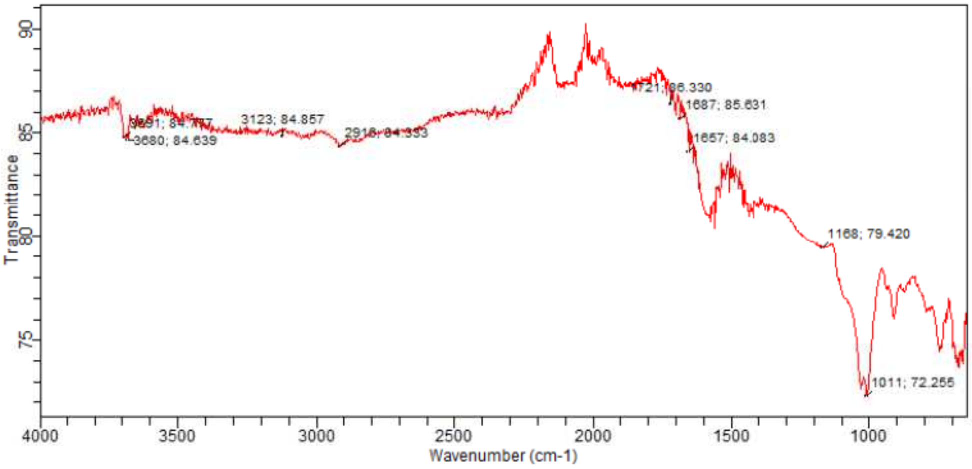


Fig. 2 : FT-IR spectraof peatsoilhumic acid (PSHA)

Evaluation of acid dissociation constant (pka) of acid hydrolysed peat soil humicacid at phenolic group

The value of the dissociation constant of the peat soil humic acid (PSHA) that underwent acidhydrolysis studied was found to be 8.9299 as shown Table 1, which is lower than the literaturevalues reported by Almeida and Szpoganics, (2015), Borges *et al*., (2005); Badr *et al*., (2012)and Fernandes *et al*,.(2009) of 9.73, 9.47 and 10.30. The difference between the obtained valuesand the reported values in this study might be probably as a result of acid hydrolysis of humicacid.

Table 1: PKa of (Hydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	$\log(\frac{nA}{1-nA})$	pKa
8.50	5.30	6.29	0.99	0.3594	-0.2510	8.2490
8.72	5.35	6.37	1.02	0.3400	-0.2880	8.4320
9.00	5.40	6.46	1.06	0.3141	-0.3391	8.6609
9.22	5.45	6.55	1.10	0.2882	-0.3927	8.8273
9.51	5.50	6.66	1.16	0.2494	-0.4786	9.0314
9.73	5.55	6.78	1.23	0.2041	-0.5910	9.1390
10.00	5.60	6.90	1.30	0.1589	-0.7238	9.2762
10.23	5.65	7.05	1.40	0.0941	-0.9835	9.2465
10.49	5.70	7.10	1.40	0.0941	-0.9835	9.5065

Average pKa = 8.9299 ± 0.4186

Table 2: PKa of (Unhydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	$\text{Log}(\frac{nA}{1-n})$	pKa
8.50	5.30	5.81	0.51	0.6619	0.2919	8.7919
8.72	5.35	5.90	0.55	0.6357	0.2418	8.9618
9.00	5.40	6.00	0.60	0.6029	0.1813	9.1813
9.22	5.45	6.10	0.65	0.5701	0.1226	9.3426
9.51	5.50	6.20	0.70	0.5376	0.0654	9.5754
9.73	5.55	6.33	0.78	0.4851	-0.0259	9.7041
10.00	5.60	6.47	0.87	0.4262	-0.1291	9.8709
10.23	5.65	6.62	0.99	0.3609	-0.2481	9.9819
10.49	5.70	6.80	1.10	0.2759	-0.4690	10.0210

Average pKa = 9.4923± 0.4410

Metal-ligand stability constant (Log K)

The stabilityconstants require the accurate values of proton-ligand stability constants (Anil and Maroti, 2008). Metal titration curves crossed over ligand titration curve indicated the formation of complex upon proton release (Santosh, *et al*., 2011). If the values of n- are within range 0.2-0.8 and 1.2-18 this indicates the formation of 1:1 and 1:2 complexes (Sayyed and Mazahar, 2012).

The metal (II)-humate stepwise stability constants (log k) at phenolic group (Tables 3-18)

Table 3: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$\log(\frac{n}{1-n})$	$\text{Log}K_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

LogK_1 (Average value) = 2.4788± 0.2203

Table 4: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$\text{Log}(\frac{n-1}{2-n})$	$\text{Log}K_2$
9.51	5.50	6.66	6.73	0.07	1.3509	1.70	-0.2671	1.4329
9.73	5.55	6.78	6.85	0.07	1.6383	1.51	0.2467	1.7567
10.00	5.60	6.90	6.98	0.08	2.1783	1.31	-0.2158	1.0942
10.23	5.65	7.05	7.13	0.08	4.1904	1.27		
10.49	5.70	7.10	7.19	0.09	4.6920			

LogK_2(Average value) = 1.4280 ± 0.3312

Table 5:Point-wise method,Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	Log($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430

$LogK_1$ **(Average value)** = 2.3059± 0.6153

Table 6:Point-wise method, Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
9.73	5.55	6.33	6.42	0.09	0.9000	1.69		
10.00	5.60	6.47	6.58	0.11	1.2578	1.44	-0.4592	0.9808
10.23	5.65	6.62	6.84	0.12	1.6137	1.26	-0.2010	1.4610
10.49	5.70	6.80	6.92	0.12	2.1052	1.03		

$LogK_2$ **(Average value)** = 1.2209± 0.3398

Table 7:Point-wise method,Pb (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n}{1-n}$)	$LogK_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.60	0.05	0.8333	1.96	0.6989	2.6589

$\mathbf{LogK_1}$ **(Average value)** = 2.5832 ±0.1614

Table 8:Point-wise method,Pb-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n-1}{2-n}$)	$logK_2$
9.51	5.50	6.66	6.71	0.05	0.9650	1.67	-0.0237	1.1963
9.73	5.55	6.78	6.83	0.05	1.1702	1.44		
10.00	5.60	6.90	6.90	0.05	1.4864	1.22		
10.23	5.65	7.05	7.10	0.05	2.0190	1.09		
10.49	5.70	7.10	7.17	0.07	3.6492	1.00		

$\mathbf{LogK_2}$**(Average value)** = 1.1963

Table 9:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log ($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.5477	2.3123
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	0.0272	2.2072
9.51	5.50	6.20	6.26	0.07	0.6417	1.89	0.2530	2.1430
9.73	5.55	6.40	6.40	0.07	0.7000	1.67	0.3680	2.0380

$LogK_1$ **(Average value)** = 2.2364 ± 0.1602

Table 10:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
10.00	5.60	6.47	6.55	0.08	1.9503	1.41		
10.23	5.65	6.62	6.72	0.11	1.4792	1.26	-0.0361	1.2239

$LogK_2$ **(Average value)** = 1.2239

Table 11:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n}{n-1}$)	$LogK_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4290	2.2110
8.72	5.35	6.37	6.39	0.02	0.2858	2.42	-0.3978	2.0222
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

$\mathbf{LogK_1}$ **(Average value)=**2.1382**±**0.1046

Table 12:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	log($\frac{n-1}{2-n}$)	LogK$_2$
9.51	5.55	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.84	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.93	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.10		
10.49	5.70	7.10	7.18	0.07	3.6492	0.83		

LogK$_2$(Average value) = 1.5453 **±** 0.3450

Table 13:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	V$_3$-V$_2$	n	pL	Log($\frac{n}{n-1}$)	Log K$_1$
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.3477	2.3123
9.00	5.40	6.00	6.04	0.04	0.3236	2.38	-0.3202	2.0598
9.22	5.45	6.10	6.15	0.05	0.4297	2.17	-0.1230	2.0470
9.51	5.50	6.20	6.26	0.06	0.5500	1.89	0.0871	1.9771
9.73	5.55	6.33	6.40	0.07	0.7000	1.67	0.3680	2.0380

LogK$_1$ **(Average value)** = 2.1568 ± 0.2069

Table 14:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	V$_3$-V$_2$	n	pL	Log($\frac{n-1}{2-n}$)	Log K$_2$
10.00	5.60	6.47	6.55	0.08	0.9148	1.41		
10.23	5.65	6.62	6.71	0.09	1.2102	1.20	-0.5749	0.6251
10.49	5.70	6.80	6.92	0.09	1.5968	1.03	0.1703	1.2003

LogK$_2$ **(Average value)** = 0.9127± 0.4070

Table15:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	Log($\frac{n}{1-n}$)	LogK$_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4210	2.2190
8.72	5.35	6.37	6.40	0.03	0.4286	2.42	-0.1249	2.2951
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.96	0.3010	2.2610
9.51	5.55	6.66	6.70	0.04	0.7720	1.67	0.5297	2.1997

LogK$_1$ (Average value) = 2.2108± 0.0825

Table 16:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	Log($\frac{n-1}{2-n}$)	Log K$_2$
9.73	5.55	6.78	6.83	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.95	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.09		
10.49	5.70	7.10	7.16	0.06	3.1429	0.89		

LogK$_2$ **(Average value)** = 1.5453± 0.3450

Table 17:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	V$_3$-V$_2$	n	pL	Log($\frac{n}{n-1}$)	Log K$_1$
8.50	5.30	5.81	5.86	0.05	0.3717	2.88	-0.2280	2.6520
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.06	0.06	0.4853	2.38	-0.0255	2.3545
9.22	5.45	6.10	6.16	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430
9.73	5.55	6.33	6.41	0.08	0.8000	1.69	0.6020	2.2920

LogK$_1$ **(Average value)** = 2.2516± 0.5380

Table 18:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$\mathrm{Log}(\frac{n-1}{2-n})$	Log K_2
10.00	5.60	6.47	6.57	0.10	1.1434	1.43		
10.23	5.65	6.62	6.72	0.10	1.3448	1.23	-0.2788	0.9512
10.49	5.70	6.80	6.90	0.10	1.7742	1.03	0.5351	1.5651

LogK_2 **(Average value)** = 1.2581± 0.4340

Table 19: Stepwise and overall Stability constants of thehydrolysed and unhydrolysed divalent metal (II) complexes

Chelates	**LogK_1**	**LogK_2**	**Logβ**
[Cu (Hydrolysed PSHA-1)$_2$]	2.4788	1.4280	3.9068
[Pb (Hydrolysed PSHA-1)$_2$]	2.5832	1.1963	3.7795
[Cd (Hydrolysed PSHA-1)$_2$]	2.2108	1.5453	3.7561
[Mg (Hydrolysed PSHA-1)$_2$]	2.1382	1.5453	3.6835
[Cu (Unhydrolysed PSHA-1)$_2$]	2.3059	1.2209	3.5268
[Pb (Unhydrolysed PSHA-1)$_2$]	2.2364	1.2239	3.4603
[Cd (Unhydrolysed PSHA-1)$_2$]	2.2516	1.2581	3.5097
[Mg (Unydrolysed PSHA-1)$_2$]	2.1568	0.9127	3.0695

The results obtained (Table19) shows the stepwise and overall stability constants to be not high indicating low stability of the complexes, because the solubility of most metal ions in the basic pH range is minimal due to metal hydroxide precipitation (Karimi, 2017). In general, the stepwise stability constants (K_1 and K_2) follow the order $K_1 > K_2$ for the copper, lead, magnesium and cadmium complexes respectively. The steady decrease of the values with increasing number of ligands is in agreement with the prediction made by researchers (Na'aliya, 2013). The decrease could be attributed to the fact that as the number of the ligands (Humate ions) that enters the coordination zone increases the aqua molecules available for replacement by the ligands become less. Thus, the metal ions become less electron loving with progressive intake of the ligand and this results in the decrease in the values of the constants (Na'aliya, 2013). Also the stability of the complexes is influenced by the size and number of the chelate rings(Mackay and Mackay,2002).All the complexes form rings in their structure as humate, a bidentate ligand, bond the metal ions in the ratio 1:2 (Boguta and Sokolowska, 2016) forming chelate rings. The values of the overall stability constants (logβ) obtained for humate complexes are not high indicating low stability as the values are not high. LogK values for copper-humates (Table 3 to 6) obtained in this study are lower than those reported for the complexes of humic acids (Pandey *et al*., 2015; Dinu, 2013; Kaschl *et al*., 2010 and Gilbeto and Jorg, 2001). The values of LogK(Table 7 to 10) forlead-humates are lower than those reported for the lead in the literature (Dinu, 2013; Gilbeto and Jorg 2001). Log K values(Table 11 to 14) for magnesium-humates obtained in this study are close to those reported by (Pandey *et al*., 2015). Log K values of cadmium-humates (Table 15 to 18) obtained in this work near to the one reported by (Dinu, 2013 and Pandey *et al*., 2015).The difference between the reported values and the values obtained in this study might be probably as a result of acid hydrolysis of humic acid. The values of the overall stability constants (log β) of the copper humates complexes presented in Table 19 is high than that of other metal humate complexes, show relatively high stability of Cu-HA complexes, show the following order of stability: Cu >Pb> Cd > Mg; which are in close agreement to the findings of (Dinu, 2013 and Pandey *et al*., 2015).The high stability of Cu-humate chelate could be attributed to the existence of coordinate covalent bond between the complexing agents and the Cu^{2+} ions. Since, Cu^{2+} being a metal of the transitional series with $3d^9$ electronic configurations can accept the electrons from the complexing agents. Similarly,the low stabilities of Pb,Cd and Mg -complexes could be explained by that Pb^{2+} with $6s^2$, Cd^{2+} with $4d^{10}$ and Mg^{2+} with $2p^6$ their electronic configuration has a completely filled d,p and s orbitals. Moreover, the stabilities of metal ions with hydrolysed humic acid from peat soil were higher than those with unhydrolysed humic acid from peat soil; which is ascribed to the high content of acidity in hydrolysed humic acid than unhydrolysed humic acid.

CONCLUSION

The values of logK for Cu(II) hydrolysed humic acid complex was higher followed by Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes as compared with metal(II) unhydrolysed humic acid complexes . This indicates acid hydrolysis of humic acid can enhance the complexation behavior of humic acid with metal (II) ions. However, the higher values of logβ for Cu(II), Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes indicates more stable stepwise complexes formed as compared with Cu(II), Pb(II), Cd(II) and Mg(II) unhydrolysed humic acid complexes.

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STABILITY CONSTANTS OF COMPLEXES OF METAL IONS WITH PEATSOIL HUMIC ACIDS UNDER NON-ACID-CONDITIONS

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ABSTRACT

Stability constants of complexes of four divalent metal ions viz. Cu^{2+}, Pb^{2+},Mg^{2+} and Cd^{2+} with humic acids (HA) were determined by potentiometric titration of humic acids with the corresponding salt of the divalent metals in aqueous media under non-acid-condition. The log K (logarithm of the stability constant) ranged from 1.0942 to 2.7471 for metal-humic acid complexes were determined using point-wise computational method. The order of stability constants were obtained as follows: Cu >Pb> Cd > Mg for metal -HA complexes respectively, indicating a higher degree of complexation with Cu metal ion.

Keywords: stability constant, humic acid, potentiometric titration, divalent metals, acid hydrolysis.

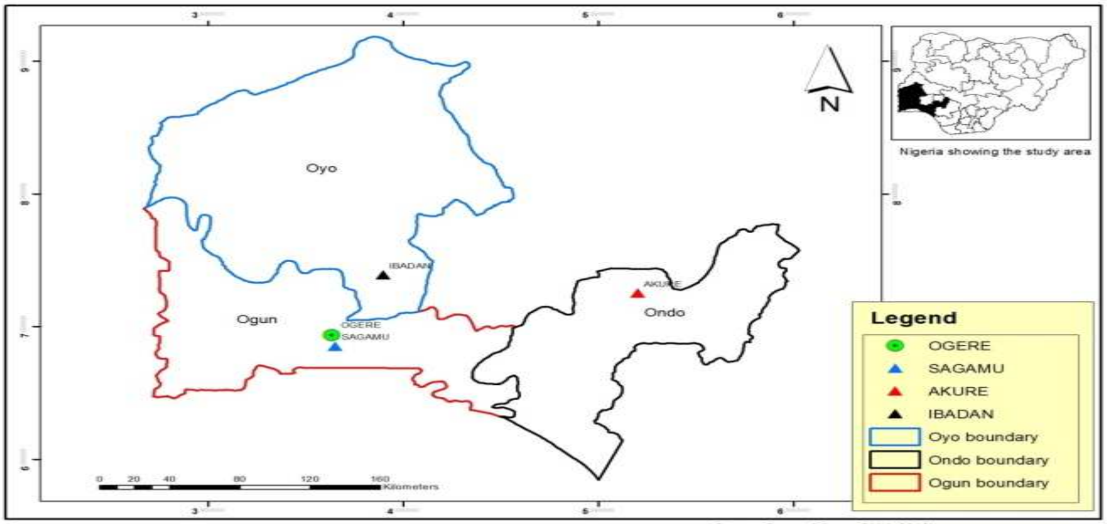
NTRODUCTION

The stability constant of a complex is the numerical expression of its stability and provides a quantitative measure of affinity of the metal ion to the complexing agent. An understanding of the relative stability of metal-complexes helps in predicting the behavior of metal ions in the soil (Ram and Raman, 1982). Extensive researches has been done to determine the stability constants of the complexes formed between humic acid (HA) with a number of metal ions. Ashok *et al.*, (2000) reported that humic acid with hydroxyl, phenoxyl and carboxyl reactive groups can form coordination compound with metal ions at pH 3.5. The stability constants(Log K) for different metal-humic acid complexes indicated the following order of the stabilities of complexes formed between humic acid and metal ion, Cu >Fe >Pb> Ni > Co > Ca > Cd > Zn >Mn> Mg. Andelkovic *et al.*, (2010) investigated the binding of Cd(II) to soil humic acid at pH 6.5 and in 0.1M KNO_3 ionic medium. The stability constant for binding indicating greater stability in the case when carboxyl groups are involved in complexation reaction. Kostic *et al.*,(2012) investigated the complexation of humic acid with certain heavy metal ions (Co(II), Ni(II),Cu(II), Zn(II), and Pb(II). The experiment was performed at 25°C, at pH 4.0 and ionic strength of 0.01M. Stability constant of complex between Pb(II) ions and humic acid is greater than stability constants of other investigated metal-humate complexes. Bogata and Sokolowska (2016) analyses the interaction between humic acids from different soils and Zn (II) ions at wide concentration ranges and at pH 5. Studies have showed significant impact of Zn concentration, pH and some properties of humic acids with zinc.But all of these studies were limited to acidic pH range. Therefore, the present study was carried out to determine and compare the stability constants of complexes of metal ions with hydrolysed peat soil humic acid and unhydrolysed peat soil humic under non-acid conditions.

MATERIALS AND METHODS

Analytical grade chemicals used includes hydrochloric acid (HCl), nitric acid (HNO_3), sodium hydroxide (NaOH), lead nitrate $Pb(NO_3)_2$, copper nitrate $Cu(NO_3)_2.3H_2O$, cadmium nitrate $Cd(NO_3)_2.4H_2O$, magnesium nitrate $Mg(NO_3)_2.6H_2O$, potassium nitrate (KNO_3), calcium chloride ($CaCl_2$), (sigma-Aldrich). Dowex 50WX8, (20-50 mesh) from Fluka.

Area of study



Source: Dept. of Geog. BUK (2016)

Figure 1: Map showing the sampling point at Sagamu Town, Ogun State.

Description of Sampling Area

Sagamu has geographical coordinates between 6°50′ north; 3° 38′ east is located in south western region of Nigeria. The region has tropical wet and dry climate with a lengthy wet season and relatively constant temperatures throughout the course of the year. Wet season runs from March to October, November to December forms the region dry season. The vegetation type of the region is savannah which is really grassland with small bushes and occasional big trees. Grassland soils have substantially higher organic matter content than forest soils (Novackova, 2011).

Sample Collection

The Peatsoil samples were collected from four different sampling points (0-10cm depth) in Sagamu into polyethylene bag with plastic spoons. Samples were taken to the laboratory, extraneous materials were removed; the samples were air-dried, crushed and ground to a fine powder in a mortar passed through a 0.20mm sieve. The samples were kept for analysis.

Isolation and purification of humic acid from peat soil sample

Peatsoil sample (100g) was mixed with 1000 cm^3 of 0.1M NaOH solution, shaken for 3hours and left to stand overnight. Dark-coloured supernatant was obtained and decanted from solid residue. The dark-coloured supernatant was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 6 hours. Yellowish brown supernatant and dark-brown precipitate were obtained. The yellowish brown supernatant was decanted followed by centrifuge and discarded. The dark-brown precipitate was mixed with 500$cm^3$of 0.1M NaOH solution followed by passing through dowex resin. The dark-brown solution was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 3 hours. The dark-brown precipitate was washed several times with deionized water. The supernatant was treated with $AgNO_3$ solution until no white precipitate observed. The humic acid was transferred to weighed crucible and dried at 60°C in an oven for 12 hours. The humic acid was cooled and dried in the desiccator, weighed and recorded. The obtained humic acid was dried again at 60°C for additional 6 hours cooled and dried in the desiccator, weighed and recorded constant weight was obtained (Baruah *et al*., 2015).

FT-IR analysis

FT-IR spectra of humic acid sample was analysed using Carry 630 FT-IR Agilent Technologies.

Unhydrolysed compost humic acid

The unhydrolysed humic acid was obtained after isolation and purification of compost humic acid and kept for investigation.

Acid hydrolysis of Peatsoil acid

Peatsoil humic acid sample (1g) was refluxed for 12 hours at (160°C) with 50cm^3 of 6M HCl. The mixture was allowed to cool, decanted, and centrifuged after hydrolysis. The insoluble residues were washed with distilled water via centrifugation several times, and the supernatant was treated with $AgNO_3$ solution until no white precipitate was observed. The residue was thoroughly dried over $CaCl_2$ in a desiccator at room temperature (Chefetz *et al*., 2002). Finally, the obtained hydrolysed humic acid was kept for investigation.

Potentiometric Titrations

Potentiometric measurements were carried out using a pH-meter Jenway (model 3510) with combine electrode, the sensitivity of the pH -meter is 0.01 units. The pH meter was switched on half an hour before starting the titration for initial warm up of the instrument. The instrument was calibrated with an aqueous standard buffer solution of pH 4.00 and 10.0 (borate buffer) prepared from a "Qualigens" buffer tablets.

The following sets of solutions were prepared in a 250cm^3 volumetric flask separately for pH metric titrations.

(i) 5 cm^3 0.1 M HCl + 40 cm^3 deionized water

(ii) 5 cm^3 0.1 M HCl + 39 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid

(iii) 5 cm^3 0.1 M HCl + 37 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid + 2 cm^3 0.01 M Cu(II)

The solutions were titrated against standardized 0.110MNaOH separately. The total volume of each mixture was adjusted to 50 cm^3 and the ionic strength of the solutions was maintained constant at by adding appropriate amount of stock solution of 1M KNO_3 (Gamal, 2015; Omar and Ali, 2015). A magnetic stirrer was used to achieve thorough mixing of the interacting solutions at 550 rpm. The same set of experimental conditions was applied for potentiometric titration of remaining samples.

Evaluation of pKa of Hydrolysed peat soil Humic Acids

The proton-ligand formation number n_A were calculated by Irving and Rossotti expression (Omar and Ali, 2015).

$$nA = Y - \frac{(V2-V1)(No-Eo)}{(Vo+V1)TcL} \quad ....1$$

Where: Y is number of dissociable proton, (V_2-V_1) is the measure of displacement of the ligand curve relative to acid curve, N^o and E^o are the resultant concentration of alkali solution, free acid solution, $T_{cL}{}^o$ is the total ligand concentration, V^o is the total volume of titration solution,V_1 is the volume of alkali added to acid solution,V_2 is the volume of alkali added to acid solution + ligand solution, acid dissociation constants (pKa - values) of ligand were calculated by algebraic method point wise calculation (Tables 1). The dissociation constants (pKa) were calculated according to the following relation:

$$pKa = pH + \log(\frac{nA}{1-nA}) \quad ....2$$

Where: pKa is the acid dissociation constant, $n_A$is the Proton-ligand formation number and pH is the pH-values (Omar and Ali, 2015).

Determination of metal-ligand stability constants (log K) of complexes

The potentiometric measurement for the determination of stability constant of a complex in solution is based on the fact that the redox potential of the couple $\frac{M^{+(m-n)}}{M^{+m}}$ is shifted significantly on complexation of the metal ion with the ligand. This method involves change in hydrogen ion concentration [H$^+$] due to the displacement or association of one or more protons taking place during complexation reaction. This change can be found out by titrating the solutions containing free acid, acid with ligand, and acid with ligand and metal ion, individually against a standard alkali solution at a constant ionic strength or temperature. Either ionic strength or temperature may be varied for different sets of solutions. In all the cases, the change in the pH of the solution is measured after each addition of a known amount of alkali to the reaction cell which contains the reaction mixture. The titration curves are then drawn by plotting the measured pH values against the corresponding volume of alkali added and the stability constants of the complexes are determined from the titration curves by employing pH-metric titration technique given by (Irving and Rossoti).

Metal-ligand stability constants (Log K) were determined by using the following relations:

$$\bar{n} = \frac{(V_3 - V_2)(E^0 + N^0)}{(V^0 + V_2)\bar{n}_A T_m^0} \quad ....3$$

and

$$PL = \log_{10}\{\frac{1 + \beta_n^H \frac{1}{[anti \ \log pH]^n}}{T_L^0 - \bar{n}T_m^0} X \frac{(V^0 + V_3)}{V^0}\} \quad ....4$$

Where $T_{L,}$ T^o, E°, and V^ohavethe same significance as in equation (1) above, T_m denotes the total concentration of metal present in solution, V_3 is the volume of metal ions present in solution and β^H is the overall proton ligand stability constant. The metal-ligand stability constants (log K) were determined by employing point wise computational Method (eq. 5 and 6).

$\mathrm{Log}K_1 = \log\left(\frac{n}{1-n}\right) + pL$ …………..5

$\mathrm{Log}K_2 = \log\left(\frac{1-n}{2-n}\right) + pL$……………………6

Where: Log K is the metal-ligand stability constant, pL is the Free ligand exponent function, **n** is the Average number of ligand attached with metal ion (Janrao*et al*., 2014).The results obtained were analyzed by an ORIGIN 2016 program using titration data and then the proton-ligand stability constants (pKa) and Metal-ligand stability constant (LogK) calculated (Omar and Ali, 2015).

RESULTS AND DISCUSSION

Fourier transformed infrared (FT-IR) spectra of isolated humic acid from peat soils Figure 2 had distinct clear absorption bands indicating the presence of major humic acid structural elemental groups such as H bonded OH ($3680cm^{-1}$ peak), C=O of carbonyl ($1721cm^{-1}$ peak), functional groups of aliphatic components CH_2 ($2918cm^{-1}$ peak) and C-O stretching of polysaccharide ($1168cm^{-1}$ peak). The positions of the absorption bands of the spectra fell within typical major absorption bands of humic acid which is at frequencies 3680, 2918, 1721, 1168 cm^{-1}. The first peak centred in the vicinity of 3680 cm^{-1} region is attributed to phenol OH group bounded by intermolecular H bonds. The $2918cm^{-1}$ band usually has absorption maximum at 2918 cm^{-1} which is due to C–H stretching of alkane group (CH_2). The next major absorption band is 1721 cm^{-1}. This band has been commonly ascribed to C=O stretching of mainly carboxyl group (COOH) with trace amount of ketones. The last peak was observed at 1168 cm^{-1} due to C–O stretching of polysaccharides and this peak appeared also in the spectra of humic acid from peat soil. The FTIR spectra of the isolated humic acid contained all major characteristic absorption peaks of humic acid. These absorption peaks indicated the presence of the major structural elements of humic acid namely H bonded OH, C=C of aromatic ring, C=O of carbonyl group (both carboxyl and ketonic), CH_2 group. This strongly supports the presence of humic acid.

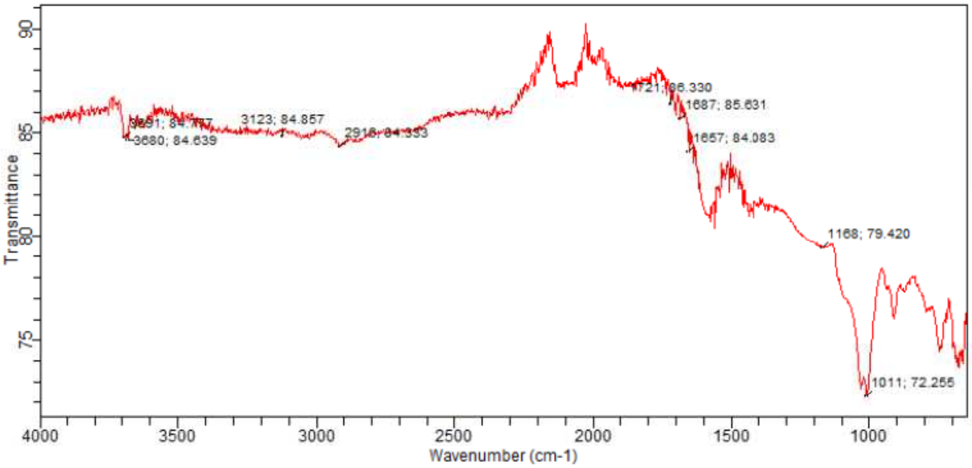


Fig. 2 : FT-IR spectraof peatsoilhumic acid (PSHA)

Evaluation of acid dissociation constant (pka) of acid hydrolysed peat soil humicacid at phenolic group

The value of the dissociation constant of the peat soil humic acid (PSHA) that underwent acidhydrolysis studied was found to be 8.9299 as shown Table 1, which is lower than the literaturevalues reported by Almeida and Szpoganics, (2015), Borges *et al*., (2005); Badr *et al*., (2012)and Fernandes *et al*,.(2009) of 9.73, 9.47 and 10.30. The difference between the obtained valuesand the reported values in this study might be probably as a result of acid hydrolysis of humicacid.

Table 1: PKa of (Hydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	$\log(\frac{nA}{1-nA})$	pKa
8.50	5.30	6.29	0.99	0.3594	-0.2510	8.2490
8.72	5.35	6.37	1.02	0.3400	-0.2880	8.4320
9.00	5.40	6.46	1.06	0.3141	-0.3391	8.6609
9.22	5.45	6.55	1.10	0.2882	-0.3927	8.8273
9.51	5.50	6.66	1.16	0.2494	-0.4786	9.0314
9.73	5.55	6.78	1.23	0.2041	-0.5910	9.1390
10.00	5.60	6.90	1.30	0.1589	-0.7238	9.2762
10.23	5.65	7.05	1.40	0.0941	-0.9835	9.2465
10.49	5.70	7.10	1.40	0.0941	-0.9835	9.5065

Average pKa = 8.9299 ± 0.4186

Table 2: PKa of (Unhydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	$\text{Log}(\frac{nA}{1-n})$	pKa
8.50	5.30	5.81	0.51	0.6619	0.2919	8.7919
8.72	5.35	5.90	0.55	0.6357	0.2418	8.9618
9.00	5.40	6.00	0.60	0.6029	0.1813	9.1813
9.22	5.45	6.10	0.65	0.5701	0.1226	9.3426
9.51	5.50	6.20	0.70	0.5376	0.0654	9.5754
9.73	5.55	6.33	0.78	0.4851	-0.0259	9.7041
10.00	5.60	6.47	0.87	0.4262	-0.1291	9.8709
10.23	5.65	6.62	0.99	0.3609	-0.2481	9.9819
10.49	5.70	6.80	1.10	0.2759	-0.4690	10.0210

Average pKa = 9.4923± 0.4410

Metal-ligand stability constant (Log K)

The stabilityconstants require the accurate values of proton-ligand stability constants (Anil and Maroti, 2008). Metal titration curves crossed over ligand titration curve indicated the formation of complex upon proton release (Santosh, *et al.*, 2011). If the values of n- are within range 0.2-0.8 and 1.2-18 this indicates the formation of 1:1 and 1:2 complexes (Sayyed and Mazahar, 2012).

The metal (II)-humate stepwise stability constants (log k) at phenolic group (Tables 3-18)

Table 3: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$\log(\frac{n}{1-n})$	LogK_1
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

LogK_1 (Average value) = 2.4788± 0.2203

Table 4: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$\text{Log}(\frac{n-1}{2-n})$	LogK_2
9.51	5.50	6.66	6.73	0.07	1.3509	1.70	-0.2671	1.4329
9.73	5.55	6.78	6.85	0.07	1.6383	1.51	0.2467	1.7567
10.00	5.60	6.90	6.98	0.08	2.1783	1.31	-0.2158	1.0942
10.23	5.65	7.05	7.13	0.08	4.1904	1.27		
10.49	5.70	7.10	7.19	0.09	4.6920			

LogK_2(Average value) = 1.4280 ± 0.3312

Table 5:Point-wise method,Cu (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	Log($\frac{n}{n-1}$)	Log K$_1$
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430

LogK$_1$ **(Average value)** = 2.3059± 0.6153

Table 6:Point-wise method, Cu (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	V$_3$-V$_2$	n	pL	Log($\frac{n-1}{2-n}$)	Log K$_2$
9.73	5.55	6.33	6.42	0.09	0.9000	1.69		
10.00	5.60	6.47	6.58	0.11	1.2578	1.44	-0.4592	0.9808
10.23	5.65	6.62	6.84	0.12	1.6137	1.26	-0.2010	1.4610
10.49	5.70	6.80	6.92	0.12	2.1052	1.03		

LogK$_2$ **(Average value)** = 1.2209± 0.3398

Table 7:Point-wise method,Pb (Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	log($\frac{n}{1-n}$)	LogK$_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.60	0.05	0.8333	1.96	0.6989	2.6589

LogK$_1$ (Average value) = 2.5832 ±0.1614

Table 8:Point-wise method,Pb-(Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	log($\frac{n-1}{2-n}$)	logK$_2$
9.51	5.50	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.83	0.05	1.1702	1.44		
10.00	5.60	6.90	6.90	0.05	1.4864	1.22	-0.0237	1.1963
10.23	5.65	7.05	7.10	0.05	2.0190	1.09		
10.49	5.70	7.10	7.17	0.07	3.6492	1.00		

LogK$_2$(Average value) = 1.1963

Table 9:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	V$_3$-V$_2$	n	pL	Log ($\frac{n}{n-1}$)	Log K$_1$
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.5477	2.3123
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	0.0272	2.2072
9.51	5.50	6.20	6.26	0.07	0.6417	1.89	0.2530	2.1430
9.73	5.55	6.40	6.40	0.07	0.7000	1.67	0.3680	2.0380

LogK$_1$ **(Average value)** = 2.2364 ± 0.1602

Table 10:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	V$_3$-V$_2$	n	pL	Log($\frac{n-1}{2-n}$)	Log K$_2$
10.00	5.60	6.47	6.55	0.08	1.9503	1.41		
10.23	5.65	6.62	6.72	0.11	1.4792	1.26	-0.0361	1.2239

LogK$_2$ **(Average value)** = 1.2239

Table 11:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	log($\frac{n}{n-1}$)	LogK$_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4290	2.2110
8.72	5.35	6.37	6.39	0.02	0.2858	2.42	-0.3978	2.0222
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

LogK$_1$ (Average value)=2.1382**±**0.1046

Table 12:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	log$(\frac{n-1}{2-n})$	LogK$_2$
9.51	5.55	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.84	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.93	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.10		
10.49	5.70	7.10	7.18	0.07	3.6492	0.83		

LogK$_2$(Average value) = 1.5453 **±** 0.3450

Table 13:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	V$_3$-V$_2$	n	pL	Log$(\frac{n}{n-1})$	Log K$_1$
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.3477	2.3123
9.00	5.40	6.00	6.04	0.04	0.3236	2.38	-0.3202	2.0598
9.22	5.45	6.10	6.15	0.05	0.4297	2.17	-0.1230	2.0470
9.51	5.50	6.20	6.26	0.06	0.5500	1.89	0.0871	1.9771
9.73	5.55	6.33	6.40	0.07	0.7000	1.67	0.3680	2.0380

LogK$_1$ **(Average value)** = 2.1568 ± 0.2069

Table 14:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	V$_3$-V$_2$	n	pL	Log$(\frac{n-1}{2-n})$	Log K$_2$
10.00	5.60	6.47	6.55	0.08	0.9148	1.41		
10.23	5.65	6.62	6.71	0.09	1.2102	1.20	-0.5749	0.6251
10.49	5.70	6.80	6.92	0.09	1.5968	1.03	0.1703	1.2003

LogK$_2$ **(Average value)** = 0.9127± 0.4070

Table15:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	Log$(\frac{n}{1-n})$	LogK$_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4210	2.2190
8.72	5.35	6.37	6.40	0.03	0.4286	2.42	-0.1249	2.2951
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.96	0.3010	2.2610
9.51	5.55	6.66	6.70	0.04	0.7720	1.67	0.5297	2.1997

LogK$_1$ (Average value) = 2.2108± 0.0825

Table 16:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	Log$(\frac{n-1}{2-n})$	Log K$_2$
9.73	5.55	6.78	6.83	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.95	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.09		
10.49	5.70	7.10	7.16	0.06	3.1429	0.89		

LogK$_2$ **(Average value)** = 1.5453± 0.3450

Table 17:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	V$_3$-V$_2$	n	pL	Log$(\frac{n}{n-1})$	Log K$_1$
8.50	5.30	5.81	5.86	0.05	0.3717	2.88	-0.2280	2.6520
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.06	0.06	0.4853	2.38	-0.0255	2.3545
9.22	5.45	6.10	6.16	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430
9.73	5.55	6.33	6.41	0.08	0.8000	1.69	0.6020	2.2920

LogK$_1$ **(Average value)** = 2.2516± 0.5380

Table 18:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$\text{Log}(\frac{n-1}{2-n})$	Log K_2
10.00	5.60	6.47	6.57	0.10	1.1434	1.43		
10.23	5.65	6.62	6.72	0.10	1.3448	1.23	-0.2788	0.9512
10.49	5.70	6.80	6.90	0.10	1.7742	1.03	0.5351	1.5651

LogK_2 **(Average value)** = 1.2581± 0.4340

Table 19: Stepwise and overall Stability constants of thehydrolysed and unhydrolysed divalent metal (II) complexes

Chelates	LogK₁	LogK₂	Logβ
[Cu (Hydrolysed PSHA-1)$_2$]	2.4788	1.4280	3.9068
[Pb (Hydrolysed PSHA-1)$_2$]	2.5832	1.1963	3.7795
[Cd (Hydrolysed PSHA-1)$_2$]	2.2108	1.5453	3.7561
[Mg (Hydrolysed PSHA-1)$_2$]	2.1382	1.5453	3.6835
[Cu (Unhydrolysed PSHA-1)$_2$]	2.3059	1.2209	3.5268
[Pb (Unhydrolysed PSHA-1)$_2$]	2.2364	1.2239	3.4603
[Cd (Unhydrolysed PSHA-1)$_2$]	2.2516	1.2581	3.5097
[Mg (Unydrolysed PSHA-1)$_2$]	2.1568	0.9127	3.0695

The results obtained (Table19) shows the stepwise and overall stability constants to be not high indicating low stability of the complexes, because the solubility of most metal ions in the basic pH range is minimal due to metal hydroxide precipitation (Karimi, 2017). In general, the stepwise stability constants (K_1 and K_2) follow the order $K_1 > K_2$ for the copper, lead, magnesium and cadmium complexes respectively. The steady decrease of the values with increasing number of ligands is in agreement with the prediction made by researchers (Na'aliya, 2013). The decrease could be attributed to the fact that as the number of the ligands (Humate ions) that enters the coordination zone increases the aqua molecules available for replacement by the ligands become less. Thus, the metal ions become less electron loving with progressive intake of the ligand and this results in the decrease in the values of the constants (Na'aliya, 2013). Also the stability of the complexes is influenced by the size and number of the chelate rings(Mackay and Mackay,2002).All the complexes form rings in their structure as humate, a bidentate ligand, bond the metal ions in the ratio 1:2 (Boguta and Sokolowska, 2016) forming chelate rings. The values of the overall stability constants (logβ) obtained for humate complexes are not high indicating low stability as the values are not high. LogK values for copper-humates (Table 3 to 6) obtained in this study are lower than those reported for the complexes of humic acids (Pandey *et al*., 2015; Dinu, 2013; Kaschl *et al*., 2010 and Gilbeto and Jorg, 2001). The values of LogK(Table 7 to 10) forlead-humates are lower than those reported for the lead in the literature (Dinu, 2013; Gilbeto and Jorg 2001). Log K values(Table 11 to 14) for magnesium-humates obtained in this study are close to those reported by (Pandey *et al*., 2015). Log K values of cadmium-humates (Table 15 to 18) obtained in this work near to the one reported by (Dinu, 2013 and Pandey *et al*., 2015).The difference between the reported values and the values obtained in this study might be probably as a result of acid hydrolysis of humic acid. The values of the overall stability constants (log β) of the copper humates complexes presented in Table 19 is high than that of other metal humate complexes, show relatively high stability of Cu-HA complexes, show the following order of stability: Cu >Pb> Cd > Mg; which are in close agreement to the findings of (Dinu, 2013 and Pandey *et al*., 2015).The high stability of Cu-humate chelate could be attributed to the existence of coordinate covalent bond between the complexing agents and the Cu^{2+} ions. Since, Cu^{2+} being a metal of the transitional series with $3d^9$ electronic configurations can accept the electrons from the complexing agents. Similarly,the low stabilities of Pb,Cd and Mg -complexes could be explained by that Pb^{2+} with $6s^2$, Cd^{2+} with $4d^{10}$ and Mg^{2+} with $2p^6$ their electronic configuration has a completely filled d,p and s orbitals. Moreover, the stabilities of metal ions with hydrolysed humic acid from peat soil were higher than those with unhydrolysed humic acid from peat soil; which is ascribed to the high content of acidity in hydrolysed humic acid than unhydrolysed humic acid.

CONCLUSION

The values of logK for Cu(II) hydrolysed humic acid complex was higher followed by Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes as compared with metal(II) unhydrolysed humic acid complexes . This indicates acid hydrolysis of humic acid can enhance the complexation behavior of humic acid with metal (II) ions. However, the higher values of logβ for Cu(II), Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes indicates more stable stepwise complexes formed as compared with Cu(II), Pb(II), Cd(II) and Mg(II) unhydrolysed humic acid complexes.

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STABILITY CONSTANTS OF COMPLEXES OF METAL IONS WITH PEATSOIL HUMIC ACIDS UNDER NON-ACID-CONDITIONS

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ABSTRACT

Stability constants of complexes of four divalent metal ions viz. Cu^{2+}, Pb^{2+},Mg^{2+} and Cd^{2+} with humic acids (HA) were determined by potentiometric titration of humic acids with the corresponding salt of the divalent metals in aqueous media under non-acid-condition. The log K (logarithm of the stability constant) ranged from 1.0942 to 2.7471 for metal-humic acid complexes were determined using point-wise computational method. The order of stability constants were obtained as follows: Cu >Pb> Cd > Mg for metal -HA complexes respectively, indicating a higher degree of complexation with Cu metal ion.

Keywords: stability constant, humic acid, potentiometric titration, divalent metals, acid hydrolysis.

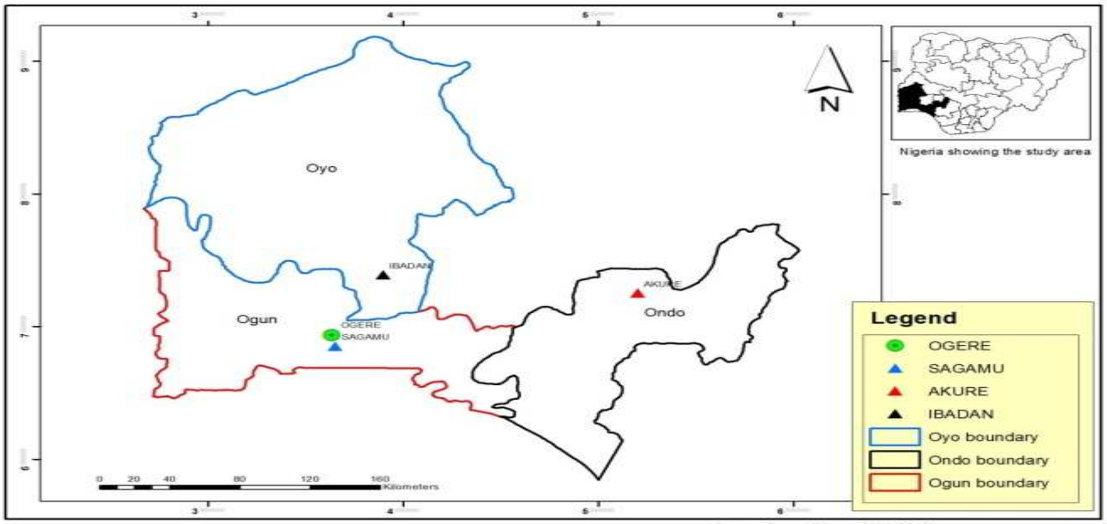
NTRODUCTION

The stability constant of a complex is the numerical expression of its stability and provides a quantitative measure of affinity of the metal ion to the complexing agent. An understanding of the relative stability of metal-complexes helps in predicting the behavior of metal ions in the soil (Ram and Raman, 1982). Extensive researches has been done to determine the stability constants of the complexes formed between humic acid (HA) with a number of metal ions. Ashok *et al.*, (2000) reported that humic acid with hydroxyl, phenoxyl and carboxyl reactive groups can form coordination compound with metal ions at pH 3.5. The stability constants(Log K) for different metal-humic acid complexes indicated the following order of the stabilities of complexes formed between humic acid and metal ion, Cu >Fe >Pb> Ni > Co > Ca > Cd > Zn >Mn> Mg. Andelkovic *et al.*, (2010) investigated the binding of Cd(II) to soil humic acid at pH 6.5 and in 0.1M KNO_3 ionic medium. The stability constant for binding indicating greater stability in the case when carboxyl groups are involved in complexation reaction. Kostic *et al.*,(2012) investigated the complexation of humic acid with certain heavy metal ions (Co(II), Ni(II),Cu(II), Zn(II), and Pb(II). The experiment was performed at 25°C, at pH 4.0 and ionic strength of 0.01M. Stability constant of complex between Pb(II) ions and humic acid is greater than stability constants of other investigated metal-humate complexes. Bogata and Sokolowska (2016) analyses the interaction between humic acids from different soils and Zn (II) ions at wide concentration ranges and at pH 5. Studies have showed significant impact of Zn concentration, pH and some properties of humic acids with zinc.But all of these studies were limited to acidic pH range. Therefore, the present study was carried out to determine and compare the stability constants of complexes of metal ions with hydrolysed peat soil humic acid and unhydrolysed peat soil humic under non-acid conditions.

MATERIALS AND METHODS

Analytical grade chemicals used includes hydrochloric acid (HCl), nitric acid (HNO_3), sodium hydroxide (NaOH), lead nitrate $Pb(NO_3)_2$, copper nitrate $Cu(NO_3)_2.3H_2O$, cadmium nitrate $Cd(NO_3)_2.4H_2O$, magnesium nitrate $Mg(NO_3)_2.6H_2O$, potassium nitrate (KNO_3), calcium chloride ($CaCl_2$), (sigma-Aldrich). Dowex 50WX8, (20-50 mesh) from Fluka.

Area of study



Source: Dept. of Geog. BUK (2016)

Figure 1: Map showing the sampling point at Sagamu Town, Ogun State.

Description of Sampling Area

Sagamu has geographical coordinates between 6°50′ north; 3° 38′ east is located in south western region of Nigeria. The region has tropical wet and dry climate with a lengthy wet season and relatively constant temperatures throughout the course of the year. Wet season runs from March to October, November to December forms the region dry season. The vegetation type of the region is savannah which is really grassland with small bushes and occasional big trees. Grassland soils have substantially higher organic matter content than forest soils (Novackova, 2011).

Sample Collection

The Peatsoil samples were collected from four different sampling points (0-10cm depth) in Sagamu into polyethylene bag with plastic spoons. Samples were taken to the laboratory, extraneous materials were removed; the samples were air-dried, crushed and ground to a fine powder in a mortar passed through a 0.20mm sieve. The samples were kept for analysis.

Isolation and purification of humic acid from peat soil sample

Peatsoil sample (100g) was mixed with 1000 cm^3 of 0.1M NaOH solution, shaken for 3hours and left to stand overnight. Dark-coloured supernatant was obtained and decanted from solid residue. The dark-coloured supernatant was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 6 hours. Yellowish brown supernatant and dark-brown precipitate were obtained. The yellowish brown supernatant was decanted followed by centrifuge and discarded. The dark-brown precipitate was mixed with $500cm^3$of 0.1M NaOH solution followed by passing through dowex resin. The dark-brown solution was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 3 hours. The dark-brown precipitate was washed several times with deionized water. The supernatant was treated with $AgNO_3$ solution until no white precipitate observed. The humic acid was transferred to weighed crucible and dried at 60°C in an oven for 12 hours. The humic acid was cooled and dried in the desiccator, weighed and recorded. The obtained humic acid was dried again at 60°C for additional 6 hours cooled and dried in the desiccator, weighed and recorded constant weight was obtained (Baruah *et al.*, 2015).

FT-IR analysis

FT-IR spectra of humic acid sample was analysed using Carry 630 FT-IR Agilent Technologies.

Unhydrolysed compost humic acid

The unhydrolysed humic acid was obtained after isolation and purification of compost humic acid and kept for investigation.

Acid hydrolysis of Peatsoil acid

Peatsoil humic acid sample (1g) was refluxed for 12 hours at (160°C) with $50cm^3$ of 6M HCl. The mixture was allowed to cool, decanted, and centrifuged after hydrolysis. The insoluble residues were washed with distilled water via centrifugation several times, and the supernatant was treated with $AgNO_3$ solution until no white precipitate was observed. The residue was thoroughly dried over $CaCl_2$ in a desiccator at room temperature (Chefetz *et al.*, 2002). Finally, the obtained hydrolysed humic acid was kept for investigation.

Potentiometric Titrations

Potentiometric measurements were carried out using a pH-meter Jenway (model 3510) with combine electrode, the sensitivity of the pH - meter is 0.01 units. The pH meter was switched on half an hour before starting the titration for initial warm up of the instrument. The instrument was calibrated with an aqueous standard buffer solution of pH 4.00 and 10.0 (borate buffer) prepared from a "Qualigens" buffer tablets.

The following sets of solutions were prepared in a 250cm^3 volumetric flask separately for pH metric titrations.

(i) 5 cm^3 0.1 M HCl + 40 cm^3 deionized water
(ii) 5 cm^3 0.1 M HCl + 39 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid
(iii) 5 cm^3 0.1 M HCl + 37 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid + 2 cm^3 0.01 M Cu(II)

The solutions were titrated against standardized 0.110MNaOH separately. The total volume of each mixture was adjusted to 50 cm^3 and the ionic strength of the solutions was maintained constant at by adding appropriate amount of stock solution of 1M KNO_3 (Gamal, 2015; Omar and Ali, 2015). A magnetic stirrer was used to achieve thorough mixing of the interacting solutions at 550 rpm. The same set of experimental conditions was applied for potentiometric titration of remaining samples.

Evaluation of pKa of Hydrolysed peat soil Humic Acids

The proton-ligand formation number n_A were calculated by Irving and Rossotti expression (Omar and Ali, 2015).

$$nA = Y - \frac{(V2-V1)(No-Eo)}{(Vo+V1)TcL} \quad ....1$$

Where: Y is number of dissociable proton, (V_2-V_1) is the measure of displacement of the ligand curve relative to acid curve, N^o and E^o are the resultant concentration of alkali solution, free acid solution, $T_{cL}{}^o$ is the total ligand concentration, V^o is the total volume of titration solution,V_1 is the volume of alkali added to acid solution,V_2 is the volume of alkali added to acid solution + ligand solution, acid dissociation constants (pKa - values) of ligand were calculated by algebraic method point wise calculation (Tables 1). The dissociation constants (pKa) were calculated according to the following relation:

$$pKa = pH + \log\left(\frac{nA}{1-nA}\right) \quad ....2$$

Where: pKa is the acid dissociation constant, $n_A$is the Proton-ligand formation number and pH is the pH-values (Omar and Ali, 2015).

Determination of metal-ligand stability constants (log K) of complexes

The potentiometric measurement for the determination of stability constant of a complex in solution is based on the fact that the redox potential of the couple $\frac{M^{+(m-n)}}{M^{+m}}$ is shifted significantly on complexation of the metal ion with the ligand. This method involves change in hydrogen ion concentration [H$^+$] due to the displacement or association of one or more protons taking place during complexation reaction. This change can be found out by titrating the solutions containing free acid, acid with ligand, and acid with ligand and metal ion, individually against a standard alkali solution at a constant ionic strength or temperature. Either ionic strength or temperature may be varied for different sets of solutions. In all the cases, the change in the pH of the solution is measured after each addition of a known amount of alkali to the reaction cell which contains the reaction mixture. The titration curves are then drawn by plotting the measured pH values against the corresponding volume of alkali added and the stability constants of the complexes are determined from the titration curves by employing pH-metric titration technique given by (Irving and Rossoti).

Metal-ligand stability constants (Log K) were determined by using the following relations:

$$\bar{n} = \frac{(V_3 - V_2)(E^0 + N^0)}{(V^0 + V_2)\bar{n}_A T_m^0} \quad ....3$$

and

$$PL = \log_{10}\left\{\frac{1 + \beta_n^H \frac{1}{[anti\ \log pH]^n}}{T_L^0 - \bar{n}T_m^0} X \frac{(V^0 + V_3)}{V^0}\right\} \quad ....4$$

Where $T_{L,}$ T^{o}, E°, and V^{o}havethe same significance as in equation (1) above, T_m denotes the total concentration of metal present in solution, V_3 is the volume of metal ions present in solution and β^H is the overall proton ligand stability constant. The metal-ligand stability constants (log K) were determined by employing point wise computational Method (eq. 5 and 6).

$$\text{LogK}_1 = \log\left(\frac{n}{1-n}\right) + \text{pL} \quad \ldots\ldots\ldots\ldots.5$$

$$\text{LogK}_2 = \log\left(\frac{1-n}{2-n}\right) + \text{pL}\ldots\ldots\ldots\ldots\ldots\ldots\ldots.6$$

Where: Log K is the metal-ligand stability constant, pL is the Free ligand exponent function, **n** is the Average number of ligand attached with metal ion (Janrao*et al*., 2014).The results obtained were analyzed by an ORIGIN 2016 program using titration data and then the proton-ligand stability constants (pKa) and Metal-ligand stability constant (LogK) calculated (Omar and Ali, 2015).

RESULTS AND DISCUSSION

Fourier transformed infrared (FT-IR) spectra of isolated humic acid from peat soils Figure 2 had distinct clear absorption bands indicating the presence of major humic acid structural elemental groups such as H bonded OH (3680cm^{-1} peak), C=O of carbonyl (1721cm^{-1} peak), functional groups of aliphatic components CH_2 (2918cm^{-1} peak) and C-O stretching of polysaccharide (1168cm^{-1} peak). The positions of the absorption bands of the spectra fell within typical major absorption bands of humic acid which is at frequencies 3680, 2918, 1721, 1168 cm^{-1}. The first peak centred in the vicinity of 3680 cm^{-1} region is attributed to phenol OH group bounded by intermolecular H bonds. The 2918cm^{-1} band usually has absorption maximum at 2918 cm^{-1} which is due to C–H stretching of alkane group (CH_2). The next major absorption band is 1721 cm^{-1}. This band has been commonly ascribed to C=O stretching of mainly carboxyl group (COOH) with trace amount of ketones. The last peak was observed at 1168 cm^{-1} due to C–O stretching of polysaccharides and this peak appeared also in the spectra of humic acid from peat soil. The FTIR spectra of the isolated humic acid contained all major characteristic absorption peaks of humic acid. These absorption peaks indicated the presence of the major structural elements of humic acid namely H bonded OH, C=C of aromatic ring, C=O of carbonyl group (both carboxyl and ketonic), CH_2 group. This strongly supports the presence of humic acid.

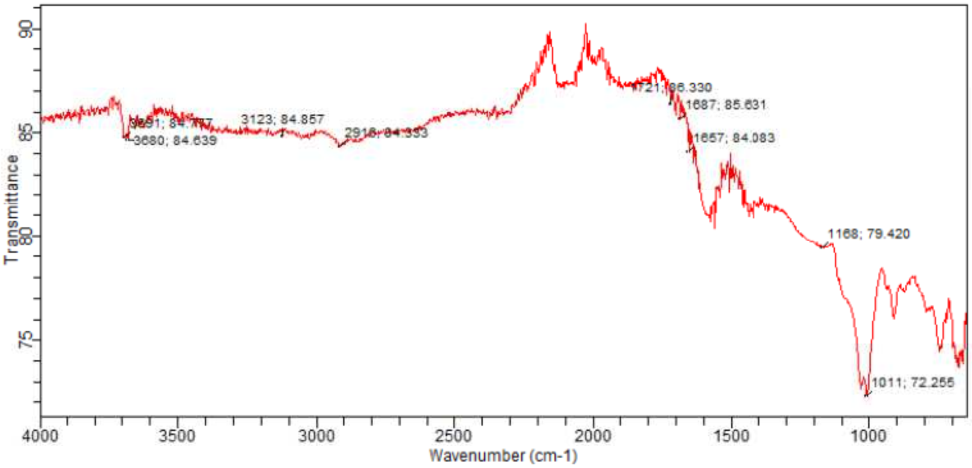


Fig. 2 : FT-IR spectraof peatsoilhumic acid (PSHA)

Evaluation of acid dissociation constant (pka) of acid hydrolysed peat soil humicacid at phenolic group

The value of the dissociation constant of the peat soil humic acid (PSHA) that underwent acidhydrolysis studied was found to be 8.9299 as shown Table 1, which is lower than the literaturevalues reported by Almeida and Szpoganics, (2015), Borges *et al*., (2005); Badr *et al*., (2012)and Fernandes *et al*,.(2009) of 9.73, 9.47 and 10.30. The difference between the obtained valuesand the reported values in this study might be probably as a result of acid hydrolysis of humicacid.

Table 1: PKa of (Hydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	$\log(\frac{nA}{1-nA})$	pKa
8.50	5.30	6.29	0.99	0.3594	-0.2510	8.2490
8.72	5.35	6.37	1.02	0.3400	-0.2880	8.4320
9.00	5.40	6.46	1.06	0.3141	-0.3391	8.6609
9.22	5.45	6.55	1.10	0.2882	-0.3927	8.8273
9.51	5.50	6.66	1.16	0.2494	-0.4786	9.0314
9.73	5.55	6.78	1.23	0.2041	-0.5910	9.1390
10.00	5.60	6.90	1.30	0.1589	-0.7238	9.2762
10.23	5.65	7.05	1.40	0.0941	-0.9835	9.2465
10.49	5.70	7.10	1.40	0.0941	-0.9835	9.5065

Average pKa = 8.9299 ± 0.4186

Table 2: PKa of (Unhydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	$\text{Log}(\frac{nA}{1-n})$	pKa
8.50	5.30	5.81	0.51	0.6619	0.2919	8.7919
8.72	5.35	5.90	0.55	0.6357	0.2418	8.9618
9.00	5.40	6.00	0.60	0.6029	0.1813	9.1813
9.22	5.45	6.10	0.65	0.5701	0.1226	9.3426
9.51	5.50	6.20	0.70	0.5376	0.0654	9.5754
9.73	5.55	6.33	0.78	0.4851	-0.0259	9.7041
10.00	5.60	6.47	0.87	0.4262	-0.1291	9.8709
10.23	5.65	6.62	0.99	0.3609	-0.2481	9.9819
10.49	5.70	6.80	1.10	0.2759	-0.4690	10.0210

Average pKa = 9.4923± 0.4410

Metal-ligand stability constant (Log K)

The stabilityconstants require the accurate values of proton-ligand stability constants (Anil and Maroti, 2008). Metal titration curves crossed over ligand titration curve indicated the formation of complex upon proton release (Santosh, *et al.*, 2011). If the values of n- are within range 0.2-0.8 and 1.2-18 this indicates the formation of 1:1 and 1:2 complexes (Sayyed and Mazahar, 2012).

The metal (II)-humate stepwise stability constants (log k) at phenolic group (Tables 3-18)

Table 3: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$\log(\frac{n}{1-n})$	$\text{Log}K_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

LogK_1 (Average value) = 2.4788± 0.2203

Table 4: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$\text{Log}(\frac{n-1}{2-n})$	$\text{Log}K_2$
9.51	5.50	6.66	6.73	0.07	1.3509	1.70	-0.2671	1.4329
9.73	5.55	6.78	6.85	0.07	1.6383	1.51	0.2467	1.7567
10.00	5.60	6.90	6.98	0.08	2.1783	1.31	-0.2158	1.0942
10.23	5.65	7.05	7.13	0.08	4.1904	1.27		
10.49	5.70	7.10	7.19	0.09	4.6920			

LogK_2(Average value) = 1.4280 ± 0.3312

Table 5:Point-wise method,Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	Log($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430

$LogK_1$ **(Average value)** = 2.3059± 0.6153

Table 6:Point-wise method, Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
9.73	5.55	6.33	6.42	0.09	0.9000	1.69		
10.00	5.60	6.47	6.58	0.11	1.2578	1.44	-0.4592	0.9808
10.23	5.65	6.62	6.84	0.12	1.6137	1.26	-0.2010	1.4610
10.49	5.70	6.80	6.92	0.12	2.1052	1.03		

$LogK_2$ **(Average value)** = 1.2209± 0.3398

Table 7:Point-wise method,Pb (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n}{1-n}$)	$LogK_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.60	0.05	0.8333	1.96	0.6989	2.6589

$LogK_1$ (Average value) = 2.5832 ±0.1614

Table 8:Point-wise method,Pb-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n-1}{2-n}$)	$logK_2$
9.51	5.50	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.83	0.05	1.1702	1.44		
10.00	5.60	6.90	6.90	0.05	1.4864	1.22	-0.0237	1.1963
10.23	5.65	7.05	7.10	0.05	2.0190	1.09		
10.49	5.70	7.10	7.17	0.07	3.6492	1.00		

$LogK_2$(Average value) = 1.1963

Table 9:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log ($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.5477	2.3123
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	0.0272	2.2072
9.51	5.50	6.20	6.26	0.07	0.6417	1.89	0.2530	2.1430
9.73	5.55	6.40	6.40	0.07	0.7000	1.67	0.3680	2.0380

$LogK_1$ **(Average value)** = 2.2364 ± 0.1602

Table 10:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
10.00	5.60	6.47	6.55	0.08	1.9503	1.41		
10.23	5.65	6.62	6.72	0.11	1.4792	1.26	-0.0361	1.2239

$LogK_2$ **(Average value)** = 1.2239

Table 11:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n}{n-1}$)	$LogK_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4290	2.2110
8.72	5.35	6.37	6.39	0.02	0.2858	2.42	-0.3978	2.0222
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

$LogK_1$ (Average value)=2.1382**±**0.1046

Table 12:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$\log(\frac{n-1}{2-n})$	$LogK_2$
9.51	5.55	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.84	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.93	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.10		
10.49	5.70	7.10	7.18	0.07	3.6492	0.83		

$LogK_2$(Average value) = 1.5453 **±** 0.3450

Table 13:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$Log(\frac{n}{n-1})$	$Log\ K_1$
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.3477	2.3123
9.00	5.40	6.00	6.04	0.04	0.3236	2.38	-0.3202	2.0598
9.22	5.45	6.10	6.15	0.05	0.4297	2.17	-0.1230	2.0470
9.51	5.50	6.20	6.26	0.06	0.5500	1.89	0.0871	1.9771
9.73	5.55	6.33	6.40	0.07	0.7000	1.67	0.3680	2.0380

$LogK_1$ **(Average value)** = 2.1568 ± 0.2069

Table 14:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$Log(\frac{n-1}{2-n})$	$Log\ K_2$
10.00	5.60	6.47	6.55	0.08	0.9148	1.41		
10.23	5.65	6.62	6.71	0.09	1.2102	1.20	-0.5749	0.6251
10.49	5.70	6.80	6.92	0.09	1.5968	1.03	0.1703	1.2003

$LogK_2$ **(Average value)** = 0.9127± 0.4070

Table15:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$Log(\frac{n}{1-n})$	$LogK_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4210	2.2190
8.72	5.35	6.37	6.40	0.03	0.4286	2.42	-0.1249	2.2951
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.96	0.3010	2.2610
9.51	5.55	6.66	6.70	0.04	0.7720	1.67	0.5297	2.1997

$LogK_1$ (Average value) = 2.2108± 0.0825

Table 16:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$Log(\frac{n-1}{2-n})$	$Log\ K_2$
9.73	5.55	6.78	6.83	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.95	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.09		
10.49	5.70	7.10	7.16	0.06	3.1429	0.89		

$LogK_2$ **(Average value)** = 1.5453± 0.3450

Table 17:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$Log(\frac{n}{n-1})$	$Log\ K_1$
8.50	5.30	5.81	5.86	0.05	0.3717	2.88	-0.2280	2.6520
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.06	0.06	0.4853	2.38	-0.0255	2.3545
9.22	5.45	6.10	6.16	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430
9.73	5.55	6.33	6.41	0.08	0.8000	1.69	0.6020	2.2920

$LogK_1$ **(Average value)** = 2.2516± 0.5380

Table 18:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$\text{Log}(\frac{n-1}{2-n})$	Log K_2
10.00	5.60	6.47	6.57	0.10	1.1434	1.43		
10.23	5.65	6.62	6.72	0.10	1.3448	1.23	-0.2788	0.9512
10.49	5.70	6.80	6.90	0.10	1.7742	1.03	0.5351	1.5651

LogK_2 **(Average value)** = 1.2581± 0.4340

Table 19: Stepwise and overall Stability constants of thehydrolysed and unhydrolysed divalent metal (II) complexes

Chelates	**LogK_1**	**LogK_2**	**Logβ**
[Cu (Hydrolysed PSHA-1)$_2$]	2.4788	1.4280	3.9068
[Pb (Hydrolysed PSHA-1)$_2$]	2.5832	1.1963	3.7795
[Cd (Hydrolysed PSHA-1)$_2$]	2.2108	1.5453	3.7561
[Mg (Hydrolysed PSHA-1)$_2$]	2.1382	1.5453	3.6835
[Cu (Unhydrolysed PSHA-1)$_2$]	2.3059	1.2209	3.5268
[Pb (Unhydrolysed PSHA-1)$_2$]	2.2364	1.2239	3.4603
[Cd (Unhydrolysed PSHA-1)$_2$]	2.2516	1.2581	3.5097
[Mg (Unydrolysed PSHA-1)$_2$]	2.1568	0.9127	3.0695

The results obtained (Table19) shows the stepwise and overall stability constants to be not high indicating low stability of the complexes, because the solubility of most metal ions in the basic pH range is minimal due to metal hydroxide precipitation (Karimi, 2017). In general, the stepwise stability constants (K_1 and K_2) follow the order $K_1 > K_2$ for the copper, lead, magnesium and cadmium complexes respectively. The steady decrease of the values with increasing number of ligands is in agreement with the prediction made by researchers (Na'aliya, 2013). The decrease could be attributed to the fact that as the number of the ligands (Humate ions) that enters the coordination zone increases the aqua molecules available for replacement by the ligands become less. Thus, the metal ions become less electron loving with progressive intake of the ligand and this results in the decrease in the values of the constants (Na'aliya, 2013). Also the stability of the complexes is influenced by the size and number of the chelate rings(Mackay and Mackay,2002).All the complexes form rings in their structure as humate, a bidentate ligand, bond the metal ions in the ratio 1:2 (Boguta and Sokolowska, 2016) forming chelate rings. The values of the overall stability constants (logβ) obtained for humate complexes are not high indicating low stability as the values are not high. LogK values for copper-humates (Table 3 to 6) obtained in this study are lower than those reported for the complexes of humic acids (Pandey *et al*., 2015; Dinu, 2013; Kaschl *et al*., 2010 and Gilbeto and Jorg, 2001). The values of LogK(Table 7 to 10) forlead-humates are lower than those reported for the lead in the literature (Dinu, 2013; Gilbeto and Jorg 2001). Log K values(Table 11 to 14) for magnesium-humates obtained in this study are close to those reported by (Pandey *et al*., 2015). Log K values of cadmium-humates (Table 15 to 18) obtained in this work near to the one reported by (Dinu, 2013 and Pandey *et al*., 2015).The difference between the reported values and the values obtained in this study might be probably as a result of acid hydrolysis of humic acid. The values of the overall stability constants (log β) of the copper humates complexes presented in Table 19 is high than that of other metal humate complexes, show relatively high stability of Cu-HA complexes, show the following order of stability: Cu >Pb> Cd > Mg; which are in close agreement to the findings of (Dinu, 2013 and Pandey *et al*., 2015).The high stability of Cu-humate chelate could be attributed to the existence of coordinate covalent bond between the complexing agents and the Cu^{2+} ions. Since, Cu^{2+} being a metal of the transitional series with $3d^9$ electronic configurations can accept the electrons from the complexing agents. Similarly,the low stabilities of Pb,Cd and Mg -complexes could be explained by that Pb^{2+} with $6s^2$, Cd^{2+} with $4d^{10}$ and Mg^{2+} with $2p^6$ their electronic configuration has a completely filled d,p and s orbitals. Moreover, the stabilities of metal ions with hydrolysed humic acid from peat soil were higher than those with unhydrolysed humic acid from peat soil; which is ascribed to the high content of acidity in hydrolysed humic acid than unhydrolysed humic acid.

CONCLUSION

The values of logK for Cu(II) hydrolysed humic acid complex was higher followed by Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes as compared with metal(II) unhydrolysed humic acid complexes . This indicates acid hydrolysis of humic acid can enhance the complexation behavior of humic acid with metal (II) ions. However, the higher values of logβ for Cu(II), Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes indicates more stable stepwise complexes formed as compared with Cu(II), Pb(II), Cd(II) and Mg(II) unhydrolysed humic acid complexes.

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STABILITY CONSTANTS OF COMPLEXES OF METAL IONS WITH PEATSOIL HUMIC ACIDS UNDER NON-ACID-CONDITIONS

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ABSTRACT

Stability constants of complexes of four divalent metal ions viz. Cu^{2+}, Pb^{2+},Mg^{2+} and Cd^{2+} with humic acids (HA) were determined by potentiometric titration of humic acids with the corresponding salt of the divalent metals in aqueous media under non-acid-condition. The log K (logarithm of the stability constant) ranged from 1.0942 to 2.7471 for metal-humic acid complexes were determined using point-wise computational method. The order of stability constants were obtained as follows: Cu >Pb> Cd > Mg for metal -HA complexes respectively, indicating a higher degree of complexation with Cu metal ion.

Keywords: stability constant, humic acid, potentiometric titration, divalent metals, acid hydrolysis.

NTRODUCTION

The stability constant of a complex is the numerical expression of its stability and provides a quantitative measure of affinity of the metal ion to the complexing agent. An understanding of the relative stability of metal-complexes helps in predicting the behavior of metal ions in the soil (Ram and Raman, 1982). Extensive researches has been done to determine the stability constants of the complexes formed between humic acid (HA) with a number of metal ions. Ashok *et al*., (2000) reported that humic acid with hydroxyl, phenoxyl and carboxyl reactive groups can form coordination compound with metal ions at pH 3.5. The stability constants(Log K) for different metal-humic acid complexes indicated the following order of the stabilities of complexes formed between humic acid and metal ion, Cu >Fe >Pb> Ni > Co > Ca > Cd > Zn >Mn> Mg. Andelkovic *et al*., (2010) investigated the binding of Cd(II) to soil humic acid at pH 6.5 and in 0.1M KNO_3 ionic medium. The stability constant for binding indicating greater stability in the case when carboxyl groups are involved in complexation reaction. Kostic *et al*.,(2012) investigated the complexation of humic acid with certain heavy metal ions (Co(II), Ni(II),Cu(II), Zn(II), and Pb(II). The experiment was performed at 25°C, at pH 4.0 and ionic strength of 0.01M. Stability constant of complex between Pb(II) ions and humic acid is greater than stability constants of other investigated metal-humate complexes. Bogata and Sokolowska (2016) analyses the interaction between humic acids from different soils and Zn (II) ions at wide concentration ranges and at pH 5. Studies have showed significant impact of Zn concentration, pH and some properties of humic acids with zinc.But all of these studies were limited to acidic pH range. Therefore, the present study was carried out to determine and compare the stability constants of complexes of metal ions with hydrolysed peat soil humic acid and unhydrolysed peat soil humic under non-acid conditions.

MATERIALS AND METHODS

Analytical grade chemicals used includes hydrochloric acid (HCl), nitric acid (HNO_3), sodium hydroxide (NaOH), lead nitrate $Pb(NO_3)_2$, copper nitrate $Cu(NO_3)_2.3H_2O$, cadmium nitrate $Cd(NO_3)_2.4H_2O$, magnesium nitrate $Mg(NO_3)_2.6H_2O$, potassium nitrate (KNO_3), calcium chloride ($CaCl_2$), (sigma-Aldrich). Dowex 50WX8, (20-50 mesh) from Fluka.

Area of study

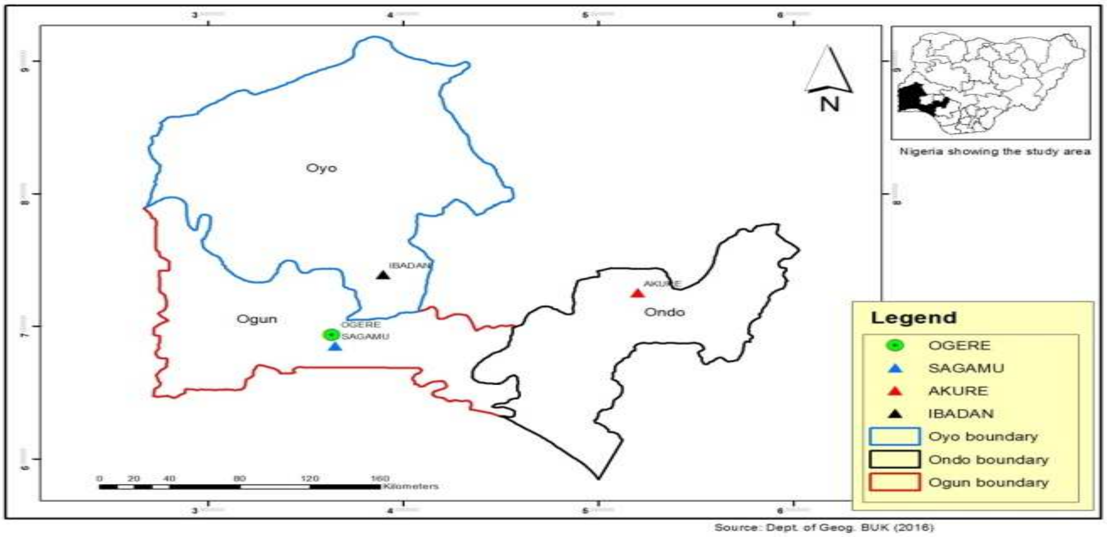

Figure 1: Map showing the sampling point at Sagamu Town, Ogun State.

Description of Sampling Area

Sagamu has geographical coordinates between 6°50′ north; 3° 38′ east is located in south western region of Nigeria. The region has tropical wet and dry climate with a lengthy wet season and relatively constant temperatures throughout the course of the year. Wet season runs from March to October, November to December forms the region dry season. The vegetation type of the region is savannah which is really grassland with small bushes and occasional big trees. Grassland soils have substantially higher organic matter content than forest soils (Novackova, 2011).

Sample Collection

The Peatsoil samples were collected from four different sampling points (0-10cm depth) in Sagamu into polyethylene bag with plastic spoons. Samples were taken to the laboratory, extraneous materials were removed; the samples were air-dried, crushed and ground to a fine powder in a mortar passed through a 0.20mm sieve. The samples were kept for analysis.

Isolation and purification of humic acid from peat soil sample

Peatsoil sample (100g) was mixed with 1000 cm^3 of 0.1M NaOH solution, shaken for 3hours and left to stand overnight. Dark-coloured supernatant was obtained and decanted from solid residue. The dark-coloured supernatant was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 6 hours. Yellowish brown supernatant and dark-brown precipitate were obtained. The yellowish brown supernatant was decanted followed by centrifuge and discarded. The dark-brown precipitate was mixed with 500$cm^3$of 0.1M NaOH solution followed by passing through dowex resin. The dark-brown solution was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 3 hours. The dark-brown precipitate was washed several times with deionized water. The supernatant was treated with $AgNO_3$ solution until no white precipitate observed. The humic acid was transferred to weighed crucible and dried at 60°C in an oven for 12 hours. The humic acid was cooled and dried in the desiccator, weighed and recorded. The obtained humic acid was dried again at 60°C for additional 6 hours cooled and dried in the desiccator, weighed and recorded constant weight was obtained (Baruah *et al*., 2015).

FT-IR analysis

FT-IR spectra of humic acid sample was analysed using Carry 630 FT-IR Agilent Technologies.

Unhydrolysed compost humic acid

The unhydrolysed humic acid was obtained after isolation and purification of compost humic acid and kept for investigation.

Acid hydrolysis of Peatsoil acid

Peatsoil humic acid sample (1g) was refluxed for 12 hours at (160°C) with 50cm^3 of 6M HCl. The mixture was allowed to cool, decanted, and centrifuged after hydrolysis. The insoluble residues were washed with distilled water via centrifugation several times, and the supernatant was treated with $AgNO_3$ solution until no white precipitate was observed. The residue was thoroughly dried over $CaCl_2$ in a desiccator at room temperature (Chefetz *et al*., 2002). Finally, the obtained hydrolysed humic acid was kept for investigation.

Potentiometric Titrations

Potentiometric measurements were carried out using a pH-meter Jenway (model 3510) with combine electrode, the sensitivity of the pH -meter is 0.01 units. The pH meter was switched on half an hour before starting the titration for initial warm up of the instrument. The instrument was calibrated with an aqueous standard buffer solution of pH 4.00 and 10.0 (borate buffer) prepared from a "Qualigens" buffer tablets.

The following sets of solutions were prepared in a 250cm^3 volumetric flask separately for pH metric titrations.

(i) 5 cm^3 0.1 M HCl + 40 cm^3 deionized water
(ii) 5 cm^3 0.1 M HCl + 39 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid
(iii) 5 cm^3 0.1 M HCl + 37 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid + 2 cm^3 0.01 M Cu(II)

The solutions were titrated against standardized 0.110MNaOH separately. The total volume of each mixture was adjusted to 50 cm^3 and the ionic strength of the solutions was maintained constant at by adding appropriate amount of stock solution of 1M KNO$_3$ (Gamal, 2015; Omar and Ali, 2015). A magnetic stirrer was used to achieve thorough mixing of the interacting solutions at 550 rpm. The same set of experimental conditions was applied for potentiometric titration of remaining samples.

Evaluation of pKa of Hydrolysed peat soil Humic Acids

The proton-ligand formation number $n_{\mathbf{A}}$ were calculated by Irving and Rossotti expression (Omar and Ali, 2015).

$$nA = Y\text{-} \frac{(V2-V1)(No-Eo)}{(Vo+V1)TcL} \quad \text{.....................................} 1$$

Where: Y is number of dissociable proton, (V_2-V_1) is the measure of displacement of the ligand curve relative to acid curve, N^o and E^o are the resultant concentration of alkali solution, free acid solution, T_{cL}^{o} is the total ligand concentration, V^o is the total volume of titration solution,V_1 is the volume of alkali added to acid solution,V_2 is the volume of alkali added to acid solution + ligand solution, acid dissociation constants (pKa - values) of ligand were calculated by algebraic method point wise calculation (Tables 1). The dissociation constants (pKa) were calculated according to the following relation:

$$\text{pKa} = \text{pH} + \log(\frac{nA}{1-nA}) \quad \text{..............................} 2$$

Where: pKa is the acid dissociation constant, $n_A$is the Proton-ligand formation number and pH is the pH-values (Omar and Ali, 2015).

Determination of metal-ligand stability constants (log K) of complexes

The potentiometric measurement for the determination of stability constant of a complex in solution is based on the fact that the redox potential of the couple $\frac{M^{+(m-n)}}{M^{+m}}$ is shifted significantly on complexation of the metal ion with the ligand. This method involves change in hydrogen ion concentration [H$^+$] due to the displacement or association of one or more protons taking place during complexation reaction. This change can be found out by titrating the solutions containing free acid, acid with ligand, and acid with ligand and metal ion, individually against a standard alkali solution at a constant ionic strength or temperature. Either ionic strength or temperature may be varied for different sets of solutions. In all the cases, the change in the pH of the solution is measured after each addition of a known amount of alkali to the reaction cell which contains the reaction mixture. The titration curves are then drawn by plotting the measured pH values against the corresponding volume of alkali added and the stability constants of the complexes are determined from the titration curves by employing pH-metric titration technique given by (Irving and Rossoti).

Metal-ligand stability constants (Log K) were determined by using the following relations:

$$\bar{n} = \frac{(V_3 - V_2)(E^0 + N^0)}{(V^0 + V_2)\bar{n}_A T_m^0} \quad \text{...} 3$$

and

$$PL = \log_{10}\{\frac{1+\beta_n^H \dfrac{1}{[anti\ \log \text{pH}]^n}}{\text{T}_\text{L}^0 - \bar{n}T_m^0} \text{X} \frac{(V^0 + V_3)}{V^0}\} \quad \text{...} 4$$

Where $T_{L,}$ T^{o}, $E°$, and V^{o}havethe same significance as in equation (1) above, T_m denotes the total concentration of metal present in solution, V_3 is the volume of metal ions present in solution and β^H is the overall proton ligand stability constant. The metal-ligand stability constants (log K) were determined by employing point wise computational Method (eq. 5 and 6).

$\text{LogK}_1 = \log\left(\frac{n}{1-n}\right) + \text{pL}$ ………….5

$\text{LogK}_2 = \log\left(\frac{1-n}{2-n}\right) + \text{pL}$……………………6

Where: Log K is the metal-ligand stability constant, pL is the Free ligand exponent function, **n** is the Average number of ligand attached with metal ion (Janrao*et al*., 2014).The results obtained were analyzed by an ORIGIN 2016 program using titration data and then the proton-ligand stability constants (pKa) and Metal-ligand stability constant (LogK) calculated (Omar and Ali, 2015).

RESULTS AND DISCUSSION

Fourier transformed infrared (FT-IR) spectra of isolated humic acid from peat soils Figure 2 had distinct clear absorption bands indicating the presence of major humic acid structural elemental groups such as H bonded OH ($3680cm^{-1}$ peak), C=O of carbonyl ($1721cm^{-1}$ peak), functional groups of aliphatic components CH_2 ($2918cm^{-1}$ peak) and C-O stretching of polysaccharide ($1168cm^{-1}$ peak). The positions of the absorption bands of the spectra fell within typical major absorption bands of humic acid which is at frequencies 3680, 2918, 1721, 1168 cm^{-1}. The first peak centred in the vicinity of 3680 cm^{-1} region is attributed to phenol OH group bounded by intermolecular H bonds. The $2918cm^{-1}$ band usually has absorption maximum at 2918 cm^{-1} which is due to C–H stretching of alkane group (CH_2). The next major absorption band is 1721 cm^{-1}. This band has been commonly ascribed to C=O stretching of mainly carboxyl group (COOH) with trace amount of ketones. The last peak was observed at 1168 cm^{-1} due to C–O stretching of polysaccharides and this peak appeared also in the spectra of humic acid from peat soil. The FTIR spectra of the isolated humic acid contained all major characteristic absorption peaks of humic acid. These absorption peaks indicated the presence of the major structural elements of humic acid namely H bonded OH, C=C of aromatic ring, C=O of carbonyl group (both carboxyl and ketonic), CH_2 group. This strongly supports the presence of humic acid.

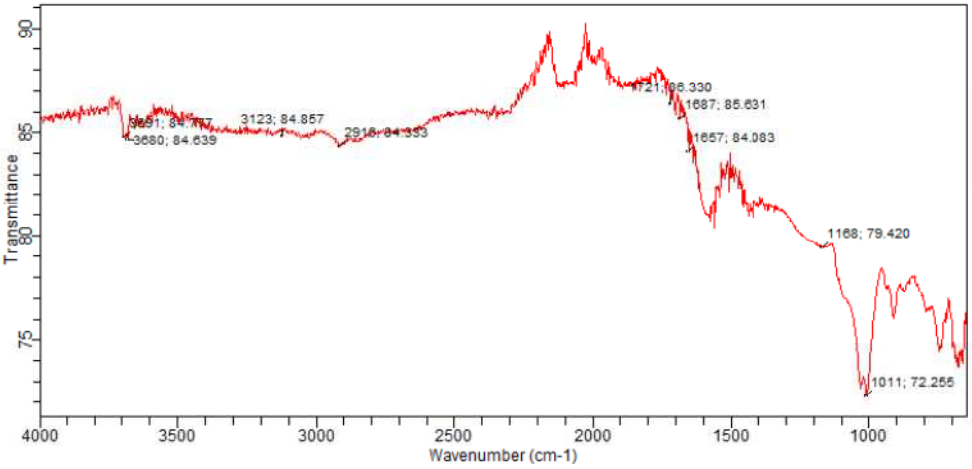

Fig. 2 : FT-IR spectraof peatsoilhumic acid (PSHA)

Evaluation of acid dissociation constant (pka) of acid hydrolysed peat soil humicacid at phenolic group

The value of the dissociation constant of the peat soil humic acid (PSHA) that underwent acidhydrolysis studied was found to be 8.9299 as shown Table 1, which is lower than the literaturevalues reported by Almeida and Szpoganics, (2015), Borges *et al*., (2005); Badr *et al*., (2012)and Fernandes *et al*,.(2009) of 9.73, 9.47 and 10.30. The difference between the obtained valuesand the reported values in this study might be probably as a result of acid hydrolysis of humicacid.

Table 1: PKa of (Hydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	log($\frac{nA}{1-nA}$)	pKa
8.50	5.30	6.29	0.99	0.3594	-0.2510	8.2490
8.72	5.35	6.37	1.02	0.3400	-0.2880	8.4320
9.00	5.40	6.46	1.06	0.3141	-0.3391	8.6609
9.22	5.45	6.55	1.10	0.2882	-0.3927	8.8273
9.51	5.50	6.66	1.16	0.2494	-0.4786	9.0314
9.73	5.55	6.78	1.23	0.2041	-0.5910	9.1390
10.00	5.60	6.90	1.30	0.1589	-0.7238	9.2762
10.23	5.65	7.05	1.40	0.0941	-0.9835	9.2465
10.49	5.70	7.10	1.40	0.0941	-0.9835	9.5065

Average pKa = 8.9299 ± 0.4186

Table 2: PKa of (Unhydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	Log($\frac{nA}{1-n}$)	pKa
8.50	5.30	5.81	0.51	0.6619	0.2919	8.7919
8.72	5.35	5.90	0.55	0.6357	0.2418	8.9618
9.00	5.40	6.00	0.60	0.6029	0.1813	9.1813
9.22	5.45	6.10	0.65	0.5701	0.1226	9.3426
9.51	5.50	6.20	0.70	0.5376	0.0654	9.5754
9.73	5.55	6.33	0.78	0.4851	-0.0259	9.7041
10.00	5.60	6.47	0.87	0.4262	-0.1291	9.8709
10.23	5.65	6.62	0.99	0.3609	-0.2481	9.9819
10.49	5.70	6.80	1.10	0.2759	-0.4690	10.0210

Average pKa = 9.4923± 0.4410

Metal-ligand stability constant (Log K)

The stabilityconstants require the accurate values of proton-ligand stability constants (Anil and Maroti, 2008). Metal titration curves crossed over ligand titration curve indicated the formation of complex upon proton release (Santosh, *et al.*, 2011). If the values of n- are within range 0.2-0.8 and 1.2-18 this indicates the formation of 1:1 and 1:2 complexes (Sayyed and Mazahar, 2012).

The metal (II)-humate stepwise stability constants (log k) at phenolic group (Tables 3-18)

Table 3: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n}{1-n}$)	$LogK_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

$LogK_1$ (Average value) = 2.4788± 0.2203

Table 4: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	Log($\frac{n-1}{2-n}$)	$LogK_2$
9.51	5.50	6.66	6.73	0.07	1.3509	1.70	-0.2671	1.4329
9.73	5.55	6.78	6.85	0.07	1.6383	1.51	0.2467	1.7567
10.00	5.60	6.90	6.98	0.08	2.1783	1.31	-0.2158	1.0942
10.23	5.65	7.05	7.13	0.08	4.1904	1.27		
10.49	5.70	7.10	7.19	0.09	4.6920			

$LogK_2$(Average value) = 1.4280 ± 0.3312

Table 5:Point-wise method,Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	Log$(\frac{n}{n-1})$	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430

$LogK_1$ **(Average value)** = 2.3059± 0.6153

Table 6:Point-wise method, Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log$(\frac{n-1}{2-n})$	Log K_2
9.73	5.55	6.33	6.42	0.09	0.9000	1.69		
10.00	5.60	6.47	6.58	0.11	1.2578	1.44	-0.4592	0.9808
10.23	5.65	6.62	6.84	0.12	1.6137	1.26	-0.2010	1.4610
10.49	5.70	6.80	6.92	0.12	2.1052	1.03		

$LogK_2$ **(Average value)** = 1.2209± 0.3398

Table 7:Point-wise method,Pb (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log$(\frac{n}{1-n})$	$LogK_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.60	0.05	0.8333	1.96	0.6989	2.6589

$LogK_1$ (Average value) = 2.5832 ±0.1614

Table 8:Point-wise method,Pb-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log$(\frac{n-1}{2-n})$	$logK_2$
9.51	5.50	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.83	0.05	1.1702	1.44		
10.00	5.60	6.90	6.90	0.05	1.4864	1.22	-0.0237	1.1963
10.23	5.65	7.05	7.10	0.05	2.0190	1.09		
10.49	5.70	7.10	7.17	0.07	3.6492	1.00		

$LogK_2$(Average value) = 1.1963

Table 9:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log $(\frac{n}{n-1})$	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.5477	2.3123
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	0.0272	2.2072
9.51	5.50	6.20	6.26	0.07	0.6417	1.89	0.2530	2.1430
9.73	5.55	6.40	6.40	0.07	0.7000	1.67	0.3680	2.0380

$LogK_1$ **(Average value)** = 2.2364 ± 0.1602

Table 10:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log$(\frac{n-1}{2-n})$	Log K_2
10.00	5.60	6.47	6.55	0.08	1.9503	1.41		
10.23	5.65	6.62	6.72	0.11	1.4792	1.26	-0.0361	1.2239

$LogK_2$ **(Average value)** = 1.2239

Table 11:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log$(\frac{n}{n-1})$	$LogK_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4290	2.2110
8.72	5.35	6.37	6.39	0.02	0.2858	2.42	-0.3978	2.0222
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

$LogK_1$ (Average value)=2.1382±0.1046

Table 12:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	$\log(\frac{n-1}{2-n})$	$LogK_2$
9.51	5.55	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.84	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.93	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.10		
10.49	5.70	7.10	7.18	0.07	3.6492	0.83		

$LogK_2$(Average value) = 1.5453 **±** 0.3450

Table 13:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$V_3\text{-}V_2$	n	pL	$Log(\frac{n}{n-1})$	$Log\ K_1$
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.3477	2.3123
9.00	5.40	6.00	6.04	0.04	0.3236	2.38	-0.3202	2.0598
9.22	5.45	6.10	6.15	0.05	0.4297	2.17	-0.1230	2.0470
9.51	5.50	6.20	6.26	0.06	0.5500	1.89	0.0871	1.9771
9.73	5.55	6.33	6.40	0.07	0.7000	1.67	0.3680	2.0380

$LogK_1$ **(Average value)** = 2.1568 ± 0.2069

Table 14:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$V_3\text{-}V_2$	n	pL	$Log(\frac{n-1}{2-n})$	$Log\ K_2$
10.00	5.60	6.47	6.55	0.08	0.9148	1.41		
10.23	5.65	6.62	6.71	0.09	1.2102	1.20	-0.5749	0.6251
10.49	5.70	6.80	6.92	0.09	1.5968	1.03	0.1703	1.2003

$LogK_2$ **(Average value)** = 0.9127± 0.4070

Table15:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	$Log(\frac{n}{1-n})$	$LogK_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4210	2.2190
8.72	5.35	6.37	6.40	0.03	0.4286	2.42	-0.1249	2.2951
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.96	0.3010	2.2610
9.51	5.55	6.66	6.70	0.04	0.7720	1.67	0.5297	2.1997

$LogK_1$ (Average value) = 2.2108± 0.0825

Table 16:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	$Log(\frac{n-1}{2-n})$	$Log\ K_2$
9.73	5.55	6.78	6.83	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.95	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.09		
10.49	5.70	7.10	7.16	0.06	3.1429	0.89		

$LogK_2$ **(Average value)** = 1.5453± 0.3450

Table 17:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$V_3\text{-}V_2$	n	pL	$Log(\frac{n}{n-1})$	$Log\ K_1$
8.50	5.30	5.81	5.86	0.05	0.3717	2.88	-0.2280	2.6520
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.06	0.06	0.4853	2.38	-0.0255	2.3545
9.22	5.45	6.10	6.16	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430
9.73	5.55	6.33	6.41	0.08	0.8000	1.69	0.6020	2.2920

$LogK_1$ **(Average value)** = 2.2516± 0.5380

Table 18:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log$(\frac{n-1}{2-n})$	Log K_2
10.00	5.60	6.47	6.57	0.10	1.1434	1.43		
10.23	5.65	6.62	6.72	0.10	1.3448	1.23	-0.2788	0.9512
10.49	5.70	6.80	6.90	0.10	1.7742	1.03	0.5351	1.5651

LogK_2 **(Average value)** = 1.2581± 0.4340

Table 19: Stepwise and overall Stability constants of thehydrolysed and unhydrolysed divalent metal (II) complexes

Chelates	**LogK_1**	**LogK_2**	**Logβ**
[Cu (Hydrolysed PSHA-1)$_2$]	2.4788	1.4280	3.9068
[Pb (Hydrolysed PSHA-1)$_2$]	2.5832	1.1963	3.7795
[Cd (Hydrolysed PSHA-1)$_2$]	2.2108	1.5453	3.7561
[Mg (Hydrolysed PSHA-1)$_2$]	2.1382	1.5453	3.6835
[Cu (Unhydrolysed PSHA-1)$_2$]	2.3059	1.2209	3.5268
[Pb (Unhydrolysed PSHA-1)$_2$]	2.2364	1.2239	3.4603
[Cd (Unhydrolysed PSHA-1)$_2$]	2.2516	1.2581	3.5097
[Mg (Unydrolysed PSHA-1)$_2$]	2.1568	0.9127	3.0695

The results obtained (Table19) shows the stepwise and overall stability constants to be not high indicating low stability of the complexes, because the solubility of most metal ions in the basic pH range is minimal due to metal hydroxide precipitation (Karimi, 2017). In general, the stepwise stability constants (K_1 and K_2) follow the order $K_1 > K_2$ for the copper, lead, magnesium and cadmium complexes respectively. The steady decrease of the values with increasing number of ligands is in agreement with the prediction made by researchers (Na'aliya, 2013). The decrease could be attributed to the fact that as the number of the ligands (Humate ions) that enters the coordination zone increases the aqua molecules available for replacement by the ligands become less. Thus, the metal ions become less electron loving with progressive intake of the ligand and this results in the decrease in the values of the constants (Na'aliya, 2013). Also the stability of the complexes is influenced by the size and number of the chelate rings(Mackay and Mackay,2002).All the complexes form rings in their structure as humate, a bidentate ligand, bond the metal ions in the ratio 1:2 (Boguta and Sokolowska, 2016) forming chelate rings. The values of the overall stability constants (logβ) obtained for humate complexes are not high indicating low stability as the values are not high. LogK values for copper-humates (Table 3 to 6) obtained in this study are lower than those reported for the complexes of humic acids (Pandey *et al.*, 2015; Dinu, 2013; Kaschl *et al.*, 2010 and Gilbeto and Jorg, 2001). The values of LogK(Table 7 to 10) forlead-humates are lower than those reported for the lead in the literature (Dinu, 2013; Gilbeto and Jorg 2001). Log K values(Table 11 to 14) for magnesium-humates obtained in this study are close to those reported by (Pandey *et al.*, 2015). Log K values of cadmium-humates (Table 15 to 18) obtained in this work near to the one reported by (Dinu, 2013 and Pandey *et al.*, 2015).The difference between the reported values and the values obtained in this study might be probably as a result of acid hydrolysis of humic acid. The values of the overall stability constants (log β) of the copper humates complexes presented in Table 19 is high than that of other metal humate complexes, show relatively high stability of Cu-HA complexes, show the following order of stability: Cu >Pb> Cd > Mg; which are in close agreement to the findings of (Dinu, 2013 and Pandey *et al.*, 2015).The high stability of Cu-humate chelate could be attributed to the existence of coordinate covalent bond between the complexing agents and the Cu^{2+} ions. Since, Cu^{2+} being a metal of the transitional series with $3d^9$ electronic configurations can accept the electrons from the complexing agents. Similarly,the low stabilities of Pb,Cd and Mg -complexes could be explained by that Pb^{2+} with $6s^2$, Cd^{2+} with $4d^{10}$ and Mg^{2+} with $2p^6$ their electronic configuration has a completely filled d,p and s orbitals. Moreover, the stabilities of metal ions with hydrolysed humic acid from peat soil were higher than those with unhydrolysed humic acid from peat soil; which is ascribed to the high content of acidity in hydrolysed humic acid than unhydrolysed humic acid.

CONCLUSION

The values of logK for Cu(II) hydrolysed humic acid complex was higher followed by Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes as compared with metal(II) unhydrolysed humic acid complexes . This indicates acid hydrolysis of humic acid can enhance the complexation behavior of humic acid with metal (II) ions. However, the higher values of logβ for Cu(II), Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes indicates more stable stepwise complexes formed as compared with Cu(II), Pb(II), Cd(II) and Mg(II) unhydrolysed humic acid complexes.

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STABILITY CONSTANTS OF COMPLEXES OF METAL IONS WITH PEATSOIL HUMIC ACIDS UNDER NON-ACID-CONDITIONS

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ABSTRACT
Stability constants of complexes of four divalent metal ions viz. Cu^{2+}, Pb^{2+},Mg^{2+} and Cd^{2+} with humic acids (HA) were determined by potentiometric titration of humic acids with the corresponding salt of the divalent metals in aqueous media under non-acid-condition. The log K (logarithm of the stability constant) ranged from 1.0942 to 2.7471 for metal-humic acid complexes were determined using point-wise computational method. The order of stability constants were obtained as follows: Cu >Pb> Cd > Mg for metal -HA complexes respectively, indicating a higher degree of complexation with Cu metal ion.
Keywords: stability constant, humic acid, potentiometric titration, divalent metals, acid hydrolysis.

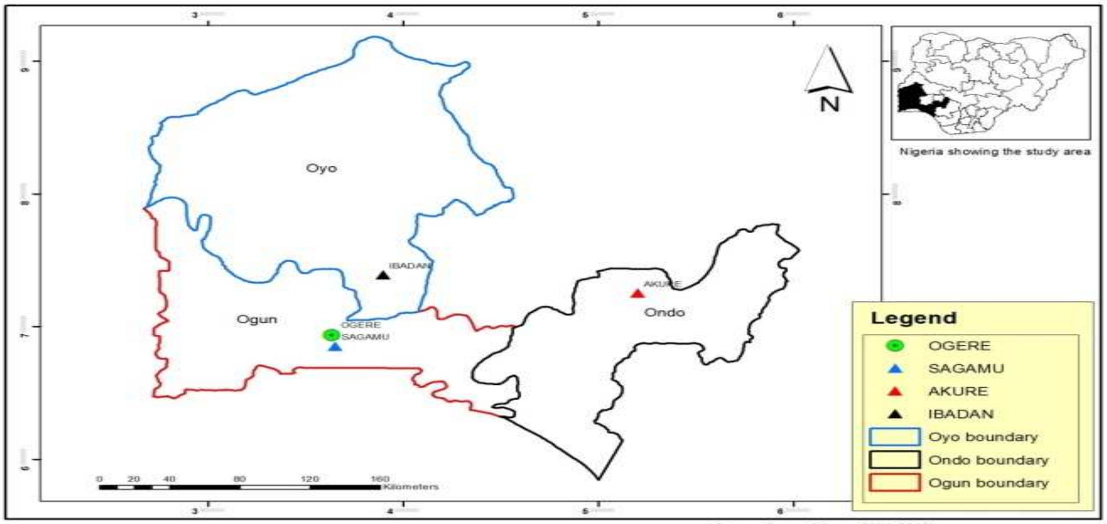
NTRODUCTION

The stability constant of a complex is the numerical expression of its stability and provides a quantitative measure of affinity of the metal ion to the complexing agent. An understanding of the relative stability of metal-complexes helps in predicting the behavior of metal ions in the soil (Ram and Raman, 1982). Extensive researches has been done to determine the stability constants of the complexes formed between humic acid (HA) with a number of metal ions. Ashok *et al*., (2000) reported that humic acid with hydroxyl, phenoxyl and carboxyl reactive groups can form coordination compound with metal ions at pH 3.5. The stability constants(Log K) for different metal-humic acid complexes indicated the following order of the stabilities of complexes formed between humic acid and metal ion, Cu >Fe >Pb> Ni > Co > Ca > Cd > Zn >Mn> Mg. Andelkovic *et al*., (2010) investigated the binding of Cd(II) to soil humic acid at pH 6.5 and in 0.1M KNO_3 ionic medium. The stability constant for binding indicating greater stability in the case when carboxyl groups are involved in complexation reaction. Kostic *et al*.,(2012) investigated the complexation of humic acid with certain heavy metal ions (Co(II), Ni(II),Cu(II), Zn(II), and Pb(II). The experiment was performed at 25°C, at pH 4.0 and ionic strength of 0.01M. Stability constant of complex between Pb(II) ions and humic acid is greater than stability constants of other investigated metal-humate complexes. Bogata and Sokolowska (2016) analyses the interaction between humic acids from different soils and Zn (II) ions at wide concentration ranges and at pH 5. Studies have showed significant impact of Zn concentration, pH and some properties of humic acids with zinc.But all of these studies were limited to acidic pH range. Therefore, the present study was carried out to determine and compare the stability constants of complexes of metal ions with hydrolysed peat soil humic acid and unhydrolysed peat soil humic under non-acid conditions.

MATERIALS AND METHODS

Analytical grade chemicals used includes hydrochloric acid (HCl), nitric acid (HNO_3), sodium hydroxide (NaOH), lead nitrate $Pb(NO_3)_2$, copper nitrate $Cu(NO_3)_2.3H_2O$, cadmium nitrate $Cd(NO_3)_2.4H_2O$, magnesium nitrate $Mg(NO_3)_2.6H_2O$, potassium nitrate (KNO_3), calcium chloride ($CaCl_2$), (sigma-Aldrich). Dowex 50WX8, (20-50 mesh) from Fluka.

Area of study



Source: Dept. of Geog. BUK (2016)

Figure 1: Map showing the sampling point at Sagamu Town, Ogun State.

Description of Sampling Area

Sagamu has geographical coordinates between 6°50′ north; 3° 38′ east is located in south western region of Nigeria. The region has tropical wet and dry climate with a lengthy wet season and relatively constant temperatures throughout the course of the year. Wet season runs from March to October, November to December forms the region dry season. The vegetation type of the region is savannah which is really grassland with small bushes and occasional big trees. Grassland soils have substantially higher organic matter content than forest soils (Novackova, 2011).

Sample Collection

The Peatsoil samples were collected from four different sampling points (0-10cm depth) in Sagamu into polyethylene bag with plastic spoons. Samples were taken to the laboratory, extraneous materials were removed; the samples were air-dried, crushed and ground to a fine powder in a mortar passed through a 0.20mm sieve. The samples were kept for analysis.

Isolation and purification of humic acid from peat soil sample

Peatsoil sample (100g) was mixed with 1000 cm^3 of 0.1M NaOH solution, shaken for 3hours and left to stand overnight. Dark-coloured supernatant was obtained and decanted from solid residue. The dark-coloured supernatant was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 6 hours. Yellowish brown supernatant and dark-brown precipitate were obtained. The yellowish brown supernatant was decanted followed by centrifuge and discarded. The dark-brown precipitate was mixed with 500$cm^3$of 0.1M NaOH solution followed by passing through dowex resin. The dark-brown solution was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 3 hours. The dark-brown precipitate was washed several times with deionized water. The supernatant was treated with $AgNO_3$ solution until no white precipitate observed. The humic acid was transferred to weighed crucible and dried at 60°C in an oven for 12 hours. The humic acid was cooled and dried in the desiccator, weighed and recorded. The obtained humic acid was dried again at 60°C for additional 6 hours cooled and dried in the desiccator, weighed and recorded constant weight was obtained (Baruah *et al*., 2015).

FT-IR analysis

FT-IR spectra of humic acid sample was analysed using Carry 630 FT-IR Agilent Technologies.

Unhydrolysed compost humic acid

The unhydrolysed humic acid was obtained after isolation and purification of compost humic acid and kept for investigation.

Acid hydrolysis of Peatsoil acid

Peatsoil humic acid sample (1g) was refluxed for 12 hours at (160°C) with 50cm^3 of 6M HCl. The mixture was allowed to cool, decanted, and centrifuged after hydrolysis. The insoluble residues were washed with distilled water via centrifugation several times, and the supernatant was treated with $AgNO_3$ solution until no white precipitate was observed. The residue was thoroughly dried over $CaCl_2$ in a desiccator at room temperature (Chefetz *et al*., 2002). Finally, the obtained hydrolysed humic acid was kept for investigation.

Potentiometric Titrations

Potentiometric measurements were carried out using a pH-meter Jenway (model 3510) with combine electrode, the sensitivity of the pH - meter is 0.01 units. The pH meter was switched on half an hour before starting the titration for initial warm up of the instrument. The instrument was calibrated with an aqueous standard buffer solution of pH 4.00 and 10.0 (borate buffer) prepared from a "Qualigens" buffer tablets.

The following sets of solutions were prepared in a 250cm^3 volumetric flask separately for pH metric titrations.

(i) 5 cm^3 0.1 M HCl + 40 cm^3 deionized water
(ii) 5 cm^3 0.1 M HCl + 39 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid
(iii) 5 cm^3 0.1 M HCl + 37 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid + 2 cm^3 0.01 M Cu(II)

The solutions were titrated against standardized 0.110MNaOH separately. The total volume of each mixture was adjusted to 50 cm^3 and the ionic strength of the solutions was maintained constant at by adding appropriate amount of stock solution of 1M KNO$_3$ (Gamal, 2015; Omar and Ali, 2015). A magnetic stirrer was used to achieve thorough mixing of the interacting solutions at 550 rpm. The same set of experimental conditions was applied for potentiometric titration of remaining samples.

Evaluation of pKa of Hydrolysed peat soil Humic Acids

The proton-ligand formation number n$_{\mathbf{A}}$ were calculated by Irving and Rossotti expression (Omar and Ali, 2015).

$$nA = Y- \frac{(V2-V1)(No-Eo)}{(Vo+V1)TcL} \quad ....1$$

Where: Y is number of dissociable proton, (V$_2$-V$_1$) is the measure of displacement of the ligand curve relative to acid curve, N^o and E^o are the resultant concentration of alkali solution, free acid solution, T$_{cL}$^{o} is the total ligand concentration, V^o is the total volume of titration solution,V$_1$ is the volume of alkali added to acid solution,V$_2$ is the volume of alkali added to acid solution + ligand solution, acid dissociation constants (pKa - values) of ligand were calculated by algebraic method point wise calculation (Tables 1). The dissociation constants (pKa) were calculated according to the following relation:

$$pKa = pH + \log\left(\frac{nA}{1-nA}\right) \quad ....2$$

Where: pKa is the acid dissociation constant, n$_A$is the Proton-ligand formation number and pH is the pH-values (Omar and Ali, 2015).

Determination of metal-ligand stability constants (log K) of complexes

The potentiometric measurement for the determination of stability constant of a complex in solution is based on the fact that the redox potential of the couple $\frac{M^{+(m-n)}}{M^{+m}}$ is shifted significantly on complexation of the metal ion with the ligand. This method involves change in hydrogen ion concentration [H$^+$] due to the displacement or association of one or more protons taking place during complexation reaction. This change can be found out by titrating the solutions containing free acid, acid with ligand, and acid with ligand and metal ion, individually against a standard alkali solution at a constant ionic strength or temperature. Either ionic strength or temperature may be varied for different sets of solutions. In all the cases, the change in the pH of the solution is measured after each addition of a known amount of alkali to the reaction cell which contains the reaction mixture. The titration curves are then drawn by plotting the measured pH values against the corresponding volume of alkali added and the stability constants of the complexes are determined from the titration curves by employing pH-metric titration technique given by (Irving and Rossoti).

Metal-ligand stability constants (Log K) were determined by using the following relations:

$$\bar{n} = \frac{(V_3 - V_2)(E^0 + N^0)}{(V^0 + V_2)\bar{n}_A T_m^0} \quad ....3$$

and

$$PL = \log_{10}\{\frac{1 + \beta_n^H \frac{1}{[anti\ \log pH]^n}}{T_L^0 - \bar{n}T_m^0} X \frac{(V^0 + V_3)}{V^0}\} \quad ....4$$

Where $T_{L,}$ T^o, E°, and V^ohavethe same significance as in equation (1) above, T_m denotes the total concentration of metal present in solution, V_3 is the volume of metal ions present in solution and β^H is the overall proton ligand stability constant. The metal-ligand stability constants (log K) were determined by employing point wise computational Method (eq. 5 and 6).

$$\mathrm{Log}K_1 = \log\left(\frac{n}{1-n}\right) + pL \qquad \ldots\ldots\ldots\ldots.5$$

$$\mathrm{Log}K_2 = \log\left(\frac{1-n}{2-n}\right) + pL\ldots\ldots\ldots\ldots\ldots\ldots\ldots.6$$

Where: Log K is the metal-ligand stability constant, pL is the Free ligand exponent function, **n** is the Average number of ligand attached with metal ion (Janrao*et al*., 2014).The results obtained were analyzed by an ORIGIN 2016 program using titration data and then the proton-ligand stability constants (pKa) and Metal-ligand stability constant (LogK) calculated (Omar and Ali, 2015).

RESULTS AND DISCUSSION

Fourier transformed infrared (FT-IR) spectra of isolated humic acid from peat soils Figure 2 had distinct clear absorption bands indicating the presence of major humic acid structural elemental groups such as H bonded OH ($3680cm^{-1}$ peak), C=O of carbonyl ($1721cm^{-1}$ peak), functional groups of aliphatic components CH_2 ($2918cm^{-1}$ peak) and C-O stretching of polysaccharide ($1168cm^{-1}$ peak). The positions of the absorption bands of the spectra fell within typical major absorption bands of humic acid which is at frequencies 3680, 2918, 1721, 1168 cm^{-1}. The first peak centred in the vicinity of 3680 cm^{-1} region is attributed to phenol OH group bounded by intermolecular H bonds. The $2918cm^{-1}$ band usually has absorption maximum at 2918 cm^{-1} which is due to C–H stretching of alkane group (CH_2). The next major absorption band is 1721 cm^{-1}. This band has been commonly ascribed to C=O stretching of mainly carboxyl group (COOH) with trace amount of ketones. The last peak was observed at 1168 cm^{-1} due to C–O stretching of polysaccharides and this peak appeared also in the spectra of humic acid from peat soil. The FTIR spectra of the isolated humic acid contained all major characteristic absorption peaks of humic acid. These absorption peaks indicated the presence of the major structural elements of humic acid namely H bonded OH, C=C of aromatic ring, C=O of carbonyl group (both carboxyl and ketonic), CH_2 group. This strongly supports the presence of humic acid.

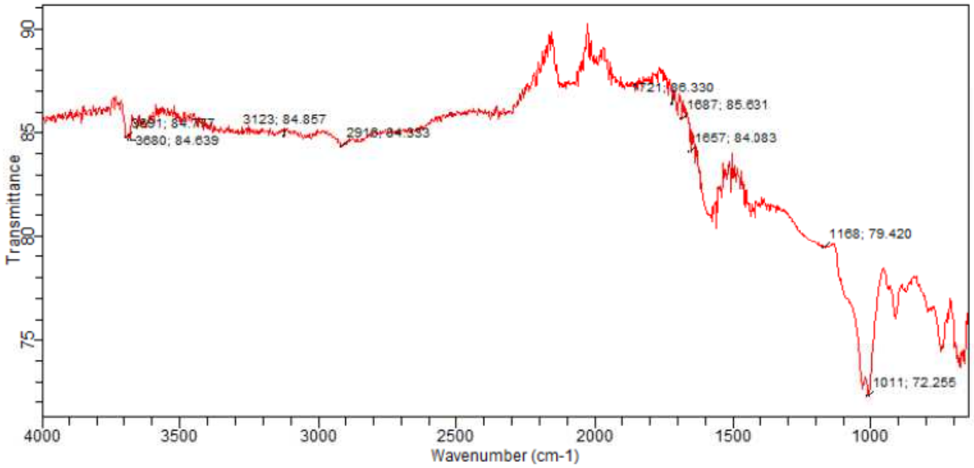


Fig. 2 : FT-IR spectraof peatsoilhumic acid (PSHA)

Evaluation of acid dissociation constant (pka) of acid hydrolysed peat soil humicacid at phenolic group

The value of the dissociation constant of the peat soil humic acid (PSHA) that underwent acidhydrolysis studied was found to be 8.9299 as shown Table 1, which is lower than the literaturevalues reported by Almeida and Szpoganics, (2015), Borges *et al*., (2005); Badr *et al*., (2012)and Fernandes *et al*,.(2009) of 9.73, 9.47 and 10.30. The difference between the obtained valuesand the reported values in this study might be probably as a result of acid hydrolysis of humicacid.

Table 1: PKa of (Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	V$_2$-V$_1$	nA	log($\frac{nA}{1-nA}$)	pKa
8.50	5.30	6.29	0.99	0.3594	-0.2510	8.2490
8.72	5.35	6.37	1.02	0.3400	-0.2880	8.4320
9.00	5.40	6.46	1.06	0.3141	-0.3391	8.6609
9.22	5.45	6.55	1.10	0.2882	-0.3927	8.8273
9.51	5.50	6.66	1.16	0.2494	-0.4786	9.0314
9.73	5.55	6.78	1.23	0.2041	-0.5910	9.1390
10.00	5.60	6.90	1.30	0.1589	-0.7238	9.2762
10.23	5.65	7.05	1.40	0.0941	-0.9835	9.2465
10.49	5.70	7.10	1.40	0.0941	-0.9835	9.5065

Average pKa = 8.9299 ± 0.4186

Table 2: PKa of (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	V$_2$-V$_1$	nA	Log($\frac{nA}{1-n}$)	pKa
8.50	5.30	5.81	0.51	0.6619	0.2919	8.7919
8.72	5.35	5.90	0.55	0.6357	0.2418	8.9618
9.00	5.40	6.00	0.60	0.6029	0.1813	9.1813
9.22	5.45	6.10	0.65	0.5701	0.1226	9.3426
9.51	5.50	6.20	0.70	0.5376	0.0654	9.5754
9.73	5.55	6.33	0.78	0.4851	-0.0259	9.7041
10.00	5.60	6.47	0.87	0.4262	-0.1291	9.8709
10.23	5.65	6.62	0.99	0.3609	-0.2481	9.9819
10.49	5.70	6.80	1.10	0.2759	-0.4690	10.0210

Average pKa = 9.4923± 0.4410

Metal-ligand stability constant (Log K)

The stabilityconstants require the accurate values of proton-ligand stability constants (Anil and Maroti, 2008). Metal titration curves crossed over ligand titration curve indicated the formation of complex upon proton release (Santosh, *et al.*, 2011). If the values of n- are within range 0.2-0.8 and 1.2-18 this indicates the formation of 1:1 and 1:2 complexes (Sayyed and Mazahar, 2012).

The metal (II)-humate stepwise stability constants (log k) at phenolic group (Tables 3-18)

Table 3: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	log($\frac{n}{1-n}$)	LogK$_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

LogK$_1$ (Average value) = 2.4788± 0.2203

Table 4: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	Log($\frac{n-1}{2-n}$)	LogK$_2$
9.51	5.50	6.66	6.73	0.07	1.3509	1.70	-0.2671	1.4329
9.73	5.55	6.78	6.85	0.07	1.6383	1.51	0.2467	1.7567
10.00	5.60	6.90	6.98	0.08	2.1783	1.31	-0.2158	1.0942
10.23	5.65	7.05	7.13	0.08	4.1904	1.27		
10.49	5.70	7.10	7.19	0.09	4.6920			

LogK$_2$(Average value) = 1.4280 ± 0.3312

Table 5:Point-wise method,Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	Log($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430

$LogK_1$ **(Average value)** = 2.3059± 0.6153

Table 6:Point-wise method, Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
9.73	5.55	6.33	6.42	0.09	0.9000	1.69		
10.00	5.60	6.47	6.58	0.11	1.2578	1.44	-0.4592	0.9808
10.23	5.65	6.62	6.84	0.12	1.6137	1.26	-0.2010	1.4610
10.49	5.70	6.80	6.92	0.12	2.1052	1.03		

$LogK_2$ **(Average value)** = 1.2209± 0.3398

Table 7:Point-wise method,Pb (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n}{1-n}$)	$LogK_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.60	0.05	0.8333	1.96	0.6989	2.6589

$LogK_1$ (Average value) = 2.5832 ±0.1614

Table 8:Point-wise method,Pb-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n-1}{2-n}$)	$logK_2$
9.51	5.50	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.83	0.05	1.1702	1.44		
10.00	5.60	6.90	6.90	0.05	1.4864	1.22	-0.0237	1.1963
10.23	5.65	7.05	7.10	0.05	2.0190	1.09		
10.49	5.70	7.10	7.17	0.07	3.6492	1.00		

$LogK_2$(Average value) = 1.1963

Table 9:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log ($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.5477	2.3123
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	0.0272	2.2072
9.51	5.50	6.20	6.26	0.07	0.6417	1.89	0.2530	2.1430
9.73	5.55	6.40	6.40	0.07	0.7000	1.67	0.3680	2.0380

$LogK_1$ **(Average value)** = 2.2364 ± 0.1602

Table 10:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
10.00	5.60	6.47	6.55	0.08	1.9503	1.41		
10.23	5.65	6.62	6.72	0.11	1.4792	1.26	-0.0361	1.2239

$LogK_2$ **(Average value)** = 1.2239

Table 11:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n}{n-1}$)	$LogK_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4290	2.2110
8.72	5.35	6.37	6.39	0.02	0.2858	2.42	-0.3978	2.0222
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

$LogK_1$ (Average value)=2.1382**±**0.1046

Table 12:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	log($\frac{n-1}{2-n}$)	LogK$_2$
9.51	5.55	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.84	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.93	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.10		
10.49	5.70	7.10	7.18	0.07	3.6492	0.83		

LogK$_2$(Average value) = 1.5453 **±** 0.3450

Table 13:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	V$_3$-V$_2$	n	pL	Log($\frac{n}{n-1}$)	Log K$_1$
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.3477	2.3123
9.00	5.40	6.00	6.04	0.04	0.3236	2.38	-0.3202	2.0598
9.22	5.45	6.10	6.15	0.05	0.4297	2.17	-0.1230	2.0470
9.51	5.50	6.20	6.26	0.06	0.5500	1.89	0.0871	1.9771
9.73	5.55	6.33	6.40	0.07	0.7000	1.67	0.3680	2.0380

LogK$_1$ **(Average value)** = 2.1568 ± 0.2069

Table 14:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	V$_3$-V$_2$	n	pL	Log($\frac{n-1}{2-n}$)	Log K$_2$
10.00	5.60	6.47	6.55	0.08	0.9148	1.41		
10.23	5.65	6.62	6.71	0.09	1.2102	1.20	-0.5749	0.6251
10.49	5.70	6.80	6.92	0.09	1.5968	1.03	0.1703	1.2003

LogK$_2$ **(Average value)** = 0.9127± 0.4070

Table15:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	Log($\frac{n}{1-n}$)	LogK$_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4210	2.2190
8.72	5.35	6.37	6.40	0.03	0.4286	2.42	-0.1249	2.2951
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.96	0.3010	2.2610
9.51	5.55	6.66	6.70	0.04	0.7720	1.67	0.5297	2.1997

LogK$_1$ (Average value) = 2.2108± 0.0825

Table 16:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	Log($\frac{n-1}{2-n}$)	Log K$_2$
9.73	5.55	6.78	6.83	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.95	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.09		
10.49	5.70	7.10	7.16	0.06	3.1429	0.89		

LogK$_2$ **(Average value)** = 1.5453± 0.3450

Table 17:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	V$_3$-V$_2$	n	pL	Log($\frac{n}{n-1}$)	Log K$_1$
8.50	5.30	5.81	5.86	0.05	0.3717	2.88	-0.2280	2.6520
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.06	0.06	0.4853	2.38	-0.0255	2.3545
9.22	5.45	6.10	6.16	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430
9.73	5.55	6.33	6.41	0.08	0.8000	1.69	0.6020	2.2920

LogK$_1$ **(Average value)** = 2.2516± 0.5380

Table 18:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
10.00	5.60	6.47	6.57	0.10	1.1434	1.43		
10.23	5.65	6.62	6.72	0.10	1.3448	1.23	-0.2788	0.9512
10.49	5.70	6.80	6.90	0.10	1.7742	1.03	0.5351	1.5651

$LogK_2$ **(Average value)** = 1.2581± 0.4340

Table 19: Stepwise and overall Stability constants of thehydrolysed and unhydrolysed divalent metal (II) complexes

Chelates	$LogK_1$	$LogK_2$	Logβ
[Cu (Hydrolysed PSHA-1)$_2$]	2.4788	1.4280	3.9068
[Pb (Hydrolysed PSHA-1)$_2$]	2.5832	1.1963	3.7795
[Cd (Hydrolysed PSHA-1)$_2$]	2.2108	1.5453	3.7561
[Mg (Hydrolysed PSHA-1)$_2$]	2.1382	1.5453	3.6835
[Cu (Unhydrolysed PSHA-1)$_2$]	2.3059	1.2209	3.5268
[Pb (Unhydrolysed PSHA-1)$_2$]	2.2364	1.2239	3.4603
[Cd (Unhydrolysed PSHA-1)$_2$]	2.2516	1.2581	3.5097
[Mg (Unydrolysed PSHA-1)$_2$]	2.1568	0.9127	3.0695

The results obtained (Table19) shows the stepwise and overall stability constants to be not high indicating low stability of the complexes, because the solubility of most metal ions in the basic pH range is minimal due to metal hydroxide precipitation (Karimi, 2017). In general, the stepwise stability constants (K_1 and K_2) follow the order $K_1 > K_2$ for the copper, lead, magnesium and cadmium complexes respectively. The steady decrease of the values with increasing number of ligands is in agreement with the prediction made by researchers (Na'aliya, 2013). The decrease could be attributed to the fact that as the number of the ligands (Humate ions) that enters the coordination zone increases the aqua molecules available for replacement by the ligands become less. Thus, the metal ions become less electron loving with progressive intake of the ligand and this results in the decrease in the values of the constants (Na'aliya, 2013). Also the stability of the complexes is influenced by the size and number of the chelate rings(Mackay and Mackay,2002).All the complexes form rings in their structure as humate, a bidentate ligand, bond the metal ions in the ratio 1:2 (Boguta and Sokolowska, 2016) forming chelate rings. The values of the overall stability constants (logβ) obtained for humate complexes are not high indicating low stability as the values are not high. LogK values for copper-humates (Table 3 to 6) obtained in this study are lower than those reported for the complexes of humic acids (Pandey *et al.*, 2015; Dinu, 2013; Kaschl *et al.*, 2010 and Gilbeto and Jorg, 2001). The values of LogK(Table 7 to 10) forlead-humates are lower than those reported for the lead in the literature (Dinu, 2013; Gilbeto and Jorg 2001). Log K values(Table 11 to 14) for magnesium-humates obtained in this study are close to those reported by (Pandey *et al.*, 2015). Log K values of cadmium-humates (Table 15 to 18) obtained in this work near to the one reported by (Dinu, 2013 and Pandey *et al.*, 2015).The difference between the reported values and the values obtained in this study might be probably as a result of acid hydrolysis of humic acid. The values of the overall stability constants (log β) of the copper humates complexes presented in Table 19 is high than that of other metal humate complexes, show relatively high stability of Cu-HA complexes, show the following order of stability: Cu >Pb> Cd > Mg; which are in close agreement to the findings of (Dinu, 2013 and Pandey *et al.*, 2015).The high stability of Cu-humate chelate could be attributed to the existence of coordinate covalent bond between the complexing agents and the Cu^{2+} ions. Since, Cu^{2+} being a metal of the transitional series with $3d^9$ electronic configurations can accept the electrons from the complexing agents. Similarly,the low stabilities of Pb,Cd and Mg -complexes could be explained by that Pb^{2+} with $6s^2$, Cd^{2+} with $4d^{10}$ and Mg^{2+} with $2p^6$ their electronic configuration has a completely filled d,p and s orbitals. Moreover, the stabilities of metal ions with hydrolysed humic acid from peat soil were higher than those with unhydrolysed humic acid from peat soil; which is ascribed to the high content of acidity in hydrolysed humic acid than unhydrolysed humic acid.

CONCLUSION

The values of logK for Cu(II) hydrolysed humic acid complex was higher followed by Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes as compared with metal(II) unhydrolysed humic acid complexes . This indicates acid hydrolysis of humic acid can enhance the complexation behavior of humic acid with metal (II) ions. However, the higher values of logβ for Cu(II), Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes indicates more stable stepwise complexes formed as compared with Cu(II), Pb(II), Cd(II) and Mg(II) unhydrolysed humic acid complexes.

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STABILITY CONSTANTS OF COMPLEXES OF METAL IONS WITH PEATSOIL HUMIC ACIDS UNDER NON-ACID-CONDITIONS

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ABSTRACT

Stability constants of complexes of four divalent metal ions viz. Cu^{2+}, Pb^{2+},Mg^{2+} and Cd^{2+} with humic acids (HA) were determined by potentiometric titration of humic acids with the corresponding salt of the divalent metals in aqueous media under non-acid-condition. The log K (logarithm of the stability constant) ranged from 1.0942 to 2.7471 for metal-humic acid complexes were determined using point-wise computational method. The order of stability constants were obtained as follows: Cu >Pb> Cd > Mg for metal -HA complexes respectively, indicating a higher degree of complexation with Cu metal ion.

Keywords: stability constant, humic acid, potentiometric titration, divalent metals, acid hydrolysis.

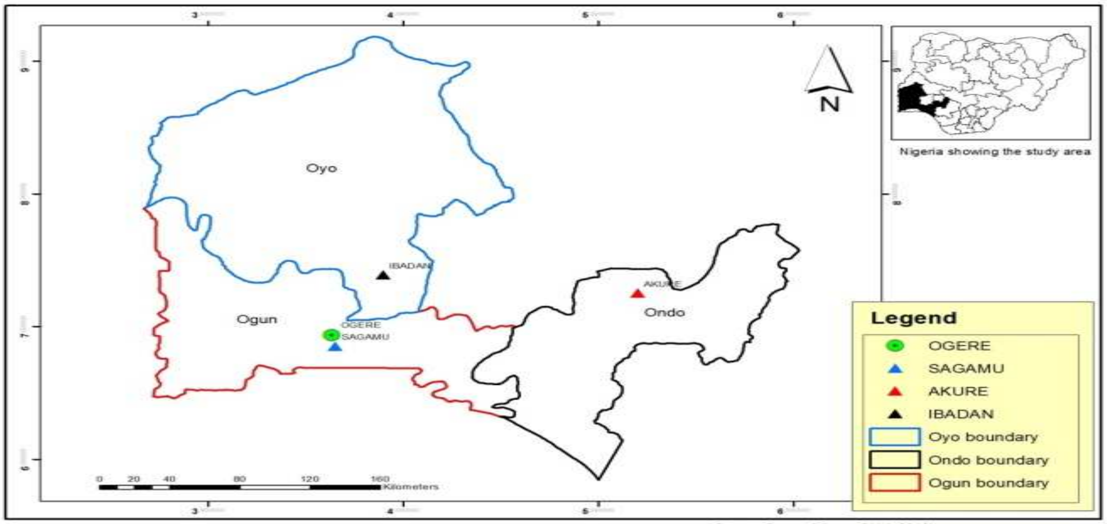
NTRODUCTION

The stability constant of a complex is the numerical expression of its stability and provides a quantitative measure of affinity of the metal ion to the complexing agent. An understanding of the relative stability of metal-complexes helps in predicting the behavior of metal ions in the soil (Ram and Raman, 1982). Extensive researches has been done to determine the stability constants of the complexes formed between humic acid (HA) with a number of metal ions. Ashok *et al.*, (2000) reported that humic acid with hydroxyl, phenoxyl and carboxyl reactive groups can form coordination compound with metal ions at pH 3.5. The stability constants(Log K) for different metal-humic acid complexes indicated the following order of the stabilities of complexes formed between humic acid and metal ion, Cu >Fe >Pb> Ni > Co > Ca > Cd > Zn >Mn> Mg. Andelkovic *et al.*, (2010) investigated the binding of Cd(II) to soil humic acid at pH 6.5 and in 0.1M KNO_3 ionic medium. The stability constant for binding indicating greater stability in the case when carboxyl groups are involved in complexation reaction. Kostic *et al.*,(2012) investigated the complexation of humic acid with certain heavy metal ions (Co(II), Ni(II),Cu(II), Zn(II), and Pb(II). The experiment was performed at 25°C, at pH 4.0 and ionic strength of 0.01M. Stability constant of complex between Pb(II) ions and humic acid is greater than stability constants of other investigated metal-humate complexes. Bogata and Sokolowska (2016) analyses the interaction between humic acids from different soils and Zn (II) ions at wide concentration ranges and at pH 5. Studies have showed significant impact of Zn concentration, pH and some properties of humic acids with zinc.But all of these studies were limited to acidic pH range. Therefore, the present study was carried out to determine and compare the stability constants of complexes of metal ions with hydrolysed peat soil humic acid and unhydrolysed peat soil humic under non-acid conditions.

MATERIALS AND METHODS

Analytical grade chemicals used includes hydrochloric acid (HCl), nitric acid (HNO_3), sodium hydroxide (NaOH), lead nitrate $Pb(NO_3)_2$, copper nitrate $Cu(NO_3)_2.3H_2O$, cadmium nitrate $Cd(NO_3)_2.4H_2O$, magnesium nitrate $Mg(NO_3)_2.6H_2O$, potassium nitrate (KNO_3), calcium chloride ($CaCl_2$), (sigma-Aldrich). Dowex 50WX8, (20-50 mesh) from Fluka.

Area of study



Source: Dept. of Geog. BUK (2016)

Figure 1: Map showing the sampling point at Sagamu Town, Ogun State.

Description of Sampling Area

Sagamu has geographical coordinates between 6°50′ north; 3° 38′ east is located in south western region of Nigeria. The region has tropical wet and dry climate with a lengthy wet season and relatively constant temperatures throughout the course of the year. Wet season runs from March to October, November to December forms the region dry season. The vegetation type of the region is savannah which is really grassland with small bushes and occasional big trees. Grassland soils have substantially higher organic matter content than forest soils (Novackova, 2011).

Sample Collection

The Peatsoil samples were collected from four different sampling points (0-10cm depth) in Sagamu into polyethylene bag with plastic spoons. Samples were taken to the laboratory, extraneous materials were removed; the samples were air-dried, crushed and ground to a fine powder in a mortar passed through a 0.20mm sieve. The samples were kept for analysis.

Isolation and purification of humic acid from peat soil sample

Peatsoil sample (100g) was mixed with 1000 cm^3 of 0.1M NaOH solution, shaken for 3hours and left to stand overnight. Dark-coloured supernatant was obtained and decanted from solid residue. The dark-coloured supernatant was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 6 hours. Yellowish brown supernatant and dark-brown precipitate were obtained. The yellowish brown supernatant was decanted followed by centrifuge and discarded. The dark-brown precipitate was mixed with 500$cm^3$of 0.1M NaOH solution followed by passing through dowex resin. The dark-brown solution was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 3 hours. The dark-brown precipitate was washed several times with deionized water. The supernatant was treated with $AgNO_3$ solution until no white precipitate observed. The humic acid was transferred to weighed crucible and dried at 60°C in an oven for 12 hours. The humic acid was cooled and dried in the desiccator, weighed and recorded. The obtained humic acid was dried again at 60°C for additional 6 hours cooled and dried in the desiccator, weighed and recorded constant weight was obtained (Baruah *et al.*, 2015).

FT-IR analysis

FT-IR spectra of humic acid sample was analysed using Carry 630 FT-IR Agilent Technologies.

Unhydrolysed compost humic acid

The unhydrolysed humic acid was obtained after isolation and purification of compost humic acid and kept for investigation.

Acid hydrolysis of Peatsoil acid

Peatsoil humic acid sample (1g) was refluxed for 12 hours at (160°C) with 50cm^3 of 6M HCl. The mixture was allowed to cool, decanted, and centrifuged after hydrolysis. The insoluble residues were washed with distilled water via centrifugation several times, and the supernatant was treated with $AgNO_3$ solution until no white precipitate was observed. The residue was thoroughly dried over $CaCl_2$ in a desiccator at room temperature (Chefetz *et al.*, 2002). Finally, the obtained hydrolysed humic acid was kept for investigation.

Potentiometric Titrations

Potentiometric measurements were carried out using a pH-meter Jenway (model 3510) with combine electrode, the sensitivity of the pH - meter is 0.01 units. The pH meter was switched on half an hour before starting the titration for initial warm up of the instrument. The instrument was calibrated with an aqueous standard buffer solution of pH 4.00 and 10.0 (borate buffer) prepared from a "Qualigens" buffer tablets.

The following sets of solutions were prepared in a 250cm^3 volumetric flask separately for pH metric titrations.

(i) 5 cm^3 0.1 M HCl + 40 cm^3 deionized water

(ii) 5 cm^3 0.1 M HCl + 39 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid

(iii) 5 cm^3 0.1 M HCl + 37 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid + 2 cm^3 0.01 M Cu(II)

The solutions were titrated against standardized 0.110MNaOH separately. The total volume of each mixture was adjusted to 50 cm^3 and the ionic strength of the solutions was maintained constant at by adding appropriate amount of stock solution of 1M KNO$_3$ (Gamal, 2015; Omar and Ali, 2015). A magnetic stirrer was used to achieve thorough mixing of the interacting solutions at 550 rpm. The same set of experimental conditions was applied for potentiometric titration of remaining samples.

Evaluation of pKa of Hydrolysed peat soil Humic Acids

The proton-ligand formation number n$_{\mathbf{A}}$ were calculated by Irving and Rossotti expression (Omar and Ali, 2015).

$$nA = Y - \frac{(V2-V1)(No-Eo)}{(Vo+V1)TcL} \quad \text{....................................1}$$

Where: Y is number of dissociable proton, (V$_2$-V$_1$) is the measure of displacement of the ligand curve relative to acid curve, N^o and E^o are the resultant concentration of alkali solution, free acid solution, T$_{cL}$^{o} is the total ligand concentration, V^o is the total volume of titration solution,V$_1$ is the volume of alkali added to acid solution,V$_2$ is the volume of alkali added to acid solution + ligand solution, acid dissociation constants (pKa - values) of ligand were calculated by algebraic method point wise calculation (Tables 1). The dissociation constants (pKa) were calculated according to the following relation:

$$pKa = pH + \log\left(\frac{nA}{1-nA}\right) \quad \text{..............................2}$$

Where: pKa is the acid dissociation constant, n$_A$is the Proton-ligand formation number and pH is the pH-values (Omar and Ali, 2015).

Determination of metal-ligand stability constants (log K) of complexes

The potentiometric measurement for the determination of stability constant of a complex in solution is based on the fact that the redox potential of the couple $\frac{M^{+(m-n)}}{M^{+m}}$ is shifted significantly on complexation of the metal ion with the ligand. This method involves change in hydrogen ion concentration [H$^+$] due to the displacement or association of one or more protons taking place during complexation reaction. This change can be found out by titrating the solutions containing free acid, acid with ligand, and acid with ligand and metal ion, individually against a standard alkali solution at a constant ionic strength or temperature. Either ionic strength or temperature may be varied for different sets of solutions. In all the cases, the change in the pH of the solution is measured after each addition of a known amount of alkali to the reaction cell which contains the reaction mixture. The titration curves are then drawn by plotting the measured pH values against the corresponding volume of alkali added and the stability constants of the complexes are determined from the titration curves by employing pH-metric titration technique given by (Irving and Rossoti).

Metal-ligand stability constants (Log K) were determined by using the following relations:

$$\bar{n} = \frac{(V_3 - V_2)(E^0 + N^0)}{(V^0 + V_2)\bar{n}_A T_m^0} \quad \text{..3}$$

and

$$PL = \log_{10}\left\{\frac{1 + \beta_n^H \dfrac{1}{[anti\ \log pH]^n}}{T_L^0 - \bar{n}T_m^0} X \frac{(V^0 + V_3)}{V^0}\right\} \quad \text{..4}$$

Where $T_{L,}$ T^{o}, E°, and V^{o}havethe same significance as in equation (1) above, T_m denotes the total concentration of metal present in solution, V_3 is the volume of metal ions present in solution and β^H is the overall proton ligand stability constant. The metal-ligand stability constants (log K) were determined by employing point wise computational Method (eq. 5 and 6).

$$\mathrm{Log}K_1 = \log\left(\frac{n}{1-n}\right) + pL \qquad \ldots\ldots\ldots\ldots.5$$

$$\mathrm{Log}K_2 = \log\left(\frac{1-n}{2-n}\right) + pL \ldots\ldots\ldots\ldots\ldots\ldots\ldots.6$$

Where: Log K is the metal-ligand stability constant, pL is the Free ligand exponent function, **n** is the Average number of ligand attached with metal ion (Janrao*et al.*, 2014).The results obtained were analyzed by an ORIGIN 2016 program using titration data and then the proton-ligand stability constants (pKa) and Metal-ligand stability constant (LogK) calculated (Omar and Ali, 2015).

RESULTS AND DISCUSSION

Fourier transformed infrared (FT-IR) spectra of isolated humic acid from peat soils Figure 2 had distinct clear absorption bands indicating the presence of major humic acid structural elemental groups such as H bonded OH ($3680cm^{-1}$ peak), C=O of carbonyl ($1721cm^{-1}$ peak), functional groups of aliphatic components CH_2 ($2918cm^{-1}$ peak) and C-O stretching of polysaccharide ($1168cm^{-1}$ peak). The positions of the absorption bands of the spectra fell within typical major absorption bands of humic acid which is at frequencies 3680, 2918, 1721, 1168 cm^{-1}. The first peak centred in the vicinity of 3680 cm^{-1} region is attributed to phenol OH group bounded by intermolecular H bonds. The $2918cm^{-1}$ band usually has absorption maximum at 2918 cm^{-1} which is due to C–H stretching of alkane group (CH_2). The next major absorption band is 1721 cm^{-1}. This band has been commonly ascribed to C=O stretching of mainly carboxyl group (COOH) with trace amount of ketones. The last peak was observed at 1168 cm^{-1} due to C–O stretching of polysaccharides and this peak appeared also in the spectra of humic acid from peat soil. The FTIR spectra of the isolated humic acid contained all major characteristic absorption peaks of humic acid. These absorption peaks indicated the presence of the major structural elements of humic acid namely H bonded OH, C=C of aromatic ring, C=O of carbonyl group (both carboxyl and ketonic), CH_2 group. This strongly supports the presence of humic acid.

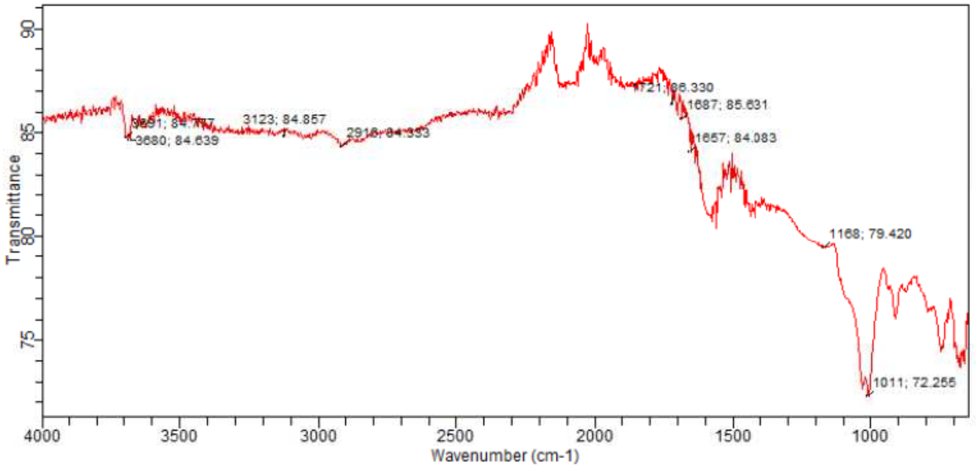


Fig. 2 : FT-IR spectraof peatsoilhumic acid (PSHA)

Evaluation of acid dissociation constant (pka) of acid hydrolysed peat soil humicacid at phenolic group

The value of the dissociation constant of the peat soil humic acid (PSHA) that underwent acidhydrolysis studied was found to be 8.9299 as shown Table 1, which is lower than the literaturevalues reported by Almeida and Szpoganics, (2015), Borges *et al.*, (2005); Badr *et al.*, (2012)and Fernandes *et al*,.(2009) of 9.73, 9.47 and 10.30. The difference between the obtained valuesand the reported values in this study might be probably as a result of acid hydrolysis of humicacid.

Table 1: PKa of (Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	V$_2$-V$_1$	nA	$\log(\frac{nA}{1-nA})$	pKa
8.50	5.30	6.29	0.99	0.3594	-0.2510	8.2490
8.72	5.35	6.37	1.02	0.3400	-0.2880	8.4320
9.00	5.40	6.46	1.06	0.3141	-0.3391	8.6609
9.22	5.45	6.55	1.10	0.2882	-0.3927	8.8273
9.51	5.50	6.66	1.16	0.2494	-0.4786	9.0314
9.73	5.55	6.78	1.23	0.2041	-0.5910	9.1390
10.00	5.60	6.90	1.30	0.1589	-0.7238	9.2762
10.23	5.65	7.05	1.40	0.0941	-0.9835	9.2465
10.49	5.70	7.10	1.40	0.0941	-0.9835	9.5065

Average pKa = 8.9299 ± 0.4186

Table 2: PKa of (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	V$_2$-V$_1$	nA	$\mathrm{Log}(\frac{nA}{1-n})$	pKa
8.50	5.30	5.81	0.51	0.6619	0.2919	8.7919
8.72	5.35	5.90	0.55	0.6357	0.2418	8.9618
9.00	5.40	6.00	0.60	0.6029	0.1813	9.1813
9.22	5.45	6.10	0.65	0.5701	0.1226	9.3426
9.51	5.50	6.20	0.70	0.5376	0.0654	9.5754
9.73	5.55	6.33	0.78	0.4851	-0.0259	9.7041
10.00	5.60	6.47	0.87	0.4262	-0.1291	9.8709
10.23	5.65	6.62	0.99	0.3609	-0.2481	9.9819
10.49	5.70	6.80	1.10	0.2759	-0.4690	10.0210

Average pKa = 9.4923± 0.4410

Metal-ligand stability constant (Log K)

The stabilityconstants require the accurate values of proton-ligand stability constants (Anil and Maroti, 2008). Metal titration curves crossed over ligand titration curve indicated the formation of complex upon proton release (Santosh, *et al.*, 2011). If the values of n- are within range 0.2-0.8 and 1.2-18 this indicates the formation of 1:1 and 1:2 complexes (Sayyed and Mazahar, 2012).

The metal (II)-humate stepwise stability constants (log k) at phenolic group (Tables 3-18)

Table 3: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	$\log(\frac{n}{1-n})$	LogK$_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

LogK$_1$ (Average value) = 2.4788± 0.2203

Table 4: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	$\mathrm{Log}(\frac{n-1}{2-n})$	LogK$_2$
9.51	5.50	6.66	6.73	0.07	1.3509	1.70	-0.2671	1.4329
9.73	5.55	6.78	6.85	0.07	1.6383	1.51	0.2467	1.7567
10.00	5.60	6.90	6.98	0.08	2.1783	1.31	-0.2158	1.0942
10.23	5.65	7.05	7.13	0.08	4.1904	1.27		
10.49	5.70	7.10	7.19	0.09	4.6920			

LogK$_2$(Average value) = 1.4280 ± 0.3312

Table 5:Point-wise method,Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	Log$(\frac{n}{n-1})$	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430

$LogK_1$ **(Average value)** = 2.3059± 0.6153

Table 6:Point-wise method, Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$V_3\text{-}V_2$	n	pL	Log$(\frac{n-1}{2-n})$	Log K_2
9.73	5.55	6.33	6.42	0.09	0.9000	1.69		
10.00	5.60	6.47	6.58	0.11	1.2578	1.44	-0.4592	0.9808
10.23	5.65	6.62	6.84	0.12	1.6137	1.26	-0.2010	1.4610
10.49	5.70	6.80	6.92	0.12	2.1052	1.03		

$LogK_2$ **(Average value)** = 1.2209± 0.3398

Table 7:Point-wise method,Pb (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	log$(\frac{n}{1-n})$	$LogK_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.60	0.05	0.8333	1.96	0.6989	2.6589

$LogK_1$ (Average value) = 2.5832 ±0.1614

Table 8:Point-wise method,Pb-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	log$(\frac{n-1}{2-n})$	$logK_2$
9.51	5.50	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.83	0.05	1.1702	1.44		
10.00	5.60	6.90	6.90	0.05	1.4864	1.22	-0.0237	1.1963
10.23	5.65	7.05	7.10	0.05	2.0190	1.09		
10.49	5.70	7.10	7.17	0.07	3.6492	1.00		

$LogK_2$(Average value) = 1.1963

Table 9:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$V_3\text{-}V_2$	n	pL	Log $(\frac{n}{n-1})$	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.5477	2.3123
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	0.0272	2.2072
9.51	5.50	6.20	6.26	0.07	0.6417	1.89	0.2530	2.1430
9.73	5.55	6.40	6.40	0.07	0.7000	1.67	0.3680	2.0380

$LogK_1$ **(Average value)** = 2.2364 ± 0.1602

Table 10:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$V_3\text{-}V_2$	n	pL	Log$(\frac{n-1}{2-n})$	Log K_2
10.00	5.60	6.47	6.55	0.08	1.9503	1.41		
10.23	5.65	6.62	6.72	0.11	1.4792	1.26	-0.0361	1.2239

$LogK_2$ **(Average value)** = 1.2239

Table 11:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	log$(\frac{n}{n-1})$	$LogK_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4290	2.2110
8.72	5.35	6.37	6.39	0.02	0.2858	2.42	-0.3978	2.0222
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

$LogK_1$ (Average value)=2.1382**±**0.1046

Table 12:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n-1}{2-n}$)	LogK_2
9.51	5.55	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.84	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.93	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.10		
10.49	5.70	7.10	7.18	0.07	3.6492	0.83		

LogK_2(Average value) = 1.5453 **±** 0.3450

Table 13:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.3477	2.3123
9.00	5.40	6.00	6.04	0.04	0.3236	2.38	-0.3202	2.0598
9.22	5.45	6.10	6.15	0.05	0.4297	2.17	-0.1230	2.0470
9.51	5.50	6.20	6.26	0.06	0.5500	1.89	0.0871	1.9771
9.73	5.55	6.33	6.40	0.07	0.7000	1.67	0.3680	2.0380

LogK_1 **(Average value)** = 2.1568 ± 0.2069

Table 14:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
10.00	5.60	6.47	6.55	0.08	0.9148	1.41		
10.23	5.65	6.62	6.71	0.09	1.2102	1.20	-0.5749	0.6251
10.49	5.70	6.80	6.92	0.09	1.5968	1.03	0.1703	1.2003

LogK_2 **(Average value)** = 0.9127± 0.4070

Table15:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	Log($\frac{n}{1-n}$)	LogK_1
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4210	2.2190
8.72	5.35	6.37	6.40	0.03	0.4286	2.42	-0.1249	2.2951
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.96	0.3010	2.2610
9.51	5.55	6.66	6.70	0.04	0.7720	1.67	0.5297	2.1997

LogK_1 (Average value) = 2.2108± 0.0825

Table 16:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
9.73	5.55	6.78	6.83	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.95	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.09		
10.49	5.70	7.10	7.16	0.06	3.1429	0.89		

LogK_2 **(Average value)** = 1.5453± 0.3450

Table 17:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.86	0.05	0.3717	2.88	-0.2280	2.6520
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.06	0.06	0.4853	2.38	-0.0255	2.3545
9.22	5.45	6.10	6.16	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430
9.73	5.55	6.33	6.41	0.08	0.8000	1.69	0.6020	2.2920

LogK_1 **(Average value)** = 2.2516± 0.5380

Table 18:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$\text{Log}(\frac{n-1}{2-n})$	Log K_2
10.00	5.60	6.47	6.57	0.10	1.1434	1.43		
10.23	5.65	6.62	6.72	0.10	1.3448	1.23	-0.2788	0.9512
10.49	5.70	6.80	6.90	0.10	1.7742	1.03	0.5351	1.5651

LogK_2 **(Average value)** = 1.2581± 0.4340

Table 19: Stepwise and overall Stability constants of thehydrolysed and unhydrolysed divalent metal (II) complexes

Chelates	**LogK_1**	**LogK_2**	**Logβ**
[Cu (Hydrolysed PSHA-1)$_2$]	2.4788	1.4280	3.9068
[Pb (Hydrolysed PSHA-1)$_2$]	2.5832	1.1963	3.7795
[Cd (Hydrolysed PSHA-1)$_2$]	2.2108	1.5453	3.7561
[Mg (Hydrolysed PSHA-1)$_2$]	2.1382	1.5453	3.6835
[Cu (Unhydrolysed PSHA-1)$_2$]	2.3059	1.2209	3.5268
[Pb (Unhydrolysed PSHA-1)$_2$]	2.2364	1.2239	3.4603
[Cd (Unhydrolysed PSHA-1)$_2$]	2.2516	1.2581	3.5097
[Mg (Unydrolysed PSHA-1)$_2$]	2.1568	0.9127	3.0695

The results obtained (Table19) shows the stepwise and overall stability constants to be not high indicating low stability of the complexes, because the solubility of most metal ions in the basic pH range is minimal due to metal hydroxide precipitation (Karimi, 2017). In general, the stepwise stability constants (K_1 and K_2) follow the order $K_1 > K_2$ for the copper, lead, magnesium and cadmium complexes respectively. The steady decrease of the values with increasing number of ligands is in agreement with the prediction made by researchers (Na'aliya, 2013). The decrease could be attributed to the fact that as the number of the ligands (Humate ions) that enters the coordination zone increases the aqua molecules available for replacement by the ligands become less. Thus, the metal ions become less electron loving with progressive intake of the ligand and this results in the decrease in the values of the constants (Na'aliya, 2013). Also the stability of the complexes is influenced by the size and number of the chelate rings(Mackay and Mackay,2002).All the complexes form rings in their structure as humate, a bidentate ligand, bond the metal ions in the ratio 1:2 (Boguta and Sokolowska, 2016) forming chelate rings. The values of the overall stability constants (logβ) obtained for humate complexes are not high indicating low stability as the values are not high. LogK values for copper-humates (Table 3 to 6) obtained in this study are lower than those reported for the complexes of humic acids (Pandey *et al.*, 2015; Dinu, 2013; Kaschl *et al.*, 2010 and Gilbeto and Jorg, 2001). The values of LogK(Table 7 to 10) forlead-humates are lower than those reported for the lead in the literature (Dinu, 2013; Gilbeto and Jorg 2001). Log K values(Table 11 to 14) for magnesium-humates obtained in this study are close to those reported by (Pandey *et al.*, 2015). Log K values of cadmium-humates (Table 15 to 18) obtained in this work near to the one reported by (Dinu, 2013 and Pandey *et al.*, 2015).The difference between the reported values and the values obtained in this study might be probably as a result of acid hydrolysis of humic acid. The values of the overall stability constants (log β) of the copper humates complexes presented in Table 19 is high than that of other metal humate complexes, show relatively high stability of Cu-HA complexes, show the following order of stability: Cu >Pb> Cd > Mg; which are in close agreement to the findings of (Dinu, 2013 and Pandey *et al.*, 2015).The high stability of Cu-humate chelate could be attributed to the existence of coordinate covalent bond between the complexing agents and the Cu^{2+} ions. Since, Cu^{2+} being a metal of the transitional series with $3d^9$ electronic configurations can accept the electrons from the complexing agents. Similarly,the low stabilities of Pb,Cd and Mg -complexes could be explained by that Pb^{2+} with $6s^2$, Cd^{2+} with $4d^{10}$ and Mg^{2+} with $2p^6$ their electronic configuration has a completely filled d,p and s orbitals. Moreover, the stabilities of metal ions with hydrolysed humic acid from peat soil were higher than those with unhydrolysed humic acid from peat soil; which is ascribed to the high content of acidity in hydrolysed humic acid than unhydrolysed humic acid.

CONCLUSION

The values of logK for Cu(II) hydrolysed humic acid complex was higher followed by Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes as compared with metal(II) unhydrolysed humic acid complexes . This indicates acid hydrolysis of humic acid can enhance the complexation behavior of humic acid with metal (II) ions. However, the higher values of logβ for Cu(II), Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes indicates more stable stepwise complexes formed as compared with Cu(II), Pb(II), Cd(II) and Mg(II) unhydrolysed humic acid complexes.

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STABILITY CONSTANTS OF COMPLEXES OF METAL IONS WITH PEATSOIL HUMIC ACIDS UNDER NON-ACID-CONDITIONS

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ABSTRACT

Stability constants of complexes of four divalent metal ions viz. Cu^{2+}, Pb^{2+},Mg^{2+} and Cd^{2+} with humic acids (HA) were determined by potentiometric titration of humic acids with the corresponding salt of the divalent metals in aqueous media under non-acid-condition. The log K (logarithm of the stability constant) ranged from 1.0942 to 2.7471 for metal-humic acid complexes were determined using point-wise computational method. The order of stability constants were obtained as follows: Cu >Pb> Cd > Mg for metal -HA complexes respectively, indicating a higher degree of complexation with Cu metal ion.

Keywords: stability constant, humic acid, potentiometric titration, divalent metals, acid hydrolysis.

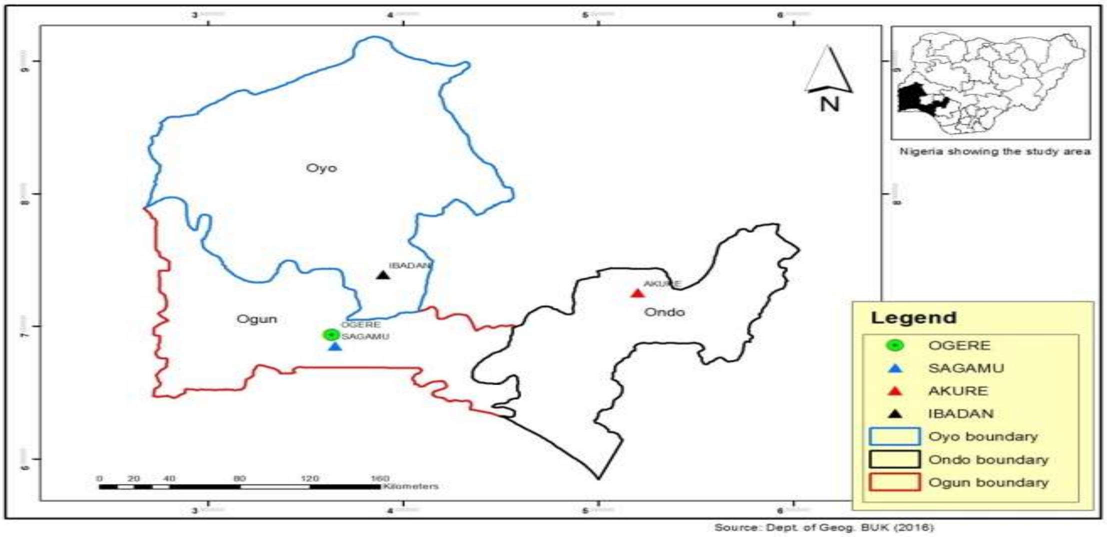
NTRODUCTION

The stability constant of a complex is the numerical expression of its stability and provides a quantitative measure of affinity of the metal ion to the complexing agent. An understanding of the relative stability of metal-complexes helps in predicting the behavior of metal ions in the soil (Ram and Raman, 1982). Extensive researches has been done to determine the stability constants of the complexes formed between humic acid (HA) with a number of metal ions. Ashok *et al.*, (2000) reported that humic acid with hydroxyl, phenoxyl and carboxyl reactive groups can form coordination compound with metal ions at pH 3.5. The stability constants(Log K) for different metal-humic acid complexes indicated the following order of the stabilities of complexes formed between humic acid and metal ion, Cu >Fe >Pb> Ni > Co > Ca > Cd > Zn >Mn> Mg. Andelkovic *et al.*, (2010) investigated the binding of Cd(II) to soil humic acid at pH 6.5 and in 0.1M KNO_3 ionic medium. The stability constant for binding indicating greater stability in the case when carboxyl groups are involved in complexation reaction. Kostic *et al.*,(2012) investigated the complexation of humic acid with certain heavy metal ions (Co(II), Ni(II),Cu(II), Zn(II), and Pb(II). The experiment was performed at 25°C, at pH 4.0 and ionic strength of 0.01M. Stability constant of complex between Pb(II) ions and humic acid is greater than stability constants of other investigated metal-humate complexes. Bogata and Sokolowska (2016) analyses the interaction between humic acids from different soils and Zn (II) ions at wide concentration ranges and at pH 5. Studies have showed significant impact of Zn concentration, pH and some properties of humic acids with zinc.But all of these studies were limited to acidic pH range. Therefore, the present study was carried out to determine and compare the stability constants of complexes of metal ions with hydrolysed peat soil humic acid and unhydrolysed peat soil humic under non-acid conditions.

MATERIALS AND METHODS

Analytical grade chemicals used includes hydrochloric acid (HCl), nitric acid (HNO_3), sodium hydroxide (NaOH), lead nitrate $Pb(NO_3)_2$, copper nitrate $Cu(NO_3)_2.3H_2O$, cadmium nitrate $Cd(NO_3)_2.4H_2O$, magnesium nitrate $Mg(NO_3)_2.6H_2O$, potassium nitrate (KNO_3), calcium chloride ($CaCl_2$), (sigma-Aldrich). Dowex 50WX8, (20-50 mesh) from Fluka.

Area of study



Source: Dept. of Geog. BUK (2016)

Figure 1: Map showing the sampling point at Sagamu Town, Ogun State.

Description of Sampling Area

Sagamu has geographical coordinates between 6°50′ north; 3° 38′ east is located in south western region of Nigeria. The region has tropical wet and dry climate with a lengthy wet season and relatively constant temperatures throughout the course of the year. Wet season runs from March to October, November to December forms the region dry season. The vegetation type of the region is savannah which is really grassland with small bushes and occasional big trees. Grassland soils have substantially higher organic matter content than forest soils (Novackova, 2011).

Sample Collection

The Peatsoil samples were collected from four different sampling points (0-10cm depth) in Sagamu into polyethylene bag with plastic spoons. Samples were taken to the laboratory, extraneous materials were removed; the samples were air-dried, crushed and ground to a fine powder in a mortar passed through a 0.20mm sieve. The samples were kept for analysis.

Isolation and purification of humic acid from peat soil sample

Peatsoil sample (100g) was mixed with 1000 cm^3 of 0.1M NaOH solution, shaken for 3hours and left to stand overnight. Dark-coloured supernatant was obtained and decanted from solid residue. The dark-coloured supernatant was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 6 hours. Yellowish brown supernatant and dark-brown precipitate were obtained. The yellowish brown supernatant was decanted followed by centrifuge and discarded. The dark-brown precipitate was mixed with $500cm^3$of 0.1M NaOH solution followed by passing through dowex resin. The dark-brown solution was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 3 hours. The dark-brown precipitate was washed several times with deionized water. The supernatant was treated with $AgNO_3$ solution until no white precipitate observed. The humic acid was transferred to weighed crucible and dried at 60°C in an oven for 12 hours. The humic acid was cooled and dried in the desiccator, weighed and recorded. The obtained humic acid was dried again at 60°C for additional 6 hours cooled and dried in the desiccator, weighed and recorded constant weight was obtained (Baruah *et al*., 2015).

FT-IR analysis

FT-IR spectra of humic acid sample was analysed using Carry 630 FT-IR Agilent Technologies.

Unhydrolysed compost humic acid

The unhydrolysed humic acid was obtained after isolation and purification of compost humic acid and kept for investigation.

Acid hydrolysis of Peatsoil acid

Peatsoil humic acid sample (1g) was refluxed for 12 hours at (160°C) with $50cm^3$ of 6M HCl. The mixture was allowed to cool, decanted, and centrifuged after hydrolysis. The insoluble residues were washed with distilled water via centrifugation several times, and the supernatant was treated with $AgNO_3$ solution until no white precipitate was observed. The residue was thoroughly dried over $CaCl_2$ in a desiccator at room temperature (Chefetz *et al*., 2002). Finally, the obtained hydrolysed humic acid was kept for investigation.

Potentiometric Titrations

Potentiometric measurements were carried out using a pH-meter Jenway (model 3510) with combine electrode, the sensitivity of the pH - meter is 0.01 units. The pH meter was switched on half an hour before starting the titration for initial warm up of the instrument. The instrument was calibrated with an aqueous standard buffer solution of pH 4.00 and 10.0 (borate buffer) prepared from a "Qualigens" buffer tablets.

The following sets of solutions were prepared in a 250cm^3 volumetric flask separately for pH metric titrations.

(i) 5 cm^3 0.1 M HCl + 40 cm^3 deionized water
(ii) 5 cm^3 0.1 M HCl + 39 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid
(iii) 5 cm^3 0.1 M HCl + 37 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid + 2 cm^3 0.01 M Cu(II)

The solutions were titrated against standardized 0.110MNaOH separately. The total volume of each mixture was adjusted to 50 cm^3 and the ionic strength of the solutions was maintained constant at by adding appropriate amount of stock solution of 1M KNO$_3$ (Gamal, 2015; Omar and Ali, 2015). A magnetic stirrer was used to achieve thorough mixing of the interacting solutions at 550 rpm. The same set of experimental conditions was applied for potentiometric titration of remaining samples.

Evaluation of pKa of Hydrolysed peat soil Humic Acids

The proton-ligand formation number n$_{\mathbf{A}}$ were calculated by Irving and Rossotti expression (Omar and Ali, 2015).

$$nA = Y- \frac{(V2-V1)(No-Eo)}{(Vo+V1)TcL} \text{ ....1}$$

Where: Y is number of dissociable proton, (V$_2$-V$_1$) is the measure of displacement of the ligand curve relative to acid curve, N^o and E^o are the resultant concentration of alkali solution, free acid solution, T$_{cL}{}^o$ is the total ligand concentration, V^o is the total volume of titration solution,V$_1$ is the volume of alkali added to acid solution,V$_2$ is the volume of alkali added to acid solution + ligand solution, acid dissociation constants (pKa - values) of ligand were calculated by algebraic method point wise calculation (Tables 1). The dissociation constants (pKa) were calculated according to the following relation:

$$pKa = pH + \log(\frac{nA}{1-nA}) \text{ ....2}$$

Where: pKa is the acid dissociation constant, n$_A$is the Proton-ligand formation number and pH is the pH-values (Omar and Ali, 2015).

Determination of metal-ligand stability constants (log K) of complexes

The potentiometric measurement for the determination of stability constant of a complex in solution is based on the fact that the redox potential of the couple $\frac{M^{+(m-n)}}{M^{+m}}$ is shifted significantly on complexation of the metal ion with the ligand. This method involves change in hydrogen ion concentration [H$^+$] due to the displacement or association of one or more protons taking place during complexation reaction. This change can be found out by titrating the solutions containing free acid, acid with ligand, and acid with ligand and metal ion, individually against a standard alkali solution at a constant ionic strength or temperature. Either ionic strength or temperature may be varied for different sets of solutions. In all the cases, the change in the pH of the solution is measured after each addition of a known amount of alkali to the reaction cell which contains the reaction mixture. The titration curves are then drawn by plotting the measured pH values against the corresponding volume of alkali added and the stability constants of the complexes are determined from the titration curves by employing pH-metric titration technique given by (Irving and Rossoti).

Metal-ligand stability constants (Log K) were determined by using the following relations:

$$\bar{n} = \frac{(V_3 - V_2)(E^0 + N^0)}{(V^0 + V_2)\bar{n}_A T_m^0} \text{ ....3}$$

and

$$PL = \log_{10}\{\frac{1+\beta_n^H \frac{1}{[anti\ \log pH]^n}}{T_L^0 - \bar{n}T_m^0} X \frac{(V^0+V_3)}{V^0}\} \text{ ....4}$$

Where $T_{L,}$ T^o, E°, and V^ohavethe same significance as in equation (1) above, T_m denotes the total concentration of metal present in solution, V_3 is the volume of metal ions present in solution and β^H is the overall proton ligand stability constant. The metal-ligand stability constants (log K) were determined by employing point wise computational Method (eq. 5 and 6).

$\mathrm{LogK}_1 = \log\left(\frac{n}{1-n}\right) + \mathrm{pL}$ …………..5

$\mathrm{LogK}_2 = \log\left(\frac{1-n}{2-n}\right) + \mathrm{pL}$……………………6

Where: Log K is the metal-ligand stability constant, pL is the Free ligand exponent function, **n** is the Average number of ligand attached with metal ion (Janrao*et al.*, 2014).The results obtained were analyzed by an ORIGIN 2016 program using titration data and then the proton-ligand stability constants (pKa) and Metal-ligand stability constant (LogK) calculated (Omar and Ali, 2015).

RESULTS AND DISCUSSION

Fourier transformed infrared (FT-IR) spectra of isolated humic acid from peat soils Figure 2 had distinct clear absorption bands indicating the presence of major humic acid structural elemental groups such as H bonded OH ($3680cm^{-1}$ peak), C=O of carbonyl ($1721cm^{-1}$ peak), functional groups of aliphatic components CH_2 ($2918cm^{-1}$ peak) and C-O stretching of polysaccharide ($1168cm^{-1}$ peak). The positions of the absorption bands of the spectra fell within typical major absorption bands of humic acid which is at frequencies 3680, 2918, 1721, 1168 cm^{-1}. The first peak centred in the vicinity of 3680 cm^{-1} region is attributed to phenol OH group bounded by intermolecular H bonds. The $2918cm^{-1}$ band usually has absorption maximum at 2918 cm^{-1} which is due to C–H stretching of alkane group (CH_2). The next major absorption band is 1721 cm^{-1}. This band has been commonly ascribed to C=O stretching of mainly carboxyl group (COOH) with trace amount of ketones. The last peak was observed at 1168 cm^{-1} due to C–O stretching of polysaccharides and this peak appeared also in the spectra of humic acid from peat soil. The FTIR spectra of the isolated humic acid contained all major characteristic absorption peaks of humic acid. These absorption peaks indicated the presence of the major structural elements of humic acid namely H bonded OH, C=C of aromatic ring, C=O of carbonyl group (both carboxyl and ketonic), CH_2 group. This strongly supports the presence of humic acid.

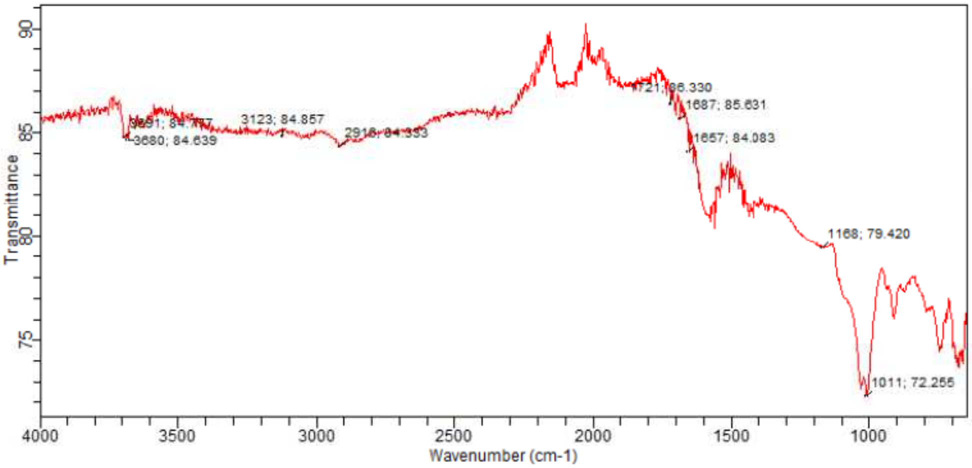


Fig. 2 : FT-IR spectraof peatsoilhumic acid (PSHA)

Evaluation of acid dissociation constant (pka) of acid hydrolysed peat soil humicacid at phenolic group

The value of the dissociation constant of the peat soil humic acid (PSHA) that underwent acidhydrolysis studied was found to be 8.9299 as shown Table 1, which is lower than the literaturevalues reported by Almeida and Szpoganics, (2015), Borges *et al.*, (2005); Badr *et al.*, (2012)and Fernandes *et al*,.(2009) of 9.73, 9.47 and 10.30. The difference between the obtained valuesand the reported values in this study might be probably as a result of acid hydrolysis of humicacid.

Table 1: PKa of (Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	V$_2$-V$_1$	nA	log($\frac{nA}{1-nA}$)	pKa
8.50	5.30	6.29	0.99	0.3594	-0.2510	8.2490
8.72	5.35	6.37	1.02	0.3400	-0.2880	8.4320
9.00	5.40	6.46	1.06	0.3141	-0.3391	8.6609
9.22	5.45	6.55	1.10	0.2882	-0.3927	8.8273
9.51	5.50	6.66	1.16	0.2494	-0.4786	9.0314
9.73	5.55	6.78	1.23	0.2041	-0.5910	9.1390
10.00	5.60	6.90	1.30	0.1589	-0.7238	9.2762
10.23	5.65	7.05	1.40	0.0941	-0.9835	9.2465
10.49	5.70	7.10	1.40	0.0941	-0.9835	9.5065

Average pKa = 8.9299 ± 0.4186

Table 2: PKa of (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	V$_2$-V$_1$	nA	Log($\frac{nA}{1-n}$)	pKa
8.50	5.30	5.81	0.51	0.6619	0.2919	8.7919
8.72	5.35	5.90	0.55	0.6357	0.2418	8.9618
9.00	5.40	6.00	0.60	0.6029	0.1813	9.1813
9.22	5.45	6.10	0.65	0.5701	0.1226	9.3426
9.51	5.50	6.20	0.70	0.5376	0.0654	9.5754
9.73	5.55	6.33	0.78	0.4851	-0.0259	9.7041
10.00	5.60	6.47	0.87	0.4262	-0.1291	9.8709
10.23	5.65	6.62	0.99	0.3609	-0.2481	9.9819
10.49	5.70	6.80	1.10	0.2759	-0.4690	10.0210

Average pKa = 9.4923± 0.4410

Metal-ligand stability constant (Log K)

The stabilityconstants require the accurate values of proton-ligand stability constants (Anil and Maroti, 2008). Metal titration curves crossed over ligand titration curve indicated the formation of complex upon proton release (Santosh, *et al.*, 2011). If the values of n- are within range 0.2-0.8 and 1.2-18 this indicates the formation of 1:1 and 1:2 complexes (Sayyed and Mazahar, 2012).

The metal (II)-humate stepwise stability constants (log k) at phenolic group (Tables 3-18)

Table 3: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	log($\frac{n}{1-n}$)	LogK$_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

LogK$_1$ (Average value) = 2.4788± 0.2203

Table 4: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	Log($\frac{n-1}{2-n}$)	LogK$_2$
9.51	5.50	6.66	6.73	0.07	1.3509	1.70	-0.2671	1.4329
9.73	5.55	6.78	6.85	0.07	1.6383	1.51	0.2467	1.7567
10.00	5.60	6.90	6.98	0.08	2.1783	1.31	-0.2158	1.0942
10.23	5.65	7.05	7.13	0.08	4.1904	1.27		
10.49	5.70	7.10	7.19	0.09	4.6920			

LogK$_2$(Average value) = 1.4280 ± 0.3312

Table 5:Point-wise method,Cu (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	$(V_3$-$V_2)$	n	pL	Log($\frac{n}{n-1}$)	Log K$_1$
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430

LogK$_1$ **(Average value)** = 2.3059± 0.6153

Table 6:Point-wise method, Cu (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	V_3-V_2	n	pL	Log($\frac{n-1}{2-n}$)	Log K$_2$
9.73	5.55	6.33	6.42	0.09	0.9000	1.69		
10.00	5.60	6.47	6.58	0.11	1.2578	1.44	-0.4592	0.9808
10.23	5.65	6.62	6.84	0.12	1.6137	1.26	-0.2010	1.4610
10.49	5.70	6.80	6.92	0.12	2.1052	1.03		

LogK$_2$ **(Average value)** = 1.2209± 0.3398

Table 7:Point-wise method,Pb (Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	$(V_3$-$V_2)$	n	pL	log($\frac{n}{1-n}$)	LogK$_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.60	0.05	0.8333	1.96	0.6989	2.6589

LogK$_1$ (Average value) = 2.5832 ±0.1614

Table 8:Point-wise method,Pb-(Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	$(V_3$-$V_2)$	n	pL	log($\frac{n-1}{2-n}$)	logK$_2$
9.51	5.50	6.66	6.71	0.05	0.9650	1.67	-0.0237	1.1963
9.73	5.55	6.78	6.83	0.05	1.1702	1.44		
10.00	5.60	6.90	6.90	0.05	1.4864	1.22		
10.23	5.65	7.05	7.10	0.05	2.0190	1.09		
10.49	5.70	7.10	7.17	0.07	3.6492	1.00		

LogK$_2$(Average value) = 1.1963

Table 9:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	V_3-V_2	n	pL	Log ($\frac{n}{n-1}$)	Log K$_1$
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.5477	2.3123
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	0.0272	2.2072
9.51	5.50	6.20	6.26	0.07	0.6417	1.89	0.2530	2.1430
9.73	5.55	6.40	6.40	0.07	0.7000	1.67	0.3680	2.0380

LogK$_1$ **(Average value)** = 2.2364 ± 0.1602

Table 10:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	V_3-V_2	n	pL	Log($\frac{n-1}{2-n}$)	Log K$_2$
10.00	5.60	6.47	6.55	0.08	1.9503	1.41	-0.0361	1.2239
10.23	5.65	6.62	6.72	0.11	1.4792	1.26		

LogK$_2$ **(Average value)** = 1.2239

Table 11:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	$(V_3$-$V_2)$	n	pL	log($\frac{n}{n-1}$)	LogK$_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4290	2.2110
8.72	5.35	6.37	6.39	0.02	0.2858	2.42	-0.3978	2.0222
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

LogK$_1$ (Average value)=2.1382**±**0.1046

Table 12:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n-1}{2-n}$)	$LogK_2$
9.51	5.55	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.84	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.93	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.10		
10.49	5.70	7.10	7.18	0.07	3.6492	0.83		

$LogK_2$(Average value) = 1.5453 **±** 0.3450

Table 13:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.3477	2.3123
9.00	5.40	6.00	6.04	0.04	0.3236	2.38	-0.3202	2.0598
9.22	5.45	6.10	6.15	0.05	0.4297	2.17	-0.1230	2.0470
9.51	5.50	6.20	6.26	0.06	0.5500	1.89	0.0871	1.9771
9.73	5.55	6.33	6.40	0.07	0.7000	1.67	0.3680	2.0380

$LogK_1$ **(Average value)** = 2.1568 ± 0.2069

Table 14:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
10.00	5.60	6.47	6.55	0.08	0.9148	1.41		
10.23	5.65	6.62	6.71	0.09	1.2102	1.20	-0.5749	0.6251
10.49	5.70	6.80	6.92	0.09	1.5968	1.03	0.1703	1.2003

$LogK_2$ **(Average value)** = 0.9127± 0.4070

Table15:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	Log($\frac{n}{1-n}$)	$LogK_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4210	2.2190
8.72	5.35	6.37	6.40	0.03	0.4286	2.42	-0.1249	2.2951
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.96	0.3010	2.2610
9.51	5.55	6.66	6.70	0.04	0.7720	1.67	0.5297	2.1997

$LogK_1$ (Average value) = 2.2108± 0.0825

Table 16:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
9.73	5.55	6.78	6.83	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.95	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.09		
10.49	5.70	7.10	7.16	0.06	3.1429	0.89		

$LogK_2$ **(Average value)** = 1.5453± 0.3450

Table 17:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.86	0.05	0.3717	2.88	-0.2280	2.6520
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.06	0.06	0.4853	2.38	-0.0255	2.3545
9.22	5.45	6.10	6.16	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430
9.73	5.55	6.33	6.41	0.08	0.8000	1.69	0.6020	2.2920

$LogK_1$ **(Average value)** = 2.2516± 0.5380

Table 18:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$\text{Log}(\frac{n-1}{2-n})$	Log K_2
10.00	5.60	6.47	6.57	0.10	1.1434	1.43		
10.23	5.65	6.62	6.72	0.10	1.3448	1.23	-0.2788	0.9512
10.49	5.70	6.80	6.90	0.10	1.7742	1.03	0.5351	1.5651

LogK_2 **(Average value)** = 1.2581± 0.4340

Table 19: Stepwise and overall Stability constants of thehydrolysed and unhydrolysed divalent metal (II) complexes

Chelates	**LogK_1**	**LogK_2**	**Logβ**
[Cu (Hydrolysed PSHA-1)$_2$]	2.4788	1.4280	3.9068
[Pb (Hydrolysed PSHA-1)$_2$]	2.5832	1.1963	3.7795
[Cd (Hydrolysed PSHA-1)$_2$]	2.2108	1.5453	3.7561
[Mg (Hydrolysed PSHA-1)$_2$]	2.1382	1.5453	3.6835
[Cu (Unhydrolysed PSHA-1)$_2$]	2.3059	1.2209	3.5268
[Pb (Unhydrolysed PSHA-1)$_2$]	2.2364	1.2239	3.4603
[Cd (Unhydrolysed PSHA-1)$_2$]	2.2516	1.2581	3.5097
[Mg (Unydrolysed PSHA-1)$_2$]	2.1568	0.9127	3.0695

The results obtained (Table19) shows the stepwise and overall stability constants to be not high indicating low stability of the complexes, because the solubility of most metal ions in the basic pH range is minimal due to metal hydroxide precipitation (Karimi, 2017). In general, the stepwise stability constants (K_1 and K_2) follow the order $K_1 > K_2$ for the copper, lead, magnesium and cadmium complexes respectively. The steady decrease of the values with increasing number of ligands is in agreement with the prediction made by researchers (Na'aliya, 2013). The decrease could be attributed to the fact that as the number of the ligands (Humate ions) that enters the coordination zone increases the aqua molecules available for replacement by the ligands become less. Thus, the metal ions become less electron loving with progressive intake of the ligand and this results in the decrease in the values of the constants (Na'aliya, 2013). Also the stability of the complexes is influenced by the size and number of the chelate rings(Mackay and Mackay,2002).All the complexes form rings in their structure as humate, a bidentate ligand, bond the metal ions in the ratio 1:2 (Boguta and Sokolowska, 2016) forming chelate rings. The values of the overall stability constants (logβ) obtained for humate complexes are not high indicating low stability as the values are not high. LogK values for copper-humates (Table 3 to 6) obtained in this study are lower than those reported for the complexes of humic acids (Pandey *et al.*, 2015; Dinu, 2013; Kaschl *et al.*, 2010 and Gilbeto and Jorg, 2001). The values of LogK(Table 7 to 10) forlead-humates are lower than those reported for the lead in the literature (Dinu, 2013; Gilbeto and Jorg 2001). Log K values(Table 11 to 14) for magnesium-humates obtained in this study are close to those reported by (Pandey *et al.*, 2015). Log K values of cadmium-humates (Table 15 to 18) obtained in this work near to the one reported by (Dinu, 2013 and Pandey *et al.*, 2015).The difference between the reported values and the values obtained in this study might be probably as a result of acid hydrolysis of humic acid. The values of the overall stability constants (log β) of the copper humates complexes presented in Table 19 is high than that of other metal humate complexes, show relatively high stability of Cu-HA complexes, show the following order of stability: Cu >Pb> Cd > Mg; which are in close agreement to the findings of (Dinu, 2013 and Pandey *et al.*, 2015).The high stability of Cu-humate chelate could be attributed to the existence of coordinate covalent bond between the complexing agents and the Cu^{2+} ions. Since, Cu^{2+} being a metal of the transitional series with $3d^9$ electronic configurations can accept the electrons from the complexing agents. Similarly,the low stabilities of Pb,Cd and Mg -complexes could be explained by that Pb^{2+} with $6s^2$, Cd^{2+} with $4d^{10}$ and Mg^{2+} with $2p^6$ their electronic configuration has a completely filled d,p and s orbitals. Moreover, the stabilities of metal ions with hydrolysed humic acid from peat soil were higher than those with unhydrolysed humic acid from peat soil; which is ascribed to the high content of acidity in hydrolysed humic acid than unhydrolysed humic acid.

CONCLUSION

The values of logK for Cu(II) hydrolysed humic acid complex was higher followed by Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes as compared with metal(II) unhydrolysed humic acid complexes . This indicates acid hydrolysis of humic acid can enhance the complexation behavior of humic acid with metal (II) ions. However, the higher values of logβ for Cu(II), Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes indicates more stable stepwise complexes formed as compared with Cu(II), Pb(II), Cd(II) and Mg(II) unhydrolysed humic acid complexes.

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STABILITY CONSTANTS OF COMPLEXES OF METAL IONS WITH PEATSOIL HUMIC ACIDS UNDER NON-ACID-CONDITIONS

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ABSTRACT

Stability constants of complexes of four divalent metal ions viz. Cu^{2+}, Pb^{2+},Mg^{2+} and Cd^{2+} with humic acids (HA) were determined by potentiometric titration of humic acids with the corresponding salt of the divalent metals in aqueous media under non-acid-condition. The log K (logarithm of the stability constant) ranged from 1.0942 to 2.7471 for metal-humic acid complexes were determined using point-wise computational method. The order of stability constants were obtained as follows: Cu >Pb> Cd > Mg for metal -HA complexes respectively, indicating a higher degree of complexation with Cu metal ion.

Keywords: stability constant, humic acid, potentiometric titration, divalent metals, acid hydrolysis.

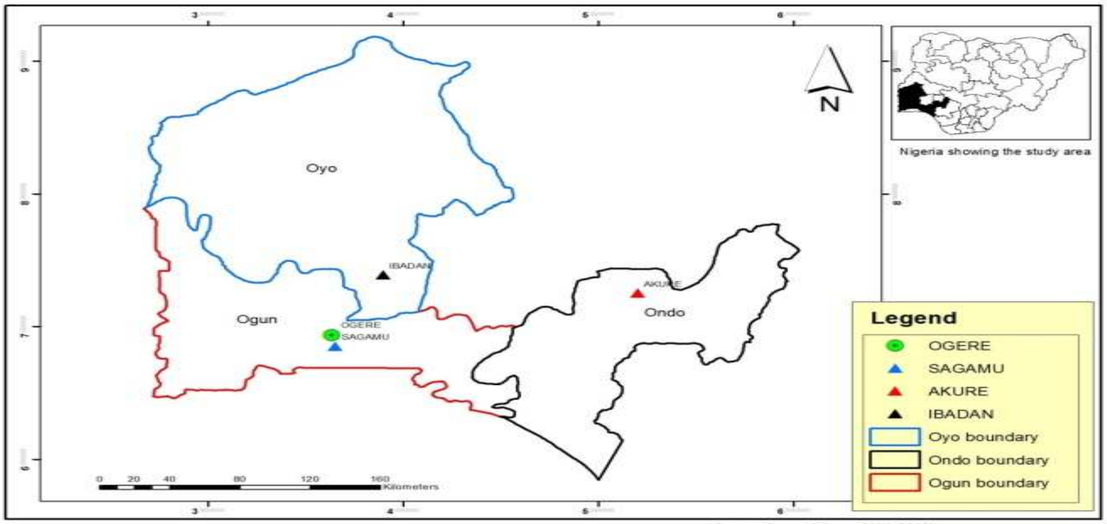
NTRODUCTION

The stability constant of a complex is the numerical expression of its stability and provides a quantitative measure of affinity of the metal ion to the complexing agent. An understanding of the relative stability of metal-complexes helps in predicting the behavior of metal ions in the soil (Ram and Raman, 1982). Extensive researches has been done to determine the stability constants of the complexes formed between humic acid (HA) with a number of metal ions. Ashok *et al*., (2000) reported that humic acid with hydroxyl, phenoxyl and carboxyl reactive groups can form coordination compound with metal ions at pH 3.5. The stability constants(Log K) for different metal-humic acid complexes indicated the following order of the stabilities of complexes formed between humic acid and metal ion, Cu >Fe >Pb> Ni > Co > Ca > Cd > Zn >Mn> Mg. Andelkovic *et al*., (2010) investigated the binding of Cd(II) to soil humic acid at pH 6.5 and in 0.1M KNO_3 ionic medium. The stability constant for binding indicating greater stability in the case when carboxyl groups are involved in complexation reaction. Kostic *et al*.,(2012) investigated the complexation of humic acid with certain heavy metal ions (Co(II), Ni(II),Cu(II), Zn(II), and Pb(II). The experiment was performed at 25°C, at pH 4.0 and ionic strength of 0.01M. Stability constant of complex between Pb(II) ions and humic acid is greater than stability constants of other investigated metal-humate complexes. Bogata and Sokolowska (2016) analyses the interaction between humic acids from different soils and Zn (II) ions at wide concentration ranges and at pH 5. Studies have showed significant impact of Zn concentration, pH and some properties of humic acids with zinc.But all of these studies were limited to acidic pH range. Therefore, the present study was carried out to determine and compare the stability constants of complexes of metal ions with hydrolysed peat soil humic acid and unhydrolysed peat soil humic under non-acid conditions.

MATERIALS AND METHODS

Analytical grade chemicals used includes hydrochloric acid (HCl), nitric acid (HNO_3), sodium hydroxide (NaOH), lead nitrate $Pb(NO_3)_2$, copper nitrate $Cu(NO_3)_2.3H_2O$, cadmium nitrate $Cd(NO_3)_2.4H_2O$, magnesium nitrate $Mg(NO_3)_2.6H_2O$, potassium nitrate (KNO_3), calcium chloride ($CaCl_2$), (sigma-Aldrich). Dowex 50WX8, (20-50 mesh) from Fluka.

Area of study



Source: Dept. of Geog. BUK (2016)

Figure 1: Map showing the sampling point at Sagamu Town, Ogun State.

Description of Sampling Area

Sagamu has geographical coordinates between 6°50′ north; 3° 38′ east is located in south western region of Nigeria. The region has tropical wet and dry climate with a lengthy wet season and relatively constant temperatures throughout the course of the year. Wet season runs from March to October, November to December forms the region dry season. The vegetation type of the region is savannah which is really grassland with small bushes and occasional big trees. Grassland soils have substantially higher organic matter content than forest soils (Novackova, 2011).

Sample Collection

The Peatsoil samples were collected from four different sampling points (0-10cm depth) in Sagamu into polyethylene bag with plastic spoons. Samples were taken to the laboratory, extraneous materials were removed; the samples were air-dried, crushed and ground to a fine powder in a mortar passed through a 0.20mm sieve. The samples were kept for analysis.

Isolation and purification of humic acid from peat soil sample

Peatsoil sample (100g) was mixed with 1000 cm^3 of 0.1M NaOH solution, shaken for 3hours and left to stand overnight. Dark-coloured supernatant was obtained and decanted from solid residue. The dark-coloured supernatant was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 6 hours. Yellowish brown supernatant and dark-brown precipitate were obtained. The yellowish brown supernatant was decanted followed by centrifuge and discarded. The dark-brown precipitate was mixed with $500cm^3$of 0.1M NaOH solution followed by passing through dowex resin. The dark-brown solution was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 3 hours. The dark-brown precipitate was washed several times with deionized water. The supernatant was treated with $AgNO_3$ solution until no white precipitate observed. The humic acid was transferred to weighed crucible and dried at 60°C in an oven for 12 hours. The humic acid was cooled and dried in the desiccator, weighed and recorded. The obtained humic acid was dried again at 60°C for additional 6 hours cooled and dried in the desiccator, weighed and recorded constant weight was obtained (Baruah *et al*., 2015).

FT-IR analysis

FT-IR spectra of humic acid sample was analysed using Carry 630 FT-IR Agilent Technologies.

Unhydrolysed compost humic acid

The unhydrolysed humic acid was obtained after isolation and purification of compost humic acid and kept for investigation.

Acid hydrolysis of Peatsoil acid

Peatsoil humic acid sample (1g) was refluxed for 12 hours at (160°C) with $50cm^3$ of 6M HCl. The mixture was allowed to cool, decanted, and centrifuged after hydrolysis. The insoluble residues were washed with distilled water via centrifugation several times, and the supernatant was treated with $AgNO_3$ solution until no white precipitate was observed. The residue was thoroughly dried over $CaCl_2$ in a desiccator at room temperature (Chefetz *et al*., 2002). Finally, the obtained hydrolysed humic acid was kept for investigation.

Potentiometric Titrations

Potentiometric measurements were carried out using a pH-meter Jenway (model 3510) with combine electrode, the sensitivity of the pH - meter is 0.01 units. The pH meter was switched on half an hour before starting the titration for initial warm up of the instrument. The instrument was calibrated with an aqueous standard buffer solution of pH 4.00 and 10.0 (borate buffer) prepared from a "Qualigens" buffer tablets.

The following sets of solutions were prepared in a 250cm^3 volumetric flask separately for pH metric titrations.

(i) 5 cm^3 0.1 M HCl + 40 cm^3 deionized water

(ii) 5 cm^3 0.1 M HCl + 39 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid

(iii) 5 cm^3 0.1 M HCl + 37 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid + 2 cm^3 0.01 M Cu(II)

The solutions were titrated against standardized 0.110MNaOH separately. The total volume of each mixture was adjusted to 50 cm^3 and the ionic strength of the solutions was maintained constant at by adding appropriate amount of stock solution of 1M KNO$_3$ (Gamal, 2015; Omar and Ali, 2015). A magnetic stirrer was used to achieve thorough mixing of the interacting solutions at 550 rpm. The same set of experimental conditions was applied for potentiometric titration of remaining samples.

Evaluation of pKa of Hydrolysed peat soil Humic Acids

The proton-ligand formation number n$_{\mathbf{A}}$ were calculated by Irving and Rossotti expression (Omar and Ali, 2015).

$$nA = Y - \frac{(V2-V1)(No-Eo)}{(Vo+V1)TcL} \quad ....1$$

Where: Y is number of dissociable proton, (V$_2$-V$_1$) is the measure of displacement of the ligand curve relative to acid curve, N^o and E^o are the resultant concentration of alkali solution, free acid solution, T$_{cL}{}^o$ is the total ligand concentration, V^o is the total volume of titration solution,V$_1$ is the volume of alkali added to acid solution,V$_2$ is the volume of alkali added to acid solution + ligand solution, acid dissociation constants (pKa - values) of ligand were calculated by algebraic method point wise calculation (Tables 1). The dissociation constants (pKa) were calculated according to the following relation:

$$pKa = pH + \log\left(\frac{nA}{1-nA}\right) \quad ....2$$

Where: pKa is the acid dissociation constant, n$_A$is the Proton-ligand formation number and pH is the pH-values (Omar and Ali, 2015).

Determination of metal-ligand stability constants (log K) of complexes

The potentiometric measurement for the determination of stability constant of a complex in solution is based on the fact that the redox potential of the couple $\frac{M^{+(m-n)}}{M^{+m}}$ is shifted significantly on complexation of the metal ion with the ligand. This method involves change in hydrogen ion concentration [H$^+$] due to the displacement or association of one or more protons taking place during complexation reaction. This change can be found out by titrating the solutions containing free acid, acid with ligand, and acid with ligand and metal ion, individually against a standard alkali solution at a constant ionic strength or temperature. Either ionic strength or temperature may be varied for different sets of solutions. In all the cases, the change in the pH of the solution is measured after each addition of a known amount of alkali to the reaction cell which contains the reaction mixture. The titration curves are then drawn by plotting the measured pH values against the corresponding volume of alkali added and the stability constants of the complexes are determined from the titration curves by employing pH-metric titration technique given by (Irving and Rossoti).

Metal-ligand stability constants (Log K) were determined by using the following relations:

$$\bar{n} = \frac{(V_3 - V_2)(E^0 + N^0)}{(V^0 + V_2)\bar{n}_A T_m^0} \quad ....3$$

and

$$PL = \log_{10}\left\{\frac{1 + \beta_n^H \dfrac{1}{[anti \ \log pH]^n}}{T_L^0 - \bar{n}T_m^0} \mathrm{X} \frac{(V^0 + V_3)}{V^0}\right\} \quad ....4$$

Where $T_{L,}$ T^{o}, E°, and V^{o}havethe same significance as in equation (1) above, T_m denotes the total concentration of metal present in solution, V_3 is the volume of metal ions present in solution and β^H is the overall proton ligand stability constant. The metal-ligand stability constants (log K) were determined by employing point wise computational Method (eq. 5 and 6).

$$\mathrm{LogK}_1 = \log\left(\frac{n}{1-n}\right) + \mathrm{pL} \quad \ldots\ldots\ldots\ldots.5$$

$$\mathrm{LogK}_2 = \log\left(\frac{1-n}{2-n}\right) + \mathrm{pL}\ldots\ldots\ldots\ldots\ldots\ldots\ldots.6$$

Where: Log K is the metal-ligand stability constant, pL is the Free ligand exponent function, **n** is the Average number of ligand attached with metal ion (Janrao*et al*., 2014).The results obtained were analyzed by an ORIGIN 2016 program using titration data and then the proton-ligand stability constants (pKa) and Metal-ligand stability constant (LogK) calculated (Omar and Ali, 2015).

RESULTS AND DISCUSSION

Fourier transformed infrared (FT-IR) spectra of isolated humic acid from peat soils Figure 2 had distinct clear absorption bands indicating the presence of major humic acid structural elemental groups such as H bonded OH (3680cm^{-1} peak), C=O of carbonyl (1721cm^{-1} peak), functional groups of aliphatic components CH_2 (2918cm^{-1} peak) and C-O stretching of polysaccharide (1168cm^{-1} peak). The positions of the absorption bands of the spectra fell within typical major absorption bands of humic acid which is at frequencies 3680, 2918, 1721, 1168 cm^{-1}. The first peak centred in the vicinity of 3680 cm^{-1} region is attributed to phenol OH group bounded by intermolecular H bonds. The 2918cm^{-1} band usually has absorption maximum at 2918 cm^{-1} which is due to C–H stretching of alkane group (CH_2). The next major absorption band is 1721 cm^{-1}. This band has been commonly ascribed to C=O stretching of mainly carboxyl group (COOH) with trace amount of ketones. The last peak was observed at 1168 cm^{-1} due to C–O stretching of polysaccharides and this peak appeared also in the spectra of humic acid from peat soil. The FTIR spectra of the isolated humic acid contained all major characteristic absorption peaks of humic acid. These absorption peaks indicated the presence of the major structural elements of humic acid namely H bonded OH, C=C of aromatic ring, C=O of carbonyl group (both carboxyl and ketonic), CH_2 group. This strongly supports the presence of humic acid.

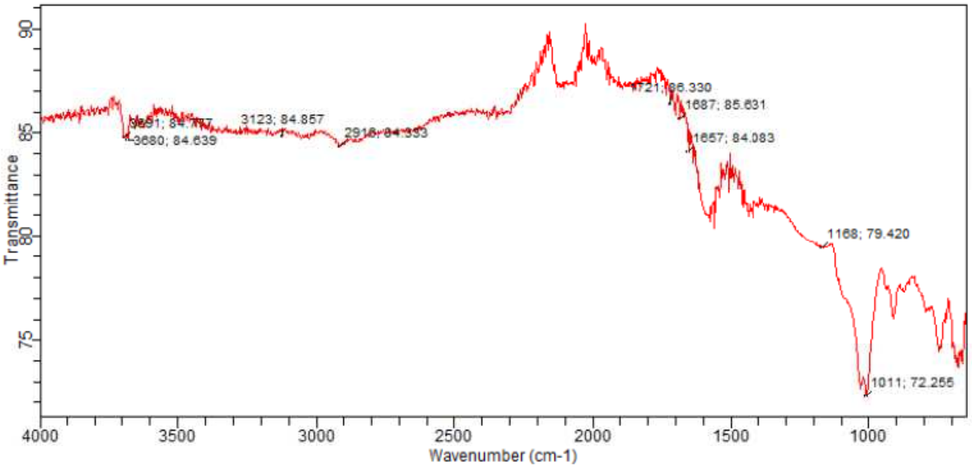


Fig. 2 : FT-IR spectraof peatsoilhumic acid (PSHA)

Evaluation of acid dissociation constant (pka) of acid hydrolysed peat soil humicacid at phenolic group

The value of the dissociation constant of the peat soil humic acid (PSHA) that underwent acidhydrolysis studied was found to be 8.9299 as shown Table 1, which is lower than the literaturevalues reported by Almeida and Szpoganics, (2015), Borges *et al*., (2005); Badr *et al*., (2012)and Fernandes *et al*,.(2009) of 9.73, 9.47 and 10.30. The difference between the obtained valuesand the reported values in this study might be probably as a result of acid hydrolysis of humicacid.

Table 1: PKa of (Hydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	$\log(\frac{nA}{1-nA})$	pKa
8.50	5.30	6.29	0.99	0.3594	-0.2510	8.2490
8.72	5.35	6.37	1.02	0.3400	-0.2880	8.4320
9.00	5.40	6.46	1.06	0.3141	-0.3391	8.6609
9.22	5.45	6.55	1.10	0.2882	-0.3927	8.8273
9.51	5.50	6.66	1.16	0.2494	-0.4786	9.0314
9.73	5.55	6.78	1.23	0.2041	-0.5910	9.1390
10.00	5.60	6.90	1.30	0.1589	-0.7238	9.2762
10.23	5.65	7.05	1.40	0.0941	-0.9835	9.2465
10.49	5.70	7.10	1.40	0.0941	-0.9835	9.5065

Average pKa = 8.9299 ± 0.4186

Table 2: PKa of (Unhydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	$\mathrm{Log}(\frac{nA}{1-n})$	pKa
8.50	5.30	5.81	0.51	0.6619	0.2919	8.7919
8.72	5.35	5.90	0.55	0.6357	0.2418	8.9618
9.00	5.40	6.00	0.60	0.6029	0.1813	9.1813
9.22	5.45	6.10	0.65	0.5701	0.1226	9.3426
9.51	5.50	6.20	0.70	0.5376	0.0654	9.5754
9.73	5.55	6.33	0.78	0.4851	-0.0259	9.7041
10.00	5.60	6.47	0.87	0.4262	-0.1291	9.8709
10.23	5.65	6.62	0.99	0.3609	-0.2481	9.9819
10.49	5.70	6.80	1.10	0.2759	-0.4690	10.0210

Average pKa = 9.4923± 0.4410

Metal-ligand stability constant (Log K)

The stabilityconstants require the accurate values of proton-ligand stability constants (Anil and Maroti, 2008). Metal titration curves crossed over ligand titration curve indicated the formation of complex upon proton release (Santosh, *et al.*, 2011). If the values of n- are within range 0.2-0.8 and 1.2-18 this indicates the formation of 1:1 and 1:2 complexes (Sayyed and Mazahar, 2012).

The metal (II)-humate stepwise stability constants (log k) at phenolic group (Tables 3-18)

Table 3: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3$-$V_2)$	n	pL	$\log(\frac{n}{1-n})$	LogK_1
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

LogK_1 (Average value) = 2.4788± 0.2203

Table 4: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3$-$V_2)$	n	pL	$\mathrm{Log}(\frac{n-1}{2-n})$	LogK_2
9.51	5.50	6.66	6.73	0.07	1.3509	1.70	-0.2671	1.4329
9.73	5.55	6.78	6.85	0.07	1.6383	1.51	0.2467	1.7567
10.00	5.60	6.90	6.98	0.08	2.1783	1.31	-0.2158	1.0942
10.23	5.65	7.05	7.13	0.08	4.1904	1.27		
10.49	5.70	7.10	7.19	0.09	4.6920			

LogK_2(Average value) = 1.4280 ± 0.3312

Table 5:Point-wise method,Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	Log$(\frac{n}{n-1})$	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430

$LogK_1$ **(Average value)** = 2.3059± 0.6153

Table 6:Point-wise method, Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log$(\frac{n-1}{2-n})$	Log K_2
9.73	5.55	6.33	6.42	0.09	0.9000	1.69		
10.00	5.60	6.47	6.58	0.11	1.2578	1.44	-0.4592	0.9808
10.23	5.65	6.62	6.84	0.12	1.6137	1.26	-0.2010	1.4610
10.49	5.70	6.80	6.92	0.12	2.1052	1.03		

$LogK_2$ **(Average value)** = 1.2209± 0.3398

Table 7:Point-wise method,Pb (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log$(\frac{n}{1-n})$	$LogK_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.60	0.05	0.8333	1.96	0.6989	2.6589

$LogK_1$ (Average value) = 2.5832 ±0.1614

Table 8:Point-wise method,Pb-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log$(\frac{n-1}{2-n})$	$logK_2$
9.51	5.50	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.83	0.05	1.1702	1.44		
10.00	5.60	6.90	6.90	0.05	1.4864	1.22	-0.0237	1.1963
10.23	5.65	7.05	7.10	0.05	2.0190	1.09		
10.49	5.70	7.10	7.17	0.07	3.6492	1.00		

$LogK_2$(Average value) = 1.1963

Table 9:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log $(\frac{n}{n-1})$	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.5477	2.3123
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	0.0272	2.2072
9.51	5.50	6.20	6.26	0.07	0.6417	1.89	0.2530	2.1430
9.73	5.55	6.40	6.40	0.07	0.7000	1.67	0.3680	2.0380

$LogK_1$ **(Average value)** = 2.2364 ± 0.1602

Table 10:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log$(\frac{n-1}{2-n})$	Log K_2
10.00	5.60	6.47	6.55	0.08	1.9503	1.41		
10.23	5.65	6.62	6.72	0.11	1.4792	1.26	-0.0361	1.2239

$LogK_2$ **(Average value)** = 1.2239

Table 11:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log$(\frac{n}{n-1})$	$LogK_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4290	2.2110
8.72	5.35	6.37	6.39	0.02	0.2858	2.42	-0.3978	2.0222
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

$LogK_1$ (Average value)=2.1382**±**0.1046

Table 12:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	log($\frac{n-1}{2-n}$)	LogK$_2$
9.51	5.55	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.84	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.93	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.10		
10.49	5.70	7.10	7.18	0.07	3.6492	0.83		

LogK$_2$(Average value) = 1.5453 **±** 0.3450

Table 13:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	V$_3$-V$_2$	n	pL	Log($\frac{n}{n-1}$)	Log K$_1$
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.3477	2.3123
9.00	5.40	6.00	6.04	0.04	0.3236	2.38	-0.3202	2.0598
9.22	5.45	6.10	6.15	0.05	0.4297	2.17	-0.1230	2.0470
9.51	5.50	6.20	6.26	0.06	0.5500	1.89	0.0871	1.9771
9.73	5.55	6.33	6.40	0.07	0.7000	1.67	0.3680	2.0380

LogK$_1$ **(Average value)** = 2.1568 ± 0.2069

Table 14:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	V$_3$-V$_2$	n	pL	Log($\frac{n-1}{2-n}$)	Log K$_2$
10.00	5.60	6.47	6.55	0.08	0.9148	1.41		
10.23	5.65	6.62	6.71	0.09	1.2102	1.20	-0.5749	0.6251
10.49	5.70	6.80	6.92	0.09	1.5968	1.03	0.1703	1.2003

LogK$_2$ **(Average value)** = 0.9127± 0.4070

Table15:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	Log($\frac{n}{1-n}$)	LogK$_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4210	2.2190
8.72	5.35	6.37	6.40	0.03	0.4286	2.42	-0.1249	2.2951
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.96	0.3010	2.2610
9.51	5.55	6.66	6.70	0.04	0.7720	1.67	0.5297	2.1997

LogK$_1$ (Average value) = 2.2108± 0.0825

Table 16:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	Log($\frac{n-1}{2-n}$)	Log K$_2$
9.73	5.55	6.78	6.83	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.95	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.09		
10.49	5.70	7.10	7.16	0.06	3.1429	0.89		

LogK$_2$ **(Average value)** = 1.5453± 0.3450

Table 17:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	V$_3$-V$_2$	n	pL	Log($\frac{n}{n-1}$)	Log K$_1$
8.50	5.30	5.81	5.86	0.05	0.3717	2.88	-0.2280	2.6520
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.06	0.06	0.4853	2.38	-0.0255	2.3545
9.22	5.45	6.10	6.16	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430
9.73	5.55	6.33	6.41	0.08	0.8000	1.69	0.6020	2.2920

LogK$_1$ **(Average value)** = 2.2516± 0.5380

Table 18:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$\mathrm{Log}(\frac{n-1}{2-n})$	Log K_2
10.00	5.60	6.47	6.57	0.10	1.1434	1.43		
10.23	5.65	6.62	6.72	0.10	1.3448	1.23	-0.2788	0.9512
10.49	5.70	6.80	6.90	0.10	1.7742	1.03	0.5351	1.5651

LogK_2 **(Average value)** = 1.2581± 0.4340

Table 19: Stepwise and overall Stability constants of thehydrolysed and unhydrolysed divalent metal (II) complexes

Chelates	**LogK_1**	**LogK_2**	**Logβ**
[Cu (Hydrolysed PSHA-1)$_2$]	2.4788	1.4280	3.9068
[Pb (Hydrolysed PSHA-1)$_2$]	2.5832	1.1963	3.7795
[Cd (Hydrolysed PSHA-1)$_2$]	2.2108	1.5453	3.7561
[Mg (Hydrolysed PSHA-1)$_2$]	2.1382	1.5453	3.6835
[Cu (Unhydrolysed PSHA-1)$_2$]	2.3059	1.2209	3.5268
[Pb (Unhydrolysed PSHA-1)$_2$]	2.2364	1.2239	3.4603
[Cd (Unhydrolysed PSHA-1)$_2$]	2.2516	1.2581	3.5097
[Mg (Unydrolysed PSHA-1)$_2$]	2.1568	0.9127	3.0695

The results obtained (Table19) shows the stepwise and overall stability constants to be not high indicating low stability of the complexes, because the solubility of most metal ions in the basic pH range is minimal due to metal hydroxide precipitation (Karimi, 2017). In general, the stepwise stability constants (K_1 and K_2) follow the order $K_1 > K_2$ for the copper, lead, magnesium and cadmium complexes respectively. The steady decrease of the values with increasing number of ligands is in agreement with the prediction made by researchers (Na'aliya, 2013). The decrease could be attributed to the fact that as the number of the ligands (Humate ions) that enters the coordination zone increases the aqua molecules available for replacement by the ligands become less. Thus, the metal ions become less electron loving with progressive intake of the ligand and this results in the decrease in the values of the constants (Na'aliya, 2013). Also the stability of the complexes is influenced by the size and number of the chelate rings(Mackay and Mackay,2002).All the complexes form rings in their structure as humate, a bidentate ligand, bond the metal ions in the ratio 1:2 (Boguta and Sokolowska, 2016) forming chelate rings. The values of the overall stability constants (logβ) obtained for humate complexes are not high indicating low stability as the values are not high. LogK values for copper-humates (Table 3 to 6) obtained in this study are lower than those reported for the complexes of humic acids (Pandey *et al.*, 2015; Dinu, 2013; Kaschl *et al.*, 2010 and Gilbeto and Jorg, 2001). The values of LogK(Table 7 to 10) forlead-humates are lower than those reported for the lead in the literature (Dinu, 2013; Gilbeto and Jorg 2001). Log K values(Table 11 to 14) for magnesium-humates obtained in this study are close to those reported by (Pandey *et al.*, 2015). Log K values of cadmium-humates (Table 15 to 18) obtained in this work near to the one reported by (Dinu, 2013 and Pandey *et al.*, 2015).The difference between the reported values and the values obtained in this study might be probably as a result of acid hydrolysis of humic acid. The values of the overall stability constants (log β) of the copper humates complexes presented in Table 19 is high than that of other metal humate complexes, show relatively high stability of Cu-HA complexes, show the following order of stability: Cu >Pb> Cd > Mg; which are in close agreement to the findings of (Dinu, 2013 and Pandey *et al.*, 2015).The high stability of Cu-humate chelate could be attributed to the existence of coordinate covalent bond between the complexing agents and the Cu^{2+} ions. Since, Cu^{2+} being a metal of the transitional series with $3d^9$ electronic configurations can accept the electrons from the complexing agents. Similarly,the low stabilities of Pb,Cd and Mg - complexes could be explained by that Pb^{2+} with $6s^2$, Cd^{2+} with $4d^{10}$ and Mg^{2+} with $2p^6$ their electronic configuration has a completely filled d,p and s orbitals. Moreover, the stabilities of metal ions with hydrolysed humic acid from peat soil were higher than those with unhydrolysed humic acid from peat soil; which is ascribed to the high content of acidity in hydrolysed humic acid than unhydrolysed humic acid.

CONCLUSION

The values of logK for Cu(II) hydrolysed humic acid complex was higher followed by Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes as compared with metal(II) unhydrolysed humic acid complexes . This indicates acid hydrolysis of humic acid can enhance the complexation behavior of humic acid with metal (II) ions. However, the higher values of logβ for Cu(II), Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes indicates more stable stepwise complexes formed as compared with Cu(II), Pb(II), Cd(II) and Mg(II) unhydrolysed humic acid complexes.

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STABILITY CONSTANTS OF COMPLEXES OF METAL IONS WITH PEATSOIL HUMIC ACIDS UNDER NON-ACID-CONDITIONS

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ABSTRACT

Stability constants of complexes of four divalent metal ions viz. Cu^{2+}, Pb^{2+},Mg^{2+} and Cd^{2+} with humic acids (HA) were determined by potentiometric titration of humic acids with the corresponding salt of the divalent metals in aqueous media under non-acid-condition. The log K (logarithm of the stability constant) ranged from 1.0942 to 2.7471 for metal-humic acid complexes were determined using point-wise computational method. The order of stability constants were obtained as follows: Cu >Pb> Cd > Mg for metal -HA complexes respectively, indicating a higher degree of complexation with Cu metal ion.

Keywords: stability constant, humic acid, potentiometric titration, divalent metals, acid hydrolysis.

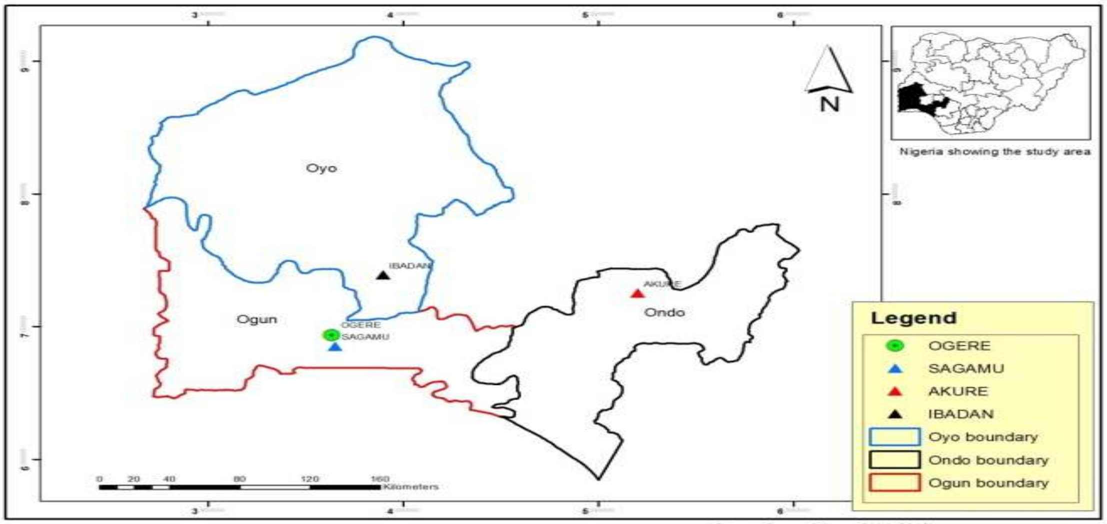
NTRODUCTION

The stability constant of a complex is the numerical expression of its stability and provides a quantitative measure of affinity of the metal ion to the complexing agent. An understanding of the relative stability of metal-complexes helps in predicting the behavior of metal ions in the soil (Ram and Raman, 1982). Extensive researches has been done to determine the stability constants of the complexes formed between humic acid (HA) with a number of metal ions. Ashok *et al*., (2000) reported that humic acid with hydroxyl, phenoxyl and carboxyl reactive groups can form coordination compound with metal ions at pH 3.5. The stability constants(Log K) for different metal-humic acid complexes indicated the following order of the stabilities of complexes formed between humic acid and metal ion, Cu >Fe >Pb> Ni > Co > Ca > Cd > Zn >Mn> Mg. Andelkovic *et al*., (2010) investigated the binding of Cd(II) to soil humic acid at pH 6.5 and in 0.1M KNO_3 ionic medium. The stability constant for binding indicating greater stability in the case when carboxyl groups are involved in complexation reaction. Kostic *et al*.,(2012) investigated the complexation of humic acid with certain heavy metal ions (Co(II), Ni(II),Cu(II), Zn(II), and Pb(II). The experiment was performed at 25°C, at pH 4.0 and ionic strength of 0.01M. Stability constant of complex between Pb(II) ions and humic acid is greater than stability constants of other investigated metal-humate complexes. Bogata and Sokolowska (2016) analyses the interaction between humic acids from different soils and Zn (II) ions at wide concentration ranges and at pH 5. Studies have showed significant impact of Zn concentration, pH and some properties of humic acids with zinc.But all of these studies were limited to acidic pH range. Therefore, the present study was carried out to determine and compare the stability constants of complexes of metal ions with hydrolysed peat soil humic acid and unhydrolysed peat soil humic under non-acid conditions.

MATERIALS AND METHODS

Analytical grade chemicals used includes hydrochloric acid (HCl), nitric acid (HNO_3), sodium hydroxide (NaOH), lead nitrate $Pb(NO_3)_2$, copper nitrate $Cu(NO_3)_2.3H_2O$, cadmium nitrate $Cd(NO_3)_2.4H_2O$, magnesium nitrate $Mg(NO_3)_2.6H_2O$, potassium nitrate (KNO_3), calcium chloride ($CaCl_2$), (sigma-Aldrich). Dowex 50WX8, (20-50 mesh) from Fluka.

Area of study



Source: Dept. of Geog. BUK (2016)

Figure 1: Map showing the sampling point at Sagamu Town, Ogun State.

Description of Sampling Area

Sagamu has geographical coordinates between 6°50′ north; 3° 38′ east is located in south western region of Nigeria. The region has tropical wet and dry climate with a lengthy wet season and relatively constant temperatures throughout the course of the year. Wet season runs from March to October, November to December forms the region dry season. The vegetation type of the region is savannah which is really grassland with small bushes and occasional big trees. Grassland soils have substantially higher organic matter content than forest soils (Novackova, 2011).

Sample Collection

The Peatsoil samples were collected from four different sampling points (0-10cm depth) in Sagamu into polyethylene bag with plastic spoons. Samples were taken to the laboratory, extraneous materials were removed; the samples were air-dried, crushed and ground to a fine powder in a mortar passed through a 0.20mm sieve. The samples were kept for analysis.

Isolation and purification of humic acid from peat soil sample

Peatsoil sample (100g) was mixed with 1000 cm^3 of 0.1M NaOH solution, shaken for 3hours and left to stand overnight. Dark-coloured supernatant was obtained and decanted from solid residue. The dark-coloured supernatant was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 6 hours. Yellowish brown supernatant and dark-brown precipitate were obtained. The yellowish brown supernatant was decanted followed by centrifuge and discarded. The dark-brown precipitate was mixed with 500$cm^3$of 0.1M NaOH solution followed by passing through dowex resin. The dark-brown solution was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 3 hours. The dark-brown precipitate was washed several times with deionized water. The supernatant was treated with $AgNO_3$ solution until no white precipitate observed. The humic acid was transferred to weighed crucible and dried at 60°C in an oven for 12 hours. The humic acid was cooled and dried in the desiccator, weighed and recorded. The obtained humic acid was dried again at 60°C for additional 6 hours cooled and dried in the desiccator, weighed and recorded constant weight was obtained (Baruah *et al*., 2015).

FT-IR analysis

FT-IR spectra of humic acid sample was analysed using Carry 630 FT-IR Agilent Technologies.

Unhydrolysed compost humic acid

The unhydrolysed humic acid was obtained after isolation and purification of compost humic acid and kept for investigation.

Acid hydrolysis of Peatsoil acid

Peatsoil humic acid sample (1g) was refluxed for 12 hours at (160°C) with 50cm^3 of 6M HCl. The mixture was allowed to cool, decanted, and centrifuged after hydrolysis. The insoluble residues were washed with distilled water via centrifugation several times, and the supernatant was treated with $AgNO_3$ solution until no white precipitate was observed. The residue was thoroughly dried over $CaCl_2$ in a desiccator at room temperature (Chefetz *et al*., 2002). Finally, the obtained hydrolysed humic acid was kept for investigation.

Potentiometric Titrations

Potentiometric measurements were carried out using a pH-meter Jenway (model 3510) with combine electrode, the sensitivity of the pH -meter is 0.01 units. The pH meter was switched on half an hour before starting the titration for initial warm up of the instrument. The instrument was calibrated with an aqueous standard buffer solution of pH 4.00 and 10.0 (borate buffer) prepared from a "Qualigens" buffer tablets.

The following sets of solutions were prepared in a 250cm^3 volumetric flask separately for pH metric titrations.

(i) 5 cm^3 0.1 M HCl + 40 cm^3 deionized water

(ii) 5 cm^3 0.1 M HCl + 39 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid

(iii) 5 cm^3 0.1 M HCl + 37 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid + 2 cm^3 0.01 M Cu(II)

The solutions were titrated against standardized 0.110MNaOH separately. The total volume of each mixture was adjusted to 50 cm^3 and the ionic strength of the solutions was maintained constant at by adding appropriate amount of stock solution of 1M KNO$_3$ (Gamal, 2015; Omar and Ali, 2015). A magnetic stirrer was used to achieve thorough mixing of the interacting solutions at 550 rpm. The same set of experimental conditions was applied for potentiometric titration of remaining samples.

Evaluation of pKa of Hydrolysed peat soil Humic Acids

The proton-ligand formation number n$_{\mathbf{A}}$ were calculated by Irving and Rossotti expression (Omar and Ali, 2015).

$$nA = Y- \frac{(V2-V1)(No-Eo)}{(Vo+V1)TcL} \quad \text{.....................................1}$$

Where: Y is number of dissociable proton, (V$_2$-V$_1$) is the measure of displacement of the ligand curve relative to acid curve, N^o and E^o are the resultant concentration of alkali solution, free acid solution, T$_{cL}$^{o} is the total ligand concentration, V^o is the total volume of titration solution,V$_1$ is the volume of alkali added to acid solution,V$_2$ is the volume of alkali added to acid solution + ligand solution, acid dissociation constants (pKa - values) of ligand were calculated by algebraic method point wise calculation (Tables 1). The dissociation constants (pKa) were calculated according to the following relation:

$$\text{pKa} = \text{pH} + \log(\frac{nA}{1-nA}) \quad \text{..............................2}$$

Where: pKa is the acid dissociation constant, n$_A$is the Proton-ligand formation number and pH is the pH-values (Omar and Ali, 2015).

Determination of metal-ligand stability constants (log K) of complexes

The potentiometric measurement for the determination of stability constant of a complex in solution is based on the fact that the redox potential of the couple $\frac{M^{+(m-n)}}{M^{+m}}$ is shifted significantly on complexation of the metal ion with the ligand. This method involves change in hydrogen ion concentration [H$^+$] due to the displacement or association of one or more protons taking place during complexation reaction. This change can be found out by titrating the solutions containing free acid, acid with ligand, and acid with ligand and metal ion, individually against a standard alkali solution at a constant ionic strength or temperature. Either ionic strength or temperature may be varied for different sets of solutions. In all the cases, the change in the pH of the solution is measured after each addition of a known amount of alkali to the reaction cell which contains the reaction mixture. The titration curves are then drawn by plotting the measured pH values against the corresponding volume of alkali added and the stability constants of the complexes are determined from the titration curves by employing pH-metric titration technique given by (Irving and Rossoti).

Metal-ligand stability constants (Log K) were determined by using the following relations:

$$\bar{n} = \frac{(V_3 - V_2)(E^0 + N^0)}{(V^0 + V_2)\bar{n}_A T_m^0} \quad \text{...3}$$

and

$$PL = \log_{10}\{\frac{1 + \beta_n^H \frac{1}{[anti \ \log \text{pH}]^n}}{T_L^0 - \bar{n} T_m^0} \text{X} \frac{(V^0 + V_3)}{V^0}\} \quad \text{...4}$$

Where $T_{L,}$ T^{o}, E°, and V^{o}havethe same significance as in equation (1) above, T_m denotes the total concentration of metal present in solution, V_3 is the volume of metal ions present in solution and β^H is the overall proton ligand stability constant. The metal-ligand stability constants (log K) were determined by employing point wise computational Method (eq. 5 and 6).

$\mathrm{Log}K_1 = \log\left(\frac{n}{1-n}\right) + pL$ 5

$\mathrm{Log}K_2 = \log\left(\frac{1-n}{2-n}\right) + pL$........................6

Where: Log K is the metal-ligand stability constant, pL is the Free ligand exponent function, **n** is the Average number of ligand attached with metal ion (Janrao*et al.*, 2014).The results obtained were analyzed by an ORIGIN 2016 program using titration data and then the proton-ligand stability constants (pKa) and Metal-ligand stability constant (LogK) calculated (Omar and Ali, 2015).

RESULTS AND DISCUSSION

Fourier transformed infrared (FT-IR) spectra of isolated humic acid from peat soils Figure 2 had distinct clear absorption bands indicating the presence of major humic acid structural elemental groups such as H bonded OH ($3680cm^{-1}$ peak), C=O of carbonyl ($1721cm^{-1}$ peak), functional groups of aliphatic components CH_2 ($2918cm^{-1}$ peak) and C-O stretching of polysaccharide ($1168cm^{-1}$ peak). The positions of the absorption bands of the spectra fell within typical major absorption bands of humic acid which is at frequencies 3680, 2918, 1721, 1168 cm^{-1}. The first peak centred in the vicinity of 3680 cm^{-1} region is attributed to phenol OH group bounded by intermolecular H bonds. The $2918cm^{-1}$ band usually has absorption maximum at 2918 cm^{-1} which is due to C–H stretching of alkane group (CH_2). The next major absorption band is 1721 cm^{-1}. This band has been commonly ascribed to C=O stretching of mainly carboxyl group (COOH) with trace amount of ketones. The last peak was observed at 1168 cm^{-1} due to C–O stretching of polysaccharides and this peak appeared also in the spectra of humic acid from peat soil. The FTIR spectra of the isolated humic acid contained all major characteristic absorption peaks of humic acid. These absorption peaks indicated the presence of the major structural elements of humic acid namely H bonded OH, C=C of aromatic ring, C=O of carbonyl group (both carboxyl and ketonic), CH_2 group. This strongly supports the presence of humic acid.

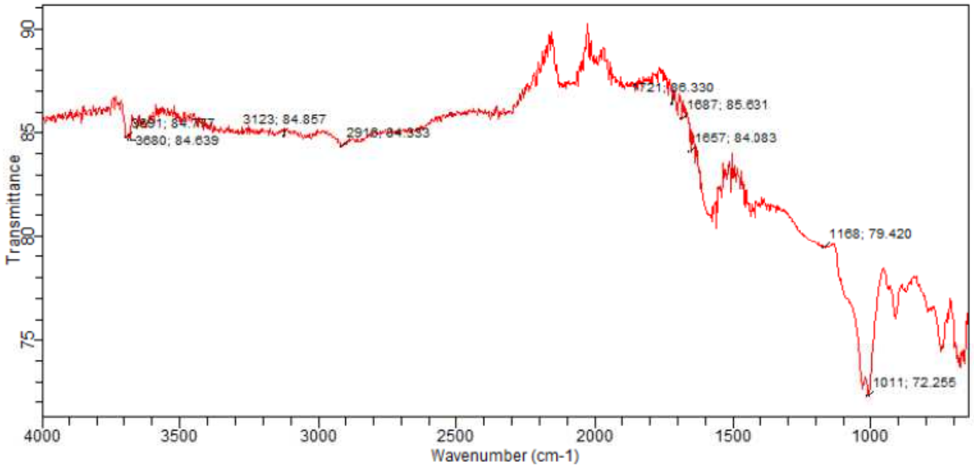


Fig. 2 : FT-IR spectraof peatsoilhumic acid (PSHA)

Evaluation of acid dissociation constant (pka) of acid hydrolysed peat soil humicacid at phenolic group

The value of the dissociation constant of the peat soil humic acid (PSHA) that underwent acidhydrolysis studied was found to be 8.9299 as shown Table 1, which is lower than the literaturevalues reported by Almeida and Szpoganics, (2015), Borges *et al.*, (2005); Badr *et al.*, (2012)and Fernandes *et al*,.(2009) of 9.73, 9.47 and 10.30. The difference between the obtained valuesand the reported values in this study might be probably as a result of acid hydrolysis of humicacid.

Table 1: PKa of (Hydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	log($\frac{nA}{1-nA}$)	pKa
8.50	5.30	6.29	0.99	0.3594	-0.2510	8.2490
8.72	5.35	6.37	1.02	0.3400	-0.2880	8.4320
9.00	5.40	6.46	1.06	0.3141	-0.3391	8.6609
9.22	5.45	6.55	1.10	0.2882	-0.3927	8.8273
9.51	5.50	6.66	1.16	0.2494	-0.4786	9.0314
9.73	5.55	6.78	1.23	0.2041	-0.5910	9.1390
10.00	5.60	6.90	1.30	0.1589	-0.7238	9.2762
10.23	5.65	7.05	1.40	0.0941	-0.9835	9.2465
10.49	5.70	7.10	1.40	0.0941	-0.9835	9.5065

Average pKa = 8.9299 ± 0.4186

Table 2: PKa of (Unhydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	Log($\frac{nA}{1-n}$)	pKa
8.50	5.30	5.81	0.51	0.6619	0.2919	8.7919
8.72	5.35	5.90	0.55	0.6357	0.2418	8.9618
9.00	5.40	6.00	0.60	0.6029	0.1813	9.1813
9.22	5.45	6.10	0.65	0.5701	0.1226	9.3426
9.51	5.50	6.20	0.70	0.5376	0.0654	9.5754
9.73	5.55	6.33	0.78	0.4851	-0.0259	9.7041
10.00	5.60	6.47	0.87	0.4262	-0.1291	9.8709
10.23	5.65	6.62	0.99	0.3609	-0.2481	9.9819
10.49	5.70	6.80	1.10	0.2759	-0.4690	10.0210

Average pKa = 9.4923± 0.4410

Metal-ligand stability constant (Log K)

The stabilityconstants require the accurate values of proton-ligand stability constants (Anil and Maroti, 2008). Metal titration curves crossed over ligand titration curve indicated the formation of complex upon proton release (Santosh, *et al.*, 2011). If the values of n- are within range 0.2-0.8 and 1.2-18 this indicates the formation of 1:1 and 1:2 complexes (Sayyed and Mazahar, 2012).

The metal (II)-humate stepwise stability constants (log k) at phenolic group (Tables 3-18)

Table 3: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n}{1-n}$)	$LogK_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

$LogK_1$ (Average value) = 2.4788± 0.2203

Table 4: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	Log($\frac{n-1}{2-n}$)	$LogK_2$
9.51	5.50	6.66	6.73	0.07	1.3509	1.70	-0.2671	1.4329
9.73	5.55	6.78	6.85	0.07	1.6383	1.51	0.2467	1.7567
10.00	5.60	6.90	6.98	0.08	2.1783	1.31	-0.2158	1.0942
10.23	5.65	7.05	7.13	0.08	4.1904	1.27		
10.49	5.70	7.10	7.19	0.09	4.6920			

$LogK_2$(Average value) = 1.4280 ± 0.3312

Table 5:Point-wise method,Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	Log($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430

$LogK_1$ **(Average value)** = 2.3059± 0.6153

Table 6:Point-wise method, Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$V_3\text{-}V_2$	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
9.73	5.55	6.33	6.42	0.09	0.9000	1.69		
10.00	5.60	6.47	6.58	0.11	1.2578	1.44	-0.4592	0.9808
10.23	5.65	6.62	6.84	0.12	1.6137	1.26	-0.2010	1.4610
10.49	5.70	6.80	6.92	0.12	2.1052	1.03		

$LogK_2$ **(Average value)** = 1.2209± 0.3398

Table 7:Point-wise method,Pb (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	log($\frac{n}{1-n}$)	$LogK_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.60	0.05	0.8333	1.96	0.6989	2.6589

$LogK_1$ (Average value) = 2.5832 ±0.1614

Table 8:Point-wise method,Pb-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	log($\frac{n-1}{2-n}$)	$logK_2$
9.51	5.50	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.83	0.05	1.1702	1.44		
10.00	5.60	6.90	6.90	0.05	1.4864	1.22	-0.0237	1.1963
10.23	5.65	7.05	7.10	0.05	2.0190	1.09		
10.49	5.70	7.10	7.17	0.07	3.6492	1.00		

$LogK_2$(Average value) = 1.1963

Table 9:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$V_3\text{-}V_2$	n	pL	Log ($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.5477	2.3123
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	0.0272	2.2072
9.51	5.50	6.20	6.26	0.07	0.6417	1.89	0.2530	2.1430
9.73	5.55	6.40	6.40	0.07	0.7000	1.67	0.3680	2.0380

$LogK_1$ **(Average value)** = 2.2364 ± 0.1602

Table 10:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$V_3\text{-}V_2$	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
10.00	5.60	6.47	6.55	0.08	1.9503	1.41		
10.23	5.65	6.62	6.72	0.11	1.4792	1.26	-0.0361	1.2239

$LogK_2$ **(Average value)** = 1.2239

Table 11:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	log($\frac{n}{n-1}$)	$LogK_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4290	2.2110
8.72	5.35	6.37	6.39	0.02	0.2858	2.42	-0.3978	2.0222
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

$LogK_1$ (Average value)=2.1382**±**0.1046

Table 12:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	log($\frac{n-1}{2-n}$)	LogK$_2$
9.51	5.55	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.84	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.93	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.10		
10.49	5.70	7.10	7.18	0.07	3.6492	0.83		

LogK$_2$(Average value) = 1.5453 **±** 0.3450

Table 13:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	V$_3$-V$_2$	n	pL	Log($\frac{n}{n-1}$)	Log K$_1$
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.3477	2.3123
9.00	5.40	6.00	6.04	0.04	0.3236	2.38	-0.3202	2.0598
9.22	5.45	6.10	6.15	0.05	0.4297	2.17	-0.1230	2.0470
9.51	5.50	6.20	6.26	0.06	0.5500	1.89	0.0871	1.9771
9.73	5.55	6.33	6.40	0.07	0.7000	1.67	0.3680	2.0380

LogK$_1$ **(Average value)** = 2.1568 ± 0.2069

Table 14:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	V$_3$-V$_2$	n	pL	Log($\frac{n-1}{2-n}$)	Log K$_2$
10.00	5.60	6.47	6.55	0.08	0.9148	1.41		
10.23	5.65	6.62	6.71	0.09	1.2102	1.20	-0.5749	0.6251
10.49	5.70	6.80	6.92	0.09	1.5968	1.03	0.1703	1.2003

LogK$_2$ **(Average value)** = 0.9127± 0.4070

Table15:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	Log($\frac{n}{1-n}$)	LogK$_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4210	2.2190
8.72	5.35	6.37	6.40	0.03	0.4286	2.42	-0.1249	2.2951
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.96	0.3010	2.2610
9.51	5.55	6.66	6.70	0.04	0.7720	1.67	0.5297	2.1997

LogK$_1$ (Average value) = 2.2108± 0.0825

Table 16:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	Log($\frac{n-1}{2-n}$)	Log K$_2$
9.73	5.55	6.78	6.83	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.95	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.09		
10.49	5.70	7.10	7.16	0.06	3.1429	0.89		

LogK$_2$ **(Average value)** = 1.5453± 0.3450

Table 17:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	V$_3$-V$_2$	n	pL	Log($\frac{n}{n-1}$)	Log K$_1$
8.50	5.30	5.81	5.86	0.05	0.3717	2.88	-0.2280	2.6520
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.06	0.06	0.4853	2.38	-0.0255	2.3545
9.22	5.45	6.10	6.16	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430
9.73	5.55	6.33	6.41	0.08	0.8000	1.69	0.6020	2.2920

LogK$_1$ **(Average value)** = 2.2516± 0.5380

Table 18:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$\mathrm{Log}(\frac{n-1}{2-n})$	Log K_2
10.00	5.60	6.47	6.57	0.10	1.1434	1.43		
10.23	5.65	6.62	6.72	0.10	1.3448	1.23	-0.2788	0.9512
10.49	5.70	6.80	6.90	0.10	1.7742	1.03	0.5351	1.5651

LogK_2 **(Average value)** = 1.2581± 0.4340

Table 19: Stepwise and overall Stability constants of thehydrolysed and unhydrolysed divalent metal (II) complexes

Chelates	**LogK_1**	**LogK_2**	**Logβ**
[Cu (Hydrolysed PSHA-1$)_2$]	2.4788	1.4280	3.9068
[Pb (Hydrolysed PSHA-1$)_2$]	2.5832	1.1963	3.7795
[Cd (Hydrolysed PSHA-1$)_2$]	2.2108	1.5453	3.7561
[Mg (Hydrolysed PSHA-1$)_2$]	2.1382	1.5453	3.6835
[Cu (Unhydrolysed PSHA-1$)_2$]	2.3059	1.2209	3.5268
[Pb (Unhydrolysed PSHA-1$)_2$]	2.2364	1.2239	3.4603
[Cd (Unhydrolysed PSHA-1$)_2$]	2.2516	1.2581	3.5097
[Mg (Unydrolysed PSHA-1$)_2$]	2.1568	0.9127	3.0695

The results obtained (Table19) shows the stepwise and overall stability constants to be not high indicating low stability of the complexes, because the solubility of most metal ions in the basic pH range is minimal due to metal hydroxide precipitation (Karimi, 2017). In general, the stepwise stability constants (K_1 and K_2) follow the order $K_1 > K_2$ for the copper, lead, magnesium and cadmium complexes respectively. The steady decrease of the values with increasing number of ligands is in agreement with the prediction made by researchers (Na'aliya, 2013). The decrease could be attributed to the fact that as the number of the ligands (Humate ions) that enters the coordination zone increases the aqua molecules available for replacement by the ligands become less. Thus, the metal ions become less electron loving with progressive intake of the ligand and this results in the decrease in the values of the constants (Na'aliya, 2013). Also the stability of the complexes is influenced by the size and number of the chelate rings(Mackay and Mackay,2002).All the complexes form rings in their structure as humate, a bidentate ligand, bond the metal ions in the ratio 1:2 (Boguta and Sokolowska, 2016) forming chelate rings. The values of the overall stability constants (logβ) obtained for humate complexes are not high indicating low stability as the values are not high. LogK values for copper-humates (Table 3 to 6) obtained in this study are lower than those reported for the complexes of humic acids (Pandey *et al*., 2015; Dinu, 2013; Kaschl *et al*., 2010 and Gilbeto and Jorg, 2001). The values of LogK(Table 7 to 10) forlead-humates are lower than those reported for the lead in the literature (Dinu, 2013; Gilbeto and Jorg 2001). Log K values(Table 11 to 14) for magnesium-humates obtained in this study are close to those reported by (Pandey *et al*., 2015). Log K values of cadmium-humates (Table 15 to 18) obtained in this work near to the one reported by (Dinu, 2013 and Pandey *et al*., 2015).The difference between the reported values and the values obtained in this study might be probably as a result of acid hydrolysis of humic acid. The values of the overall stability constants (log β) of the copper humates complexes presented in Table 19 is high than that of other metal humate complexes, show relatively high stability of Cu-HA complexes, show the following order of stability: Cu >Pb> Cd > Mg; which are in close agreement to the findings of (Dinu, 2013 and Pandey *et al*., 2015).The high stability of Cu-humate chelate could be attributed to the existence of coordinate covalent bond between the complexing agents and the Cu^{2+} ions. Since, Cu^{2+} being a metal of the transitional series with $3d^9$ electronic configurations can accept the electrons from the complexing agents. Similarly,the low stabilities of Pb,Cd and Mg -complexes could be explained by that Pb^{2+} with $6s^2$, Cd^{2+} with $4d^{10}$ and Mg^{2+} with $2p^6$ their electronic configuration has a completely filled d,p and s orbitals. Moreover, the stabilities of metal ions with hydrolysed humic acid from peat soil were higher than those with unhydrolysed humic acid from peat soil; which is ascribed to the high content of acidity in hydrolysed humic acid than unhydrolysed humic acid.

CONCLUSION

The values of logK for Cu(II) hydrolysed humic acid complex was higher followed by Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes as compared with metal(II) unhydrolysed humic acid complexes . This indicates acid hydrolysis of humic acid can enhance the complexation behavior of humic acid with metal (II) ions. However, the higher values of logβ for Cu(II), Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes indicates more stable stepwise complexes formed as compared with Cu(II), Pb(II), Cd(II) and Mg(II) unhydrolysed humic acid complexes.

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STABILITY CONSTANTS OF COMPLEXES OF METAL IONS WITH PEATSOIL HUMIC ACIDS UNDER NON-ACID-CONDITIONS

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ABSTRACT

Stability constants of complexes of four divalent metal ions viz. Cu^{2+}, Pb^{2+},Mg^{2+} and Cd^{2+} with humic acids (HA) were determined by potentiometric titration of humic acids with the corresponding salt of the divalent metals in aqueous media under non-acid-condition. The log K (logarithm of the stability constant) ranged from 1.0942 to 2.7471 for metal-humic acid complexes were determined using point-wise computational method. The order of stability constants were obtained as follows: Cu >Pb> Cd > Mg for metal -HA complexes respectively, indicating a higher degree of complexation with Cu metal ion.

Keywords: stability constant, humic acid, potentiometric titration, divalent metals, acid hydrolysis.

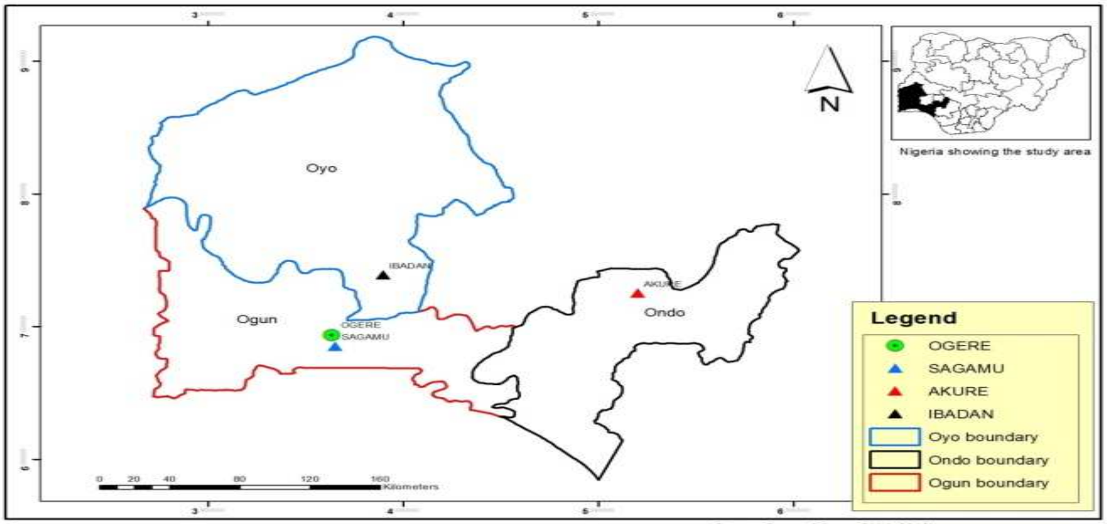
NTRODUCTION

The stability constant of a complex is the numerical expression of its stability and provides a quantitative measure of affinity of the metal ion to the complexing agent. An understanding of the relative stability of metal-complexes helps in predicting the behavior of metal ions in the soil (Ram and Raman, 1982). Extensive researches has been done to determine the stability constants of the complexes formed between humic acid (HA) with a number of metal ions. Ashok *et al*., (2000) reported that humic acid with hydroxyl, phenoxyl and carboxyl reactive groups can form coordination compound with metal ions at pH 3.5. The stability constants(Log K) for different metal-humic acid complexes indicated the following order of the stabilities of complexes formed between humic acid and metal ion, Cu >Fe >Pb> Ni > Co > Ca > Cd > Zn >Mn> Mg. Andelkovic *et al*., (2010) investigated the binding of Cd(II) to soil humic acid at pH 6.5 and in 0.1M KNO_3 ionic medium. The stability constant for binding indicating greater stability in the case when carboxyl groups are involved in complexation reaction. Kostic *et al*.,(2012) investigated the complexation of humic acid with certain heavy metal ions (Co(II), Ni(II),Cu(II), Zn(II), and Pb(II). The experiment was performed at 25°C, at pH 4.0 and ionic strength of 0.01M. Stability constant of complex between Pb(II) ions and humic acid is greater than stability constants of other investigated metal-humate complexes. Bogata and Sokolowska (2016) analyses the interaction between humic acids from different soils and Zn (II) ions at wide concentration ranges and at pH 5. Studies have showed significant impact of Zn concentration, pH and some properties of humic acids with zinc.But all of these studies were limited to acidic pH range. Therefore, the present study was carried out to determine and compare the stability constants of complexes of metal ions with hydrolysed peat soil humic acid and unhydrolysed peat soil humic under non-acid conditions.

MATERIALS AND METHODS

Analytical grade chemicals used includes hydrochloric acid (HCl), nitric acid (HNO_3), sodium hydroxide (NaOH), lead nitrate $Pb(NO_3)_2$, copper nitrate $Cu(NO_3)_2.3H_2O$, cadmium nitrate $Cd(NO_3)_2.4H_2O$, magnesium nitrate $Mg(NO_3)_2.6H_2O$, potassium nitrate (KNO_3), calcium chloride ($CaCl_2$), (sigma-Aldrich). Dowex 50WX8, (20-50 mesh) from Fluka.

Area of study



Source: Dept. of Geog. BUK (2016)

Figure 1: Map showing the sampling point at Sagamu Town, Ogun State.

Description of Sampling Area

Sagamu has geographical coordinates between 6°50′ north; 3° 38′ east is located in south western region of Nigeria. The region has tropical wet and dry climate with a lengthy wet season and relatively constant temperatures throughout the course of the year. Wet season runs from March to October, November to December forms the region dry season. The vegetation type of the region is savannah which is really grassland with small bushes and occasional big trees. Grassland soils have substantially higher organic matter content than forest soils (Novackova, 2011).

Sample Collection

The Peatsoil samples were collected from four different sampling points (0-10cm depth) in Sagamu into polyethylene bag with plastic spoons. Samples were taken to the laboratory, extraneous materials were removed; the samples were air-dried, crushed and ground to a fine powder in a mortar passed through a 0.20mm sieve. The samples were kept for analysis.

Isolation and purification of humic acid from peat soil sample

Peatsoil sample (100g) was mixed with 1000 cm^3 of 0.1M NaOH solution, shaken for 3hours and left to stand overnight. Dark-coloured supernatant was obtained and decanted from solid residue. The dark-coloured supernatant was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 6 hours. Yellowish brown supernatant and dark-brown precipitate were obtained. The yellowish brown supernatant was decanted followed by centrifuge and discarded. The dark-brown precipitate was mixed with $500cm^3$of 0.1M NaOH solution followed by passing through dowex resin. The dark-brown solution was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 3 hours. The dark-brown precipitate was washed several times with deionized water. The supernatant was treated with $AgNO_3$ solution until no white precipitate observed. The humic acid was transferred to weighed crucible and dried at 60°C in an oven for 12 hours. The humic acid was cooled and dried in the desiccator, weighed and recorded. The obtained humic acid was dried again at 60°C for additional 6 hours cooled and dried in the desiccator, weighed and recorded constant weight was obtained (Baruah *et al*., 2015).

FT-IR analysis

FT-IR spectra of humic acid sample was analysed using Carry 630 FT-IR Agilent Technologies.

Unhydrolysed compost humic acid

The unhydrolysed humic acid was obtained after isolation and purification of compost humic acid and kept for investigation.

Acid hydrolysis of Peatsoil acid

Peatsoil humic acid sample (1g) was refluxed for 12 hours at (160°C) with $50cm^3$ of 6M HCl. The mixture was allowed to cool, decanted, and centrifuged after hydrolysis. The insoluble residues were washed with distilled water via centrifugation several times, and the supernatant was treated with $AgNO_3$ solution until no white precipitate was observed. The residue was thoroughly dried over $CaCl_2$ in a desiccator at room temperature (Chefetz *et al*., 2002). Finally, the obtained hydrolysed humic acid was kept for investigation.

Potentiometric Titrations

Potentiometric measurements were carried out using a pH-meter Jenway (model 3510) with combine electrode, the sensitivity of the pH - meter is 0.01 units. The pH meter was switched on half an hour before starting the titration for initial warm up of the instrument. The instrument was calibrated with an aqueous standard buffer solution of pH 4.00 and 10.0 (borate buffer) prepared from a "Qualigens" buffer tablets.

The following sets of solutions were prepared in a 250cm^3 volumetric flask separately for pH metric titrations.

(i) 5 cm^3 0.1 M HCl + 40 cm^3 deionized water
(ii) 5 cm^3 0.1 M HCl + 39 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid
(iii) 5 cm^3 0.1 M HCl + 37 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid
+ 2 cm^3 0.01 M Cu(II)

The solutions were titrated against standardized 0.110MNaOH separately. The total volume of each mixture was adjusted to 50 cm^3 and the ionic strength of the solutions was maintained constant at by adding appropriate amount of stock solution of 1M KNO$_3$ (Gamal, 2015; Omar and Ali, 2015). A magnetic stirrer was used to achieve thorough mixing of the interacting solutions at 550 rpm. The same set of experimental conditions was applied for potentiometric titration of remaining samples.

Evaluation of pKa of Hydrolysed peat soil Humic Acids

The proton-ligand formation number n$_{\mathbf{A}}$ were calculated by Irving and Rossotti expression (Omar and Ali, 2015).

$$nA = Y - \frac{(V2-V1)(No-Eo)}{(Vo+V1)TcL} \quad \text{....................................1}$$

Where: Y is number of dissociable proton, (V$_2$-V$_1$) is the measure of displacement of the ligand curve relative to acid curve, N^o and E^o are the resultant concentration of alkali solution, free acid solution, T$_{cL}$^{o} is the total ligand concentration, V^o is the total volume of titration solution,V$_1$ is the volume of alkali added to acid solution,V$_2$ is the volume of alkali added to acid solution + ligand solution, acid dissociation constants (pKa - values) of ligand were calculated by algebraic method point wise calculation (Tables 1). The dissociation constants (pKa) were calculated according to the following relation:

$$pKa = pH + \log\left(\frac{nA}{1-nA}\right) \quad \text{..............................2}$$

Where: pKa is the acid dissociation constant, n$_A$is the Proton-ligand formation number and pH is the pH-values (Omar and Ali, 2015).

Determination of metal-ligand stability constants (log K) of complexes

The potentiometric measurement for the determination of stability constant of a complex in solution is based on the fact that the redox potential of the couple $\frac{M^{+(m-n)}}{M^{+m}}$ is shifted significantly on complexation of the metal ion with the ligand. This method involves change in hydrogen ion concentration [H$^+$] due to the displacement or association of one or more protons taking place during complexation reaction. This change can be found out by titrating the solutions containing free acid, acid with ligand, and acid with ligand and metal ion, individually against a standard alkali solution at a constant ionic strength or temperature. Either ionic strength or temperature may be varied for different sets of solutions. In all the cases, the change in the pH of the solution is measured after each addition of a known amount of alkali to the reaction cell which contains the reaction mixture. The titration curves are then drawn by plotting the measured pH values against the corresponding volume of alkali added and the stability constants of the complexes are determined from the titration curves by employing pH-metric titration technique given by (Irving and Rossoti).

Metal-ligand stability constants (Log K) were determined by using the following relations:

$$\bar{n} = \frac{(V_3 - V_2)(E^0 + N^0)}{(V^0 + V_2)\bar{n}_A T_m^0} \quad \text{..3}$$

and

$$PL = \log_{10}\left\{\frac{1 + \beta_n^H \frac{1}{[anti\ \log \mathrm{pH}]^n}}{T_L^0 - \bar{n} T_m^0} \mathrm{X} \frac{(V^0 + V_3)}{V^0}\right\} \quad \text{..4}$$

Where $T_{L,}$ T^o, E°, and V^ohavethe same significance as in equation (1) above, T_m denotes the total concentration of metal present in solution, V_3 is the volume of metal ions present in solution and β^H is the overall proton ligand stability constant. The metal-ligand stability constants (log K) were determined by employing point wise computational Method (eq. 5 and 6).

$$\text{Log}K_1 = \log\left(\frac{n}{1-n}\right) + pL \qquad ....5$$

$$\text{Log}K_2 = \log\left(\frac{1-n}{2-n}\right) + pL........................6$$

Where: Log K is the metal-ligand stability constant, pL is the Free ligand exponent function, **n** is the Average number of ligand attached with metal ion (Janrao*et al.*, 2014).The results obtained were analyzed by an ORIGIN 2016 program using titration data and then the proton-ligand stability constants (pKa) and Metal-ligand stability constant (LogK) calculated (Omar and Ali, 2015).

RESULTS AND DISCUSSION

Fourier transformed infrared (FT-IR) spectra of isolated humic acid from peat soils Figure 2 had distinct clear absorption bands indicating the presence of major humic acid structural elemental groups such as H bonded OH ($3680cm^{-1}$ peak), C=O of carbonyl ($1721cm^{-1}$ peak), functional groups of aliphatic components CH_2 ($2918cm^{-1}$ peak) and C-O stretching of polysaccharide ($1168cm^{-1}$ peak). The positions of the absorption bands of the spectra fell within typical major absorption bands of humic acid which is at frequencies 3680, 2918, 1721, 1168 cm^{-1}. The first peak centred in the vicinity of 3680 cm^{-1} region is attributed to phenol OH group bounded by intermolecular H bonds. The $2918cm^{-1}$ band usually has absorption maximum at 2918 cm^{-1} which is due to C–H stretching of alkane group (CH_2). The next major absorption band is 1721 cm^{-1}. This band has been commonly ascribed to C=O stretching of mainly carboxyl group (COOH) with trace amount of ketones. The last peak was observed at 1168 cm^{-1} due to C–O stretching of polysaccharides and this peak appeared also in the spectra of humic acid from peat soil. The FTIR spectra of the isolated humic acid contained all major characteristic absorption peaks of humic acid. These absorption peaks indicated the presence of the major structural elements of humic acid namely H bonded OH, C=C of aromatic ring, C=O of carbonyl group (both carboxyl and ketonic), CH_2 group. This strongly supports the presence of humic acid.

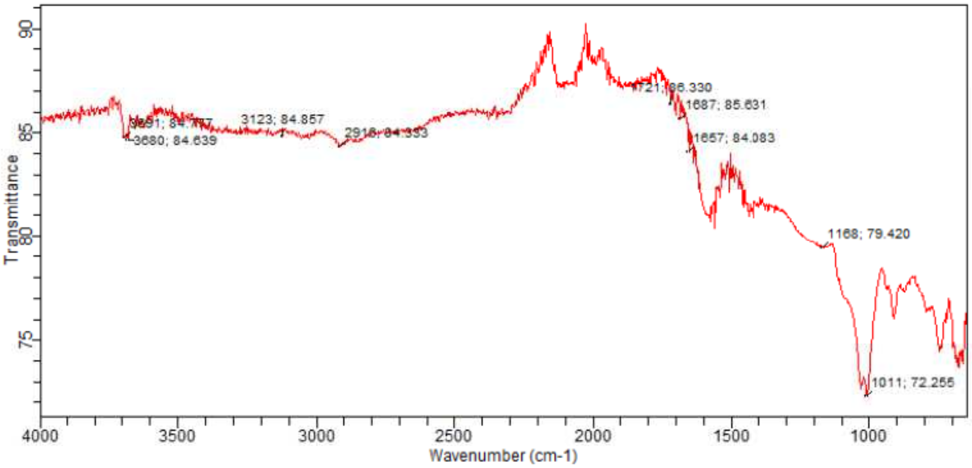


Fig. 2 : FT-IR spectraof peatsoilhumic acid (PSHA)

Evaluation of acid dissociation constant (pka) of acid hydrolysed peat soil humicacid at phenolic group

The value of the dissociation constant of the peat soil humic acid (PSHA) that underwent acidhydrolysis studied was found to be 8.9299 as shown Table 1, which is lower than the literaturevalues reported by Almeida and Szpoganics, (2015), Borges *et al.*, (2005); Badr *et al.*, (2012)and Fernandes *et al*,.(2009) of 9.73, 9.47 and 10.30. The difference between the obtained valuesand the reported values in this study might be probably as a result of acid hydrolysis of humicacid.

Table 1: PKa of (Hydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	$\log(\frac{nA}{1-nA})$	pKa
8.50	5.30	6.29	0.99	0.3594	-0.2510	8.2490
8.72	5.35	6.37	1.02	0.3400	-0.2880	8.4320
9.00	5.40	6.46	1.06	0.3141	-0.3391	8.6609
9.22	5.45	6.55	1.10	0.2882	-0.3927	8.8273
9.51	5.50	6.66	1.16	0.2494	-0.4786	9.0314
9.73	5.55	6.78	1.23	0.2041	-0.5910	9.1390
10.00	5.60	6.90	1.30	0.1589	-0.7238	9.2762
10.23	5.65	7.05	1.40	0.0941	-0.9835	9.2465
10.49	5.70	7.10	1.40	0.0941	-0.9835	9.5065

Average pKa = 8.9299 ± 0.4186

Table 2: PKa of (Unhydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	$\text{Log}(\frac{nA}{1-n})$	pKa
8.50	5.30	5.81	0.51	0.6619	0.2919	8.7919
8.72	5.35	5.90	0.55	0.6357	0.2418	8.9618
9.00	5.40	6.00	0.60	0.6029	0.1813	9.1813
9.22	5.45	6.10	0.65	0.5701	0.1226	9.3426
9.51	5.50	6.20	0.70	0.5376	0.0654	9.5754
9.73	5.55	6.33	0.78	0.4851	-0.0259	9.7041
10.00	5.60	6.47	0.87	0.4262	-0.1291	9.8709
10.23	5.65	6.62	0.99	0.3609	-0.2481	9.9819
10.49	5.70	6.80	1.10	0.2759	-0.4690	10.0210

Average pKa = 9.4923± 0.4410

Metal-ligand stability constant (Log K)

The stabilityconstants require the accurate values of proton-ligand stability constants (Anil and Maroti, 2008). Metal titration curves crossed over ligand titration curve indicated the formation of complex upon proton release (Santosh, *et al.*, 2011). If the values of n- are within range 0.2-0.8 and 1.2-18 this indicates the formation of 1:1 and 1:2 complexes (Sayyed and Mazahar, 2012).

The metal (II)-humate stepwise stability constants (log k) at phenolic group (Tables 3-18)

Table 3: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3$-$V_2)$	n	pL	$\log(\frac{n}{1-n})$	LogK_1
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

LogK_1 (Average value) = 2.4788± 0.2203

Table 4: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3$-$V_2)$	n	pL	$\text{Log}(\frac{n-1}{2-n})$	LogK_2
9.51	5.50	6.66	6.73	0.07	1.3509	1.70	-0.2671	1.4329
9.73	5.55	6.78	6.85	0.07	1.6383	1.51	0.2467	1.7567
10.00	5.60	6.90	6.98	0.08	2.1783	1.31	-0.2158	1.0942
10.23	5.65	7.05	7.13	0.08	4.1904	1.27		
10.49	5.70	7.10	7.19	0.09	4.6920			

LogK_2(Average value) = 1.4280 ± 0.3312

Table 5:Point-wise method,Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	Log($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430

$LogK_1$ **(Average value)** = 2.3059± 0.6153

Table 6:Point-wise method, Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$V_3\text{-}V_2$	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
9.73	5.55	6.33	6.42	0.09	0.9000	1.69		
10.00	5.60	6.47	6.58	0.11	1.2578	1.44	-0.4592	0.9808
10.23	5.65	6.62	6.84	0.12	1.6137	1.26	-0.2010	1.4610
10.49	5.70	6.80	6.92	0.12	2.1052	1.03		

$LogK_2$ **(Average value)** = 1.2209± 0.3398

Table 7:Point-wise method,Pb (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	log($\frac{n}{1-n}$)	$LogK_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.60	0.05	0.8333	1.96	0.6989	2.6589

$LogK_1$ (Average value) = 2.5832 ±0.1614

Table 8:Point-wise method,Pb-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	log($\frac{n-1}{2-n}$)	$logK_2$
9.51	5.50	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.83	0.05	1.1702	1.44		
10.00	5.60	6.90	6.90	0.05	1.4864	1.22	-0.0237	1.1963
10.23	5.65	7.05	7.10	0.05	2.0190	1.09		
10.49	5.70	7.10	7.17	0.07	3.6492	1.00		

$LogK_2$(Average value) = 1.1963

Table 9:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$V_3\text{-}V_2$	n	pL	Log ($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.5477	2.3123
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	0.0272	2.2072
9.51	5.50	6.20	6.26	0.07	0.6417	1.89	0.2530	2.1430
9.73	5.55	6.40	6.40	0.07	0.7000	1.67	0.3680	2.0380

$LogK_1$ **(Average value)** = 2.2364 ± 0.1602

Table 10:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$V_3\text{-}V_2$	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
10.00	5.60	6.47	6.55	0.08	1.9503	1.41		
10.23	5.65	6.62	6.72	0.11	1.4792	1.26	-0.0361	1.2239

$LogK_2$ **(Average value)** = 1.2239

Table 11:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	log($\frac{n}{n-1}$)	$LogK_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4290	2.2110
8.72	5.35	6.37	6.39	0.02	0.2858	2.42	-0.3978	2.0222
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

$LogK_1$ (Average value)=2.1382**±**0.1046

Table 12:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n-1}{2-n}$)	$LogK_2$
9.51	5.55	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.84	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.93	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.10		
10.49	5.70	7.10	7.18	0.07	3.6492	0.83		

$LogK_2$(Average value) = 1.5453 **±** 0.3450

Table 13:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.3477	2.3123
9.00	5.40	6.00	6.04	0.04	0.3236	2.38	-0.3202	2.0598
9.22	5.45	6.10	6.15	0.05	0.4297	2.17	-0.1230	2.0470
9.51	5.50	6.20	6.26	0.06	0.5500	1.89	0.0871	1.9771
9.73	5.55	6.33	6.40	0.07	0.7000	1.67	0.3680	2.0380

$LogK_1$ **(Average value)** = 2.1568 ± 0.2069

Table 14:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
10.00	5.60	6.47	6.55	0.08	0.9148	1.41		
10.23	5.65	6.62	6.71	0.09	1.2102	1.20	-0.5749	0.6251
10.49	5.70	6.80	6.92	0.09	1.5968	1.03	0.1703	1.2003

$LogK_2$ **(Average value)** = 0.9127± 0.4070

Table15:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	Log($\frac{n}{1-n}$)	$LogK_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4210	2.2190
8.72	5.35	6.37	6.40	0.03	0.4286	2.42	-0.1249	2.2951
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.96	0.3010	2.2610
9.51	5.55	6.66	6.70	0.04	0.7720	1.67	0.5297	2.1997

$LogK_1$ (Average value) = 2.2108± 0.0825

Table 16:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
9.73	5.55	6.78	6.83	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.95	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.09		
10.49	5.70	7.10	7.16	0.06	3.1429	0.89		

$LogK_2$ **(Average value)** = 1.5453± 0.3450

Table 17:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.86	0.05	0.3717	2.88	-0.2280	2.6520
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.06	0.06	0.4853	2.38	-0.0255	2.3545
9.22	5.45	6.10	6.16	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430
9.73	5.55	6.33	6.41	0.08	0.8000	1.69	0.6020	2.2920

$LogK_1$ **(Average value)** = 2.2516± 0.5380

Table 18:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$\mathrm{Log}(\frac{n-1}{2-n})$	Log K_2
10.00	5.60	6.47	6.57	0.10	1.1434	1.43		
10.23	5.65	6.62	6.72	0.10	1.3448	1.23	-0.2788	0.9512
10.49	5.70	6.80	6.90	0.10	1.7742	1.03	0.5351	1.5651

$\mathrm{LogK_2}$ **(Average value)** = 1.2581± 0.4340

Table 19: Stepwise and overall Stability constants of thehydrolysed and unhydrolysed divalent metal (II) complexes

Chelates	**$\mathrm{LogK_1}$**	**$\mathrm{LogK_2}$**	**Logβ**
[Cu (Hydrolysed PSHA-1)$_2$]	2.4788	1.4280	3.9068
[Pb (Hydrolysed PSHA-1)$_2$]	2.5832	1.1963	3.7795
[Cd (Hydrolysed PSHA-1)$_2$]	2.2108	1.5453	3.7561
[Mg (Hydrolysed PSHA-1)$_2$]	2.1382	1.5453	3.6835
[Cu (Unhydrolysed PSHA-1)$_2$]	2.3059	1.2209	3.5268
[Pb (Unhydrolysed PSHA-1)$_2$]	2.2364	1.2239	3.4603
[Cd (Unhydrolysed PSHA-1)$_2$]	2.2516	1.2581	3.5097
[Mg (Unydrolysed PSHA-1)$_2$]	2.1568	0.9127	3.0695

The results obtained (Table19) shows the stepwise and overall stability constants to be not high indicating low stability of the complexes, because the solubility of most metal ions in the basic pH range is minimal due to metal hydroxide precipitation (Karimi, 2017). In general, the stepwise stability constants (K_1 and K_2) follow the order $K_1 > K_2$ for the copper, lead, magnesium and cadmium complexes respectively. The steady decrease of the values with increasing number of ligands is in agreement with the prediction made by researchers (Na'aliya, 2013). The decrease could be attributed to the fact that as the number of the ligands (Humate ions) that enters the coordination zone increases the aqua molecules available for replacement by the ligands become less. Thus, the metal ions become less electron loving with progressive intake of the ligand and this results in the decrease in the values of the constants (Na'aliya, 2013). Also the stability of the complexes is influenced by the size and number of the chelate rings(Mackay and Mackay,2002).All the complexes form rings in their structure as humate, a bidentate ligand, bond the metal ions in the ratio 1:2 (Boguta and Sokolowska, 2016) forming chelate rings. The values of the overall stability constants (logβ) obtained for humate complexes are not high indicating low stability as the values are not high. LogK values for copper-humates (Table 3 to 6) obtained in this study are lower than those reported for the complexes of humic acids (Pandey *et al.*, 2015; Dinu, 2013; Kaschl *et al.*, 2010 and Gilbeto and Jorg, 2001). The values of LogK(Table 7 to 10) forlead-humates are lower than those reported for the lead in the literature (Dinu, 2013; Gilbeto and Jorg 2001). Log K values(Table 11 to 14) for magnesium-humates obtained in this study are close to those reported by (Pandey *et al.*, 2015). Log K values of cadmium-humates (Table 15 to 18) obtained in this work near to the one reported by (Dinu, 2013 and Pandey *et al.*, 2015).The difference between the reported values and the values obtained in this study might be probably as a result of acid hydrolysis of humic acid. The values of the overall stability constants (log β) of the copper humates complexes presented in Table 19 is high than that of other metal humate complexes, show relatively high stability of Cu-HA complexes, show the following order of stability: Cu >Pb> Cd > Mg; which are in close agreement to the findings of (Dinu, 2013 and Pandey *et al.*, 2015).The high stability of Cu-humate chelate could be attributed to the existence of coordinate covalent bond between the complexing agents and the Cu^{2+} ions. Since, Cu^{2+} being a metal of the transitional series with $3d^9$ electronic configurations can accept the electrons from the complexing agents. Similarly,the low stabilities of Pb,Cd and Mg - complexes could be explained by that Pb^{2+} with $6s^2$, Cd^{2+} with $4d^{10}$ and Mg^{2+} with $2p^6$ their electronic configuration has a completely filled d,p and s orbitals. Moreover, the stabilities of metal ions with hydrolysed humic acid from peat soil were higher than those with unhydrolysed humic acid from peat soil; which is ascribed to the high content of acidity in hydrolysed humic acid than unhydrolysed humic acid.

CONCLUSION

The values of logK for Cu(II) hydrolysed humic acid complex was higher followed by Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes as compared with metal(II) unhydrolysed humic acid complexes . This indicates acid hydrolysis of humic acid can enhance the complexation behavior of humic acid with metal (II) ions. However, the higher values of logβ for Cu(II), Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes indicates more stable stepwise complexes formed as compared with Cu(II), Pb(II), Cd(II) and Mg(II) unhydrolysed humic acid complexes.

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STABILITY CONSTANTS OF COMPLEXES OF METAL IONS WITH PEATSOIL HUMIC ACIDS UNDER NON-ACID-CONDITIONS

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ABSTRACT

Stability constants of complexes of four divalent metal ions viz. Cu^{2+}, Pb^{2+},Mg^{2+} and Cd^{2+} with humic acids (HA) were determined by potentiometric titration of humic acids with the corresponding salt of the divalent metals in aqueous media under non-acid-condition. The log K (logarithm of the stability constant) ranged from 1.0942 to 2.7471 for metal-humic acid complexes were determined using point-wise computational method. The order of stability constants were obtained as follows: Cu >Pb> Cd > Mg for metal -HA complexes respectively, indicating a higher degree of complexation with Cu metal ion.

Keywords: stability constant, humic acid, potentiometric titration, divalent metals, acid hydrolysis.

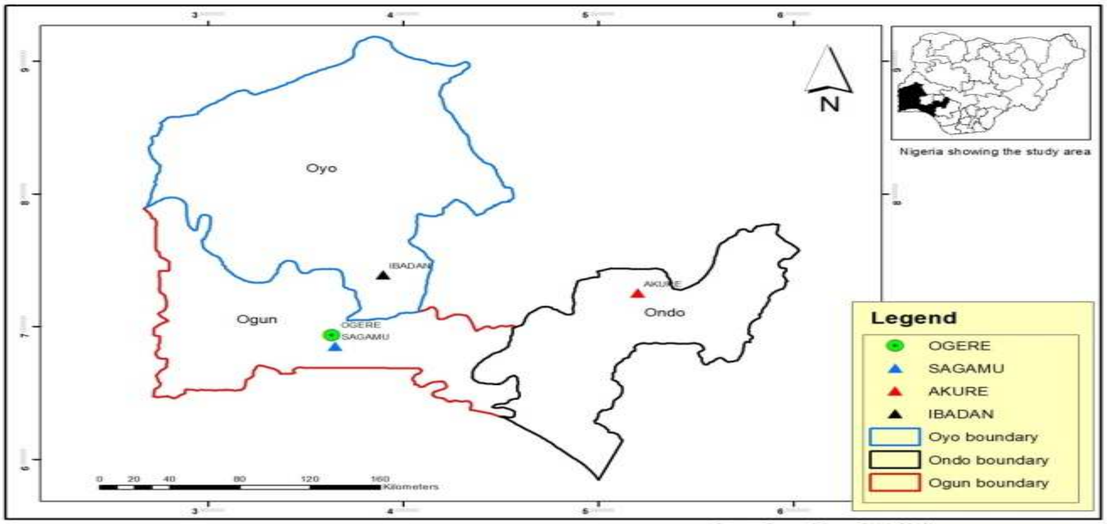
NTRODUCTION

The stability constant of a complex is the numerical expression of its stability and provides a quantitative measure of affinity of the metal ion to the complexing agent. An understanding of the relative stability of metal-complexes helps in predicting the behavior of metal ions in the soil (Ram and Raman, 1982). Extensive researches has been done to determine the stability constants of the complexes formed between humic acid (HA) with a number of metal ions. Ashok *et al.*, (2000) reported that humic acid with hydroxyl, phenoxyl and carboxyl reactive groups can form coordination compound with metal ions at pH 3.5. The stability constants(Log K) for different metal-humic acid complexes indicated the following order of the stabilities of complexes formed between humic acid and metal ion, Cu >Fe >Pb> Ni > Co > Ca > Cd > Zn >Mn> Mg. Andelkovic *et al.*, (2010) investigated the binding of Cd(II) to soil humic acid at pH 6.5 and in 0.1M KNO_3 ionic medium. The stability constant for binding indicating greater stability in the case when carboxyl groups are involved in complexation reaction. Kostic *et al.*,(2012) investigated the complexation of humic acid with certain heavy metal ions (Co(II), Ni(II),Cu(II), Zn(II), and Pb(II). The experiment was performed at 25°C, at pH 4.0 and ionic strength of 0.01M. Stability constant of complex between Pb(II) ions and humic acid is greater than stability constants of other investigated metal-humate complexes. Bogata and Sokolowska (2016) analyses the interaction between humic acids from different soils and Zn (II) ions at wide concentration ranges and at pH 5. Studies have showed significant impact of Zn concentration, pH and some properties of humic acids with zinc.But all of these studies were limited to acidic pH range. Therefore, the present study was carried out to determine and compare the stability constants of complexes of metal ions with hydrolysed peat soil humic acid and unhydrolysed peat soil humic under non-acid conditions.

MATERIALS AND METHODS

Analytical grade chemicals used includes hydrochloric acid (HCl), nitric acid (HNO_3), sodium hydroxide (NaOH), lead nitrate $Pb(NO_3)_2$, copper nitrate $Cu(NO_3)_2.3H_2O$, cadmium nitrate $Cd(NO_3)_2.4H_2O$, magnesium nitrate $Mg(NO_3)_2.6H_2O$, potassium nitrate (KNO_3), calcium chloride ($CaCl_2$), (sigma-Aldrich). Dowex 50WX8, (20-50 mesh) from Fluka.

Area of study



Source: Dept. of Geog. BUK (2016)

Figure 1: Map showing the sampling point at Sagamu Town, Ogun State.

Description of Sampling Area

Sagamu has geographical coordinates between 6°50′ north; 3° 38′ east is located in south western region of Nigeria. The region has tropical wet and dry climate with a lengthy wet season and relatively constant temperatures throughout the course of the year. Wet season runs from March to October, November to December forms the region dry season. The vegetation type of the region is savannah which is really grassland with small bushes and occasional big trees. Grassland soils have substantially higher organic matter content than forest soils (Novackova, 2011).

Sample Collection

The Peatsoil samples were collected from four different sampling points (0-10cm depth) in Sagamu into polyethylene bag with plastic spoons. Samples were taken to the laboratory, extraneous materials were removed; the samples were air-dried, crushed and ground to a fine powder in a mortar passed through a 0.20mm sieve. The samples were kept for analysis.

Isolation and purification of humic acid from peat soil sample

Peatsoil sample (100g) was mixed with 1000 cm^3 of 0.1M NaOH solution, shaken for 3hours and left to stand overnight. Dark-coloured supernatant was obtained and decanted from solid residue. The dark-coloured supernatant was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 6 hours. Yellowish brown supernatant and dark-brown precipitate were obtained. The yellowish brown supernatant was decanted followed by centrifuge and discarded. The dark-brown precipitate was mixed with $500cm^3$of 0.1M NaOH solution followed by passing through dowex resin. The dark-brown solution was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 3 hours. The dark-brown precipitate was washed several times with deionized water. The supernatant was treated with $AgNO_3$ solution until no white precipitate observed. The humic acid was transferred to weighed crucible and dried at 60°C in an oven for 12 hours. The humic acid was cooled and dried in the desiccator, weighed and recorded. The obtained humic acid was dried again at 60°C for additional 6 hours cooled and dried in the desiccator, weighed and recorded constant weight was obtained (Baruah *et al*., 2015).

FT-IR analysis

FT-IR spectra of humic acid sample was analysed using Carry 630 FT-IR Agilent Technologies.

Unhydrolysed compost humic acid

The unhydrolysed humic acid was obtained after isolation and purification of compost humic acid and kept for investigation.

Acid hydrolysis of Peatsoil acid

Peatsoil humic acid sample (1g) was refluxed for 12 hours at (160°C) with $50cm^3$ of 6M HCl. The mixture was allowed to cool, decanted, and centrifuged after hydrolysis. The insoluble residues were washed with distilled water via centrifugation several times, and the supernatant was treated with $AgNO_3$ solution until no white precipitate was observed. The residue was thoroughly dried over $CaCl_2$ in a desiccator at room temperature (Chefetz *et al*., 2002). Finally, the obtained hydrolysed humic acid was kept for investigation.

Potentiometric Titrations

Potentiometric measurements were carried out using a pH-meter Jenway (model 3510) with combine electrode, the sensitivity of the pH - meter is 0.01 units. The pH meter was switched on half an hour before starting the titration for initial warm up of the instrument. The instrument was calibrated with an aqueous standard buffer solution of pH 4.00 and 10.0 (borate buffer) prepared from a "Qualigens" buffer tablets.

The following sets of solutions were prepared in a 250cm^3 volumetric flask separately for pH metric titrations.

(i) 5 cm^3 0.1 M HCl + 40 cm^3 deionized water

(ii) 5 cm^3 0.1 M HCl + 39 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid

(iii) 5 cm^3 0.1 M HCl + 37 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid + 2 cm^3 0.01 M Cu(II)

The solutions were titrated against standardized 0.110MNaOH separately. The total volume of each mixture was adjusted to 50 cm^3 and the ionic strength of the solutions was maintained constant at by adding appropriate amount of stock solution of 1M KNO$_3$ (Gamal, 2015; Omar and Ali, 2015). A magnetic stirrer was used to achieve thorough mixing of the interacting solutions at 550 rpm. The same set of experimental conditions was applied for potentiometric titration of remaining samples.

Evaluation of pKa of Hydrolysed peat soil Humic Acids

The proton-ligand formation number n$_{\mathbf{A}}$ were calculated by Irving and Rossotti expression (Omar and Ali, 2015).

$$nA = Y\text{-}\ \frac{(V2-V1)(No-Eo)}{(Vo+V1)TcL} \quad \text{..................................}1$$

Where: Y is number of dissociable proton, (V$_2$-V$_1$) is the measure of displacement of the ligand curve relative to acid curve, N^o and E^o are the resultant concentration of alkali solution, free acid solution, T$_{cL}$^{o} is the total ligand concentration, V^o is the total volume of titration solution,V$_1$ is the volume of alkali added to acid solution,V$_2$ is the volume of alkali added to acid solution + ligand solution, acid dissociation constants (pKa - values) of ligand were calculated by algebraic method point wise calculation (Tables 1). The dissociation constants (pKa) were calculated according to the following relation:

$$pKa = pH + \log\left(\frac{nA}{1-nA}\right) \quad \text{.............................}2$$

Where: pKa is the acid dissociation constant, n$_A$is the Proton-ligand formation number and pH is the pH-values (Omar and Ali, 2015).

Determination of metal-ligand stability constants (log K) of complexes

The potentiometric measurement for the determination of stability constant of a complex in solution is based on the fact that the redox potential of the couple $\frac{M^{+(m-n)}}{M^{+m}}$ is shifted significantly on complexation of the metal ion with the ligand. This method involves change in hydrogen ion concentration [H$^+$] due to the displacement or association of one or more protons taking place during complexation reaction. This change can be found out by titrating the solutions containing free acid, acid with ligand, and acid with ligand and metal ion, individually against a standard alkali solution at a constant ionic strength or temperature. Either ionic strength or temperature may be varied for different sets of solutions. In all the cases, the change in the pH of the solution is measured after each addition of a known amount of alkali to the reaction cell which contains the reaction mixture. The titration curves are then drawn by plotting the measured pH values against the corresponding volume of alkali added and the stability constants of the complexes are determined from the titration curves by employing pH-metric titration technique given by (Irving and Rossoti).

Metal-ligand stability constants (Log K) were determined by using the following relations:

$$\bar{n} = \frac{(V_3 - V_2)(E^0 + N^0)}{(V^0 + V_2)\bar{n}_A T_m^0} \quad \text{..}3$$

and

$$PL = \log_{10}\left\{\frac{1 + \beta_n^H \dfrac{1}{[anti\ \log \mathrm{pH}]^n}}{T_L^0 - \bar{n}T_m^0} \mathrm{X} \frac{(V^0 + V_3)}{V^0}\right\} \quad \text{..}4$$

Where $T_{L,}$ T^{o}, E°, and V^{o}havethe same significance as in equation (1) above, T_m denotes the total concentration of metal present in solution, V_3 is the volume of metal ions present in solution and β^H is the overall proton ligand stability constant. The metal-ligand stability constants (log K) were determined by employing point wise computational Method (eq. 5 and 6).

$$\text{LogK}_1 = \log\left(\frac{n}{1-n}\right) + \text{pL} \qquad \ldots\ldots\ldots\ldots.5$$

$$\text{LogK}_2 = \log\left(\frac{1-n}{2-n}\right) + \text{pL}\ldots\ldots\ldots\ldots\ldots\ldots\ldots..6$$

Where: Log K is the metal-ligand stability constant, pL is the Free ligand exponent function, **n** is the Average number of ligand attached with metal ion (Janrao*et al.*, 2014).The results obtained were analyzed by an ORIGIN 2016 program using titration data and then the proton-ligand stability constants (pKa) and Metal-ligand stability constant (LogK) calculated (Omar and Ali, 2015).

RESULTS AND DISCUSSION

Fourier transformed infrared (FT-IR) spectra of isolated humic acid from peat soils Figure 2 had distinct clear absorption bands indicating the presence of major humic acid structural elemental groups such as H bonded OH ($3680 cm^{-1}$ peak), C=O of carbonyl ($1721 cm^{-1}$ peak), functional groups of aliphatic components CH_2 ($2918 cm^{-1}$ peak) and C-O stretching of polysaccharide ($1168 cm^{-1}$ peak). The positions of the absorption bands of the spectra fell within typical major absorption bands of humic acid which is at frequencies 3680, 2918, 1721, 1168 cm^{-1}. The first peak centred in the vicinity of 3680 cm^{-1} region is attributed to phenol OH group bounded by intermolecular H bonds. The $2918 cm^{-1}$ band usually has absorption maximum at 2918 cm^{-1} which is due to C–H stretching of alkane group (CH_2). The next major absorption band is 1721 cm^{-1}. This band has been commonly ascribed to C=O stretching of mainly carboxyl group (COOH) with trace amount of ketones. The last peak was observed at 1168 cm^{-1} due to C–O stretching of polysaccharides and this peak appeared also in the spectra of humic acid from peat soil. The FTIR spectra of the isolated humic acid contained all major characteristic absorption peaks of humic acid. These absorption peaks indicated the presence of the major structural elements of humic acid namely H bonded OH, C=C of aromatic ring, C=O of carbonyl group (both carboxyl and ketonic), CH_2 group. This strongly supports the presence of humic acid.

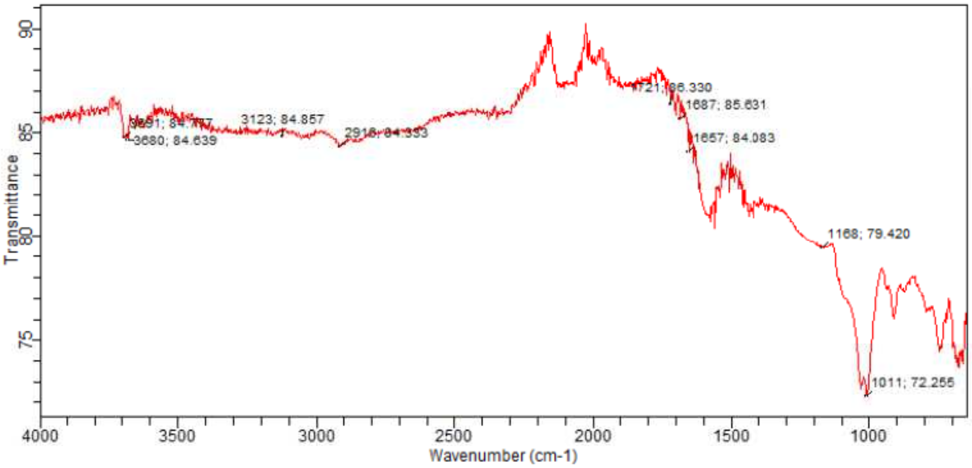


Fig. 2 : FT-IR spectraof peatsoilhumic acid (PSHA)

Evaluation of acid dissociation constant (pka) of acid hydrolysed peat soil humicacid at phenolic group

The value of the dissociation constant of the peat soil humic acid (PSHA) that underwent acidhydrolysis studied was found to be 8.9299 as shown Table 1, which is lower than the literaturevalues reported by Almeida and Szpoganics, (2015), Borges *et al.*, (2005); Badr *et al.*, (2012)and Fernandes *et al*,.(2009) of 9.73, 9.47 and 10.30. The difference between the obtained valuesand the reported values in this study might be probably as a result of acid hydrolysis of humicacid.

Table 1: PKa of (Hydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	$\log(\frac{nA}{1-nA})$	pKa
8.50	5.30	6.29	0.99	0.3594	-0.2510	8.2490
8.72	5.35	6.37	1.02	0.3400	-0.2880	8.4320
9.00	5.40	6.46	1.06	0.3141	-0.3391	8.6609
9.22	5.45	6.55	1.10	0.2882	-0.3927	8.8273
9.51	5.50	6.66	1.16	0.2494	-0.4786	9.0314
9.73	5.55	6.78	1.23	0.2041	-0.5910	9.1390
10.00	5.60	6.90	1.30	0.1589	-0.7238	9.2762
10.23	5.65	7.05	1.40	0.0941	-0.9835	9.2465
10.49	5.70	7.10	1.40	0.0941	-0.9835	9.5065

Average pKa = 8.9299 ± 0.4186

Table 2: PKa of (Unhydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	$\mathrm{Log}(\frac{nA}{1-n})$	pKa
8.50	5.30	5.81	0.51	0.6619	0.2919	8.7919
8.72	5.35	5.90	0.55	0.6357	0.2418	8.9618
9.00	5.40	6.00	0.60	0.6029	0.1813	9.1813
9.22	5.45	6.10	0.65	0.5701	0.1226	9.3426
9.51	5.50	6.20	0.70	0.5376	0.0654	9.5754
9.73	5.55	6.33	0.78	0.4851	-0.0259	9.7041
10.00	5.60	6.47	0.87	0.4262	-0.1291	9.8709
10.23	5.65	6.62	0.99	0.3609	-0.2481	9.9819
10.49	5.70	6.80	1.10	0.2759	-0.4690	10.0210

Average pKa = 9.4923± 0.4410

Metal-ligand stability constant (Log K)

The stabilityconstants require the accurate values of proton-ligand stability constants (Anil and Maroti, 2008). Metal titration curves crossed over ligand titration curve indicated the formation of complex upon proton release (Santosh, *et al.*, 2011). If the values of n- are within range 0.2-0.8 and 1.2-18 this indicates the formation of 1:1 and 1:2 complexes (Sayyed and Mazahar, 2012).

The metal (II)-humate stepwise stability constants (log k) at phenolic group (Tables 3-18)

Table 3: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$\log(\frac{n}{1-n})$	$\mathrm{Log}K_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

$\mathrm{LogK_1}$ (Average value) = 2.4788± 0.2203

Table 4: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$\mathrm{Log}(\frac{n-1}{2-n})$	$\mathrm{Log}K_2$
9.51	5.50	6.66	6.73	0.07	1.3509	1.70	-0.2671	1.4329
9.73	5.55	6.78	6.85	0.07	1.6383	1.51	0.2467	1.7567
10.00	5.60	6.90	6.98	0.08	2.1783	1.31	-0.2158	1.0942
10.23	5.65	7.05	7.13	0.08	4.1904	1.27		
10.49	5.70	7.10	7.19	0.09	4.6920			

$\mathrm{LogK_2}$(Average value) = 1.4280 ± 0.3312

Table 5:Point-wise method,Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	Log($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430

$LogK_1$ **(Average value)** = 2.3059± 0.6153

Table 6:Point-wise method, Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
9.73	5.55	6.33	6.42	0.09	0.9000	1.69		
10.00	5.60	6.47	6.58	0.11	1.2578	1.44	-0.4592	0.9808
10.23	5.65	6.62	6.84	0.12	1.6137	1.26	-0.2010	1.4610
10.49	5.70	6.80	6.92	0.12	2.1052	1.03		

$LogK_2$ **(Average value)** = 1.2209± 0.3398

Table 7:Point-wise method,Pb (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n}{1-n}$)	$LogK_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.60	0.05	0.8333	1.96	0.6989	2.6589

$LogK_1$ (Average value) = 2.5832 ±0.1614

Table 8:Point-wise method,Pb-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n-1}{2-n}$)	$logK_2$
9.51	5.50	6.66	6.71	0.05	0.9650	1.67	-0.0237	1.1963
9.73	5.55	6.78	6.83	0.05	1.1702	1.44		
10.00	5.60	6.90	6.90	0.05	1.4864	1.22		
10.23	5.65	7.05	7.10	0.05	2.0190	1.09		
10.49	5.70	7.10	7.17	0.07	3.6492	1.00		

$LogK_2$(Average value) = 1.1963

Table 9:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log ($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.5477	2.3123
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	0.0272	2.2072
9.51	5.50	6.20	6.26	0.07	0.6417	1.89	0.2530	2.1430
9.73	5.55	6.40	6.40	0.07	0.7000	1.67	0.3680	2.0380

$LogK_1$ **(Average value)** = 2.2364 ± 0.1602

Table 10:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
10.00	5.60	6.47	6.55	0.08	1.9503	1.41	-0.0361	1.2239
10.23	5.65	6.62	6.72	0.11	1.4792	1.26		

$LogK_2$ **(Average value)** = 1.2239

Table 11:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n}{n-1}$)	$LogK_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4290	2.2110
8.72	5.35	6.37	6.39	0.02	0.2858	2.42	-0.3978	2.0222
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

$LogK_1$ (Average value)=2.1382**±**0.1046

Table 12:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$\log(\frac{n-1}{2-n})$	$LogK_2$
9.51	5.55	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.84	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.93	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.10		
10.49	5.70	7.10	7.18	0.07	3.6492	0.83		

$LogK_2$(Average value) = 1.5453 **±** 0.3450

Table 13:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$Log(\frac{n}{n-1})$	$Log\ K_1$
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.3477	2.3123
9.00	5.40	6.00	6.04	0.04	0.3236	2.38	-0.3202	2.0598
9.22	5.45	6.10	6.15	0.05	0.4297	2.17	-0.1230	2.0470
9.51	5.50	6.20	6.26	0.06	0.5500	1.89	0.0871	1.9771
9.73	5.55	6.33	6.40	0.07	0.7000	1.67	0.3680	2.0380

$LogK_1$ **(Average value)** = 2.1568 ± 0.2069

Table 14:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$Log(\frac{n-1}{2-n})$	$Log\ K_2$
10.00	5.60	6.47	6.55	0.08	0.9148	1.41		
10.23	5.65	6.62	6.71	0.09	1.2102	1.20	-0.5749	0.6251
10.49	5.70	6.80	6.92	0.09	1.5968	1.03	0.1703	1.2003

$LogK_2$ **(Average value)** = 0.9127± 0.4070

Table15:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$Log(\frac{n}{1-n})$	$LogK_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4210	2.2190
8.72	5.35	6.37	6.40	0.03	0.4286	2.42	-0.1249	2.2951
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.96	0.3010	2.2610
9.51	5.55	6.66	6.70	0.04	0.7720	1.67	0.5297	2.1997

$LogK_1$ (Average value) = 2.2108± 0.0825

Table 16:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$Log(\frac{n-1}{2-n})$	$Log\ K_2$
9.73	5.55	6.78	6.83	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.95	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.09		
10.49	5.70	7.10	7.16	0.06	3.1429	0.89		

$LogK_2$ **(Average value)** = 1.5453± 0.3450

Table 17:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$Log(\frac{n}{n-1})$	$Log\ K_1$
8.50	5.30	5.81	5.86	0.05	0.3717	2.88	-0.2280	2.6520
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.06	0.06	0.4853	2.38	-0.0255	2.3545
9.22	5.45	6.10	6.16	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430
9.73	5.55	6.33	6.41	0.08	0.8000	1.69	0.6020	2.2920

$LogK_1$ **(Average value)** = 2.2516± 0.5380

Table 18:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$\text{Log}(\frac{n-1}{2-n})$	Log K_2
10.00	5.60	6.47	6.57	0.10	1.1434	1.43		
10.23	5.65	6.62	6.72	0.10	1.3448	1.23	-0.2788	0.9512
10.49	5.70	6.80	6.90	0.10	1.7742	1.03	0.5351	1.5651

LogK_2 **(Average value)** = 1.2581± 0.4340

Table 19: Stepwise and overall Stability constants of thehydrolysed and unhydrolysed divalent metal (II) complexes

Chelates	**LogK_1**	**LogK_2**	**Logβ**
[Cu (Hydrolysed PSHA-1)$_2$]	2.4788	1.4280	3.9068
[Pb (Hydrolysed PSHA-1)$_2$]	2.5832	1.1963	3.7795
[Cd (Hydrolysed PSHA-1)$_2$]	2.2108	1.5453	3.7561
[Mg (Hydrolysed PSHA-1)$_2$]	2.1382	1.5453	3.6835
[Cu (Unhydrolysed PSHA-1)$_2$]	2.3059	1.2209	3.5268
[Pb (Unhydrolysed PSHA-1)$_2$]	2.2364	1.2239	3.4603
[Cd (Unhydrolysed PSHA-1)$_2$]	2.2516	1.2581	3.5097
[Mg (Unydrolysed PSHA-1)$_2$]	2.1568	0.9127	3.0695

The results obtained (Table19) shows the stepwise and overall stability constants to be not high indicating low stability of the complexes, because the solubility of most metal ions in the basic pH range is minimal due to metal hydroxide precipitation (Karimi, 2017). In general, the stepwise stability constants (K_1 and K_2) follow the order $K_1 > K_2$ for the copper, lead, magnesium and cadmium complexes respectively. The steady decrease of the values with increasing number of ligands is in agreement with the prediction made by researchers (Na'aliya, 2013). The decrease could be attributed to the fact that as the number of the ligands (Humate ions) that enters the coordination zone increases the aqua molecules available for replacement by the ligands become less. Thus, the metal ions become less electron loving with progressive intake of the ligand and this results in the decrease in the values of the constants (Na'aliya, 2013). Also the stability of the complexes is influenced by the size and number of the chelate rings(Mackay and Mackay,2002).All the complexes form rings in their structure as humate, a bidentate ligand, bond the metal ions in the ratio 1:2 (Boguta and Sokolowska, 2016) forming chelate rings. The values of the overall stability constants (logβ) obtained for humate complexes are not high indicating low stability as the values are not high. LogK values for copper-humates (Table 3 to 6) obtained in this study are lower than those reported for the complexes of humic acids (Pandey *et al.*, 2015; Dinu, 2013; Kaschl *et al.*, 2010 and Gilbeto and Jorg, 2001). The values of LogK(Table 7 to 10) forlead-humates are lower than those reported for the lead in the literature (Dinu, 2013; Gilbeto and Jorg 2001). Log K values(Table 11 to 14) for magnesium-humates obtained in this study are close to those reported by (Pandey *et al.*, 2015). Log K values of cadmium-humates (Table 15 to 18) obtained in this work near to the one reported by (Dinu, 2013 and Pandey *et al.*, 2015).The difference between the reported values and the values obtained in this study might be probably as a result of acid hydrolysis of humic acid. The values of the overall stability constants (log β) of the copper humates complexes presented in Table 19 is high than that of other metal humate complexes, show relatively high stability of Cu-HA complexes, show the following order of stability: Cu >Pb> Cd > Mg; which are in close agreement to the findings of (Dinu, 2013 and Pandey *et al.*, 2015).The high stability of Cu-humate chelate could be attributed to the existence of coordinate covalent bond between the complexing agents and the Cu^{2+} ions. Since, Cu^{2+} being a metal of the transitional series with $3d^9$ electronic configurations can accept the electrons from the complexing agents. Similarly,the low stabilities of Pb,Cd and Mg -complexes could be explained by that Pb^{2+} with $6s^2$, Cd^{2+} with $4d^{10}$ and Mg^{2+} with $2p^6$ their electronic configuration has a completely filled d,p and s orbitals. Moreover, the stabilities of metal ions with hydrolysed humic acid from peat soil were higher than those with unhydrolysed humic acid from peat soil; which is ascribed to the high content of acidity in hydrolysed humic acid than unhydrolysed humic acid.

CONCLUSION

The values of logK for Cu(II) hydrolysed humic acid complex was higher followed by Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes as compared with metal(II) unhydrolysed humic acid complexes . This indicates acid hydrolysis of humic acid can enhance the complexation behavior of humic acid with metal (II) ions. However, the higher values of logβ for Cu(II), Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes indicates more stable stepwise complexes formed as compared with Cu(II), Pb(II), Cd(II) and Mg(II) unhydrolysed humic acid complexes.

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STABILITY CONSTANTS OF COMPLEXES OF METAL IONS WITH PEATSOIL HUMIC ACIDS UNDER NON-ACID-CONDITIONS

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ABSTRACT

Stability constants of complexes of four divalent metal ions viz. Cu^{2+}, Pb^{2+},Mg^{2+} and Cd^{2+} with humic acids (HA) were determined by potentiometric titration of humic acids with the corresponding salt of the divalent metals in aqueous media under non-acid-condition. The log K (logarithm of the stability constant) ranged from 1.0942 to 2.7471 for metal-humic acid complexes were determined using point-wise computational method. The order of stability constants were obtained as follows: Cu >Pb> Cd > Mg for metal -HA complexes respectively, indicating a higher degree of complexation with Cu metal ion.

Keywords: stability constant, humic acid, potentiometric titration, divalent metals, acid hydrolysis.

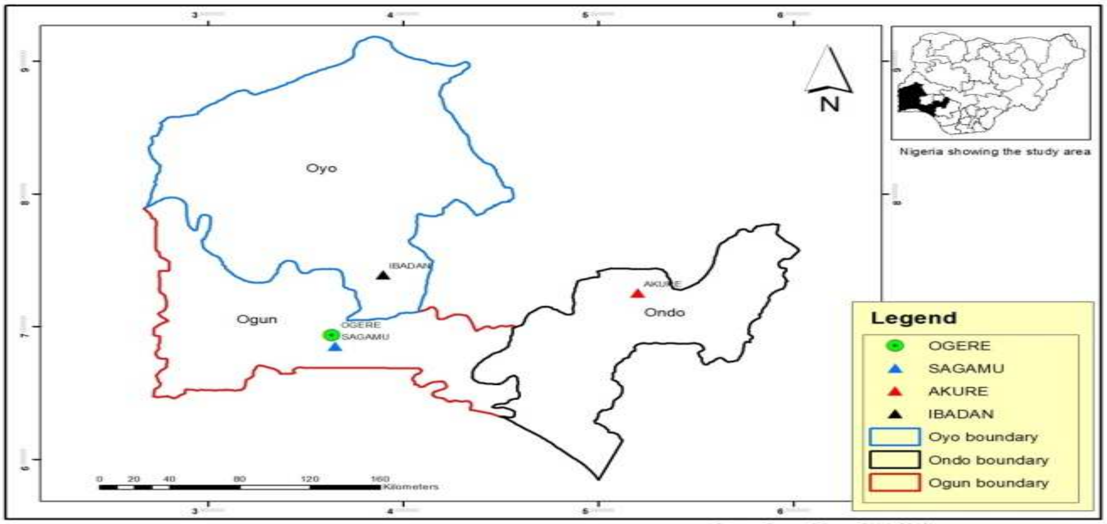
NTRODUCTION

The stability constant of a complex is the numerical expression of its stability and provides a quantitative measure of affinity of the metal ion to the complexing agent. An understanding of the relative stability of metal-complexes helps in predicting the behavior of metal ions in the soil (Ram and Raman, 1982). Extensive researches has been done to determine the stability constants of the complexes formed between humic acid (HA) with a number of metal ions. Ashok *et al*., (2000) reported that humic acid with hydroxyl, phenoxyl and carboxyl reactive groups can form coordination compound with metal ions at pH 3.5. The stability constants(Log K) for different metal-humic acid complexes indicated the following order of the stabilities of complexes formed between humic acid and metal ion, Cu >Fe >Pb> Ni > Co > Ca > Cd > Zn >Mn> Mg. Andelkovic *et al*., (2010) investigated the binding of Cd(II) to soil humic acid at pH 6.5 and in 0.1M KNO_3 ionic medium. The stability constant for binding indicating greater stability in the case when carboxyl groups are involved in complexation reaction. Kostic *et al*.,(2012) investigated the complexation of humic acid with certain heavy metal ions (Co(II), Ni(II),Cu(II), Zn(II), and Pb(II). The experiment was performed at 25°C, at pH 4.0 and ionic strength of 0.01M. Stability constant of complex between Pb(II) ions and humic acid is greater than stability constants of other investigated metal-humate complexes. Bogata and Sokolowska (2016) analyses the interaction between humic acids from different soils and Zn (II) ions at wide concentration ranges and at pH 5. Studies have showed significant impact of Zn concentration, pH and some properties of humic acids with zinc.But all of these studies were limited to acidic pH range. Therefore, the present study was carried out to determine and compare the stability constants of complexes of metal ions with hydrolysed peat soil humic acid and unhydrolysed peat soil humic under non-acid conditions.

MATERIALS AND METHODS

Analytical grade chemicals used includes hydrochloric acid (HCl), nitric acid (HNO_3), sodium hydroxide (NaOH), lead nitrate $Pb(NO_3)_2$, copper nitrate $Cu(NO_3)_2.3H_2O$, cadmium nitrate $Cd(NO_3)_2.4H_2O$, magnesium nitrate $Mg(NO_3)_2.6H_2O$, potassium nitrate (KNO_3), calcium chloride ($CaCl_2$), (sigma-Aldrich). Dowex 50WX8, (20-50 mesh) from Fluka.

Area of study



Source: Dept. of Geog. BUK (2016)

Figure 1: Map showing the sampling point at Sagamu Town, Ogun State.

Description of Sampling Area

Sagamu has geographical coordinates between 6°50′ north; 3° 38′ east is located in south western region of Nigeria. The region has tropical wet and dry climate with a lengthy wet season and relatively constant temperatures throughout the course of the year. Wet season runs from March to October, November to December forms the region dry season. The vegetation type of the region is savannah which is really grassland with small bushes and occasional big trees. Grassland soils have substantially higher organic matter content than forest soils (Novackova, 2011).

Sample Collection

The Peatsoil samples were collected from four different sampling points (0-10cm depth) in Sagamu into polyethylene bag with plastic spoons. Samples were taken to the laboratory, extraneous materials were removed; the samples were air-dried, crushed and ground to a fine powder in a mortar passed through a 0.20mm sieve. The samples were kept for analysis.

Isolation and purification of humic acid from peat soil sample

Peatsoil sample (100g) was mixed with 1000 cm^3 of 0.1M NaOH solution, shaken for 3hours and left to stand overnight. Dark-coloured supernatant was obtained and decanted from solid residue. The dark-coloured supernatant was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 6 hours. Yellowish brown supernatant and dark-brown precipitate were obtained. The yellowish brown supernatant was decanted followed by centrifuge and discarded. The dark-brown precipitate was mixed with $500cm^3$of 0.1M NaOH solution followed by passing through dowex resin. The dark-brown solution was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 3 hours. The dark-brown precipitate was washed several times with deionized water. The supernatant was treated with $AgNO_3$ solution until no white precipitate observed. The humic acid was transferred to weighed crucible and dried at 60°C in an oven for 12 hours. The humic acid was cooled and dried in the desiccator, weighed and recorded. The obtained humic acid was dried again at 60°C for additional 6 hours cooled and dried in the desiccator, weighed and recorded constant weight was obtained (Baruah *et al.*, 2015).

FT-IR analysis

FT-IR spectra of humic acid sample was analysed using Carry 630 FT-IR Agilent Technologies.

Unhydrolysed compost humic acid

The unhydrolysed humic acid was obtained after isolation and purification of compost humic acid and kept for investigation.

Acid hydrolysis of Peatsoil acid

Peatsoil humic acid sample (1g) was refluxed for 12 hours at (160°C) with $50cm^3$ of 6M HCl. The mixture was allowed to cool, decanted, and centrifuged after hydrolysis. The insoluble residues were washed with distilled water via centrifugation several times, and the supernatant was treated with $AgNO_3$ solution until no white precipitate was observed. The residue was thoroughly dried over $CaCl_2$ in a desiccator at room temperature (Chefetz *et al.*, 2002). Finally, the obtained hydrolysed humic acid was kept for investigation.

Potentiometric Titrations

Potentiometric measurements were carried out using a pH-meter Jenway (model 3510) with combine electrode, the sensitivity of the pH - meter is 0.01 units. The pH meter was switched on half an hour before starting the titration for initial warm up of the instrument. The instrument was calibrated with an aqueous standard buffer solution of pH 4.00 and 10.0 (borate buffer) prepared from a "Qualigens" buffer tablets.

The following sets of solutions were prepared in a 250cm^3 volumetric flask separately for pH metric titrations.

(i) 5 cm^3 0.1 M HCl + 40 cm^3 deionized water
(ii) 5 cm^3 0.1 M HCl + 39 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid
(iii) 5 cm^3 0.1 M HCl + 37 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid + 2 cm^3 0.01 M Cu(II)

The solutions were titrated against standardized 0.110MNaOH separately. The total volume of each mixture was adjusted to 50 cm^3 and the ionic strength of the solutions was maintained constant at by adding appropriate amount of stock solution of 1M KNO_3 (Gamal, 2015; Omar and Ali, 2015). A magnetic stirrer was used to achieve thorough mixing of the interacting solutions at 550 rpm. The same set of experimental conditions was applied for potentiometric titration of remaining samples.

Evaluation of pKa of Hydrolysed peat soil Humic Acids

The proton-ligand formation number n$_{\mathbf{A}}$ were calculated by Irving and Rossotti expression (Omar and Ali, 2015).

$$nA = Y- \frac{(V2-V1)(No-Eo)}{(Vo+V1)TcL} \text{ ……………………………1}$$

Where: Y is number of dissociable proton, (V_2-V_1) is the measure of displacement of the ligand curve relative to acid curve, N^o and E^o are the resultant concentration of alkali solution, free acid solution, $T_{cL}{}^o$ is the total ligand concentration, V^o is the total volume of titration solution,V_1 is the volume of alkali added to acid solution,V_2 is the volume of alkali added to acid solution + ligand solution, acid dissociation constants (pKa - values) of ligand were calculated by algebraic method point wise calculation (Tables 1). The dissociation constants (pKa) were calculated according to the following relation:

$$pKa = pH + \log(\frac{nA}{1-nA}) \text{ ………………………..2}$$

Where: pKa is the acid dissociation constant, $n_A$is the Proton-ligand formation number and pH is the pH-values (Omar and Ali, 2015).

Determination of metal-ligand stability constants (log K) of complexes

The potentiometric measurement for the determination of stability constant of a complex in solution is based on the fact that the redox potential of the couple $\frac{M^{+(m-n)}}{M^{+m}}$ is shifted significantly on complexation of the metal ion with the ligand. This method involves change in hydrogen ion concentration [H$^+$] due to the displacement or association of one or more protons taking place during complexation reaction. This change can be found out by titrating the solutions containing free acid, acid with ligand, and acid with ligand and metal ion, individually against a standard alkali solution at a constant ionic strength or temperature. Either ionic strength or temperature may be varied for different sets of solutions. In all the cases, the change in the pH of the solution is measured after each addition of a known amount of alkali to the reaction cell which contains the reaction mixture. The titration curves are then drawn by plotting the measured pH values against the corresponding volume of alkali added and the stability constants of the complexes are determined from the titration curves by employing pH-metric titration technique given by (Irving and Rossoti).

Metal-ligand stability constants (Log K) were determined by using the following relations:

$$\bar{n} = \frac{(V_3 - V_2)(E^0 + N^0)}{(V^0 + V_2)\bar{n}_A T_m^0} \text{ ……..……………………………………………………………..3}$$

and

$$PL = \log_{10}\{\frac{1+\beta_n^H \frac{1}{[anti\ \log pH]^n}}{T_L^0 - \bar{n}T_m^0} X \frac{(V^0 + V_3)}{V^0}\} \text{ …………………………………………………….4}$$

Where $T_{L,}$ T^o, E°, and V^ohavethe same significance as in equation (1) above, T_m denotes the total concentration of metal present in solution, V_3 is the volume of metal ions present in solution and β^H is the overall proton ligand stability constant. The metal-ligand stability constants (log K) were determined by employing point wise computational Method (eq. 5 and 6).

$$\text{LogK}_1 = \log\left(\frac{n}{1-n}\right) + \text{pL} \qquad \ldots\ldots\ldots\ldots.5$$

$$\text{LogK}_2 = \log\left(\frac{1-n}{2-n}\right) + \text{pL}\ldots\ldots\ldots\ldots\ldots\ldots\ldots.6$$

Where: Log K is the metal-ligand stability constant, pL is the Free ligand exponent function, **n** is the Average number of ligand attached with metal ion (Janrao*et al.*, 2014).The results obtained were analyzed by an ORIGIN 2016 program using titration data and then the proton-ligand stability constants (pKa) and Metal-ligand stability constant (LogK) calculated (Omar and Ali, 2015).

RESULTS AND DISCUSSION

Fourier transformed infrared (FT-IR) spectra of isolated humic acid from peat soils Figure 2 had distinct clear absorption bands indicating the presence of major humic acid structural elemental groups such as H bonded OH ($3680cm^{-1}$ peak), C=O of carbonyl ($1721cm^{-1}$ peak), functional groups of aliphatic components CH_2 ($2918cm^{-1}$ peak) and C-O stretching of polysaccharide ($1168cm^{-1}$ peak). The positions of the absorption bands of the spectra fell within typical major absorption bands of humic acid which is at frequencies 3680, 2918, 1721, 1168 cm^{-1}. The first peak centred in the vicinity of 3680 cm^{-1} region is attributed to phenol OH group bounded by intermolecular H bonds. The $2918cm^{-1}$ band usually has absorption maximum at 2918 cm^{-1} which is due to C–H stretching of alkane group (CH_2). The next major absorption band is 1721 cm^{-1}. This band has been commonly ascribed to C=O stretching of mainly carboxyl group (COOH) with trace amount of ketones. The last peak was observed at 1168 cm^{-1} due to C–O stretching of polysaccharides and this peak appeared also in the spectra of humic acid from peat soil. The FTIR spectra of the isolated humic acid contained all major characteristic absorption peaks of humic acid. These absorption peaks indicated the presence of the major structural elements of humic acid namely H bonded OH, C=C of aromatic ring, C=O of carbonyl group (both carboxyl and ketonic), CH_2 group. This strongly supports the presence of humic acid.

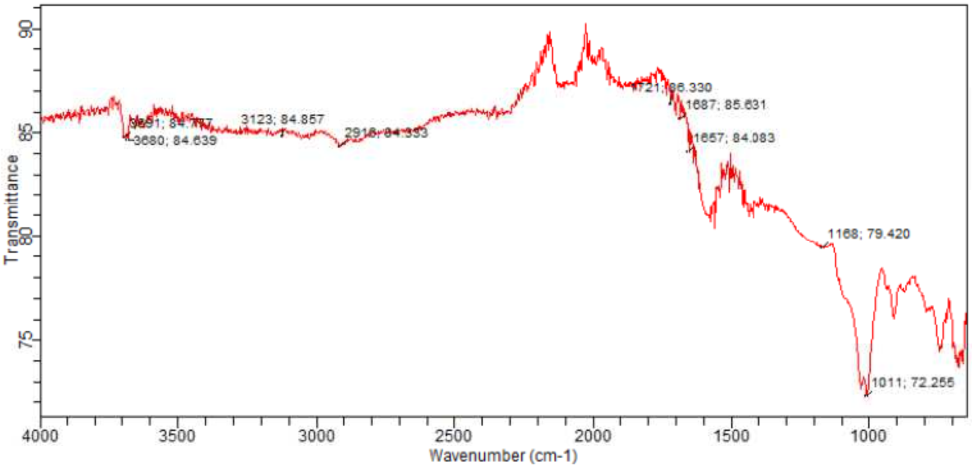


Fig. 2 : FT-IR spectraof peatsoilhumic acid (PSHA)

Evaluation of acid dissociation constant (pka) of acid hydrolysed peat soil humicacid at phenolic group

The value of the dissociation constant of the peat soil humic acid (PSHA) that underwent acidhydrolysis studied was found to be 8.9299 as shown Table 1, which is lower than the literaturevalues reported by Almeida and Szpoganics, (2015), Borges *et al.*, (2005); Badr *et al.*, (2012)and Fernandes *et al*,.(2009) of 9.73, 9.47 and 10.30. The difference between the obtained valuesand the reported values in this study might be probably as a result of acid hydrolysis of humicacid.

Table 1: PKa of (Hydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	log$(\frac{nA}{1-nA})$	pKa
8.50	5.30	6.29	0.99	0.3594	-0.2510	8.2490
8.72	5.35	6.37	1.02	0.3400	-0.2880	8.4320
9.00	5.40	6.46	1.06	0.3141	-0.3391	8.6609
9.22	5.45	6.55	1.10	0.2882	-0.3927	8.8273
9.51	5.50	6.66	1.16	0.2494	-0.4786	9.0314
9.73	5.55	6.78	1.23	0.2041	-0.5910	9.1390
10.00	5.60	6.90	1.30	0.1589	-0.7238	9.2762
10.23	5.65	7.05	1.40	0.0941	-0.9835	9.2465
10.49	5.70	7.10	1.40	0.0941	-0.9835	9.5065

Average pKa = 8.9299 ± 0.4186

Table 2: PKa of (Unhydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	Log$(\frac{nA}{1-n})$	pKa
8.50	5.30	5.81	0.51	0.6619	0.2919	8.7919
8.72	5.35	5.90	0.55	0.6357	0.2418	8.9618
9.00	5.40	6.00	0.60	0.6029	0.1813	9.1813
9.22	5.45	6.10	0.65	0.5701	0.1226	9.3426
9.51	5.50	6.20	0.70	0.5376	0.0654	9.5754
9.73	5.55	6.33	0.78	0.4851	-0.0259	9.7041
10.00	5.60	6.47	0.87	0.4262	-0.1291	9.8709
10.23	5.65	6.62	0.99	0.3609	-0.2481	9.9819
10.49	5.70	6.80	1.10	0.2759	-0.4690	10.0210

Average pKa = 9.4923± 0.4410

Metal-ligand stability constant (Log K)

The stabilityconstants require the accurate values of proton-ligand stability constants (Anil and Maroti, 2008). Metal titration curves crossed over ligand titration curve indicated the formation of complex upon proton release (Santosh, *et al.*, 2011). If the values of n- are within range 0.2-0.8 and 1.2-18 this indicates the formation of 1:1 and 1:2 complexes (Sayyed and Mazahar, 2012).

The metal (II)-humate stepwise stability constants (log k) at phenolic group (Tables 3-18)

Table 3: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log$(\frac{n}{1-n})$	LogK_1
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

LogK_1 (Average value) = 2.4788± 0.2203

Table 4: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	Log$(\frac{n-1}{2-n})$	LogK_2
9.51	5.50	6.66	6.73	0.07	1.3509	1.70	-0.2671	1.4329
9.73	5.55	6.78	6.85	0.07	1.6383	1.51	0.2467	1.7567
10.00	5.60	6.90	6.98	0.08	2.1783	1.31	-0.2158	1.0942
10.23	5.65	7.05	7.13	0.08	4.1904	1.27		
10.49	5.70	7.10	7.19	0.09	4.6920			

LogK_2(Average value) = 1.4280 ± 0.3312

Table 5:Point-wise method,Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	$\text{Log}(\frac{n}{n-1})$	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430

LogK_1 **(Average value)** = 2.3059± 0.6153

Table 6:Point-wise method, Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$V_3\text{-}V_2$	n	pL	$\text{Log}(\frac{n-1}{2-n})$	Log K_2
9.73	5.55	6.33	6.42	0.09	0.9000	1.69		
10.00	5.60	6.47	6.58	0.11	1.2578	1.44	-0.4592	0.9808
10.23	5.65	6.62	6.84	0.12	1.6137	1.26	-0.2010	1.4610
10.49	5.70	6.80	6.92	0.12	2.1052	1.03		

LogK_2 **(Average value)** = 1.2209± 0.3398

Table 7:Point-wise method,Pb (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	$\log(\frac{n}{1-n})$	LogK_1
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.60	0.05	0.8333	1.96	0.6989	2.6589

LogK_1 (Average value) = 2.5832 ±0.1614

Table 8:Point-wise method,Pb-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	$\log(\frac{n-1}{2-n})$	logK_2
9.51	5.50	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.83	0.05	1.1702	1.44		
10.00	5.60	6.90	6.90	0.05	1.4864	1.22	-0.0237	1.1963
10.23	5.65	7.05	7.10	0.05	2.0190	1.09		
10.49	5.70	7.10	7.17	0.07	3.6492	1.00		

LogK_2(Average value) = 1.1963

Table 9:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$V_3\text{-}V_2$	n	pL	Log $(\frac{n}{n-1})$	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.5477	2.3123
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	0.0272	2.2072
9.51	5.50	6.20	6.26	0.07	0.6417	1.89	0.2530	2.1430
9.73	5.55	6.40	6.40	0.07	0.7000	1.67	0.3680	2.0380

LogK_1 **(Average value)** = 2.2364 ± 0.1602

Table 10:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$V_3\text{-}V_2$	n	pL	$\text{Log}(\frac{n-1}{2-n})$	Log K_2
10.00	5.60	6.47	6.55	0.08	1.9503	1.41		
10.23	5.65	6.62	6.72	0.11	1.4792	1.26	-0.0361	1.2239

LogK_2 **(Average value)** = 1.2239

Table 11:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	$\log(\frac{n}{n-1})$	LogK_1
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4290	2.2110
8.72	5.35	6.37	6.39	0.02	0.2858	2.42	-0.3978	2.0222
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

LogK_1 (Average value)=2.1382±0.1046

Table 12:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n-1}{2-n}$)	$LogK_2$
9.51	5.55	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.84	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.93	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.10		
10.49	5.70	7.10	7.18	0.07	3.6492	0.83		

$LogK_2$(Average value) = 1.5453 **±** 0.3450

Table 13:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.3477	2.3123
9.00	5.40	6.00	6.04	0.04	0.3236	2.38	-0.3202	2.0598
9.22	5.45	6.10	6.15	0.05	0.4297	2.17	-0.1230	2.0470
9.51	5.50	6.20	6.26	0.06	0.5500	1.89	0.0871	1.9771
9.73	5.55	6.33	6.40	0.07	0.7000	1.67	0.3680	2.0380

$LogK_1$ **(Average value)** = 2.1568 ± 0.2069

Table 14:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
10.00	5.60	6.47	6.55	0.08	0.9148	1.41		
10.23	5.65	6.62	6.71	0.09	1.2102	1.20	-0.5749	0.6251
10.49	5.70	6.80	6.92	0.09	1.5968	1.03	0.1703	1.2003

$LogK_2$ **(Average value)** = 0.9127± 0.4070

Table15:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	Log($\frac{n}{1-n}$)	$LogK_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4210	2.2190
8.72	5.35	6.37	6.40	0.03	0.4286	2.42	-0.1249	2.2951
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.96	0.3010	2.2610
9.51	5.55	6.66	6.70	0.04	0.7720	1.67	0.5297	2.1997

$LogK_1$ (Average value) = 2.2108± 0.0825

Table 16:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
9.73	5.55	6.78	6.83	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.95	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.09		
10.49	5.70	7.10	7.16	0.06	3.1429	0.89		

$LogK_2$ **(Average value)** = 1.5453± 0.3450

Table 17:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.86	0.05	0.3717	2.88	-0.2280	2.6520
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.06	0.06	0.4853	2.38	-0.0255	2.3545
9.22	5.45	6.10	6.16	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430
9.73	5.55	6.33	6.41	0.08	0.8000	1.69	0.6020	2.2920

$LogK_1$ **(Average value)** = 2.2516± 0.5380

Table 18:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$\text{Log}(\frac{n-1}{2-n})$	Log K_2
10.00	5.60	6.47	6.57	0.10	1.1434	1.43		
10.23	5.65	6.62	6.72	0.10	1.3448	1.23	-0.2788	0.9512
10.49	5.70	6.80	6.90	0.10	1.7742	1.03	0.5351	1.5651

LogK_2 **(Average value)** = 1.2581± 0.4340

Table 19: Stepwise and overall Stability constants of thehydrolysed and unhydrolysed divalent metal (II) complexes

Chelates	**LogK_1**	**LogK_2**	**Logβ**
[Cu (Hydrolysed PSHA-1)$_2$]	2.4788	1.4280	3.9068
[Pb (Hydrolysed PSHA-1)$_2$]	2.5832	1.1963	3.7795
[Cd (Hydrolysed PSHA-1)$_2$]	2.2108	1.5453	3.7561
[Mg (Hydrolysed PSHA-1)$_2$]	2.1382	1.5453	3.6835
[Cu (Unhydrolysed PSHA-1)$_2$]	2.3059	1.2209	3.5268
[Pb (Unhydrolysed PSHA-1)$_2$]	2.2364	1.2239	3.4603
[Cd (Unhydrolysed PSHA-1)$_2$]	2.2516	1.2581	3.5097
[Mg (Unydrolysed PSHA-1)$_2$]	2.1568	0.9127	3.0695

The results obtained (Table19) shows the stepwise and overall stability constants to be not high indicating low stability of the complexes, because the solubility of most metal ions in the basic pH range is minimal due to metal hydroxide precipitation (Karimi, 2017). In general, the stepwise stability constants (K_1 and K_2) follow the order $K_1 > K_2$ for the copper, lead, magnesium and cadmium complexes respectively. The steady decrease of the values with increasing number of ligands is in agreement with the prediction made by researchers (Na'aliya, 2013). The decrease could be attributed to the fact that as the number of the ligands (Humate ions) that enters the coordination zone increases the aqua molecules available for replacement by the ligands become less. Thus, the metal ions become less electron loving with progressive intake of the ligand and this results in the decrease in the values of the constants (Na'aliya, 2013). Also the stability of the complexes is influenced by the size and number of the chelate rings(Mackay and Mackay,2002).All the complexes form rings in their structure as humate, a bidentate ligand, bond the metal ions in the ratio 1:2 (Boguta and Sokolowska, 2016) forming chelate rings. The values of the overall stability constants (logβ) obtained for humate complexes are not high indicating low stability as the values are not high. LogK values for copper-humates (Table 3 to 6) obtained in this study are lower than those reported for the complexes of humic acids (Pandey *et al*., 2015; Dinu, 2013; Kaschl *et al*., 2010 and Gilbeto and Jorg, 2001). The values of LogK(Table 7 to 10) forlead-humates are lower than those reported for the lead in the literature (Dinu, 2013; Gilbeto and Jorg 2001). Log K values(Table 11 to 14) for magnesium-humates obtained in this study are close to those reported by (Pandey *et al*., 2015). Log K values of cadmium-humates (Table 15 to 18) obtained in this work near to the one reported by (Dinu, 2013 and Pandey *et al*., 2015).The difference between the reported values and the values obtained in this study might be probably as a result of acid hydrolysis of humic acid. The values of the overall stability constants (log β) of the copper humates complexes presented in Table 19 is high than that of other metal humate complexes, show relatively high stability of Cu-HA complexes, show the following order of stability: Cu >Pb> Cd > Mg; which are in close agreement to the findings of (Dinu, 2013 and Pandey *et al*., 2015).The high stability of Cu-humate chelate could be attributed to the existence of coordinate covalent bond between the complexing agents and the Cu^{2+} ions. Since, Cu^{2+} being a metal of the transitional series with $3d^9$ electronic configurations can accept the electrons from the complexing agents. Similarly,the low stabilities of Pb,Cd and Mg -complexes could be explained by that Pb^{2+} with $6s^2$, Cd^{2+} with $4d^{10}$ and Mg^{2+} with $2p^6$ their electronic configuration has a completely filled d,p and s orbitals. Moreover, the stabilities of metal ions with hydrolysed humic acid from peat soil were higher than those with unhydrolysed humic acid from peat soil; which is ascribed to the high content of acidity in hydrolysed humic acid than unhydrolysed humic acid.

CONCLUSION

The values of logK for Cu(II) hydrolysed humic acid complex was higher followed by Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes as compared with metal(II) unhydrolysed humic acid complexes . This indicates acid hydrolysis of humic acid can enhance the complexation behavior of humic acid with metal (II) ions. However, the higher values of logβ for Cu(II), Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes indicates more stable stepwise complexes formed as compared with Cu(II), Pb(II), Cd(II) and Mg(II) unhydrolysed humic acid complexes.

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STABILITY CONSTANTS OF COMPLEXES OF METAL IONS WITH PEATSOIL HUMIC ACIDS UNDER NON-ACID-CONDITIONS

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ABSTRACT

Stability constants of complexes of four divalent metal ions viz. Cu^{2+}, Pb^{2+},Mg^{2+} and Cd^{2+} with humic acids (HA) were determined by potentiometric titration of humic acids with the corresponding salt of the divalent metals in aqueous media under non-acid-condition. The log K (logarithm of the stability constant) ranged from 1.0942 to 2.7471 for metal-humic acid complexes were determined using point-wise computational method. The order of stability constants were obtained as follows: Cu >Pb> Cd > Mg for metal -HA complexes respectively, indicating a higher degree of complexation with Cu metal ion.

Keywords: stability constant, humic acid, potentiometric titration, divalent metals, acid hydrolysis.

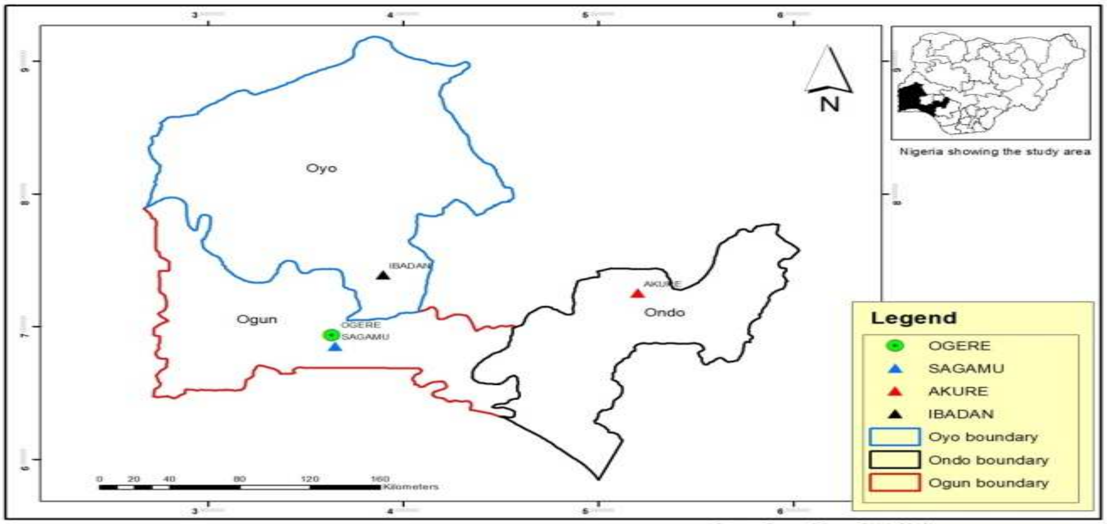
NTRODUCTION

The stability constant of a complex is the numerical expression of its stability and provides a quantitative measure of affinity of the metal ion to the complexing agent. An understanding of the relative stability of metal-complexes helps in predicting the behavior of metal ions in the soil (Ram and Raman, 1982). Extensive researches has been done to determine the stability constants of the complexes formed between humic acid (HA) with a number of metal ions. Ashok *et al.*, (2000) reported that humic acid with hydroxyl, phenoxyl and carboxyl reactive groups can form coordination compound with metal ions at pH 3.5. The stability constants(Log K) for different metal-humic acid complexes indicated the following order of the stabilities of complexes formed between humic acid and metal ion, Cu >Fe >Pb> Ni > Co > Ca > Cd > Zn >Mn> Mg. Andelkovic *et al.*, (2010) investigated the binding of Cd(II) to soil humic acid at pH 6.5 and in 0.1M KNO_3 ionic medium. The stability constant for binding indicating greater stability in the case when carboxyl groups are involved in complexation reaction. Kostic *et al.*,(2012) investigated the complexation of humic acid with certain heavy metal ions (Co(II), Ni(II),Cu(II), Zn(II), and Pb(II). The experiment was performed at 25°C, at pH 4.0 and ionic strength of 0.01M. Stability constant of complex between Pb(II) ions and humic acid is greater than stability constants of other investigated metal-humate complexes. Bogata and Sokolowska (2016) analyses the interaction between humic acids from different soils and Zn (II) ions at wide concentration ranges and at pH 5. Studies have showed significant impact of Zn concentration, pH and some properties of humic acids with zinc.But all of these studies were limited to acidic pH range. Therefore, the present study was carried out to determine and compare the stability constants of complexes of metal ions with hydrolysed peat soil humic acid and unhydrolysed peat soil humic under non-acid conditions.

MATERIALS AND METHODS

Analytical grade chemicals used includes hydrochloric acid (HCl), nitric acid (HNO_3), sodium hydroxide (NaOH), lead nitrate $Pb(NO_3)_2$, copper nitrate $Cu(NO_3)_2.3H_2O$, cadmium nitrate $Cd(NO_3)_2.4H_2O$, magnesium nitrate $Mg(NO_3)_2.6H_2O$, potassium nitrate (KNO_3), calcium chloride ($CaCl_2$), (sigma-Aldrich). Dowex 50WX8, (20-50 mesh) from Fluka.

Area of study



Source: Dept. of Geog. BUK (2016)

Figure 1: Map showing the sampling point at Sagamu Town, Ogun State.

Description of Sampling Area

Sagamu has geographical coordinates between 6°50′ north; 3° 38′ east is located in south western region of Nigeria. The region has tropical wet and dry climate with a lengthy wet season and relatively constant temperatures throughout the course of the year. Wet season runs from March to October, November to December forms the region dry season. The vegetation type of the region is savannah which is really grassland with small bushes and occasional big trees. Grassland soils have substantially higher organic matter content than forest soils (Novackova, 2011).

Sample Collection

The Peatsoil samples were collected from four different sampling points (0-10cm depth) in Sagamu into polyethylene bag with plastic spoons. Samples were taken to the laboratory, extraneous materials were removed; the samples were air-dried, crushed and ground to a fine powder in a mortar passed through a 0.20mm sieve. The samples were kept for analysis.

Isolation and purification of humic acid from peat soil sample

Peatsoil sample (100g) was mixed with 1000 cm^3 of 0.1M NaOH solution, shaken for 3hours and left to stand overnight. Dark-coloured supernatant was obtained and decanted from solid residue. The dark-coloured supernatant was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 6 hours. Yellowish brown supernatant and dark-brown precipitate were obtained. The yellowish brown supernatant was decanted followed by centrifuge and discarded. The dark-brown precipitate was mixed with 500$cm^3$of 0.1M NaOH solution followed by passing through dowex resin. The dark-brown solution was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 3 hours. The dark-brown precipitate was washed several times with deionized water. The supernatant was treated with $AgNO_3$ solution until no white precipitate observed. The humic acid was transferred to weighed crucible and dried at 60°C in an oven for 12 hours. The humic acid was cooled and dried in the desiccator, weighed and recorded. The obtained humic acid was dried again at 60°C for additional 6 hours cooled and dried in the desiccator, weighed and recorded constant weight was obtained (Baruah *et al*., 2015).

FT-IR analysis

FT-IR spectra of humic acid sample was analysed using Carry 630 FT-IR Agilent Technologies.

Unhydrolysed compost humic acid

The unhydrolysed humic acid was obtained after isolation and purification of compost humic acid and kept for investigation.

Acid hydrolysis of Peatsoil acid

Peatsoil humic acid sample (1g) was refluxed for 12 hours at (160°C) with 50cm^3 of 6M HCl. The mixture was allowed to cool, decanted, and centrifuged after hydrolysis. The insoluble residues were washed with distilled water via centrifugation several times, and the supernatant was treated with $AgNO_3$ solution until no white precipitate was observed. The residue was thoroughly dried over $CaCl_2$ in a desiccator at room temperature (Chefetz *et al*., 2002). Finally, the obtained hydrolysed humic acid was kept for investigation.

Potentiometric Titrations

Potentiometric measurements were carried out using a pH-meter Jenway (model 3510) with combine electrode, the sensitivity of the pH - meter is 0.01 units. The pH meter was switched on half an hour before starting the titration for initial warm up of the instrument. The instrument was calibrated with an aqueous standard buffer solution of pH 4.00 and 10.0 (borate buffer) prepared from a "Qualigens" buffer tablets.

The following sets of solutions were prepared in a 250cm^3 volumetric flask separately for pH metric titrations.

(i) 5 cm^3 0.1 M HCl + 40 cm^3 deionized water
(ii) 5 cm^3 0.1 M HCl + 39 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid
(iii) 5 cm^3 0.1 M HCl + 37 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid + 2 cm^3 0.01 M Cu(II)

The solutions were titrated against standardized 0.110MNaOH separately. The total volume of each mixture was adjusted to 50 cm^3 and the ionic strength of the solutions was maintained constant at by adding appropriate amount of stock solution of 1M KNO_3 (Gamal, 2015; Omar and Ali, 2015). A magnetic stirrer was used to achieve thorough mixing of the interacting solutions at 550 rpm. The same set of experimental conditions was applied for potentiometric titration of remaining samples.

Evaluation of pKa of Hydrolysed peat soil Humic Acids

The proton-ligand formation number n_A were calculated by Irving and Rossotti expression (Omar and Ali, 2015).

$$nA = Y - \frac{(V2-V1)(No-Eo)}{(Vo+V1)TcL} \text{ ....1}$$

Where: Y is number of dissociable proton, (V_2-V_1) is the measure of displacement of the ligand curve relative to acid curve, N^o and E^o are the resultant concentration of alkali solution, free acid solution, $T_{cL}{}^o$ is the total ligand concentration, V^o is the total volume of titration solution,V_1 is the volume of alkali added to acid solution,V_2 is the volume of alkali added to acid solution + ligand solution, acid dissociation constants (pKa - values) of ligand were calculated by algebraic method point wise calculation (Tables 1). The dissociation constants (pKa) were calculated according to the following relation:

$$pKa = pH + \log\left(\frac{nA}{1-nA}\right) \text{ ....2}$$

Where: pKa is the acid dissociation constant, $n_A$is the Proton-ligand formation number and pH is the pH-values (Omar and Ali, 2015).

Determination of metal-ligand stability constants (log K) of complexes

The potentiometric measurement for the determination of stability constant of a complex in solution is based on the fact that the redox potential of the couple $\frac{M^{+(m-n)}}{M^{+m}}$ is shifted significantly on complexation of the metal ion with the ligand. This method involves change in hydrogen ion concentration [H$^+$] due to the displacement or association of one or more protons taking place during complexation reaction. This change can be found out by titrating the solutions containing free acid, acid with ligand, and acid with ligand and metal ion, individually against a standard alkali solution at a constant ionic strength or temperature. Either ionic strength or temperature may be varied for different sets of solutions. In all the cases, the change in the pH of the solution is measured after each addition of a known amount of alkali to the reaction cell which contains the reaction mixture. The titration curves are then drawn by plotting the measured pH values against the corresponding volume of alkali added and the stability constants of the complexes are determined from the titration curves by employing pH-metric titration technique given by (Irving and Rossoti).

Metal-ligand stability constants (Log K) were determined by using the following relations:

$$\bar{n} = \frac{(V_3 - V_2)(E^0 + N^0)}{(V^0 + V_2)\bar{n}_A T_m^0} \text{ ....3}$$

and

$$PL = \log_{10}\left\{\frac{1 + \beta_n^H \frac{1}{[anti\ \log pH]^n}}{T_L^0 - \bar{n}T_m^0} X \frac{(V^0 + V_3)}{V^0}\right\} \text{ ....4}$$

Where $T_{L,}$ T^o, E°, and V^ohavethe same significance as in equation (1) above, T_m denotes the total concentration of metal present in solution, V_3 is the volume of metal ions present in solution and β^H is the overall proton ligand stability constant. The metal-ligand stability constants (log K) were determined by employing point wise computational Method (eq. 5 and 6).

$$\mathrm{Log}K_1 = \log\left(\frac{n}{1-n}\right) + pL \qquad ....5$$

$$\mathrm{Log}K_2 = \log\left(\frac{1-n}{2-n}\right) + pL.......................6$$

Where: Log K is the metal-ligand stability constant, pL is the Free ligand exponent function, **n** is the Average number of ligand attached with metal ion (Janrao*et al*., 2014).The results obtained were analyzed by an ORIGIN 2016 program using titration data and then the proton-ligand stability constants (pKa) and Metal-ligand stability constant (LogK) calculated (Omar and Ali, 2015).

RESULTS AND DISCUSSION

Fourier transformed infrared (FT-IR) spectra of isolated humic acid from peat soils Figure 2 had distinct clear absorption bands indicating the presence of major humic acid structural elemental groups such as H bonded OH ($3680cm^{-1}$ peak), C=O of carbonyl ($1721cm^{-1}$ peak), functional groups of aliphatic components CH_2 ($2918cm^{-1}$ peak) and C-O stretching of polysaccharide ($1168cm^{-1}$ peak). The positions of the absorption bands of the spectra fell within typical major absorption bands of humic acid which is at frequencies 3680, 2918, 1721, 1168 cm^{-1}. The first peak centred in the vicinity of 3680 cm^{-1} region is attributed to phenol OH group bounded by intermolecular H bonds. The $2918cm^{-1}$ band usually has absorption maximum at 2918 cm^{-1} which is due to C–H stretching of alkane group (CH_2). The next major absorption band is 1721 cm^{-1}. This band has been commonly ascribed to C=O stretching of mainly carboxyl group (COOH) with trace amount of ketones. The last peak was observed at 1168 cm^{-1} due to C–O stretching of polysaccharides and this peak appeared also in the spectra of humic acid from peat soil. The FTIR spectra of the isolated humic acid contained all major characteristic absorption peaks of humic acid. These absorption peaks indicated the presence of the major structural elements of humic acid namely H bonded OH, C=C of aromatic ring, C=O of carbonyl group (both carboxyl and ketonic), CH_2 group. This strongly supports the presence of humic acid.

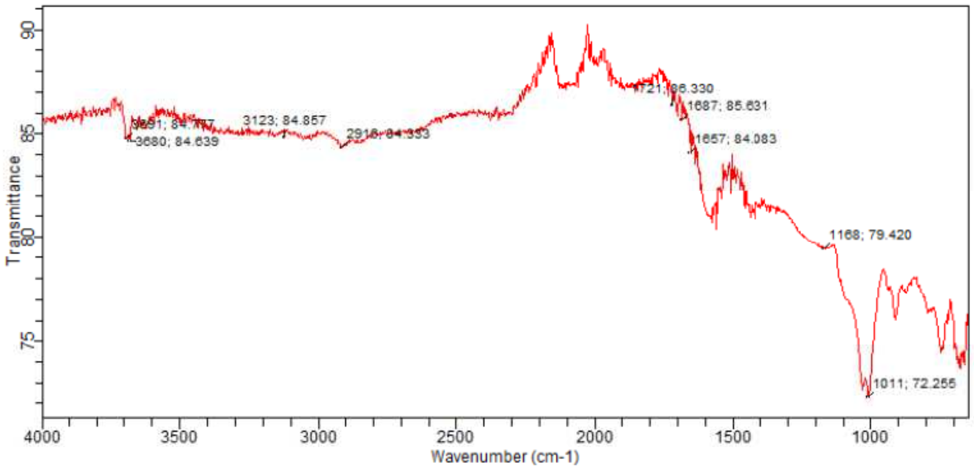


Fig. 2 : FT-IR spectraof peatsoilhumic acid (PSHA)

Evaluation of acid dissociation constant (pka) of acid hydrolysed peat soil humicacid at phenolic group

The value of the dissociation constant of the peat soil humic acid (PSHA) that underwent acidhydrolysis studied was found to be 8.9299 as shown Table 1, which is lower than the literaturevalues reported by Almeida and Szpoganics, (2015), Borges *et al*., (2005); Badr *et al*., (2012)and Fernandes *et al*,.(2009) of 9.73, 9.47 and 10.30. The difference between the obtained valuesand the reported values in this study might be probably as a result of acid hydrolysis of humicacid.

Table 1: PKa of (Hydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	log($\frac{nA}{1-nA}$)	pKa
8.50	5.30	6.29	0.99	0.3594	-0.2510	8.2490
8.72	5.35	6.37	1.02	0.3400	-0.2880	8.4320
9.00	5.40	6.46	1.06	0.3141	-0.3391	8.6609
9.22	5.45	6.55	1.10	0.2882	-0.3927	8.8273
9.51	5.50	6.66	1.16	0.2494	-0.4786	9.0314
9.73	5.55	6.78	1.23	0.2041	-0.5910	9.1390
10.00	5.60	6.90	1.30	0.1589	-0.7238	9.2762
10.23	5.65	7.05	1.40	0.0941	-0.9835	9.2465
10.49	5.70	7.10	1.40	0.0941	-0.9835	9.5065

Average pKa = 8.9299 ± 0.4186

Table 2: PKa of (Unhydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	Log($\frac{nA}{1-n}$)	pKa
8.50	5.30	5.81	0.51	0.6619	0.2919	8.7919
8.72	5.35	5.90	0.55	0.6357	0.2418	8.9618
9.00	5.40	6.00	0.60	0.6029	0.1813	9.1813
9.22	5.45	6.10	0.65	0.5701	0.1226	9.3426
9.51	5.50	6.20	0.70	0.5376	0.0654	9.5754
9.73	5.55	6.33	0.78	0.4851	-0.0259	9.7041
10.00	5.60	6.47	0.87	0.4262	-0.1291	9.8709
10.23	5.65	6.62	0.99	0.3609	-0.2481	9.9819
10.49	5.70	6.80	1.10	0.2759	-0.4690	10.0210

Average pKa = 9.4923± 0.4410

Metal-ligand stability constant (Log K)

The stabilityconstants require the accurate values of proton-ligand stability constants (Anil and Maroti, 2008). Metal titration curves crossed over ligand titration curve indicated the formation of complex upon proton release (Santosh, *et al.*, 2011). If the values of n- are within range 0.2-0.8 and 1.2-18 this indicates the formation of 1:1 and 1:2 complexes (Sayyed and Mazahar, 2012).

The metal (II)-humate stepwise stability constants (log k) at phenolic group (Tables 3-18)

Table 3: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n}{1-n}$)	$LogK_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

$LogK_1$ (Average value) = 2.4788± 0.2203

Table 4: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	Log($\frac{n-1}{2-n}$)	$LogK_2$
9.51	5.50	6.66	6.73	0.07	1.3509	1.70	-0.2671	1.4329
9.73	5.55	6.78	6.85	0.07	1.6383	1.51	0.2467	1.7567
10.00	5.60	6.90	6.98	0.08	2.1783	1.31	-0.2158	1.0942
10.23	5.65	7.05	7.13	0.08	4.1904	1.27		
10.49	5.70	7.10	7.19	0.09	4.6920			

$LogK_2$(Average value) = 1.4280 ± 0.3312

Table 5:Point-wise method,Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	Log($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430

$LogK_1$ **(Average value)** = 2.3059± 0.6153

Table 6:Point-wise method, Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
9.73	5.55	6.33	6.42	0.09	0.9000	1.69		
10.00	5.60	6.47	6.58	0.11	1.2578	1.44	-0.4592	0.9808
10.23	5.65	6.62	6.84	0.12	1.6137	1.26	-0.2010	1.4610
10.49	5.70	6.80	6.92	0.12	2.1052	1.03		

$LogK_2$ **(Average value)** = 1.2209± 0.3398

Table 7:Point-wise method,Pb (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n}{1-n}$)	$LogK_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.60	0.05	0.8333	1.96	0.6989	2.6589

$LogK_1$ (Average value) = 2.5832 ±0.1614

Table 8:Point-wise method,Pb-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n-1}{2-n}$)	$logK_2$
9.51	5.50	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.83	0.05	1.1702	1.44		
10.00	5.60	6.90	6.90	0.05	1.4864	1.22	-0.0237	1.1963
10.23	5.65	7.05	7.10	0.05	2.0190	1.09		
10.49	5.70	7.10	7.17	0.07	3.6492	1.00		

$LogK_2$(Average value) = 1.1963

Table 9:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log ($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.5477	2.3123
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	0.0272	2.2072
9.51	5.50	6.20	6.26	0.07	0.6417	1.89	0.2530	2.1430
9.73	5.55	6.40	6.40	0.07	0.7000	1.67	0.3680	2.0380

$LogK_1$ **(Average value)** = 2.2364 ± 0.1602

Table 10:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
10.00	5.60	6.47	6.55	0.08	1.9503	1.41		
10.23	5.65	6.62	6.72	0.11	1.4792	1.26	-0.0361	1.2239

$LogK_2$ **(Average value)** = 1.2239

Table 11:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n}{n-1}$)	$LogK_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4290	2.2110
8.72	5.35	6.37	6.39	0.02	0.2858	2.42	-0.3978	2.0222
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

$LogK_1$ (Average value)=2.1382**±**0.1046

Table 12:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	log($\frac{n-1}{2-n}$)	LogK$_2$
9.51	5.55	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.84	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.93	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.10		
10.49	5.70	7.10	7.18	0.07	3.6492	0.83		

LogK$_2$(Average value) = 1.5453 **±** 0.3450

Table 13:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	V$_3$-V$_2$	n	pL	Log($\frac{n}{n-1}$)	Log K$_1$
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.3477	2.3123
9.00	5.40	6.00	6.04	0.04	0.3236	2.38	-0.3202	2.0598
9.22	5.45	6.10	6.15	0.05	0.4297	2.17	-0.1230	2.0470
9.51	5.50	6.20	6.26	0.06	0.5500	1.89	0.0871	1.9771
9.73	5.55	6.33	6.40	0.07	0.7000	1.67	0.3680	2.0380

LogK$_1$ **(Average value)** = 2.1568 ± 0.2069

Table 14:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	V$_3$-V$_2$	n	pL	Log($\frac{n-1}{2-n}$)	Log K$_2$
10.00	5.60	6.47	6.55	0.08	0.9148	1.41		
10.23	5.65	6.62	6.71	0.09	1.2102	1.20	-0.5749	0.6251
10.49	5.70	6.80	6.92	0.09	1.5968	1.03	0.1703	1.2003

LogK$_2$ **(Average value)** = 0.9127± 0.4070

Table15:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	Log($\frac{n}{1-n}$)	LogK$_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4210	2.2190
8.72	5.35	6.37	6.40	0.03	0.4286	2.42	-0.1249	2.2951
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.96	0.3010	2.2610
9.51	5.55	6.66	6.70	0.04	0.7720	1.67	0.5297	2.1997

LogK$_1$ (Average value) = 2.2108± 0.0825

Table 16:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	Log($\frac{n-1}{2-n}$)	Log K$_2$
9.73	5.55	6.78	6.83	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.95	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.09		
10.49	5.70	7.10	7.16	0.06	3.1429	0.89		

LogK$_2$ **(Average value)** = 1.5453± 0.3450

Table 17:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	V$_3$-V$_2$	n	pL	Log($\frac{n}{n-1}$)	Log K$_1$
8.50	5.30	5.81	5.86	0.05	0.3717	2.88	-0.2280	2.6520
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.06	0.06	0.4853	2.38	-0.0255	2.3545
9.22	5.45	6.10	6.16	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430
9.73	5.55	6.33	6.41	0.08	0.8000	1.69	0.6020	2.2920

LogK$_1$ **(Average value)** = 2.2516± 0.5380

Table 18:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$\text{Log}(\frac{n-1}{2-n})$	Log K_2
10.00	5.60	6.47	6.57	0.10	1.1434	1.43		
10.23	5.65	6.62	6.72	0.10	1.3448	1.23	-0.2788	0.9512
10.49	5.70	6.80	6.90	0.10	1.7742	1.03	0.5351	1.5651

LogK_2 **(Average value)** = 1.2581± 0.4340

Table 19: Stepwise and overall Stability constants of thehydrolysed and unhydrolysed divalent metal (II) complexes

Chelates	**LogK_1**	**LogK_2**	**Logβ**
[Cu (Hydrolysed PSHA-1)$_2$]	2.4788	1.4280	3.9068
[Pb (Hydrolysed PSHA-1)$_2$]	2.5832	1.1963	3.7795
[Cd (Hydrolysed PSHA-1)$_2$]	2.2108	1.5453	3.7561
[Mg (Hydrolysed PSHA-1)$_2$]	2.1382	1.5453	3.6835
[Cu (Unhydrolysed PSHA-1)$_2$]	2.3059	1.2209	3.5268
[Pb (Unhydrolysed PSHA-1)$_2$]	2.2364	1.2239	3.4603
[Cd (Unhydrolysed PSHA-1)$_2$]	2.2516	1.2581	3.5097
[Mg (Unydrolysed PSHA-1)$_2$]	2.1568	0.9127	3.0695

The results obtained (Table19) shows the stepwise and overall stability constants to be not high indicating low stability of the complexes, because the solubility of most metal ions in the basic pH range is minimal due to metal hydroxide precipitation (Karimi, 2017). In general, the stepwise stability constants (K_1 and K_2) follow the order $K_1 > K_2$ for the copper, lead, magnesium and cadmium complexes respectively. The steady decrease of the values with increasing number of ligands is in agreement with the prediction made by researchers (Na'aliya, 2013). The decrease could be attributed to the fact that as the number of the ligands (Humate ions) that enters the coordination zone increases the aqua molecules available for replacement by the ligands become less. Thus, the metal ions become less electron loving with progressive intake of the ligand and this results in the decrease in the values of the constants (Na'aliya, 2013). Also the stability of the complexes is influenced by the size and number of the chelate rings(Mackay and Mackay,2002).All the complexes form rings in their structure as humate, a bidentate ligand, bond the metal ions in the ratio 1:2 (Boguta and Sokolowska, 2016) forming chelate rings. The values of the overall stability constants (logβ) obtained for humate complexes are not high indicating low stability as the values are not high. LogK values for copper-humates (Table 3 to 6) obtained in this study are lower than those reported for the complexes of humic acids (Pandey *et al.*, 2015; Dinu, 2013; Kaschl *et al.*, 2010 and Gilbeto and Jorg, 2001). The values of LogK(Table 7 to 10) forlead-humates are lower than those reported for the lead in the literature (Dinu, 2013; Gilbeto and Jorg 2001). Log K values(Table 11 to 14) for magnesium-humates obtained in this study are close to those reported by (Pandey *et al.*, 2015). Log K values of cadmium-humates (Table 15 to 18) obtained in this work near to the one reported by (Dinu, 2013 and Pandey *et al.*, 2015).The difference between the reported values and the values obtained in this study might be probably as a result of acid hydrolysis of humic acid. The values of the overall stability constants (log β) of the copper humates complexes presented in Table 19 is high than that of other metal humate complexes, show relatively high stability of Cu-HA complexes, show the following order of stability: Cu >Pb> Cd > Mg; which are in close agreement to the findings of (Dinu, 2013 and Pandey *et al.*, 2015).The high stability of Cu-humate chelate could be attributed to the existence of coordinate covalent bond between the complexing agents and the Cu^{2+} ions. Since, Cu^{2+} being a metal of the transitional series with $3d^9$ electronic configurations can accept the electrons from the complexing agents. Similarly,the low stabilities of Pb,Cd and Mg - complexes could be explained by that Pb^{2+} with $6s^2$, Cd^{2+} with $4d^{10}$ and Mg^{2+} with $2p^6$ their electronic configuration has a completely filled d,p and s orbitals. Moreover, the stabilities of metal ions with hydrolysed humic acid from peat soil were higher than those with unhydrolysed humic acid from peat soil; which is ascribed to the high content of acidity in hydrolysed humic acid than unhydrolysed humic acid.

CONCLUSION

The values of logK for Cu(II) hydrolysed humic acid complex was higher followed by Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes as compared with metal(II) unhydrolysed humic acid complexes . This indicates acid hydrolysis of humic acid can enhance the complexation behavior of humic acid with metal (II) ions. However, the higher values of logβ for Cu(II), Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes indicates more stable stepwise complexes formed as compared with Cu(II), Pb(II), Cd(II) and Mg(II) unhydrolysed humic acid complexes.

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STABILITY CONSTANTS OF COMPLEXES OF METAL IONS WITH PEATSOIL HUMIC ACIDS UNDER NON-ACID-CONDITIONS

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ABSTRACT

Stability constants of complexes of four divalent metal ions viz. Cu^{2+}, Pb^{2+},Mg^{2+} and Cd^{2+} with humic acids (HA) were determined by potentiometric titration of humic acids with the corresponding salt of the divalent metals in aqueous media under non-acid-condition. The log K (logarithm of the stability constant) ranged from 1.0942 to 2.7471 for metal-humic acid complexes were determined using point-wise computational method. The order of stability constants were obtained as follows: Cu >Pb> Cd > Mg for metal -HA complexes respectively, indicating a higher degree of complexation with Cu metal ion.

Keywords: stability constant, humic acid, potentiometric titration, divalent metals, acid hydrolysis.

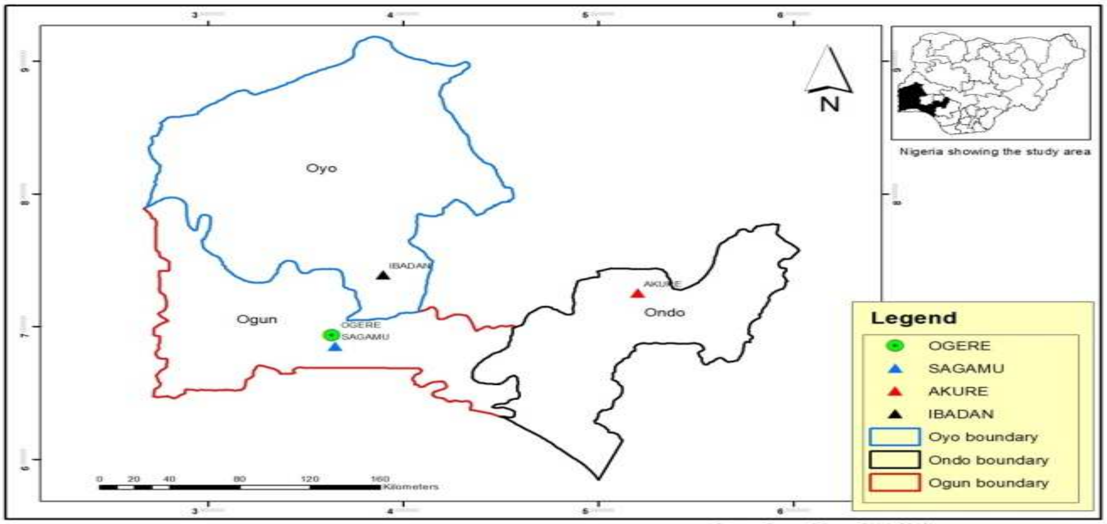
NTRODUCTION

The stability constant of a complex is the numerical expression of its stability and provides a quantitative measure of affinity of the metal ion to the complexing agent. An understanding of the relative stability of metal-complexes helps in predicting the behavior of metal ions in the soil (Ram and Raman, 1982). Extensive researches has been done to determine the stability constants of the complexes formed between humic acid (HA) with a number of metal ions. Ashok *et al.*, (2000) reported that humic acid with hydroxyl, phenoxyl and carboxyl reactive groups can form coordination compound with metal ions at pH 3.5. The stability constants(Log K) for different metal-humic acid complexes indicated the following order of the stabilities of complexes formed between humic acid and metal ion, Cu >Fe >Pb> Ni > Co > Ca > Cd > Zn >Mn> Mg. Andelkovic *et al.*, (2010) investigated the binding of Cd(II) to soil humic acid at pH 6.5 and in 0.1M KNO_3 ionic medium. The stability constant for binding indicating greater stability in the case when carboxyl groups are involved in complexation reaction. Kostic *et al.*,(2012) investigated the complexation of humic acid with certain heavy metal ions (Co(II), Ni(II),Cu(II), Zn(II), and Pb(II). The experiment was performed at 25°C, at pH 4.0 and ionic strength of 0.01M. Stability constant of complex between Pb(II) ions and humic acid is greater than stability constants of other investigated metal-humate complexes. Bogata and Sokolowska (2016) analyses the interaction between humic acids from different soils and Zn (II) ions at wide concentration ranges and at pH 5. Studies have showed significant impact of Zn concentration, pH and some properties of humic acids with zinc.But all of these studies were limited to acidic pH range. Therefore, the present study was carried out to determine and compare the stability constants of complexes of metal ions with hydrolysed peat soil humic acid and unhydrolysed peat soil humic under non-acid conditions.

MATERIALS AND METHODS

Analytical grade chemicals used includes hydrochloric acid (HCl), nitric acid (HNO_3), sodium hydroxide (NaOH), lead nitrate $Pb(NO_3)_2$, copper nitrate $Cu(NO_3)_2.3H_2O$, cadmium nitrate $Cd(NO_3)_2.4H_2O$, magnesium nitrate $Mg(NO_3)_2.6H_2O$, potassium nitrate (KNO_3), calcium chloride ($CaCl_2$), (sigma-Aldrich). Dowex 50WX8, (20-50 mesh) from Fluka.

Area of study



Source: Dept. of Geog. BUK (2016)

Figure 1: Map showing the sampling point at Sagamu Town, Ogun State.

Description of Sampling Area

Sagamu has geographical coordinates between 6°50′ north; 3° 38′ east is located in south western region of Nigeria. The region has tropical wet and dry climate with a lengthy wet season and relatively constant temperatures throughout the course of the year. Wet season runs from March to October, November to December forms the region dry season. The vegetation type of the region is savannah which is really grassland with small bushes and occasional big trees. Grassland soils have substantially higher organic matter content than forest soils (Novackova, 2011).

Sample Collection

The Peatsoil samples were collected from four different sampling points (0-10cm depth) in Sagamu into polyethylene bag with plastic spoons. Samples were taken to the laboratory, extraneous materials were removed; the samples were air-dried, crushed and ground to a fine powder in a mortar passed through a 0.20mm sieve. The samples were kept for analysis.

Isolation and purification of humic acid from peat soil sample

Peatsoil sample (100g) was mixed with 1000 cm^3 of 0.1M NaOH solution, shaken for 3hours and left to stand overnight. Dark-coloured supernatant was obtained and decanted from solid residue. The dark-coloured supernatant was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 6 hours. Yellowish brown supernatant and dark-brown precipitate were obtained. The yellowish brown supernatant was decanted followed by centrifuge and discarded. The dark-brown precipitate was mixed with $500cm^3$of 0.1M NaOH solution followed by passing through dowex resin. The dark-brown solution was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 3 hours. The dark-brown precipitate was washed several times with deionized water. The supernatant was treated with $AgNO_3$ solution until no white precipitate observed. The humic acid was transferred to weighed crucible and dried at 60°C in an oven for 12 hours. The humic acid was cooled and dried in the desiccator, weighed and recorded. The obtained humic acid was dried again at 60°C for additional 6 hours cooled and dried in the desiccator, weighed and recorded constant weight was obtained (Baruah *et al*., 2015).

FT-IR analysis

FT-IR spectra of humic acid sample was analysed using Carry 630 FT-IR Agilent Technologies.

Unhydrolysed compost humic acid

The unhydrolysed humic acid was obtained after isolation and purification of compost humic acid and kept for investigation.

Acid hydrolysis of Peatsoil acid

Peatsoil humic acid sample (1g) was refluxed for 12 hours at (160°C) with $50cm^3$ of 6M HCl. The mixture was allowed to cool, decanted, and centrifuged after hydrolysis. The insoluble residues were washed with distilled water via centrifugation several times, and the supernatant was treated with $AgNO_3$ solution until no white precipitate was observed. The residue was thoroughly dried over $CaCl_2$ in a desiccator at room temperature (Chefetz *et al*., 2002). Finally, the obtained hydrolysed humic acid was kept for investigation.

Potentiometric Titrations

Potentiometric measurements were carried out using a pH-meter Jenway (model 3510) with combine electrode, the sensitivity of the pH - meter is 0.01 units. The pH meter was switched on half an hour before starting the titration for initial warm up of the instrument. The instrument was calibrated with an aqueous standard buffer solution of pH 4.00 and 10.0 (borate buffer) prepared from a "Qualigens" buffer tablets.

The following sets of solutions were prepared in a 250cm^3 volumetric flask separately for pH metric titrations.

(i) 5 cm^3 0.1 M HCl + 40 cm^3 deionized water

(ii) 5 cm^3 0.1 M HCl + 39 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid

(iii) 5 cm^3 0.1 M HCl + 37 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid + 2 cm^3 0.01 M Cu(II)

The solutions were titrated against standardized 0.110MNaOH separately. The total volume of each mixture was adjusted to 50 cm^3 and the ionic strength of the solutions was maintained constant at by adding appropriate amount of stock solution of 1M KNO$_3$ (Gamal, 2015; Omar and Ali, 2015). A magnetic stirrer was used to achieve thorough mixing of the interacting solutions at 550 rpm. The same set of experimental conditions was applied for potentiometric titration of remaining samples.

Evaluation of pKa of Hydrolysed peat soil Humic Acids

The proton-ligand formation number n$_\mathbf{A}$ were calculated by Irving and Rossotti expression (Omar and Ali, 2015).

nA = Y- $\frac{(V2-V1)(No-Eo)}{(Vo+V1)TcL}$ ………………………………1

Where: Y is number of dissociable proton, (V$_2$-V$_1$) is the measure of displacement of the ligand curve relative to acid curve, N^o and E^o are the resultant concentration of alkali solution, free acid solution, T$_{cL}$^{o} is the total ligand concentration, V^o is the total volume of titration solution,V$_1$ is the volume of alkali added to acid solution,V$_2$ is the volume of alkali added to acid solution + ligand solution, acid dissociation constants (pKa - values) of ligand were calculated by algebraic method point wise calculation (Tables 1). The dissociation constants (pKa) were calculated according to the following relation:

pKa = pH + log($\frac{nA}{1-nA}$) ………………………..2

Where: pKa is the acid dissociation constant, n$_A$is the Proton-ligand formation number and pH is the pH-values (Omar and Ali, 2015).

Determination of metal-ligand stability constants (log K) of complexes

The potentiometric measurement for the determination of stability constant of a complex in solution is based on the fact that the redox potential of the couple $\frac{M^{+(m-n)}}{M^{+m}}$ is shifted significantly on complexation of the metal ion with the ligand. This method involves change in hydrogen ion concentration [H$^+$] due to the displacement or association of one or more protons taking place during complexation reaction. This change can be found out by titrating the solutions containing free acid, acid with ligand, and acid with ligand and metal ion, individually against a standard alkali solution at a constant ionic strength or temperature. Either ionic strength or temperature may be varied for different sets of solutions. In all the cases, the change in the pH of the solution is measured after each addition of a known amount of alkali to the reaction cell which contains the reaction mixture. The titration curves are then drawn by plotting the measured pH values against the corresponding volume of alkali added and the stability constants of the complexes are determined from the titration curves by employing pH-metric titration technique given by (Irving and Rossoti).

Metal-ligand stability constants (Log K) were determined by using the following relations:

$$\bar{n} = \frac{(V_3 - V_2)(E^0 + N^0)}{(V^0 + V_2)\bar{n}_A T_m^0} \quad \text{…………………………………………………………………3}$$

and

$$PL = \log_{10}\{\frac{1 + \beta_n^H \frac{1}{[anti\ \log pH]^n}}{T_L^0 - \bar{n}T_m^0} X \frac{(V^0 + V_3)}{V^0}\} \quad \text{…………………………………………………4}$$

Where $T_{L,}$ T^o, E°, and V^ohavethe same significance as in equation (1) above, T_m denotes the total concentration of metal present in solution, V_3 is the volume of metal ions present in solution and β^H is the overall proton ligand stability constant. The metal-ligand stability constants (log K) were determined by employing point wise computational Method (eq. 5 and 6).

$\text{Log}K_1 = \log\left(\frac{n}{1-n}\right) + pL$ 5

$\text{Log}K_2 = \log\left(\frac{1-n}{2-n}\right) + pL$.......................6

Where: Log K is the metal-ligand stability constant, pL is the Free ligand exponent function, **n** is the Average number of ligand attached with metal ion (Janrao*et al.*, 2014).The results obtained were analyzed by an ORIGIN 2016 program using titration data and then the proton-ligand stability constants (pKa) and Metal-ligand stability constant (LogK) calculated (Omar and Ali, 2015).

RESULTS AND DISCUSSION

Fourier transformed infrared (FT-IR) spectra of isolated humic acid from peat soils Figure 2 had distinct clear absorption bands indicating the presence of major humic acid structural elemental groups such as H bonded OH ($3680cm^{-1}$ peak), C=O of carbonyl ($1721cm^{-1}$ peak), functional groups of aliphatic components CH_2 ($2918cm^{-1}$ peak) and C-O stretching of polysaccharide ($1168cm^{-1}$ peak). The positions of the absorption bands of the spectra fell within typical major absorption bands of humic acid which is at frequencies 3680, 2918, 1721, 1168 cm^{-1}. The first peak centred in the vicinity of 3680 cm^{-1} region is attributed to phenol OH group bounded by intermolecular H bonds. The $2918cm^{-1}$ band usually has absorption maximum at 2918 cm^{-1} which is due to C–H stretching of alkane group (CH_2). The next major absorption band is 1721 cm^{-1}. This band has been commonly ascribed to C=O stretching of mainly carboxyl group (COOH) with trace amount of ketones. The last peak was observed at 1168 cm^{-1} due to C–O stretching of polysaccharides and this peak appeared also in the spectra of humic acid from peat soil. The FTIR spectra of the isolated humic acid contained all major characteristic absorption peaks of humic acid. These absorption peaks indicated the presence of the major structural elements of humic acid namely H bonded OH, C=C of aromatic ring, C=O of carbonyl group (both carboxyl and ketonic), CH_2 group. This strongly supports the presence of humic acid.

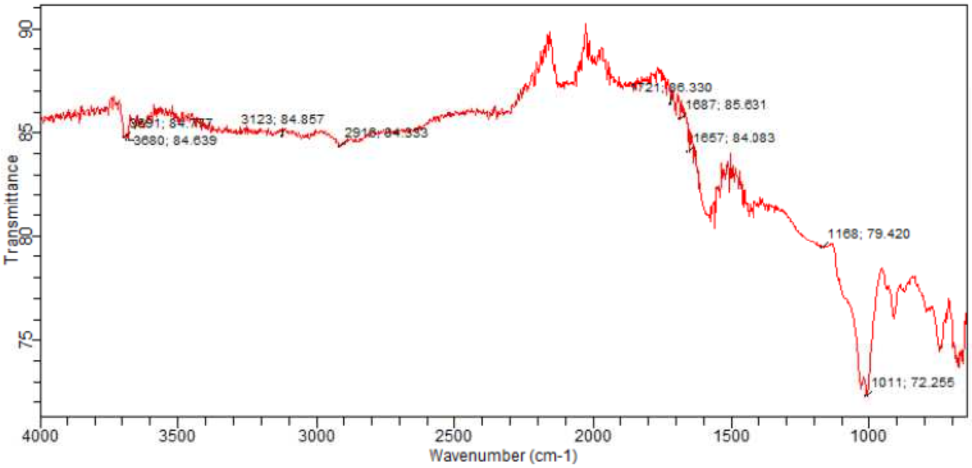


Fig. 2 : FT-IR spectraof peatsoilhumic acid (PSHA)

Evaluation of acid dissociation constant (pka) of acid hydrolysed peat soil humicacid at phenolic group

The value of the dissociation constant of the peat soil humic acid (PSHA) that underwent acidhydrolysis studied was found to be 8.9299 as shown Table 1, which is lower than the literaturevalues reported by Almeida and Szpoganics, (2015), Borges *et al.*, (2005); Badr *et al.*, (2012)and Fernandes *et al*,.(2009) of 9.73, 9.47 and 10.30. The difference between the obtained valuesand the reported values in this study might be probably as a result of acid hydrolysis of humicacid.

Table 1: PKa of (Hydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	log($\frac{nA}{1-nA}$)	pKa
8.50	5.30	6.29	0.99	0.3594	-0.2510	8.2490
8.72	5.35	6.37	1.02	0.3400	-0.2880	8.4320
9.00	5.40	6.46	1.06	0.3141	-0.3391	8.6609
9.22	5.45	6.55	1.10	0.2882	-0.3927	8.8273
9.51	5.50	6.66	1.16	0.2494	-0.4786	9.0314
9.73	5.55	6.78	1.23	0.2041	-0.5910	9.1390
10.00	5.60	6.90	1.30	0.1589	-0.7238	9.2762
10.23	5.65	7.05	1.40	0.0941	-0.9835	9.2465
10.49	5.70	7.10	1.40	0.0941	-0.9835	9.5065

Average pKa = 8.9299 ± 0.4186

Table 2: PKa of (Unhydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	Log($\frac{nA}{1-n}$)	pKa
8.50	5.30	5.81	0.51	0.6619	0.2919	8.7919
8.72	5.35	5.90	0.55	0.6357	0.2418	8.9618
9.00	5.40	6.00	0.60	0.6029	0.1813	9.1813
9.22	5.45	6.10	0.65	0.5701	0.1226	9.3426
9.51	5.50	6.20	0.70	0.5376	0.0654	9.5754
9.73	5.55	6.33	0.78	0.4851	-0.0259	9.7041
10.00	5.60	6.47	0.87	0.4262	-0.1291	9.8709
10.23	5.65	6.62	0.99	0.3609	-0.2481	9.9819
10.49	5.70	6.80	1.10	0.2759	-0.4690	10.0210

Average pKa = 9.4923± 0.4410

Metal-ligand stability constant (Log K)

The stabilityconstants require the accurate values of proton-ligand stability constants (Anil and Maroti, 2008). Metal titration curves crossed over ligand titration curve indicated the formation of complex upon proton release (Santosh, *et al.*, 2011). If the values of n- are within range 0.2-0.8 and 1.2-18 this indicates the formation of 1:1 and 1:2 complexes (Sayyed and Mazahar, 2012).

The metal (II)-humate stepwise stability constants (log k) at phenolic group (Tables 3-18)

Table 3: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n}{1-n}$)	$LogK_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

$LogK_1$ (Average value) = 2.4788± 0.2203

Table 4: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	Log($\frac{n-1}{2-n}$)	$LogK_2$
9.51	5.50	6.66	6.73	0.07	1.3509	1.70	-0.2671	1.4329
9.73	5.55	6.78	6.85	0.07	1.6383	1.51	0.2467	1.7567
10.00	5.60	6.90	6.98	0.08	2.1783	1.31	-0.2158	1.0942
10.23	5.65	7.05	7.13	0.08	4.1904	1.27		
10.49	5.70	7.10	7.19	0.09	4.6920			

$LogK_2$(Average value) = 1.4280 ± 0.3312

Table 5:Point-wise method,Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$\mathrm{Log}(\frac{n}{n-1})$	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430

LogK_1 **(Average value)** = 2.3059± 0.6153

Table 6:Point-wise method, Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$\mathrm{Log}(\frac{n-1}{2-n})$	Log K_2
9.73	5.55	6.33	6.42	0.09	0.9000	1.69		
10.00	5.60	6.47	6.58	0.11	1.2578	1.44	-0.4592	0.9808
10.23	5.65	6.62	6.84	0.12	1.6137	1.26	-0.2010	1.4610
10.49	5.70	6.80	6.92	0.12	2.1052	1.03		

LogK_2 **(Average value)** = 1.2209± 0.3398

Table 7:Point-wise method,Pb (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$\log(\frac{n}{1-n})$	LogK_1
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.60	0.05	0.8333	1.96	0.6989	2.6589

LogK_1 (Average value) = 2.5832 ±0.1614

Table 8:Point-wise method,Pb-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$\log(\frac{n-1}{2-n})$	$\log K_2$
9.51	5.50	6.66	6.71	0.05	0.9650	1.67	-0.0237	1.1963
9.73	5.55	6.78	6.83	0.05	1.1702	1.44		
10.00	5.60	6.90	6.90	0.05	1.4864	1.22		
10.23	5.65	7.05	7.10	0.05	2.0190	1.09		
10.49	5.70	7.10	7.17	0.07	3.6492	1.00		

LogK_2(Average value) = 1.1963

Table 9:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log $(\frac{n}{n-1})$	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.5477	2.3123
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	0.0272	2.2072
9.51	5.50	6.20	6.26	0.07	0.6417	1.89	0.2530	2.1430
9.73	5.55	6.40	6.40	0.07	0.7000	1.67	0.3680	2.0380

LogK_1 **(Average value)** = 2.2364 ± 0.1602

Table 10:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$\mathrm{Log}(\frac{n-1}{2-n})$	Log K_2
10.00	5.60	6.47	6.55	0.08	1.9503	1.41		
10.23	5.65	6.62	6.72	0.11	1.4792	1.26	-0.0361	1.2239

LogK_2 **(Average value)** = 1.2239

Table 11:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$\log(\frac{n}{n-1})$	LogK_1
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4290	2.2110
8.72	5.35	6.37	6.39	0.02	0.2858	2.42	-0.3978	2.0222
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

LogK_1 (Average value)=2.1382**±**0.1046

Table 12:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	log($\frac{n-1}{2-n}$)	LogK$_2$
9.51	5.55	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.84	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.93	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.10		
10.49	5.70	7.10	7.18	0.07	3.6492	0.83		

LogK$_2$(Average value) = 1.5453 **±** 0.3450

Table 13:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	V$_3$-V$_2$	n	pL	Log($\frac{n}{n-1}$)	Log K$_1$
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.3477	2.3123
9.00	5.40	6.00	6.04	0.04	0.3236	2.38	-0.3202	2.0598
9.22	5.45	6.10	6.15	0.05	0.4297	2.17	-0.1230	2.0470
9.51	5.50	6.20	6.26	0.06	0.5500	1.89	0.0871	1.9771
9.73	5.55	6.33	6.40	0.07	0.7000	1.67	0.3680	2.0380

LogK$_1$ **(Average value)** = 2.1568 ± 0.2069

Table 14:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	V$_3$-V$_2$	n	pL	Log($\frac{n-1}{2-n}$)	Log K$_2$
10.00	5.60	6.47	6.55	0.08	0.9148	1.41		
10.23	5.65	6.62	6.71	0.09	1.2102	1.20	-0.5749	0.6251
10.49	5.70	6.80	6.92	0.09	1.5968	1.03	0.1703	1.2003

LogK$_2$ **(Average value)** = 0.9127± 0.4070

Table15:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	Log($\frac{n}{1-n}$)	LogK$_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4210	2.2190
8.72	5.35	6.37	6.40	0.03	0.4286	2.42	-0.1249	2.2951
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.96	0.3010	2.2610
9.51	5.55	6.66	6.70	0.04	0.7720	1.67	0.5297	2.1997

LogK$_1$ (Average value) = 2.2108± 0.0825

Table 16:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	Log($\frac{n-1}{2-n}$)	Log K$_2$
9.73	5.55	6.78	6.83	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.95	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.09		
10.49	5.70	7.10	7.16	0.06	3.1429	0.89		

LogK$_2$ **(Average value)** = 1.5453± 0.3450

Table 17:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	V$_3$-V$_2$	n	pL	Log($\frac{n}{n-1}$)	Log K$_1$
8.50	5.30	5.81	5.86	0.05	0.3717	2.88	-0.2280	2.6520
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.06	0.06	0.4853	2.38	-0.0255	2.3545
9.22	5.45	6.10	6.16	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430
9.73	5.55	6.33	6.41	0.08	0.8000	1.69	0.6020	2.2920

LogK$_1$ **(Average value)** = 2.2516± 0.5380

Table 18:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$\text{Log}(\frac{n-1}{2-n})$	Log K_2
10.00	5.60	6.47	6.57	0.10	1.1434	1.43		
10.23	5.65	6.62	6.72	0.10	1.3448	1.23	-0.2788	0.9512
10.49	5.70	6.80	6.90	0.10	1.7742	1.03	0.5351	1.5651

LogK_2 **(Average value)** = 1.2581± 0.4340

Table 19: Stepwise and overall Stability constants of thehydrolysed and unhydrolysed divalent metal (II) complexes

Chelates	**LogK_1**	**LogK_2**	**Logβ**
[Cu (Hydrolysed PSHA-1)$_2$]	2.4788	1.4280	3.9068
[Pb (Hydrolysed PSHA-1)$_2$]	2.5832	1.1963	3.7795
[Cd (Hydrolysed PSHA-1)$_2$]	2.2108	1.5453	3.7561
[Mg (Hydrolysed PSHA-1)$_2$]	2.1382	1.5453	3.6835
[Cu (Unhydrolysed PSHA-1)$_2$]	2.3059	1.2209	3.5268
[Pb (Unhydrolysed PSHA-1)$_2$]	2.2364	1.2239	3.4603
[Cd (Unhydrolysed PSHA-1)$_2$]	2.2516	1.2581	3.5097
[Mg (Unydrolysed PSHA-1)$_2$]	2.1568	0.9127	3.0695

The results obtained (Table19) shows the stepwise and overall stability constants to be not high indicating low stability of the complexes, because the solubility of most metal ions in the basic pH range is minimal due to metal hydroxide precipitation (Karimi, 2017). In general, the stepwise stability constants (K_1 and K_2) follow the order $K_1 > K_2$ for the copper, lead, magnesium and cadmium complexes respectively. The steady decrease of the values with increasing number of ligands is in agreement with the prediction made by researchers (Na'aliya, 2013). The decrease could be attributed to the fact that as the number of the ligands (Humate ions) that enters the coordination zone increases the aqua molecules available for replacement by the ligands become less. Thus, the metal ions become less electron loving with progressive intake of the ligand and this results in the decrease in the values of the constants (Na'aliya, 2013). Also the stability of the complexes is influenced by the size and number of the chelate rings(Mackay and Mackay,2002).All the complexes form rings in their structure as humate, a bidentate ligand, bond the metal ions in the ratio 1:2 (Boguta and Sokolowska, 2016) forming chelate rings. The values of the overall stability constants (logβ) obtained for humate complexes are not high indicating low stability as the values are not high. LogK values for copper-humates (Table 3 to 6) obtained in this study are lower than those reported for the complexes of humic acids (Pandey *et al.*, 2015; Dinu, 2013; Kaschl *et al.*, 2010 and Gilbeto and Jorg, 2001). The values of LogK(Table 7 to 10) forlead-humates are lower than those reported for the lead in the literature (Dinu, 2013; Gilbeto and Jorg 2001). Log K values(Table 11 to 14) for magnesium-humates obtained in this study are close to those reported by (Pandey *et al.*, 2015). Log K values of cadmium-humates (Table 15 to 18) obtained in this work near to the one reported by (Dinu, 2013 and Pandey *et al.*, 2015).The difference between the reported values and the values obtained in this study might be probably as a result of acid hydrolysis of humic acid. The values of the overall stability constants (log β) of the copper humates complexes presented in Table 19 is high than that of other metal humate complexes, show relatively high stability of Cu-HA complexes, show the following order of stability: Cu >Pb> Cd > Mg; which are in close agreement to the findings of (Dinu, 2013 and Pandey *et al.*, 2015).The high stability of Cu-humate chelate could be attributed to the existence of coordinate covalent bond between the complexing agents and the Cu^{2+} ions. Since, Cu^{2+} being a metal of the transitional series with $3d^9$ electronic configurations can accept the electrons from the complexing agents. Similarly,the low stabilities of Pb,Cd and Mg - complexes could be explained by that Pb^{2+} with $6s^2$, Cd^{2+} with $4d^{10}$ and Mg^{2+} with $2p^6$ their electronic configuration has a completely filled d,p and s orbitals. Moreover, the stabilities of metal ions with hydrolysed humic acid from peat soil were higher than those with unhydrolysed humic acid from peat soil; which is ascribed to the high content of acidity in hydrolysed humic acid than unhydrolysed humic acid.

CONCLUSION

The values of logK for Cu(II) hydrolysed humic acid complex was higher followed by Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes as compared with metal(II) unhydrolysed humic acid complexes . This indicates acid hydrolysis of humic acid can enhance the complexation behavior of humic acid with metal (II) ions. However, the higher values of logβ for Cu(II), Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes indicates more stable stepwise complexes formed as compared with Cu(II), Pb(II), Cd(II) and Mg(II) unhydrolysed humic acid complexes.

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STABILITY CONSTANTS OF COMPLEXES OF METAL IONS WITH PEATSOIL HUMIC ACIDS UNDER NON-ACID-CONDITIONS

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ABSTRACT

Stability constants of complexes of four divalent metal ions viz. Cu^{2+}, Pb^{2+},Mg^{2+} and Cd^{2+} with humic acids (HA) were determined by potentiometric titration of humic acids with the corresponding salt of the divalent metals in aqueous media under non-acid-condition. The log K (logarithm of the stability constant) ranged from 1.0942 to 2.7471 for metal-humic acid complexes were determined using point-wise computational method. The order of stability constants were obtained as follows: Cu >Pb> Cd > Mg for metal -HA complexes respectively, indicating a higher degree of complexation with Cu metal ion.

Keywords: stability constant, humic acid, potentiometric titration, divalent metals, acid hydrolysis.

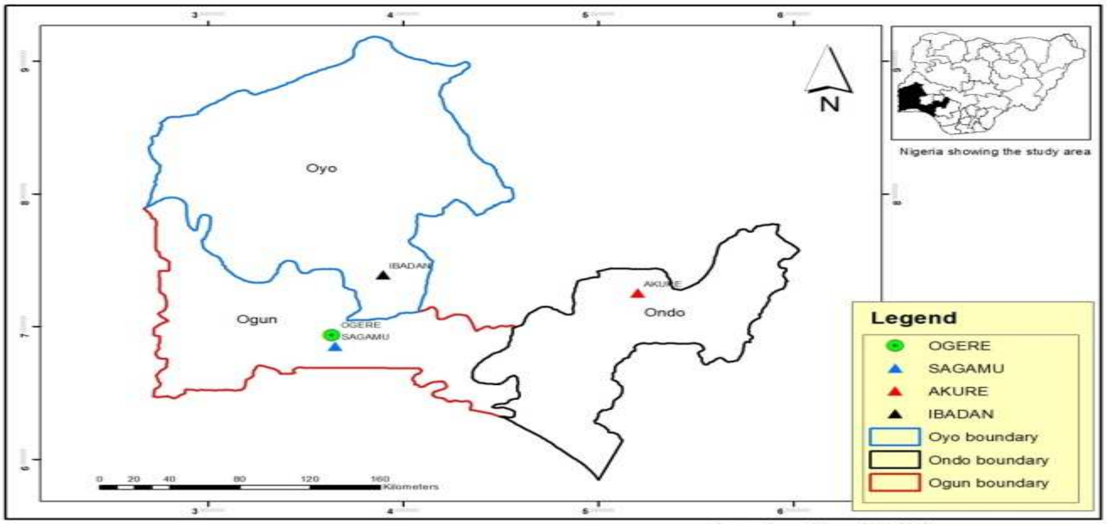
NTRODUCTION

The stability constant of a complex is the numerical expression of its stability and provides a quantitative measure of affinity of the metal ion to the complexing agent. An understanding of the relative stability of metal-complexes helps in predicting the behavior of metal ions in the soil (Ram and Raman, 1982). Extensive researches has been done to determine the stability constants of the complexes formed between humic acid (HA) with a number of metal ions. Ashok *et al*., (2000) reported that humic acid with hydroxyl, phenoxyl and carboxyl reactive groups can form coordination compound with metal ions at pH 3.5. The stability constants(Log K) for different metal-humic acid complexes indicated the following order of the stabilities of complexes formed between humic acid and metal ion, Cu >Fe >Pb> Ni > Co > Ca > Cd > Zn >Mn> Mg. Andelkovic *et al*., (2010) investigated the binding of Cd(II) to soil humic acid at pH 6.5 and in 0.1M KNO_3 ionic medium. The stability constant for binding indicating greater stability in the case when carboxyl groups are involved in complexation reaction. Kostic *et al*.,(2012) investigated the complexation of humic acid with certain heavy metal ions (Co(II), Ni(II),Cu(II), Zn(II), and Pb(II). The experiment was performed at $25^{o}C$, at pH 4.0 and ionic strength of 0.01M. Stability constant of complex between Pb(II) ions and humic acid is greater than stability constants of other investigated metal-humate complexes. Bogata and Sokolowska (2016) analyses the interaction between humic acids from different soils and Zn (II) ions at wide concentration ranges and at pH 5. Studies have showed significant impact of Zn concentration, pH and some properties of humic acids with zinc.But all of these studies were limited to acidic pH range. Therefore, the present study was carried out to determine and compare the stability constants of complexes of metal ions with hydrolysed peat soil humic acid and unhydrolysed peat soil humic under non-acid conditions.

MATERIALS AND METHODS

Analytical grade chemicals used includes hydrochloric acid (HCl), nitric acid (HNO_3), sodium hydroxide (NaOH), lead nitrate $Pb(NO_3)_2$, copper nitrate $Cu(NO_3)_2.3H_2O$, cadmium nitrate $Cd(NO_3)_2.4H_2O$, magnesium nitrate $Mg(NO_3)_2.6H_2O$, potassium nitrate (KNO_3), calcium chloride ($CaCl_2$), (sigma-Aldrich). Dowex 50WX8, (20-50 mesh) from Fluka.

Area of study



Source: Dept. of Geog. BUK (2016)

Figure 1: Map showing the sampling point at Sagamu Town, Ogun State.

Description of Sampling Area

Sagamu has geographical coordinates between 6°50′ north; 3° 38′ east is located in south western region of Nigeria. The region has tropical wet and dry climate with a lengthy wet season and relatively constant temperatures throughout the course of the year. Wet season runs from March to October, November to December forms the region dry season. The vegetation type of the region is savannah which is really grassland with small bushes and occasional big trees. Grassland soils have substantially higher organic matter content than forest soils (Novackova, 2011).

Sample Collection

The Peatsoil samples were collected from four different sampling points (0-10cm depth) in Sagamu into polyethylene bag with plastic spoons. Samples were taken to the laboratory, extraneous materials were removed; the samples were air-dried, crushed and ground to a fine powder in a mortar passed through a 0.20mm sieve. The samples were kept for analysis.

Isolation and purification of humic acid from peat soil sample

Peatsoil sample (100g) was mixed with 1000 cm^3 of 0.1M NaOH solution, shaken for 3hours and left to stand overnight. Dark-coloured supernatant was obtained and decanted from solid residue. The dark-coloured supernatant was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 6 hours. Yellowish brown supernatant and dark-brown precipitate were obtained. The yellowish brown supernatant was decanted followed by centrifuge and discarded. The dark-brown precipitate was mixed with $500cm^3$of 0.1M NaOH solution followed by passing through dowex resin. The dark-brown solution was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 3 hours. The dark-brown precipitate was washed several times with deionized water. The supernatant was treated with $AgNO_3$ solution until no white precipitate observed. The humic acid was transferred to weighed crucible and dried at 60°C in an oven for 12 hours. The humic acid was cooled and dried in the desiccator, weighed and recorded. The obtained humic acid was dried again at 60°C for additional 6 hours cooled and dried in the desiccator, weighed and recorded constant weight was obtained (Baruah *et al.*, 2015).

FT-IR analysis

FT-IR spectra of humic acid sample was analysed using Carry 630 FT-IR Agilent Technologies.

Unhydrolysed compost humic acid

The unhydrolysed humic acid was obtained after isolation and purification of compost humic acid and kept for investigation.

Acid hydrolysis of Peatsoil acid

Peatsoil humic acid sample (1g) was refluxed for 12 hours at (160°C) with $50cm^3$ of 6M HCl. The mixture was allowed to cool, decanted, and centrifuged after hydrolysis. The insoluble residues were washed with distilled water via centrifugation several times, and the supernatant was treated with $AgNO_3$ solution until no white precipitate was observed. The residue was thoroughly dried over $CaCl_2$ in a desiccator at room temperature (Chefetz *et al.*, 2002). Finally, the obtained hydrolysed humic acid was kept for investigation.

Potentiometric Titrations

Potentiometric measurements were carried out using a pH-meter Jenway (model 3510) with combine electrode, the sensitivity of the pH - meter is 0.01 units. The pH meter was switched on half an hour before starting the titration for initial warm up of the instrument. The instrument was calibrated with an aqueous standard buffer solution of pH 4.00 and 10.0 (borate buffer) prepared from a "Qualigens" buffer tablets.

The following sets of solutions were prepared in a 250cm^3 volumetric flask separately for pH metric titrations.

(i) 5 cm^3 0.1 M HCl + 40 cm^3 deionized water
(ii) 5 cm^3 0.1 M HCl + 39 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid
(iii) 5 cm^3 0.1 M HCl + 37 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid
+ 2 cm^3 0.01 M Cu(II)

The solutions were titrated against standardized 0.110MNaOH separately. The total volume of each mixture was adjusted to 50 cm^3 and the ionic strength of the solutions was maintained constant at by adding appropriate amount of stock solution of 1M KNO$_3$ (Gamal, 2015; Omar and Ali, 2015). A magnetic stirrer was used to achieve thorough mixing of the interacting solutions at 550 rpm. The same set of experimental conditions was applied for potentiometric titration of remaining samples.

Evaluation of pKa of Hydrolysed peat soil Humic Acids

The proton-ligand formation number n$_{\mathbf{A}}$ were calculated by Irving and Rossotti expression (Omar and Ali, 2015).

$$nA = Y - \frac{(V2-V1)(No-Eo)}{(Vo+V1)TcL} \quad \text{..................................1}$$

Where: Y is number of dissociable proton, (V$_2$-V$_1$) is the measure of displacement of the ligand curve relative to acid curve, N^o and E^o are the resultant concentration of alkali solution, free acid solution, $T_{cL}{}^{o}$ is the total ligand concentration, V^o is the total volume of titration solution,V$_1$ is the volume of alkali added to acid solution,V$_2$ is the volume of alkali added to acid solution + ligand solution, acid dissociation constants (pKa - values) of ligand were calculated by algebraic method point wise calculation (Tables 1). The dissociation constants (pKa) were calculated according to the following relation:

$$pKa = pH + \log\left(\frac{nA}{1-nA}\right) \quad \text{.............................2}$$

Where: pKa is the acid dissociation constant, n$_A$is the Proton-ligand formation number and pH is the pH-values (Omar and Ali, 2015).

Determination of metal-ligand stability constants (log K) of complexes

The potentiometric measurement for the determination of stability constant of a complex in solution is based on the fact that the redox potential of the couple $\frac{M^{+(m-n)}}{M^{+m}}$ is shifted significantly on complexation of the metal ion with the ligand. This method involves change in hydrogen ion concentration [H$^+$] due to the displacement or association of one or more protons taking place during complexation reaction. This change can be found out by titrating the solutions containing free acid, acid with ligand, and acid with ligand and metal ion, individually against a standard alkali solution at a constant ionic strength or temperature. Either ionic strength or temperature may be varied for different sets of solutions. In all the cases, the change in the pH of the solution is measured after each addition of a known amount of alkali to the reaction cell which contains the reaction mixture. The titration curves are then drawn by plotting the measured pH values against the corresponding volume of alkali added and the stability constants of the complexes are determined from the titration curves by employing pH-metric titration technique given by (Irving and Rossoti).

Metal-ligand stability constants (Log K) were determined by using the following relations:

$$\bar{n} = \frac{(V_3 - V_2)(E^0 + N^0)}{(V^0 + V_2)\bar{n}_A T_m^0} \quad \text{..3}$$

and

$$PL = \log_{10}\left\{\frac{1 + \beta_n^H \dfrac{1}{[anti\ \log pH]^n}}{T_L^0 - \bar{n}T_m^0} \mathrm{X} \frac{(V^0 + V_3)}{V^0}\right\} \quad \text{..4}$$

Where $T_{L,}$ T^{o}, E°, and V^{o}havethe same significance as in equation (1) above, T_m denotes the total concentration of metal present in solution, V_3 is the volume of metal ions present in solution and β^{H} is the overall proton ligand stability constant. The metal-ligand stability constants (log K) were determined by employing point wise computational Method (eq. 5 and 6).

$$LogK_1 = \log\left(\frac{n}{1-n}\right) + pL \qquad \text{.............}5$$

$$LogK_2 = \log\left(\frac{1-n}{2-n}\right) + pL\text{.......................}6$$

Where: Log K is the metal-ligand stability constant, pL is the Free ligand exponent function, **n** is the Average number of ligand attached with metal ion (Janrao*et al.*, 2014).The results obtained were analyzed by an ORIGIN 2016 program using titration data and then the proton-ligand stability constants (pKa) and Metal-ligand stability constant (LogK) calculated (Omar and Ali, 2015).

RESULTS AND DISCUSSION

Fourier transformed infrared (FT-IR) spectra of isolated humic acid from peat soils Figure 2 had distinct clear absorption bands indicating the presence of major humic acid structural elemental groups such as H bonded OH ($3680cm^{-1}$ peak), C=O of carbonyl ($1721cm^{-1}$ peak), functional groups of aliphatic components CH_2 ($2918cm^{-1}$ peak) and C-O stretching of polysaccharide ($1168cm^{-1}$ peak). The positions of the absorption bands of the spectra fell within typical major absorption bands of humic acid which is at frequencies 3680, 2918, 1721, 1168 cm^{-1}. The first peak centred in the vicinity of 3680 cm^{-1} region is attributed to phenol OH group bounded by intermolecular H bonds. The $2918cm^{-1}$ band usually has absorption maximum at 2918 cm^{-1} which is due to C–H stretching of alkane group (CH_2). The next major absorption band is 1721 cm^{-1}. This band has been commonly ascribed to C=O stretching of mainly carboxyl group (COOH) with trace amount of ketones. The last peak was observed at 1168 cm^{-1} due to C–O stretching of polysaccharides and this peak appeared also in the spectra of humic acid from peat soil. The FTIR spectra of the isolated humic acid contained all major characteristic absorption peaks of humic acid. These absorption peaks indicated the presence of the major structural elements of humic acid namely H bonded OH, C=C of aromatic ring, C=O of carbonyl group (both carboxyl and ketonic), CH_2 group. This strongly supports the presence of humic acid.

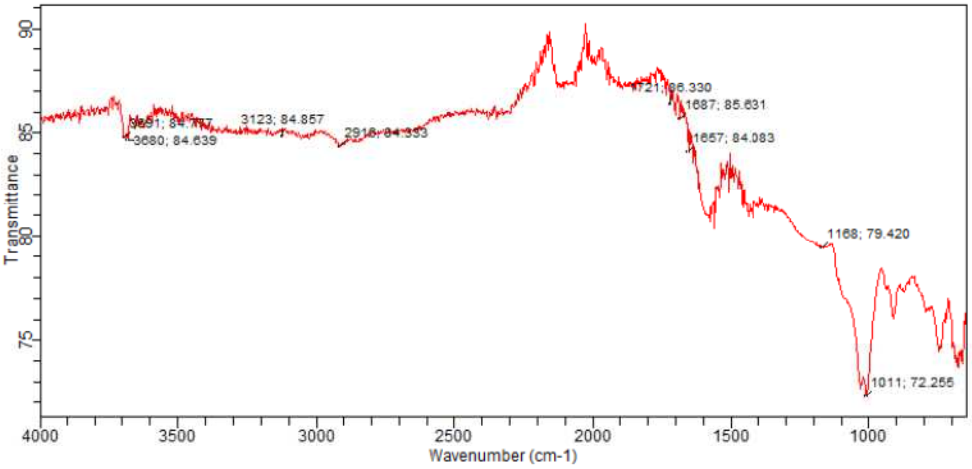


Fig. 2 : FT-IR spectraof peatsoilhumic acid (PSHA)

Evaluation of acid dissociation constant (pka) of acid hydrolysed peat soil humicacid at phenolic group

The value of the dissociation constant of the peat soil humic acid (PSHA) that underwent acidhydrolysis studied was found to be 8.9299 as shown Table 1, which is lower than the literaturevalues reported by Almeida and Szpoganics, (2015), Borges *et al.*, (2005); Badr *et al.*, (2012)and Fernandes *et al*,.(2009) of 9.73, 9.47 and 10.30. The difference between the obtained valuesand the reported values in this study might be probably as a result of acid hydrolysis of humicacid.

Table 1: PKa of (Hydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	log($\frac{nA}{1-nA}$)	pKa
8.50	5.30	6.29	0.99	0.3594	-0.2510	8.2490
8.72	5.35	6.37	1.02	0.3400	-0.2880	8.4320
9.00	5.40	6.46	1.06	0.3141	-0.3391	8.6609
9.22	5.45	6.55	1.10	0.2882	-0.3927	8.8273
9.51	5.50	6.66	1.16	0.2494	-0.4786	9.0314
9.73	5.55	6.78	1.23	0.2041	-0.5910	9.1390
10.00	5.60	6.90	1.30	0.1589	-0.7238	9.2762
10.23	5.65	7.05	1.40	0.0941	-0.9835	9.2465
10.49	5.70	7.10	1.40	0.0941	-0.9835	9.5065

Average pKa = 8.9299 ± 0.4186

Table 2: PKa of (Unhydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	Log($\frac{nA}{1-n}$)	pKa
8.50	5.30	5.81	0.51	0.6619	0.2919	8.7919
8.72	5.35	5.90	0.55	0.6357	0.2418	8.9618
9.00	5.40	6.00	0.60	0.6029	0.1813	9.1813
9.22	5.45	6.10	0.65	0.5701	0.1226	9.3426
9.51	5.50	6.20	0.70	0.5376	0.0654	9.5754
9.73	5.55	6.33	0.78	0.4851	-0.0259	9.7041
10.00	5.60	6.47	0.87	0.4262	-0.1291	9.8709
10.23	5.65	6.62	0.99	0.3609	-0.2481	9.9819
10.49	5.70	6.80	1.10	0.2759	-0.4690	10.0210

Average pKa = 9.4923± 0.4410

Metal-ligand stability constant (Log K)

The stabilityconstants require the accurate values of proton-ligand stability constants (Anil and Maroti, 2008). Metal titration curves crossed over ligand titration curve indicated the formation of complex upon proton release (Santosh, *et al.*, 2011). If the values of n- are within range 0.2-0.8 and 1.2-18 this indicates the formation of 1:1 and 1:2 complexes (Sayyed and Mazahar, 2012).

The metal (II)-humate stepwise stability constants (log k) at phenolic group (Tables 3-18)

Table 3: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n}{1-n}$)	$LogK_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

$LogK_1$ (Average value) = 2.4788± 0.2203

Table 4: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	Log($\frac{n-1}{2-n}$)	$LogK_2$
9.51	5.50	6.66	6.73	0.07	1.3509	1.70	-0.2671	1.4329
9.73	5.55	6.78	6.85	0.07	1.6383	1.51	0.2467	1.7567
10.00	5.60	6.90	6.98	0.08	2.1783	1.31	-0.2158	1.0942
10.23	5.65	7.05	7.13	0.08	4.1904	1.27		
10.49	5.70	7.10	7.19	0.09	4.6920			

$LogK_2$(Average value) = 1.4280 ± 0.3312

Table 5:Point-wise method,Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3$-$V_2)$	n	pL	Log($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430

$LogK_1$ **(Average value)** = 2.3059± 0.6153

Table 6:Point-wise method, Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
9.73	5.55	6.33	6.42	0.09	0.9000	1.69		
10.00	5.60	6.47	6.58	0.11	1.2578	1.44	-0.4592	0.9808
10.23	5.65	6.62	6.84	0.12	1.6137	1.26	-0.2010	1.4610
10.49	5.70	6.80	6.92	0.12	2.1052	1.03		

$LogK_2$ **(Average value)** = 1.2209± 0.3398

Table 7:Point-wise method,Pb (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3$-$V_2)$	n	pL	log($\frac{n}{1-n}$)	$LogK_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.60	0.05	0.8333	1.96	0.6989	2.6589

$LogK_1$ (Average value) = 2.5832 ±0.1614

Table 8:Point-wise method,Pb-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3$-$V_2)$	n	pL	log($\frac{n-1}{2-n}$)	$logK_2$
9.51	5.50	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.83	0.05	1.1702	1.44		
10.00	5.60	6.90	6.90	0.05	1.4864	1.22	-0.0237	1.1963
10.23	5.65	7.05	7.10	0.05	2.0190	1.09		
10.49	5.70	7.10	7.17	0.07	3.6492	1.00		

$LogK_2$(Average value) = 1.1963

Table 9:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log ($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.5477	2.3123
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	0.0272	2.2072
9.51	5.50	6.20	6.26	0.07	0.6417	1.89	0.2530	2.1430
9.73	5.55	6.40	6.40	0.07	0.7000	1.67	0.3680	2.0380

$LogK_1$ **(Average value)** = 2.2364 ± 0.1602

Table 10:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
10.00	5.60	6.47	6.55	0.08	1.9503	1.41		
10.23	5.65	6.62	6.72	0.11	1.4792	1.26	-0.0361	1.2239

$LogK_2$ **(Average value)** = 1.2239

Table 11:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3$-$V_2)$	n	pL	log($\frac{n}{n-1}$)	$LogK_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4290	2.2110
8.72	5.35	6.37	6.39	0.02	0.2858	2.42	-0.3978	2.0222
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

$LogK_1$ (Average value)=2.1382±0.1046

Table 12:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$\log(\frac{n-1}{2-n})$	$LogK_2$
9.51	5.55	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.84	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.93	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.10		
10.49	5.70	7.10	7.18	0.07	3.6492	0.83		

$LogK_2$(Average value) = 1.5453 **±** 0.3450

Table 13:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$Log(\frac{n}{n-1})$	$Log\ K_1$
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.3477	2.3123
9.00	5.40	6.00	6.04	0.04	0.3236	2.38	-0.3202	2.0598
9.22	5.45	6.10	6.15	0.05	0.4297	2.17	-0.1230	2.0470
9.51	5.50	6.20	6.26	0.06	0.5500	1.89	0.0871	1.9771
9.73	5.55	6.33	6.40	0.07	0.7000	1.67	0.3680	2.0380

$LogK_1$ **(Average value)** = 2.1568 ± 0.2069

Table 14:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$Log(\frac{n-1}{2-n})$	$Log\ K_2$
10.00	5.60	6.47	6.55	0.08	0.9148	1.41		
10.23	5.65	6.62	6.71	0.09	1.2102	1.20	-0.5749	0.6251
10.49	5.70	6.80	6.92	0.09	1.5968	1.03	0.1703	1.2003

$LogK_2$ **(Average value)** = 0.9127± 0.4070

Table15:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$Log(\frac{n}{1-n})$	$LogK_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4210	2.2190
8.72	5.35	6.37	6.40	0.03	0.4286	2.42	-0.1249	2.2951
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.96	0.3010	2.2610
9.51	5.55	6.66	6.70	0.04	0.7720	1.67	0.5297	2.1997

$LogK_1$ (Average value) = 2.2108± 0.0825

Table 16:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$Log(\frac{n-1}{2-n})$	$Log\ K_2$
9.73	5.55	6.78	6.83	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.95	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.09		
10.49	5.70	7.10	7.16	0.06	3.1429	0.89		

$LogK_2$ **(Average value)** = 1.5453± 0.3450

Table 17:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$Log(\frac{n}{n-1})$	$Log\ K_1$
8.50	5.30	5.81	5.86	0.05	0.3717	2.88	-0.2280	2.6520
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.06	0.06	0.4853	2.38	-0.0255	2.3545
9.22	5.45	6.10	6.16	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430
9.73	5.55	6.33	6.41	0.08	0.8000	1.69	0.6020	2.2920

$LogK_1$ **(Average value)** = 2.2516± 0.5380

Table 18:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$\text{Log}(\frac{n-1}{2-n})$	Log K_2
10.00	5.60	6.47	6.57	0.10	1.1434	1.43		
10.23	5.65	6.62	6.72	0.10	1.3448	1.23	-0.2788	0.9512
10.49	5.70	6.80	6.90	0.10	1.7742	1.03	0.5351	1.5651

LogK_2 **(Average value)** = 1.2581± 0.4340

Table 19: Stepwise and overall Stability constants of thehydrolysed and unhydrolysed divalent metal (II) complexes

Chelates	**LogK_1**	**LogK_2**	**Logβ**
[Cu (Hydrolysed PSHA-1)$_2$]	2.4788	1.4280	3.9068
[Pb (Hydrolysed PSHA-1)$_2$]	2.5832	1.1963	3.7795
[Cd (Hydrolysed PSHA-1)$_2$]	2.2108	1.5453	3.7561
[Mg (Hydrolysed PSHA-1)$_2$]	2.1382	1.5453	3.6835
[Cu (Unhydrolysed PSHA-1)$_2$]	2.3059	1.2209	3.5268
[Pb (Unhydrolysed PSHA-1)$_2$]	2.2364	1.2239	3.4603
[Cd (Unhydrolysed PSHA-1)$_2$]	2.2516	1.2581	3.5097
[Mg (Unydrolysed PSHA-1)$_2$]	2.1568	0.9127	3.0695

The results obtained (Table19) shows the stepwise and overall stability constants to be not high indicating low stability of the complexes, because the solubility of most metal ions in the basic pH range is minimal due to metal hydroxide precipitation (Karimi, 2017). In general, the stepwise stability constants (K_1 and K_2) follow the order $K_1 > K_2$ for the copper, lead, magnesium and cadmium complexes respectively. The steady decrease of the values with increasing number of ligands is in agreement with the prediction made by researchers (Na'aliya, 2013). The decrease could be attributed to the fact that as the number of the ligands (Humate ions) that enters the coordination zone increases the aqua molecules available for replacement by the ligands become less. Thus, the metal ions become less electron loving with progressive intake of the ligand and this results in the decrease in the values of the constants (Na'aliya, 2013). Also the stability of the complexes is influenced by the size and number of the chelate rings(Mackay and Mackay,2002).All the complexes form rings in their structure as humate, a bidentate ligand, bond the metal ions in the ratio 1:2 (Boguta and Sokolowska, 2016) forming chelate rings. The values of the overall stability constants (logβ) obtained for humate complexes are not high indicating low stability as the values are not high. LogK values for copper-humates (Table 3 to 6) obtained in this study are lower than those reported for the complexes of humic acids (Pandey *et al.*, 2015; Dinu, 2013; Kaschl *et al.*, 2010 and Gilbeto and Jorg, 2001). The values of LogK(Table 7 to 10) forlead-humates are lower than those reported for the lead in the literature (Dinu, 2013; Gilbeto and Jorg 2001). Log K values(Table 11 to 14) for magnesium-humates obtained in this study are close to those reported by (Pandey *et al.*, 2015). Log K values of cadmium-humates (Table 15 to 18) obtained in this work near to the one reported by (Dinu, 2013 and Pandey *et al.*, 2015).The difference between the reported values and the values obtained in this study might be probably as a result of acid hydrolysis of humic acid. The values of the overall stability constants (log β) of the copper humates complexes presented in Table 19 is high than that of other metal humate complexes, show relatively high stability of Cu-HA complexes, show the following order of stability: Cu >Pb> Cd > Mg; which are in close agreement to the findings of (Dinu, 2013 and Pandey *et al.*, 2015).The high stability of Cu-humate chelate could be attributed to the existence of coordinate covalent bond between the complexing agents and the Cu^{2+} ions. Since, Cu^{2+} being a metal of the transitional series with $3d^9$ electronic configurations can accept the electrons from the complexing agents. Similarly,the low stabilities of Pb,Cd and Mg -complexes could be explained by that Pb^{2+} with $6s^2$, Cd^{2+} with $4d^{10}$ and Mg^{2+} with $2p^6$ their electronic configuration has a completely filled d,p and s orbitals. Moreover, the stabilities of metal ions with hydrolysed humic acid from peat soil were higher than those with unhydrolysed humic acid from peat soil; which is ascribed to the high content of acidity in hydrolysed humic acid than unhydrolysed humic acid.

CONCLUSION

The values of logK for Cu(II) hydrolysed humic acid complex was higher followed by Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes as compared with metal(II) unhydrolysed humic acid complexes . This indicates acid hydrolysis of humic acid can enhance the complexation behavior of humic acid with metal (II) ions. However, the higher values of logβ for Cu(II), Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes indicates more stable stepwise complexes formed as compared with Cu(II), Pb(II), Cd(II) and Mg(II) unhydrolysed humic acid complexes.

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STABILITY CONSTANTS OF COMPLEXES OF METAL IONS WITH PEATSOIL HUMIC ACIDS UNDER NON-ACID-CONDITIONS

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ABSTRACT

Stability constants of complexes of four divalent metal ions viz. Cu^{2+}, Pb^{2+},Mg^{2+} and Cd^{2+} with humic acids (HA) were determined by potentiometric titration of humic acids with the corresponding salt of the divalent metals in aqueous media under non-acid-condition. The log K (logarithm of the stability constant) ranged from 1.0942 to 2.7471 for metal-humic acid complexes were determined using point-wise computational method. The order of stability constants were obtained as follows: Cu >Pb> Cd > Mg for metal -HA complexes respectively, indicating a higher degree of complexation with Cu metal ion.

Keywords: stability constant, humic acid, potentiometric titration, divalent metals, acid hydrolysis.

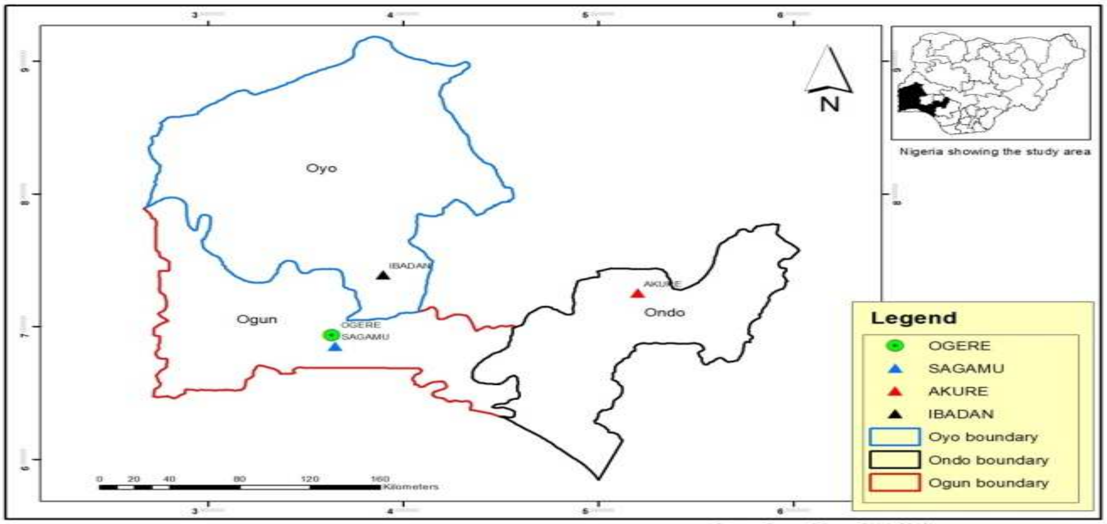
NTRODUCTION

The stability constant of a complex is the numerical expression of its stability and provides a quantitative measure of affinity of the metal ion to the complexing agent. An understanding of the relative stability of metal-complexes helps in predicting the behavior of metal ions in the soil (Ram and Raman, 1982). Extensive researches has been done to determine the stability constants of the complexes formed between humic acid (HA) with a number of metal ions. Ashok *et al*., (2000) reported that humic acid with hydroxyl, phenoxyl and carboxyl reactive groups can form coordination compound with metal ions at pH 3.5. The stability constants(Log K) for different metal-humic acid complexes indicated the following order of the stabilities of complexes formed between humic acid and metal ion, Cu >Fe >Pb> Ni > Co > Ca > Cd > Zn >Mn> Mg. Andelkovic *et al*., (2010) investigated the binding of Cd(II) to soil humic acid at pH 6.5 and in 0.1M KNO_3 ionic medium. The stability constant for binding indicating greater stability in the case when carboxyl groups are involved in complexation reaction. Kostic *et al*.,(2012) investigated the complexation of humic acid with certain heavy metal ions (Co(II), Ni(II),Cu(II), Zn(II), and Pb(II). The experiment was performed at 25°C, at pH 4.0 and ionic strength of 0.01M. Stability constant of complex between Pb(II) ions and humic acid is greater than stability constants of other investigated metal-humate complexes. Bogata and Sokolowska (2016) analyses the interaction between humic acids from different soils and Zn (II) ions at wide concentration ranges and at pH 5. Studies have showed significant impact of Zn concentration, pH and some properties of humic acids with zinc.But all of these studies were limited to acidic pH range. Therefore, the present study was carried out to determine and compare the stability constants of complexes of metal ions with hydrolysed peat soil humic acid and unhydrolysed peat soil humic under non-acid conditions.

MATERIALS AND METHODS

Analytical grade chemicals used includes hydrochloric acid (HCl), nitric acid (HNO_3), sodium hydroxide (NaOH), lead nitrate $Pb(NO_3)_2$, copper nitrate $Cu(NO_3)_2.3H_2O$, cadmium nitrate $Cd(NO_3)_2.4H_2O$, magnesium nitrate $Mg(NO_3)_2.6H_2O$, potassium nitrate (KNO_3), calcium chloride ($CaCl_2$), (sigma-Aldrich). Dowex 50WX8, (20-50 mesh) from Fluka.

Area of study



Source: Dept. of Geog. BUK (2016)

Figure 1: Map showing the sampling point at Sagamu Town, Ogun State.

Description of Sampling Area

Sagamu has geographical coordinates between 6°50′ north; 3° 38′ east is located in south western region of Nigeria. The region has tropical wet and dry climate with a lengthy wet season and relatively constant temperatures throughout the course of the year. Wet season runs from March to October, November to December forms the region dry season. The vegetation type of the region is savannah which is really grassland with small bushes and occasional big trees. Grassland soils have substantially higher organic matter content than forest soils (Novackova, 2011).

Sample Collection

The Peatsoil samples were collected from four different sampling points (0-10cm depth) in Sagamu into polyethylene bag with plastic spoons. Samples were taken to the laboratory, extraneous materials were removed; the samples were air-dried, crushed and ground to a fine powder in a mortar passed through a 0.20mm sieve. The samples were kept for analysis.

Isolation and purification of humic acid from peat soil sample

Peatsoil sample (100g) was mixed with 1000 cm^3 of 0.1M NaOH solution, shaken for 3hours and left to stand overnight. Dark-coloured supernatant was obtained and decanted from solid residue. The dark-coloured supernatant was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 6 hours. Yellowish brown supernatant and dark-brown precipitate were obtained. The yellowish brown supernatant was decanted followed by centrifuge and discarded. The dark-brown precipitate was mixed with 500$cm^3$of 0.1M NaOH solution followed by passing through dowex resin. The dark-brown solution was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 3 hours. The dark-brown precipitate was washed several times with deionized water. The supernatant was treated with $AgNO_3$ solution until no white precipitate observed. The humic acid was transferred to weighed crucible and dried at 60°C in an oven for 12 hours. The humic acid was cooled and dried in the desiccator, weighed and recorded. The obtained humic acid was dried again at 60°C for additional 6 hours cooled and dried in the desiccator, weighed and recorded constant weight was obtained (Baruah *et al*., 2015).

FT-IR analysis

FT-IR spectra of humic acid sample was analysed using Carry 630 FT-IR Agilent Technologies.

Unhydrolysed compost humic acid

The unhydrolysed humic acid was obtained after isolation and purification of compost humic acid and kept for investigation.

Acid hydrolysis of Peatsoil acid

Peatsoil humic acid sample (1g) was refluxed for 12 hours at (160°C) with 50cm^3 of 6M HCl. The mixture was allowed to cool, decanted, and centrifuged after hydrolysis. The insoluble residues were washed with distilled water via centrifugation several times, and the supernatant was treated with $AgNO_3$ solution until no white precipitate was observed. The residue was thoroughly dried over $CaCl_2$ in a desiccator at room temperature (Chefetz *et al*., 2002). Finally, the obtained hydrolysed humic acid was kept for investigation.

Potentiometric Titrations

Potentiometric measurements were carried out using a pH-meter Jenway (model 3510) with combine electrode, the sensitivity of the pH - meter is 0.01 units. The pH meter was switched on half an hour before starting the titration for initial warm up of the instrument. The instrument was calibrated with an aqueous standard buffer solution of pH 4.00 and 10.0 (borate buffer) prepared from a "Qualigens" buffer tablets.

The following sets of solutions were prepared in a 250cm^3 volumetric flask separately for pH metric titrations.

(i) 5 cm^3 0.1 M HCl + 40 cm^3 deionized water
(ii) 5 cm^3 0.1 M HCl + 39 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid
(iii) 5 cm^3 0.1 M HCl + 37 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid + 2 cm^3 0.01 M Cu(II)

The solutions were titrated against standardized 0.110MNaOH separately. The total volume of each mixture was adjusted to 50 cm^3 and the ionic strength of the solutions was maintained constant at by adding appropriate amount of stock solution of 1M KNO$_3$ (Gamal, 2015; Omar and Ali, 2015). A magnetic stirrer was used to achieve thorough mixing of the interacting solutions at 550 rpm. The same set of experimental conditions was applied for potentiometric titration of remaining samples.

Evaluation of pKa of Hydrolysed peat soil Humic Acids

The proton-ligand formation number n$_{\mathbf{A}}$ were calculated by Irving and Rossotti expression (Omar and Ali, 2015).

$$nA = Y- \frac{(V2-V1)(No-Eo)}{(Vo+V1)TcL} \quad \text{.................................1}$$

Where: Y is number of dissociable proton, (V$_2$-V$_1$) is the measure of displacement of the ligand curve relative to acid curve, N^o and E^o are the resultant concentration of alkali solution, free acid solution, T$_{cL}{}^o$ is the total ligand concentration, V^o is the total volume of titration solution,V$_1$ is the volume of alkali added to acid solution,V$_2$ is the volume of alkali added to acid solution + ligand solution, acid dissociation constants (pKa - values) of ligand were calculated by algebraic method point wise calculation (Tables 1). The dissociation constants (pKa) were calculated according to the following relation:

$$pKa = pH + \log(\frac{nA}{1-nA}) \quad \text{............................2}$$

Where: pKa is the acid dissociation constant, n$_A$is the Proton-ligand formation number and pH is the pH-values (Omar and Ali, 2015).

Determination of metal-ligand stability constants (log K) of complexes

The potentiometric measurement for the determination of stability constant of a complex in solution is based on the fact that the redox potential of the couple $\frac{M^{+(m-n)}}{M^{+m}}$ is shifted significantly on complexation of the metal ion with the ligand. This method involves change in hydrogen ion concentration [H$^+$] due to the displacement or association of one or more protons taking place during complexation reaction. This change can be found out by titrating the solutions containing free acid, acid with ligand, and acid with ligand and metal ion, individually against a standard alkali solution at a constant ionic strength or temperature. Either ionic strength or temperature may be varied for different sets of solutions. In all the cases, the change in the pH of the solution is measured after each addition of a known amount of alkali to the reaction cell which contains the reaction mixture. The titration curves are then drawn by plotting the measured pH values against the corresponding volume of alkali added and the stability constants of the complexes are determined from the titration curves by employing pH-metric titration technique given by (Irving and Rossoti).

Metal-ligand stability constants (Log K) were determined by using the following relations:

$$\bar{n} = \frac{(V_3 - V_2)(E^0 + N^0)}{(V^0 + V_2)\bar{n}_A T_m^0} \quad \text{..3}$$

and

$$PL = \log_{10}\{\frac{1+\beta_n^H \frac{1}{[anti\ \log pH]^n}}{T_L^0 - \bar{n}T_m^0} X \frac{(V^0 + V_3)}{V^0}\} \quad \text{..4}$$

Where $T_{L,}$ T^o, E°, and V^ohavethe same significance as in equation (1) above, T_m denotes the total concentration of metal present in solution, V_3 is the volume of metal ions present in solution and β^H is the overall proton ligand stability constant. The metal-ligand stability constants (log K) were determined by employing point wise computational Method (eq. 5 and 6).

$$\text{Log}K_1 = \log\left(\frac{n}{1-n}\right) + pL \qquad \ldots\ldots\ldots\ldots.5$$

$$\text{Log}K_2 = \log\left(\frac{1-n}{2-n}\right) + pL\ldots\ldots\ldots\ldots\ldots\ldots\ldots.6$$

Where: Log K is the metal-ligand stability constant, pL is the Free ligand exponent function, **n** is the Average number of ligand attached with metal ion (Janrao*et al.*, 2014).The results obtained were analyzed by an ORIGIN 2016 program using titration data and then the proton-ligand stability constants (pKa) and Metal-ligand stability constant (LogK) calculated (Omar and Ali, 2015).

RESULTS AND DISCUSSION

Fourier transformed infrared (FT-IR) spectra of isolated humic acid from peat soils Figure 2 had distinct clear absorption bands indicating the presence of major humic acid structural elemental groups such as H bonded OH ($3680cm^{-1}$ peak), C=O of carbonyl ($1721cm^{-1}$ peak), functional groups of aliphatic components CH_2 ($2918cm^{-1}$ peak) and C-O stretching of polysaccharide ($1168cm^{-1}$ peak). The positions of the absorption bands of the spectra fell within typical major absorption bands of humic acid which is at frequencies 3680, 2918, 1721, 1168 cm^{-1}. The first peak centred in the vicinity of 3680 cm^{-1} region is attributed to phenol OH group bounded by intermolecular H bonds. The $2918cm^{-1}$ band usually has absorption maximum at 2918 cm^{-1} which is due to C–H stretching of alkane group (CH_2). The next major absorption band is 1721 cm^{-1}. This band has been commonly ascribed to C=O stretching of mainly carboxyl group (COOH) with trace amount of ketones. The last peak was observed at 1168 cm^{-1} due to C–O stretching of polysaccharides and this peak appeared also in the spectra of humic acid from peat soil. The FTIR spectra of the isolated humic acid contained all major characteristic absorption peaks of humic acid. These absorption peaks indicated the presence of the major structural elements of humic acid namely H bonded OH, C=C of aromatic ring, C=O of carbonyl group (both carboxyl and ketonic), CH_2 group. This strongly supports the presence of humic acid.

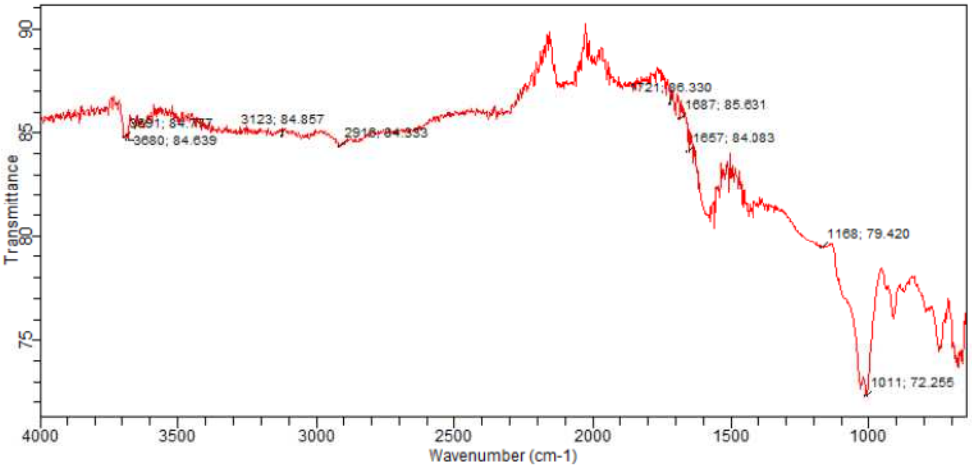


Fig. 2 : FT-IR spectraof peatsoilhumic acid (PSHA)

Evaluation of acid dissociation constant (pka) of acid hydrolysed peat soil humicacid at phenolic group

The value of the dissociation constant of the peat soil humic acid (PSHA) that underwent acidhydrolysis studied was found to be 8.9299 as shown Table 1, which is lower than the literaturevalues reported by Almeida and Szpoganics, (2015), Borges *et al.*, (2005); Badr *et al.*, (2012)and Fernandes *et al*,.(2009) of 9.73, 9.47 and 10.30. The difference between the obtained valuesand the reported values in this study might be probably as a result of acid hydrolysis of humicacid.

Table 1: PKa of (Hydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	log($\frac{nA}{1-nA}$)	pKa
8.50	5.30	6.29	0.99	0.3594	-0.2510	8.2490
8.72	5.35	6.37	1.02	0.3400	-0.2880	8.4320
9.00	5.40	6.46	1.06	0.3141	-0.3391	8.6609
9.22	5.45	6.55	1.10	0.2882	-0.3927	8.8273
9.51	5.50	6.66	1.16	0.2494	-0.4786	9.0314
9.73	5.55	6.78	1.23	0.2041	-0.5910	9.1390
10.00	5.60	6.90	1.30	0.1589	-0.7238	9.2762
10.23	5.65	7.05	1.40	0.0941	-0.9835	9.2465
10.49	5.70	7.10	1.40	0.0941	-0.9835	9.5065

Average pKa = 8.9299 ± 0.4186

Table 2: PKa of (Unhydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	Log($\frac{nA}{1-n}$)	pKa
8.50	5.30	5.81	0.51	0.6619	0.2919	8.7919
8.72	5.35	5.90	0.55	0.6357	0.2418	8.9618
9.00	5.40	6.00	0.60	0.6029	0.1813	9.1813
9.22	5.45	6.10	0.65	0.5701	0.1226	9.3426
9.51	5.50	6.20	0.70	0.5376	0.0654	9.5754
9.73	5.55	6.33	0.78	0.4851	-0.0259	9.7041
10.00	5.60	6.47	0.87	0.4262	-0.1291	9.8709
10.23	5.65	6.62	0.99	0.3609	-0.2481	9.9819
10.49	5.70	6.80	1.10	0.2759	-0.4690	10.0210

Average pKa = 9.4923± 0.4410

Metal-ligand stability constant (Log K)

The stabilityconstants require the accurate values of proton-ligand stability constants (Anil and Maroti, 2008). Metal titration curves crossed over ligand titration curve indicated the formation of complex upon proton release (Santosh, *et al.*, 2011). If the values of n- are within range 0.2-0.8 and 1.2-18 this indicates the formation of 1:1 and 1:2 complexes (Sayyed and Mazahar, 2012).

The metal (II)-humate stepwise stability constants (log k) at phenolic group (Tables 3-18)

Table 3: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n}{1-n}$)	$LogK_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

$LogK_1$ (Average value) = 2.4788± 0.2203

Table 4: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	Log($\frac{n-1}{2-n}$)	$LogK_2$
9.51	5.50	6.66	6.73	0.07	1.3509	1.70	-0.2671	1.4329
9.73	5.55	6.78	6.85	0.07	1.6383	1.51	0.2467	1.7567
10.00	5.60	6.90	6.98	0.08	2.1783	1.31	-0.2158	1.0942
10.23	5.65	7.05	7.13	0.08	4.1904	1.27		
10.49	5.70	7.10	7.19	0.09	4.6920			

$LogK_2$(Average value) = 1.4280 ± 0.3312

Table 5:Point-wise method,Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	Log($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430

$LogK_1$ **(Average value)** = 2.3059± 0.6153

Table 6:Point-wise method, Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
9.73	5.55	6.33	6.42	0.09	0.9000	1.69		
10.00	5.60	6.47	6.58	0.11	1.2578	1.44	-0.4592	0.9808
10.23	5.65	6.62	6.84	0.12	1.6137	1.26	-0.2010	1.4610
10.49	5.70	6.80	6.92	0.12	2.1052	1.03		

$LogK_2$ **(Average value)** = 1.2209± 0.3398

Table 7:Point-wise method,Pb (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n}{1-n}$)	$LogK_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.60	0.05	0.8333	1.96	0.6989	2.6589

$LogK_1$ (Average value) = 2.5832 ±0.1614

Table 8:Point-wise method,Pb-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n-1}{2-n}$)	$logK_2$
9.51	5.50	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.83	0.05	1.1702	1.44		
10.00	5.60	6.90	6.90	0.05	1.4864	1.22	-0.0237	1.1963
10.23	5.65	7.05	7.10	0.05	2.0190	1.09		
10.49	5.70	7.10	7.17	0.07	3.6492	1.00		

$LogK_2$(Average value) = 1.1963

Table 9:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log ($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.5477	2.3123
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	0.0272	2.2072
9.51	5.50	6.20	6.26	0.07	0.6417	1.89	0.2530	2.1430
9.73	5.55	6.40	6.40	0.07	0.7000	1.67	0.3680	2.0380

$LogK_1$ **(Average value)** = 2.2364 ± 0.1602

Table 10:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
10.00	5.60	6.47	6.55	0.08	1.9503	1.41		
10.23	5.65	6.62	6.72	0.11	1.4792	1.26	-0.0361	1.2239

$LogK_2$ **(Average value)** = 1.2239

Table 11:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n}{n-1}$)	$LogK_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4290	2.2110
8.72	5.35	6.37	6.39	0.02	0.2858	2.42	-0.3978	2.0222
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

$LogK_1$ (Average value)=2.1382±0.1046

Table 12:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	log($\frac{n-1}{2-n}$)	LogK$_2$
9.51	5.55	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.84	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.93	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.10		
10.49	5.70	7.10	7.18	0.07	3.6492	0.83		

LogK$_2$(Average value) = 1.5453 **±** 0.3450

Table 13:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	V$_3$-V$_2$	n	pL	Log($\frac{n}{n-1}$)	Log K$_1$
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.3477	2.3123
9.00	5.40	6.00	6.04	0.04	0.3236	2.38	-0.3202	2.0598
9.22	5.45	6.10	6.15	0.05	0.4297	2.17	-0.1230	2.0470
9.51	5.50	6.20	6.26	0.06	0.5500	1.89	0.0871	1.9771
9.73	5.55	6.33	6.40	0.07	0.7000	1.67	0.3680	2.0380

LogK$_1$ **(Average value)** = 2.1568 ± 0.2069

Table 14:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	V$_3$-V$_2$	n	pL	Log($\frac{n-1}{2-n}$)	Log K$_2$
10.00	5.60	6.47	6.55	0.08	0.9148	1.41		
10.23	5.65	6.62	6.71	0.09	1.2102	1.20	-0.5749	0.6251
10.49	5.70	6.80	6.92	0.09	1.5968	1.03	0.1703	1.2003

LogK$_2$ **(Average value)** = 0.9127± 0.4070

Table15:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	Log($\frac{n}{1-n}$)	LogK$_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4210	2.2190
8.72	5.35	6.37	6.40	0.03	0.4286	2.42	-0.1249	2.2951
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.96	0.3010	2.2610
9.51	5.55	6.66	6.70	0.04	0.7720	1.67	0.5297	2.1997

LogK$_1$ (Average value) = 2.2108± 0.0825

Table 16:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	Log($\frac{n-1}{2-n}$)	Log K$_2$
9.73	5.55	6.78	6.83	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.95	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.09		
10.49	5.70	7.10	7.16	0.06	3.1429	0.89		

LogK$_2$ **(Average value)** = 1.5453± 0.3450

Table 17:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	V$_3$-V$_2$	n	pL	Log($\frac{n}{n-1}$)	Log K$_1$
8.50	5.30	5.81	5.86	0.05	0.3717	2.88	-0.2280	2.6520
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.06	0.06	0.4853	2.38	-0.0255	2.3545
9.22	5.45	6.10	6.16	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430
9.73	5.55	6.33	6.41	0.08	0.8000	1.69	0.6020	2.2920

LogK$_1$ **(Average value)** = 2.2516± 0.5380

Table 18:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
10.00	5.60	6.47	6.57	0.10	1.1434	1.43		
10.23	5.65	6.62	6.72	0.10	1.3448	1.23	-0.2788	0.9512
10.49	5.70	6.80	6.90	0.10	1.7742	1.03	0.5351	1.5651

LogK_2 **(Average value)** = 1.2581± 0.4340

Table 19: Stepwise and overall Stability constants of thehydrolysed and unhydrolysed divalent metal (II) complexes

Chelates	**LogK₁**	**LogK₂**	**Logβ**
[Cu (Hydrolysed PSHA-1)$_2$]	2.4788	1.4280	3.9068
[Pb (Hydrolysed PSHA-1)$_2$]	2.5832	1.1963	3.7795
[Cd (Hydrolysed PSHA-1)$_2$]	2.2108	1.5453	3.7561
[Mg (Hydrolysed PSHA-1)$_2$]	2.1382	1.5453	3.6835
[Cu (Unhydrolysed PSHA-1)$_2$]	2.3059	1.2209	3.5268
[Pb (Unhydrolysed PSHA-1)$_2$]	2.2364	1.2239	3.4603
[Cd (Unhydrolysed PSHA-1)$_2$]	2.2516	1.2581	3.5097
[Mg (Unydrolysed PSHA-1)$_2$]	2.1568	0.9127	3.0695

The results obtained (Table19) shows the stepwise and overall stability constants to be not high indicating low stability of the complexes, because the solubility of most metal ions in the basic pH range is minimal due to metal hydroxide precipitation (Karimi, 2017). In general, the stepwise stability constants (K_1 and K_2) follow the order $K_1 > K_2$ for the copper, lead, magnesium and cadmium complexes respectively. The steady decrease of the values with increasing number of ligands is in agreement with the prediction made by researchers (Na'aliya, 2013). The decrease could be attributed to the fact that as the number of the ligands (Humate ions) that enters the coordination zone increases the aqua molecules available for replacement by the ligands become less. Thus, the metal ions become less electron loving with progressive intake of the ligand and this results in the decrease in the values of the constants (Na'aliya, 2013). Also the stability of the complexes is influenced by the size and number of the chelate rings(Mackay and Mackay,2002).All the complexes form rings in their structure as humate, a bidentate ligand, bond the metal ions in the ratio 1:2 (Boguta and Sokolowska, 2016) forming chelate rings. The values of the overall stability constants (logβ) obtained for humate complexes are not high indicating low stability as the values are not high. LogK values for copper-humates (Table 3 to 6) obtained in this study are lower than those reported for the complexes of humic acids (Pandey *et al*., 2015; Dinu, 2013; Kaschl *et al*., 2010 and Gilbeto and Jorg, 2001). The values of LogK(Table 7 to 10) forlead-humates are lower than those reported for the lead in the literature (Dinu, 2013; Gilbeto and Jorg 2001). Log K values(Table 11 to 14) for magnesium-humates obtained in this study are close to those reported by (Pandey *et al*., 2015). Log K values of cadmium-humates (Table 15 to 18) obtained in this work near to the one reported by (Dinu, 2013 and Pandey *et al*., 2015).The difference between the reported values and the values obtained in this study might be probably as a result of acid hydrolysis of humic acid. The values of the overall stability constants (log β) of the copper humates complexes presented in Table 19 is high than that of other metal humate complexes, show relatively high stability of Cu-HA complexes, show the following order of stability: Cu >Pb> Cd > Mg; which are in close agreement to the findings of (Dinu, 2013 and Pandey *et al*., 2015).The high stability of Cu-humate chelate could be attributed to the existence of coordinate covalent bond between the complexing agents and the Cu^{2+} ions. Since, Cu^{2+} being a metal of the transitional series with $3d^9$ electronic configurations can accept the electrons from the complexing agents. Similarly,the low stabilities of Pb,Cd and Mg -complexes could be explained by that Pb^{2+} with $6s^2$, Cd^{2+} with $4d^{10}$ and Mg^{2+} with $2p^6$ their electronic configuration has a completely filled d,p and s orbitals. Moreover, the stabilities of metal ions with hydrolysed humic acid from peat soil were higher than those with unhydrolysed humic acid from peat soil; which is ascribed to the high content of acidity in hydrolysed humic acid than unhydrolysed humic acid.

CONCLUSION

The values of logK for Cu(II) hydrolysed humic acid complex was higher followed by Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes as compared with metal(II) unhydrolysed humic acid complexes . This indicates acid hydrolysis of humic acid can enhance the complexation behavior of humic acid with metal (II) ions. However, the higher values of logβ for Cu(II), Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes indicates more stable stepwise complexes formed as compared with Cu(II), Pb(II), Cd(II) and Mg(II) unhydrolysed humic acid complexes.

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STABILITY CONSTANTS OF COMPLEXES OF METAL IONS WITH PEATSOIL HUMIC ACIDS UNDER NON-ACID-CONDITIONS

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ABSTRACT

Stability constants of complexes of four divalent metal ions viz. Cu^{2+}, Pb^{2+},Mg^{2+} and Cd^{2+} with humic acids (HA) were determined by potentiometric titration of humic acids with the corresponding salt of the divalent metals in aqueous media under non-acid-condition. The log K (logarithm of the stability constant) ranged from 1.0942 to 2.7471 for metal-humic acid complexes were determined using point-wise computational method. The order of stability constants were obtained as follows: Cu >Pb> Cd > Mg for metal -HA complexes respectively, indicating a higher degree of complexation with Cu metal ion.

Keywords: stability constant, humic acid, potentiometric titration, divalent metals, acid hydrolysis.

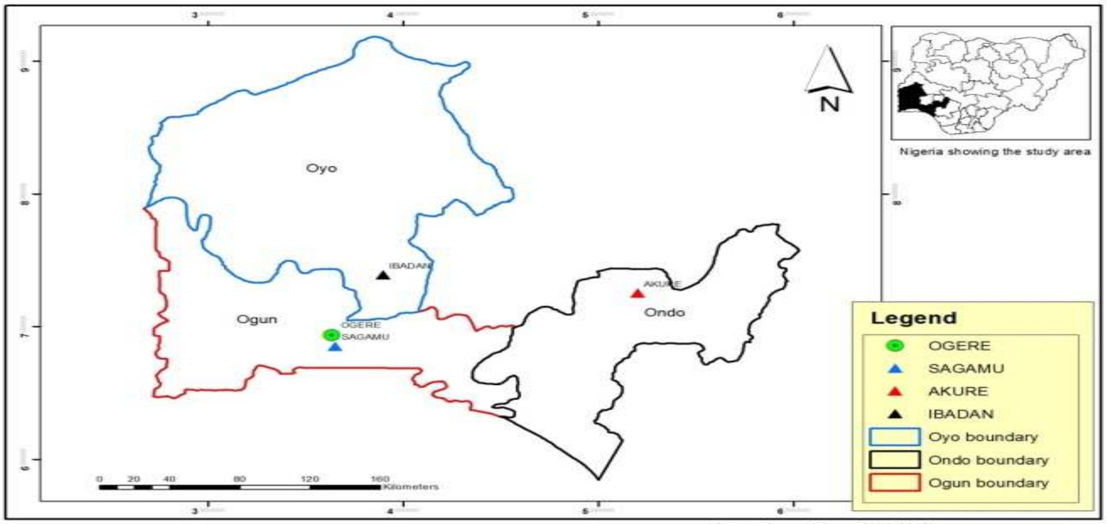
NTRODUCTION

The stability constant of a complex is the numerical expression of its stability and provides a quantitative measure of affinity of the metal ion to the complexing agent. An understanding of the relative stability of metal-complexes helps in predicting the behavior of metal ions in the soil (Ram and Raman, 1982). Extensive researches has been done to determine the stability constants of the complexes formed between humic acid (HA) with a number of metal ions. Ashok *et al*., (2000) reported that humic acid with hydroxyl, phenoxyl and carboxyl reactive groups can form coordination compound with metal ions at pH 3.5. The stability constants(Log K) for different metal-humic acid complexes indicated the following order of the stabilities of complexes formed between humic acid and metal ion, Cu >Fe >Pb> Ni > Co > Ca > Cd > Zn >Mn> Mg. Andelkovic *et al*., (2010) investigated the binding of Cd(II) to soil humic acid at pH 6.5 and in 0.1M KNO_3 ionic medium. The stability constant for binding indicating greater stability in the case when carboxyl groups are involved in complexation reaction. Kostic *et al*.,(2012) investigated the complexation of humic acid with certain heavy metal ions (Co(II), Ni(II),Cu(II), Zn(II), and Pb(II). The experiment was performed at 25°C, at pH 4.0 and ionic strength of 0.01M. Stability constant of complex between Pb(II) ions and humic acid is greater than stability constants of other investigated metal-humate complexes. Bogata and Sokolowska (2016) analyses the interaction between humic acids from different soils and Zn (II) ions at wide concentration ranges and at pH 5. Studies have showed significant impact of Zn concentration, pH and some properties of humic acids with zinc.But all of these studies were limited to acidic pH range. Therefore, the present study was carried out to determine and compare the stability constants of complexes of metal ions with hydrolysed peat soil humic acid and unhydrolysed peat soil humic under non-acid conditions.

MATERIALS AND METHODS

Analytical grade chemicals used includes hydrochloric acid (HCl), nitric acid (HNO_3), sodium hydroxide (NaOH), lead nitrate $Pb(NO_3)_2$, copper nitrate $Cu(NO_3)_2.3H_2O$, cadmium nitrate $Cd(NO_3)_2.4H_2O$, magnesium nitrate $Mg(NO_3)_2.6H_2O$, potassium nitrate (KNO_3), calcium chloride ($CaCl_2$), (sigma-Aldrich). Dowex 50WX8, (20-50 mesh) from Fluka.

Area of study



Source: Dept. of Geog. BUK (2016)

Figure 1: Map showing the sampling point at Sagamu Town, Ogun State.

Description of Sampling Area

Sagamu has geographical coordinates between 6°50′ north; 3° 38′ east is located in south western region of Nigeria. The region has tropical wet and dry climate with a lengthy wet season and relatively constant temperatures throughout the course of the year. Wet season runs from March to October, November to December forms the region dry season. The vegetation type of the region is savannah which is really grassland with small bushes and occasional big trees. Grassland soils have substantially higher organic matter content than forest soils (Novackova, 2011).

Sample Collection

The Peatsoil samples were collected from four different sampling points (0-10cm depth) in Sagamu into polyethylene bag with plastic spoons. Samples were taken to the laboratory, extraneous materials were removed; the samples were air-dried, crushed and ground to a fine powder in a mortar passed through a 0.20mm sieve. The samples were kept for analysis.

Isolation and purification of humic acid from peat soil sample

Peatsoil sample (100g) was mixed with 1000 cm^3 of 0.1M NaOH solution, shaken for 3hours and left to stand overnight. Dark-coloured supernatant was obtained and decanted from solid residue. The dark-coloured supernatant was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 6 hours. Yellowish brown supernatant and dark-brown precipitate were obtained. The yellowish brown supernatant was decanted followed by centrifuge and discarded. The dark-brown precipitate was mixed with 500cm^{3}of 0.1M NaOH solution followed by passing through dowex resin. The dark-brown solution was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 3 hours. The dark-brown precipitate was washed several times with deionized water. The supernatant was treated with $AgNO_3$ solution until no white precipitate observed. The humic acid was transferred to weighed crucible and dried at 60^{o}C in an oven for 12 hours. The humic acid was cooled and dried in the desiccator, weighed and recorded. The obtained humic acid was dried again at 60^{o}C for additional 6 hours cooled and dried in the desiccator, weighed and recorded constant weight was obtained (Baruah *et al*., 2015).

FT-IR analysis

FT-IR spectra of humic acid sample was analysed using Carry 630 FT-IR Agilent Technologies.

Unhydrolysed compost humic acid

The unhydrolysed humic acid was obtained after isolation and purification of compost humic acid and kept for investigation.

Acid hydrolysis of Peatsoil acid

Peatsoil humic acid sample (1g) was refluxed for 12 hours at (160^{o}C) with 50cm^3 of 6M HCl. The mixture was allowed to cool, decanted, and centrifuged after hydrolysis. The insoluble residues were washed with distilled water via centrifugation several times, and the supernatant was treated with $AgNO_3$ solution until no white precipitate was observed. The residue was thoroughly dried over $CaCl_2$ in a desiccator at room temperature (Chefetz *et al*., 2002). Finally, the obtained hydrolysed humic acid was kept for investigation.

Potentiometric Titrations

Potentiometric measurements were carried out using a pH-meter Jenway (model 3510) with combine electrode, the sensitivity of the pH - meter is 0.01 units. The pH meter was switched on half an hour before starting the titration for initial warm up of the instrument. The instrument was calibrated with an aqueous standard buffer solution of pH 4.00 and 10.0 (borate buffer) prepared from a "Qualigens" buffer tablets.

The following sets of solutions were prepared in a 250cm^3 volumetric flask separately for pH metric titrations.

(i) 5 cm^3 0.1 M HCl + 40 cm^3 deionized water

(ii) 5 cm^3 0.1 M HCl + 39 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid

(iii) 5 cm^3 0.1 M HCl + 37 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid + 2 cm^3 0.01 M Cu(II)

The solutions were titrated against standardized 0.110MNaOH separately. The total volume of each mixture was adjusted to 50 cm^3 and the ionic strength of the solutions was maintained constant at by adding appropriate amount of stock solution of 1M KNO$_3$ (Gamal, 2015; Omar and Ali, 2015). A magnetic stirrer was used to achieve thorough mixing of the interacting solutions at 550 rpm. The same set of experimental conditions was applied for potentiometric titration of remaining samples.

Evaluation of pKa of Hydrolysed peat soil Humic Acids

The proton-ligand formation number n_A were calculated by Irving and Rossotti expression (Omar and Ali, 2015).

$$nA = Y - \frac{(V2-V1)(No-Eo)}{(Vo+V1)TcL} \quad \text{..................................1}$$

Where: Y is number of dissociable proton, (V_2-V_1) is the measure of displacement of the ligand curve relative to acid curve, N^o and E^o are the resultant concentration of alkali solution, free acid solution, $T_{cL}{}^o$ is the total ligand concentration, V^o is the total volume of titration solution,V_1 is the volume of alkali added to acid solution,V_2 is the volume of alkali added to acid solution + ligand solution, acid dissociation constants (pKa - values) of ligand were calculated by algebraic method point wise calculation (Tables 1). The dissociation constants (pKa) were calculated according to the following relation:

$$pKa = pH + \log\left(\frac{nA}{1-nA}\right) \quad \text{.............................2}$$

Where: pKa is the acid dissociation constant, $n_A$is the Proton-ligand formation number and pH is the pH-values (Omar and Ali, 2015).

Determination of metal-ligand stability constants (log K) of complexes

The potentiometric measurement for the determination of stability constant of a complex in solution is based on the fact that the redox potential of the couple $\frac{M^{+(m-n)}}{M^{+m}}$ is shifted significantly on complexation of the metal ion with the ligand. This method involves change in hydrogen ion concentration [H$^+$] due to the displacement or association of one or more protons taking place during complexation reaction. This change can be found out by titrating the solutions containing free acid, acid with ligand, and acid with ligand and metal ion, individually against a standard alkali solution at a constant ionic strength or temperature. Either ionic strength or temperature may be varied for different sets of solutions. In all the cases, the change in the pH of the solution is measured after each addition of a known amount of alkali to the reaction cell which contains the reaction mixture. The titration curves are then drawn by plotting the measured pH values against the corresponding volume of alkali added and the stability constants of the complexes are determined from the titration curves by employing pH-metric titration technique given by (Irving and Rossoti).

Metal-ligand stability constants (Log K) were determined by using the following relations:

$$\bar{n} = \frac{(V_3 - V_2)(E^0 + N^0)}{(V^0 + V_2)\bar{n}_A T_m^0} \quad \text{...3}$$

and

$$PL = \log_{10}\left\{\frac{1+\beta_n^H \dfrac{1}{[anti\ \log pH]^n}}{T_L^0 - \bar{n}T_m^0} X \frac{(V^0 + V_3)}{V^0}\right\} \quad \text{...4}$$

Where $T_{L,}$ T^{o}, E°, and V^{o}havethe same significance as in equation (1) above, T_m denotes the total concentration of metal present in solution, V_3 is the volume of metal ions present in solution and β^{H} is the overall proton ligand stability constant. The metal-ligand stability constants (log K) were determined by employing point wise computational Method (eq. 5 and 6).

$$\text{Log}K_1 = \log\left(\frac{n}{1-n}\right) + pL \qquad \ldots\ldots\ldots\ldots.5$$

$$\text{Log}K_2 = \log\left(\frac{1-n}{2-n}\right) + pL\ldots\ldots\ldots\ldots\ldots\ldots\ldots.6$$

Where: Log K is the metal-ligand stability constant, pL is the Free ligand exponent function, **n** is the Average number of ligand attached with metal ion (Janrao*et al.*, 2014).The results obtained were analyzed by an ORIGIN 2016 program using titration data and then the proton-ligand stability constants (pKa) and Metal-ligand stability constant (LogK) calculated (Omar and Ali, 2015).

RESULTS AND DISCUSSION

Fourier transformed infrared (FT-IR) spectra of isolated humic acid from peat soils Figure 2 had distinct clear absorption bands indicating the presence of major humic acid structural elemental groups such as H bonded OH ($3680cm^{-1}$ peak), C=O of carbonyl ($1721cm^{-1}$ peak), functional groups of aliphatic components CH_2 ($2918cm^{-1}$ peak) and C-O stretching of polysaccharide ($1168cm^{-1}$ peak). The positions of the absorption bands of the spectra fell within typical major absorption bands of humic acid which is at frequencies 3680, 2918, 1721, 1168 cm^{-1}. The first peak centred in the vicinity of 3680 cm^{-1} region is attributed to phenol OH group bounded by intermolecular H bonds. The $2918cm^{-1}$ band usually has absorption maximum at 2918 cm^{-1} which is due to C–H stretching of alkane group (CH_2). The next major absorption band is 1721 cm^{-1}. This band has been commonly ascribed to C=O stretching of mainly carboxyl group (COOH) with trace amount of ketones. The last peak was observed at 1168 cm^{-1} due to C–O stretching of polysaccharides and this peak appeared also in the spectra of humic acid from peat soil. The FTIR spectra of the isolated humic acid contained all major characteristic absorption peaks of humic acid. These absorption peaks indicated the presence of the major structural elements of humic acid namely H bonded OH, C=C of aromatic ring, C=O of carbonyl group (both carboxyl and ketonic), CH_2 group. This strongly supports the presence of humic acid.

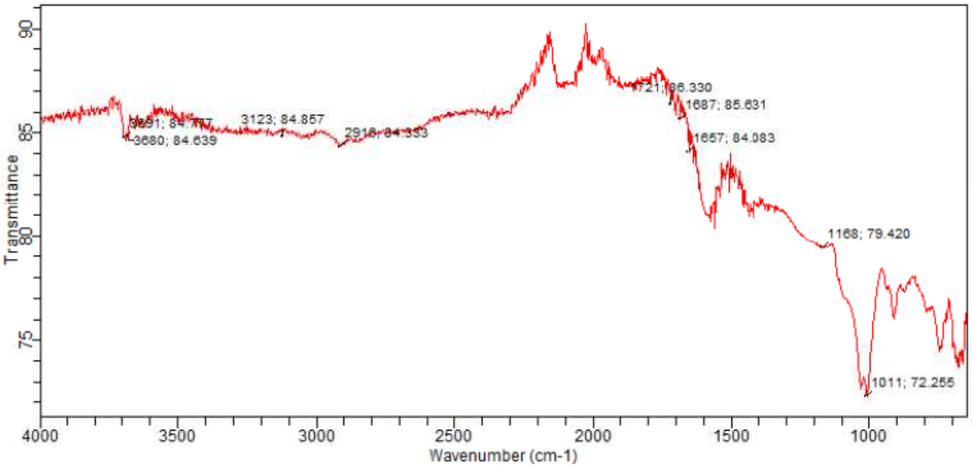


Fig. 2 : FT-IR spectraof peatsoilhumic acid (PSHA)

Evaluation of acid dissociation constant (pka) of acid hydrolysed peat soil humicacid at phenolic group

The value of the dissociation constant of the peat soil humic acid (PSHA) that underwent acidhydrolysis studied was found to be 8.9299 as shown Table 1, which is lower than the literaturevalues reported by Almeida and Szpoganics, (2015), Borges *et al.*, (2005); Badr *et al.*, (2012)and Fernandes *et al*,.(2009) of 9.73, 9.47 and 10.30. The difference between the obtained valuesand the reported values in this study might be probably as a result of acid hydrolysis of humicacid.

Table 1: PKa of (Hydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	log($\frac{nA}{1-nA}$)	pKa
8.50	5.30	6.29	0.99	0.3594	-0.2510	8.2490
8.72	5.35	6.37	1.02	0.3400	-0.2880	8.4320
9.00	5.40	6.46	1.06	0.3141	-0.3391	8.6609
9.22	5.45	6.55	1.10	0.2882	-0.3927	8.8273
9.51	5.50	6.66	1.16	0.2494	-0.4786	9.0314
9.73	5.55	6.78	1.23	0.2041	-0.5910	9.1390
10.00	5.60	6.90	1.30	0.1589	-0.7238	9.2762
10.23	5.65	7.05	1.40	0.0941	-0.9835	9.2465
10.49	5.70	7.10	1.40	0.0941	-0.9835	9.5065

Average pKa = 8.9299 ± 0.4186

Table 2: PKa of (Unhydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	Log($\frac{nA}{1-n}$)	pKa
8.50	5.30	5.81	0.51	0.6619	0.2919	8.7919
8.72	5.35	5.90	0.55	0.6357	0.2418	8.9618
9.00	5.40	6.00	0.60	0.6029	0.1813	9.1813
9.22	5.45	6.10	0.65	0.5701	0.1226	9.3426
9.51	5.50	6.20	0.70	0.5376	0.0654	9.5754
9.73	5.55	6.33	0.78	0.4851	-0.0259	9.7041
10.00	5.60	6.47	0.87	0.4262	-0.1291	9.8709
10.23	5.65	6.62	0.99	0.3609	-0.2481	9.9819
10.49	5.70	6.80	1.10	0.2759	-0.4690	10.0210

Average pKa = 9.4923± 0.4410

Metal-ligand stability constant (Log K)

The stabilityconstants require the accurate values of proton-ligand stability constants (Anil and Maroti, 2008). Metal titration curves crossed over ligand titration curve indicated the formation of complex upon proton release (Santosh, *et al.*, 2011). If the values of n- are within range 0.2-0.8 and 1.2-18 this indicates the formation of 1:1 and 1:2 complexes (Sayyed and Mazahar, 2012).

The metal (II)-humate stepwise stability constants (log k) at phenolic group (Tables 3-18)

Table 3: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n}{1-n}$)	$LogK_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

$LogK_1$ (Average value) = 2.4788± 0.2203

Table 4: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	Log($\frac{n-1}{2-n}$)	$LogK_2$
9.51	5.50	6.66	6.73	0.07	1.3509	1.70	-0.2671	1.4329
9.73	5.55	6.78	6.85	0.07	1.6383	1.51	0.2467	1.7567
10.00	5.60	6.90	6.98	0.08	2.1783	1.31	-0.2158	1.0942
10.23	5.65	7.05	7.13	0.08	4.1904	1.27		
10.49	5.70	7.10	7.19	0.09	4.6920			

$LogK_2$(Average value) = 1.4280 ± 0.3312

Table 5:Point-wise method,Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	Log($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430

$LogK_1$ **(Average value)** = 2.3059± 0.6153

Table 6:Point-wise method, Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$V_3\text{-}V_2$	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
9.73	5.55	6.33	6.42	0.09	0.9000	1.69		
10.00	5.60	6.47	6.58	0.11	1.2578	1.44	-0.4592	0.9808
10.23	5.65	6.62	6.84	0.12	1.6137	1.26	-0.2010	1.4610
10.49	5.70	6.80	6.92	0.12	2.1052	1.03		

$LogK_2$ **(Average value)** = 1.2209± 0.3398

Table 7:Point-wise method,Pb (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	log($\frac{n}{1-n}$)	$LogK_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.60	0.05	0.8333	1.96	0.6989	2.6589

$LogK_1$ (Average value) = 2.5832 ±0.1614

Table 8:Point-wise method,Pb-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	log($\frac{n-1}{2-n}$)	$logK_2$
9.51	5.50	6.66	6.71	0.05	0.9650	1.67	-0.0237	1.1963
9.73	5.55	6.78	6.83	0.05	1.1702	1.44		
10.00	5.60	6.90	6.90	0.05	1.4864	1.22		
10.23	5.65	7.05	7.10	0.05	2.0190	1.09		
10.49	5.70	7.10	7.17	0.07	3.6492	1.00		

$LogK_2$(Average value) = 1.1963

Table 9:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$V_3\text{-}V_2$	n	pL	Log ($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.5477	2.3123
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	0.0272	2.2072
9.51	5.50	6.20	6.26	0.07	0.6417	1.89	0.2530	2.1430
9.73	5.55	6.40	6.40	0.07	0.7000	1.67	0.3680	2.0380

$LogK_1$ **(Average value)** = 2.2364 ± 0.1602

Table 10:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$V_3\text{-}V_2$	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
10.00	5.60	6.47	6.55	0.08	1.9503	1.41		
10.23	5.65	6.62	6.72	0.11	1.4792	1.26	-0.0361	1.2239

$LogK_2$ **(Average value)** = 1.2239

Table 11:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	log($\frac{n}{n-1}$)	$LogK_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4290	2.2110
8.72	5.35	6.37	6.39	0.02	0.2858	2.42	-0.3978	2.0222
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

$LogK_1$ (Average value)=2.1382**±**0.1046

Table 12:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n-1}{2-n}$)	$LogK_2$
9.51	5.55	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.84	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.93	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.10		
10.49	5.70	7.10	7.18	0.07	3.6492	0.83		

$LogK_2$(Average value) = 1.5453 **±** 0.3450

Table 13:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.3477	2.3123
9.00	5.40	6.00	6.04	0.04	0.3236	2.38	-0.3202	2.0598
9.22	5.45	6.10	6.15	0.05	0.4297	2.17	-0.1230	2.0470
9.51	5.50	6.20	6.26	0.06	0.5500	1.89	0.0871	1.9771
9.73	5.55	6.33	6.40	0.07	0.7000	1.67	0.3680	2.0380

$LogK_1$ **(Average value)** = 2.1568 ± 0.2069

Table 14:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
10.00	5.60	6.47	6.55	0.08	0.9148	1.41		
10.23	5.65	6.62	6.71	0.09	1.2102	1.20	-0.5749	0.6251
10.49	5.70	6.80	6.92	0.09	1.5968	1.03	0.1703	1.2003

$LogK_2$ **(Average value)** = 0.9127± 0.4070

Table15:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	Log($\frac{n}{1-n}$)	$LogK_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4210	2.2190
8.72	5.35	6.37	6.40	0.03	0.4286	2.42	-0.1249	2.2951
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.96	0.3010	2.2610
9.51	5.55	6.66	6.70	0.04	0.7720	1.67	0.5297	2.1997

$LogK_1$ (Average value) = 2.2108± 0.0825

Table 16:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
9.73	5.55	6.78	6.83	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.95	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.09		
10.49	5.70	7.10	7.16	0.06	3.1429	0.89		

$LogK_2$ **(Average value)** = 1.5453± 0.3450

Table 17:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.86	0.05	0.3717	2.88	-0.2280	2.6520
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.06	0.06	0.4853	2.38	-0.0255	2.3545
9.22	5.45	6.10	6.16	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430
9.73	5.55	6.33	6.41	0.08	0.8000	1.69	0.6020	2.2920

$LogK_1$ **(Average value)** = 2.2516± 0.5380

Table 18:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$\text{Log}(\frac{n-1}{2-n})$	Log K_2
10.00	5.60	6.47	6.57	0.10	1.1434	1.43		
10.23	5.65	6.62	6.72	0.10	1.3448	1.23	-0.2788	0.9512
10.49	5.70	6.80	6.90	0.10	1.7742	1.03	0.5351	1.5651

LogK_2 **(Average value)** = 1.2581± 0.4340

Table 19: Stepwise and overall Stability constants of thehydrolysed and unhydrolysed divalent metal (II) complexes

Chelates	LogK_1	LogK_2	Logβ
[Cu (Hydrolysed PSHA-1)$_2$]	2.4788	1.4280	3.9068
[Pb (Hydrolysed PSHA-1)$_2$]	2.5832	1.1963	3.7795
[Cd (Hydrolysed PSHA-1)$_2$]	2.2108	1.5453	3.7561
[Mg (Hydrolysed PSHA-1)$_2$]	2.1382	1.5453	3.6835
[Cu (Unhydrolysed PSHA-1)$_2$]	2.3059	1.2209	3.5268
[Pb (Unhydrolysed PSHA-1)$_2$]	2.2364	1.2239	3.4603
[Cd (Unhydrolysed PSHA-1)$_2$]	2.2516	1.2581	3.5097
[Mg (Unydrolysed PSHA-1)$_2$]	2.1568	0.9127	3.0695

The results obtained (Table19) shows the stepwise and overall stability constants to be not high indicating low stability of the complexes, because the solubility of most metal ions in the basic pH range is minimal due to metal hydroxide precipitation (Karimi, 2017). In general, the stepwise stability constants (K_1 and K_2) follow the order $K_1 > K_2$ for the copper, lead, magnesium and cadmium complexes respectively. The steady decrease of the values with increasing number of ligands is in agreement with the prediction made by researchers (Na'aliya, 2013). The decrease could be attributed to the fact that as the number of the ligands (Humate ions) that enters the coordination zone increases the aqua molecules available for replacement by the ligands become less. Thus, the metal ions become less electron loving with progressive intake of the ligand and this results in the decrease in the values of the constants (Na'aliya, 2013). Also the stability of the complexes is influenced by the size and number of the chelate rings(Mackay and Mackay,2002).All the complexes form rings in their structure as humate, a bidentate ligand, bond the metal ions in the ratio 1:2 (Boguta and Sokolowska, 2016) forming chelate rings. The values of the overall stability constants (logβ) obtained for humate complexes are not high indicating low stability as the values are not high. LogK values for copper-humates (Table 3 to 6) obtained in this study are lower than those reported for the complexes of humic acids (Pandey *et al.*, 2015; Dinu, 2013; Kaschl *et al.*, 2010 and Gilbeto and Jorg, 2001). The values of LogK(Table 7 to 10) forlead-humates are lower than those reported for the lead in the literature (Dinu, 2013; Gilbeto and Jorg 2001). Log K values(Table 11 to 14) for magnesium-humates obtained in this study are close to those reported by (Pandey *et al.*, 2015). Log K values of cadmium-humates (Table 15 to 18) obtained in this work near to the one reported by (Dinu, 2013 and Pandey *et al.*, 2015).The difference between the reported values and the values obtained in this study might be probably as a result of acid hydrolysis of humic acid. The values of the overall stability constants (log β) of the copper humates complexes presented in Table 19 is high than that of other metal humate complexes, show relatively high stability of Cu-HA complexes, show the following order of stability: Cu >Pb> Cd > Mg; which are in close agreement to the findings of (Dinu, 2013 and Pandey *et al.*, 2015).The high stability of Cu-humate chelate could be attributed to the existence of coordinate covalent bond between the complexing agents and the Cu^{2+} ions. Since, Cu^{2+} being a metal of the transitional series with $3d^9$ electronic configurations can accept the electrons from the complexing agents. Similarly,the low stabilities of Pb,Cd and Mg -complexes could be explained by that Pb^{2+} with $6s^2$, Cd^{2+} with $4d^{10}$ and Mg^{2+} with $2p^6$ their electronic configuration has a completely filled d,p and s orbitals. Moreover, the stabilities of metal ions with hydrolysed humic acid from peat soil were higher than those with unhydrolysed humic acid from peat soil; which is ascribed to the high content of acidity in hydrolysed humic acid than unhydrolysed humic acid.

CONCLUSION

The values of logK for Cu(II) hydrolysed humic acid complex was higher followed by Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes as compared with metal(II) unhydrolysed humic acid complexes . This indicates acid hydrolysis of humic acid can enhance the complexation behavior of humic acid with metal (II) ions. However, the higher values of logβ for Cu(II), Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes indicates more stable stepwise complexes formed as compared with Cu(II), Pb(II), Cd(II) and Mg(II) unhydrolysed humic acid complexes.

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STABILITY CONSTANTS OF COMPLEXES OF METAL IONS WITH PEATSOIL HUMIC ACIDS UNDER NON-ACID-CONDITIONS

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ABSTRACT

Stability constants of complexes of four divalent metal ions viz. Cu^{2+}, Pb^{2+},Mg^{2+} and Cd^{2+} with humic acids (HA) were determined by potentiometric titration of humic acids with the corresponding salt of the divalent metals in aqueous media under non-acid-condition. The log K (logarithm of the stability constant) ranged from 1.0942 to 2.7471 for metal-humic acid complexes were determined using point-wise computational method. The order of stability constants were obtained as follows: Cu >Pb> Cd > Mg for metal -HA complexes respectively, indicating a higher degree of complexation with Cu metal ion.

Keywords: stability constant, humic acid, potentiometric titration, divalent metals, acid hydrolysis.

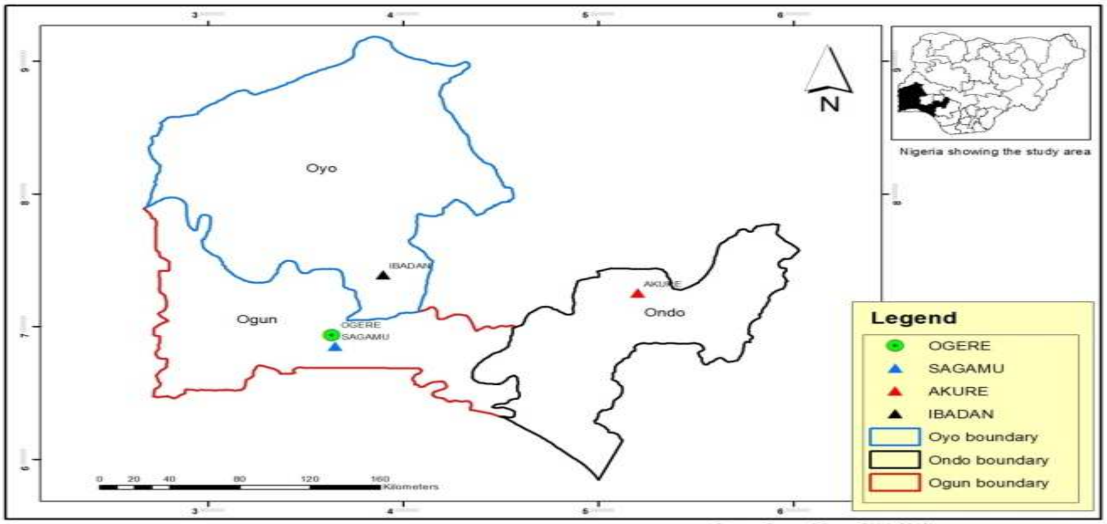
NTRODUCTION

The stability constant of a complex is the numerical expression of its stability and provides a quantitative measure of affinity of the metal ion to the complexing agent. An understanding of the relative stability of metal-complexes helps in predicting the behavior of metal ions in the soil (Ram and Raman, 1982). Extensive researches has been done to determine the stability constants of the complexes formed between humic acid (HA) with a number of metal ions. Ashok *et al.*, (2000) reported that humic acid with hydroxyl, phenoxyl and carboxyl reactive groups can form coordination compound with metal ions at pH 3.5. The stability constants(Log K) for different metal-humic acid complexes indicated the following order of the stabilities of complexes formed between humic acid and metal ion, Cu >Fe >Pb> Ni > Co > Ca > Cd > Zn >Mn> Mg. Andelkovic *et al.*, (2010) investigated the binding of Cd(II) to soil humic acid at pH 6.5 and in 0.1M KNO_3 ionic medium. The stability constant for binding indicating greater stability in the case when carboxyl groups are involved in complexation reaction. Kostic *et al.*,(2012) investigated the complexation of humic acid with certain heavy metal ions (Co(II), Ni(II),Cu(II), Zn(II), and Pb(II). The experiment was performed at 25°C, at pH 4.0 and ionic strength of 0.01M. Stability constant of complex between Pb(II) ions and humic acid is greater than stability constants of other investigated metal-humate complexes. Bogata and Sokolowska (2016) analyses the interaction between humic acids from different soils and Zn (II) ions at wide concentration ranges and at pH 5. Studies have showed significant impact of Zn concentration, pH and some properties of humic acids with zinc.But all of these studies were limited to acidic pH range. Therefore, the present study was carried out to determine and compare the stability constants of complexes of metal ions with hydrolysed peat soil humic acid and unhydrolysed peat soil humic under non-acid conditions.

MATERIALS AND METHODS

Analytical grade chemicals used includes hydrochloric acid (HCl), nitric acid (HNO_3), sodium hydroxide (NaOH), lead nitrate $Pb(NO_3)_2$, copper nitrate $Cu(NO_3)_2.3H_2O$, cadmium nitrate $Cd(NO_3)_2.4H_2O$, magnesium nitrate $Mg(NO_3)_2.6H_2O$, potassium nitrate (KNO_3), calcium chloride ($CaCl_2$), (sigma-Aldrich). Dowex 50WX8, (20-50 mesh) from Fluka.

Area of study



Source: Dept. of Geog. BUK (2016)

Figure 1: Map showing the sampling point at Sagamu Town, Ogun State.

Description of Sampling Area

Sagamu has geographical coordinates between 6°50′ north; 3° 38′ east is located in south western region of Nigeria. The region has tropical wet and dry climate with a lengthy wet season and relatively constant temperatures throughout the course of the year. Wet season runs from March to October, November to December forms the region dry season. The vegetation type of the region is savannah which is really grassland with small bushes and occasional big trees. Grassland soils have substantially higher organic matter content than forest soils (Novackova, 2011).

Sample Collection

The Peatsoil samples were collected from four different sampling points (0-10cm depth) in Sagamu into polyethylene bag with plastic spoons. Samples were taken to the laboratory, extraneous materials were removed; the samples were air-dried, crushed and ground to a fine powder in a mortar passed through a 0.20mm sieve. The samples were kept for analysis.

Isolation and purification of humic acid from peat soil sample

Peatsoil sample (100g) was mixed with 1000 cm^3 of 0.1M NaOH solution, shaken for 3hours and left to stand overnight. Dark-coloured supernatant was obtained and decanted from solid residue. The dark-coloured supernatant was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 6 hours. Yellowish brown supernatant and dark-brown precipitate were obtained. The yellowish brown supernatant was decanted followed by centrifuge and discarded. The dark-brown precipitate was mixed with $500cm^3$of 0.1M NaOH solution followed by passing through dowex resin. The dark-brown solution was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 3 hours. The dark-brown precipitate was washed several times with deionized water. The supernatant was treated with $AgNO_3$ solution until no white precipitate observed. The humic acid was transferred to weighed crucible and dried at 60^oC in an oven for 12 hours. The humic acid was cooled and dried in the desiccator, weighed and recorded. The obtained humic acid was dried again at 60^oC for additional 6 hours cooled and dried in the desiccator, weighed and recorded constant weight was obtained (Baruah *et al.*, 2015).

FT-IR analysis

FT-IR spectra of humic acid sample was analysed using Carry 630 FT-IR Agilent Technologies.

Unhydrolysed compost humic acid

The unhydrolysed humic acid was obtained after isolation and purification of compost humic acid and kept for investigation.

Acid hydrolysis of Peatsoil acid

Peatsoil humic acid sample (1g) was refluxed for 12 hours at (160^oC) with $50cm^3$ of 6M HCl. The mixture was allowed to cool, decanted, and centrifuged after hydrolysis. The insoluble residues were washed with distilled water via centrifugation several times, and the supernatant was treated with $AgNO_3$ solution until no white precipitate was observed. The residue was thoroughly dried over $CaCl_2$ in a desiccator at room temperature (Chefetz *et al.*, 2002). Finally, the obtained hydrolysed humic acid was kept for investigation.

Potentiometric Titrations

Potentiometric measurements were carried out using a pH-meter Jenway (model 3510) with combine electrode, the sensitivity of the pH - meter is 0.01 units. The pH meter was switched on half an hour before starting the titration for initial warm up of the instrument. The instrument was calibrated with an aqueous standard buffer solution of pH 4.00 and 10.0 (borate buffer) prepared from a "Qualigens" buffer tablets.

The following sets of solutions were prepared in a 250cm^3 volumetric flask separately for pH metric titrations.

(i) 5 cm^3 0.1 M HCl + 40 cm^3 deionized water
(ii) 5 cm^3 0.1 M HCl + 39 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid
(iii) 5 cm^3 0.1 M HCl + 37 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid + 2 cm^3 0.01 M Cu(II)

The solutions were titrated against standardized 0.110MNaOH separately. The total volume of each mixture was adjusted to 50 cm^3 and the ionic strength of the solutions was maintained constant at by adding appropriate amount of stock solution of 1M KNO_3 (Gamal, 2015; Omar and Ali, 2015). A magnetic stirrer was used to achieve thorough mixing of the interacting solutions at 550 rpm. The same set of experimental conditions was applied for potentiometric titration of remaining samples.

Evaluation of pKa of Hydrolysed peat soil Humic Acids

The proton-ligand formation number $n_{\mathbf{A}}$ were calculated by Irving and Rossotti expression (Omar and Ali, 2015).

$$nA = Y - \frac{(V2-V1)(No-Eo)}{(Vo+V1)TcL} \quad ....1$$

Where: Y is number of dissociable proton, (V_2-V_1) is the measure of displacement of the ligand curve relative to acid curve, N^o and E^o are the resultant concentration of alkali solution, free acid solution, $T_{cL}{}^o$ is the total ligand concentration, V^o is the total volume of titration solution,V_1 is the volume of alkali added to acid solution,V_2 is the volume of alkali added to acid solution + ligand solution, acid dissociation constants (pKa - values) of ligand were calculated by algebraic method point wise calculation (Tables 1). The dissociation constants (pKa) were calculated according to the following relation:

$$pKa = pH + \log(\frac{nA}{1-nA}) \quad ....2$$

Where: pKa is the acid dissociation constant, $n_A$is the Proton-ligand formation number and pH is the pH-values (Omar and Ali, 2015).

Determination of metal-ligand stability constants (log K) of complexes

The potentiometric measurement for the determination of stability constant of a complex in solution is based on the fact that the redox potential of the couple $\frac{M^{+(m-n)}}{M^{+m}}$ is shifted significantly on complexation of the metal ion with the ligand. This method involves change in hydrogen ion concentration [H^+] due to the displacement or association of one or more protons taking place during complexation reaction. This change can be found out by titrating the solutions containing free acid, acid with ligand, and acid with ligand and metal ion, individually against a standard alkali solution at a constant ionic strength or temperature. Either ionic strength or temperature may be varied for different sets of solutions. In all the cases, the change in the pH of the solution is measured after each addition of a known amount of alkali to the reaction cell which contains the reaction mixture. The titration curves are then drawn by plotting the measured pH values against the corresponding volume of alkali added and the stability constants of the complexes are determined from the titration curves by employing pH-metric titration technique given by (Irving and Rossoti).

Metal-ligand stability constants (Log K) were determined by using the following relations:

$$\bar{n} = \frac{(V_3 - V_2)(E^0 + N^0)}{(V^0 + V_2)\bar{n}_A T_m^0} \quad ....3$$

and

$$PL = \log_{10}\{\frac{1 + \beta_n^H \frac{1}{[anti\ \log pH]^n}}{T_L^0 - \bar{n}T_m^0} X \frac{(V^0 + V_3)}{V^0}\} \quad ....4$$

Where $T_{L,}$ T^o, E°, and V^ohavethe same significance as in equation (1) above, T_m denotes the total concentration of metal present in solution, V_3 is the volume of metal ions present in solution and β^H is the overall proton ligand stability constant. The metal-ligand stability constants (log K) were determined by employing point wise computational Method (eq. 5 and 6).

$LogK_1 = \log\left(\frac{n}{1-n}\right) + pL$ 5

$LogK_2 = \log\left(\frac{1-n}{2-n}\right) + pL$.......................6

Where: Log K is the metal-ligand stability constant, pL is the Free ligand exponent function, **n** is the Average number of ligand attached with metal ion (Janrao*et al.*, 2014).The results obtained were analyzed by an ORIGIN 2016 program using titration data and then the proton-ligand stability constants (pKa) and Metal-ligand stability constant (LogK) calculated (Omar and Ali, 2015).

RESULTS AND DISCUSSION

Fourier transformed infrared (FT-IR) spectra of isolated humic acid from peat soils Figure 2 had distinct clear absorption bands indicating the presence of major humic acid structural elemental groups such as H bonded OH ($3680cm^{-1}$ peak), C=O of carbonyl ($1721cm^{-1}$ peak), functional groups of aliphatic components CH_2 ($2918cm^{-1}$ peak) and C-O stretching of polysaccharide ($1168cm^{-1}$ peak). The positions of the absorption bands of the spectra fell within typical major absorption bands of humic acid which is at frequencies 3680, 2918, 1721, 1168 cm^{-1}. The first peak centred in the vicinity of 3680 cm^{-1} region is attributed to phenol OH group bounded by intermolecular H bonds. The $2918cm^{-1}$ band usually has absorption maximum at 2918 cm^{-1} which is due to C–H stretching of alkane group (CH_2). The next major absorption band is 1721 cm^{-1}. This band has been commonly ascribed to C=O stretching of mainly carboxyl group (COOH) with trace amount of ketones. The last peak was observed at 1168 cm^{-1} due to C–O stretching of polysaccharides and this peak appeared also in the spectra of humic acid from peat soil. The FTIR spectra of the isolated humic acid contained all major characteristic absorption peaks of humic acid. These absorption peaks indicated the presence of the major structural elements of humic acid namely H bonded OH, C=C of aromatic ring, C=O of carbonyl group (both carboxyl and ketonic), CH_2 group. This strongly supports the presence of humic acid.

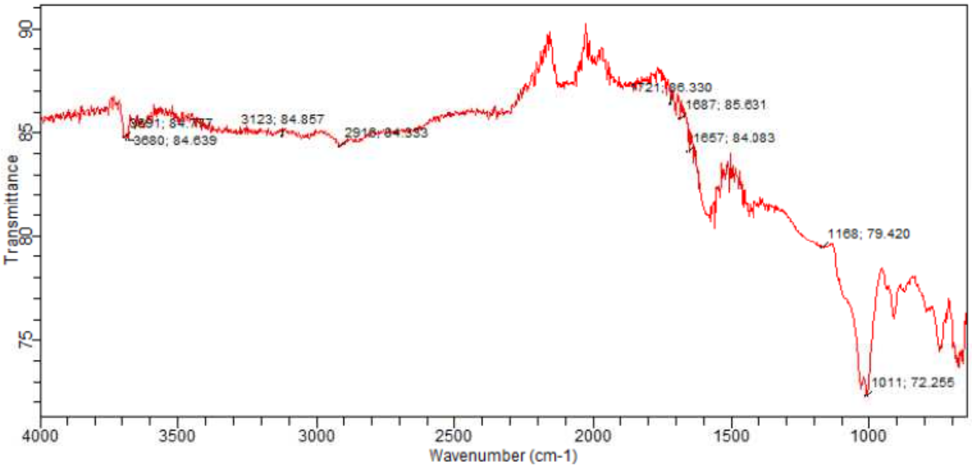


Fig. 2 : FT-IR spectraof peatsoilhumic acid (PSHA)

Evaluation of acid dissociation constant (pka) of acid hydrolysed peat soil humicacid at phenolic group

The value of the dissociation constant of the peat soil humic acid (PSHA) that underwent acidhydrolysis studied was found to be 8.9299 as shown Table 1, which is lower than the literaturevalues reported by Almeida and Szpoganics, (2015), Borges *et al.*, (2005); Badr *et al.*, (2012)and Fernandes *et al*,.(2009) of 9.73, 9.47 and 10.30. The difference between the obtained valuesand the reported values in this study might be probably as a result of acid hydrolysis of humicacid.

Table 1: PKa of (Hydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	$\log(\frac{nA}{1-nA})$	pKa
8.50	5.30	6.29	0.99	0.3594	-0.2510	8.2490
8.72	5.35	6.37	1.02	0.3400	-0.2880	8.4320
9.00	5.40	6.46	1.06	0.3141	-0.3391	8.6609
9.22	5.45	6.55	1.10	0.2882	-0.3927	8.8273
9.51	5.50	6.66	1.16	0.2494	-0.4786	9.0314
9.73	5.55	6.78	1.23	0.2041	-0.5910	9.1390
10.00	5.60	6.90	1.30	0.1589	-0.7238	9.2762
10.23	5.65	7.05	1.40	0.0941	-0.9835	9.2465
10.49	5.70	7.10	1.40	0.0941	-0.9835	9.5065

Average pKa = 8.9299 ± 0.4186

Table 2: PKa of (Unhydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	$\text{Log}(\frac{nA}{1-n})$	pKa
8.50	5.30	5.81	0.51	0.6619	0.2919	8.7919
8.72	5.35	5.90	0.55	0.6357	0.2418	8.9618
9.00	5.40	6.00	0.60	0.6029	0.1813	9.1813
9.22	5.45	6.10	0.65	0.5701	0.1226	9.3426
9.51	5.50	6.20	0.70	0.5376	0.0654	9.5754
9.73	5.55	6.33	0.78	0.4851	-0.0259	9.7041
10.00	5.60	6.47	0.87	0.4262	-0.1291	9.8709
10.23	5.65	6.62	0.99	0.3609	-0.2481	9.9819
10.49	5.70	6.80	1.10	0.2759	-0.4690	10.0210

Average pKa = 9.4923± 0.4410

Metal-ligand stability constant (Log K)

The stabilityconstants require the accurate values of proton-ligand stability constants (Anil and Maroti, 2008). Metal titration curves crossed over ligand titration curve indicated the formation of complex upon proton release (Santosh, *et al.*, 2011). If the values of n- are within range 0.2-0.8 and 1.2-18 this indicates the formation of 1:1 and 1:2 complexes (Sayyed and Mazahar, 2012).

The metal (II)-humate stepwise stability constants (log k) at phenolic group (Tables 3-18)

Table 3: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$\log(\frac{n}{1-n})$	$\text{Log}K_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

$\text{Log}K_1$ (Average value) = 2.4788± 0.2203

Table 4: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$\text{Log}(\frac{n-1}{2-n})$	$\text{Log}K_2$
9.51	5.50	6.66	6.73	0.07	1.3509	1.70	-0.2671	1.4329
9.73	5.55	6.78	6.85	0.07	1.6383	1.51	0.2467	1.7567
10.00	5.60	6.90	6.98	0.08	2.1783	1.31	-0.2158	1.0942
10.23	5.65	7.05	7.13	0.08	4.1904	1.27		
10.49	5.70	7.10	7.19	0.09	4.6920			

$\text{Log}K_2$(Average value) = 1.4280 ± 0.3312

Table 5:Point-wise method,Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	Log($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430

$LogK_1$ **(Average value)** = 2.3059± 0.6153

Table 6:Point-wise method, Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
9.73	5.55	6.33	6.42	0.09	0.9000	1.69		
10.00	5.60	6.47	6.58	0.11	1.2578	1.44	-0.4592	0.9808
10.23	5.65	6.62	6.84	0.12	1.6137	1.26	-0.2010	1.4610
10.49	5.70	6.80	6.92	0.12	2.1052	1.03		

$LogK_2$ **(Average value)** = 1.2209± 0.3398

Table 7:Point-wise method,Pb (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n}{1-n}$)	$LogK_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.60	0.05	0.8333	1.96	0.6989	2.6589

$LogK_1$ (Average value) = 2.5832 ±0.1614

Table 8:Point-wise method,Pb-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n-1}{2-n}$)	$logK_2$
9.51	5.50	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.83	0.05	1.1702	1.44		
10.00	5.60	6.90	6.90	0.05	1.4864	1.22	-0.0237	1.1963
10.23	5.65	7.05	7.10	0.05	2.0190	1.09		
10.49	5.70	7.10	7.17	0.07	3.6492	1.00		

$LogK_2$(Average value) = 1.1963

Table 9:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log ($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.5477	2.3123
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	0.0272	2.2072
9.51	5.50	6.20	6.26	0.07	0.6417	1.89	0.2530	2.1430
9.73	5.55	6.40	6.40	0.07	0.7000	1.67	0.3680	2.0380

$LogK_1$ **(Average value)** = 2.2364 ± 0.1602

Table 10:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
10.00	5.60	6.47	6.55	0.08	1.9503	1.41		
10.23	5.65	6.62	6.72	0.11	1.4792	1.26	-0.0361	1.2239

$LogK_2$ **(Average value)** = 1.2239

Table 11:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n}{n-1}$)	$LogK_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4290	2.2110
8.72	5.35	6.37	6.39	0.02	0.2858	2.42	-0.3978	2.0222
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

$LogK_1$ (Average value)=2.1382**±**0.1046

Table 12:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	$\log(\frac{n-1}{2-n})$	$LogK_2$
9.51	5.55	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.84	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.93	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.10		
10.49	5.70	7.10	7.18	0.07	3.6492	0.83		

$LogK_2$(Average value) = 1.5453 **±** 0.3450

Table 13:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$V_3\text{-}V_2$	n	pL	$Log(\frac{n}{n-1})$	$Log\ K_1$
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.3477	2.3123
9.00	5.40	6.00	6.04	0.04	0.3236	2.38	-0.3202	2.0598
9.22	5.45	6.10	6.15	0.05	0.4297	2.17	-0.1230	2.0470
9.51	5.50	6.20	6.26	0.06	0.5500	1.89	0.0871	1.9771
9.73	5.55	6.33	6.40	0.07	0.7000	1.67	0.3680	2.0380

$LogK_1$ **(Average value)** = 2.1568 ± 0.2069

Table 14:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$V_3\text{-}V_2$	n	pL	$Log(\frac{n-1}{2-n})$	$Log\ K_2$
10.00	5.60	6.47	6.55	0.08	0.9148	1.41		
10.23	5.65	6.62	6.71	0.09	1.2102	1.20	-0.5749	0.6251
10.49	5.70	6.80	6.92	0.09	1.5968	1.03	0.1703	1.2003

$LogK_2$ **(Average value)** = 0.9127± 0.4070

Table15:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	$Log(\frac{n}{1-n})$	$LogK_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4210	2.2190
8.72	5.35	6.37	6.40	0.03	0.4286	2.42	-0.1249	2.2951
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.96	0.3010	2.2610
9.51	5.55	6.66	6.70	0.04	0.7720	1.67	0.5297	2.1997

$LogK_1$ (Average value) = 2.2108± 0.0825

Table 16:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	$Log(\frac{n-1}{2-n})$	$Log\ K_2$
9.73	5.55	6.78	6.83	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.95	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.09		
10.49	5.70	7.10	7.16	0.06	3.1429	0.89		

$LogK_2$ **(Average value)** = 1.5453± 0.3450

Table 17:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$V_3\text{-}V_2$	n	pL	$Log(\frac{n}{n-1})$	$Log\ K_1$
8.50	5.30	5.81	5.86	0.05	0.3717	2.88	-0.2280	2.6520
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.06	0.06	0.4853	2.38	-0.0255	2.3545
9.22	5.45	6.10	6.16	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430
9.73	5.55	6.33	6.41	0.08	0.8000	1.69	0.6020	2.2920

$LogK_1$ **(Average value)** = 2.2516± 0.5380

Table 18:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$\text{Log}(\frac{n-1}{2-n})$	Log K_2
10.00	5.60	6.47	6.57	0.10	1.1434	1.43		
10.23	5.65	6.62	6.72	0.10	1.3448	1.23	-0.2788	0.9512
10.49	5.70	6.80	6.90	0.10	1.7742	1.03	0.5351	1.5651

LogK_2 **(Average value)** = 1.2581± 0.4340

Table 19: Stepwise and overall Stability constants of thehydrolysed and unhydrolysed divalent metal (II) complexes

Chelates	**LogK₁**	**LogK₂**	**Logβ**
[Cu (Hydrolysed PSHA-1)$_2$]	2.4788	1.4280	3.9068
[Pb (Hydrolysed PSHA-1)$_2$]	2.5832	1.1963	3.7795
[Cd (Hydrolysed PSHA-1)$_2$]	2.2108	1.5453	3.7561
[Mg (Hydrolysed PSHA-1)$_2$]	2.1382	1.5453	3.6835
[Cu (Unhydrolysed PSHA-1)$_2$]	2.3059	1.2209	3.5268
[Pb (Unhydrolysed PSHA-1)$_2$]	2.2364	1.2239	3.4603
[Cd (Unhydrolysed PSHA-1)$_2$]	2.2516	1.2581	3.5097
[Mg (Unydrolysed PSHA-1)$_2$]	2.1568	0.9127	3.0695

The results obtained (Table19) shows the stepwise and overall stability constants to be not high indicating low stability of the complexes, because the solubility of most metal ions in the basic pH range is minimal due to metal hydroxide precipitation (Karimi, 2017). In general, the stepwise stability constants (K_1 and K_2) follow the order $K_1 > K_2$ for the copper, lead, magnesium and cadmium complexes respectively. The steady decrease of the values with increasing number of ligands is in agreement with the prediction made by researchers (Na'aliya, 2013). The decrease could be attributed to the fact that as the number of the ligands (Humate ions) that enters the coordination zone increases the aqua molecules available for replacement by the ligands become less. Thus, the metal ions become less electron loving with progressive intake of the ligand and this results in the decrease in the values of the constants (Na'aliya, 2013). Also the stability of the complexes is influenced by the size and number of the chelate rings(Mackay and Mackay,2002).All the complexes form rings in their structure as humate, a bidentate ligand, bond the metal ions in the ratio 1:2 (Boguta and Sokolowska, 2016) forming chelate rings. The values of the overall stability constants (logβ) obtained for humate complexes are not high indicating low stability as the values are not high. LogK values for copper-humates (Table 3 to 6) obtained in this study are lower than those reported for the complexes of humic acids (Pandey *et al*., 2015; Dinu, 2013; Kaschl *et al*., 2010 and Gilbeto and Jorg, 2001). The values of LogK(Table 7 to 10) forlead-humates are lower than those reported for the lead in the literature (Dinu, 2013; Gilbeto and Jorg 2001). Log K values(Table 11 to 14) for magnesium-humates obtained in this study are close to those reported by (Pandey *et al*., 2015). Log K values of cadmium-humates (Table 15 to 18) obtained in this work near to the one reported by (Dinu, 2013 and Pandey *et al*., 2015).The difference between the reported values and the values obtained in this study might be probably as a result of acid hydrolysis of humic acid. The values of the overall stability constants (log β) of the copper humates complexes presented in Table 19 is high than that of other metal humate complexes, show relatively high stability of Cu-HA complexes, show the following order of stability: Cu >Pb> Cd > Mg; which are in close agreement to the findings of (Dinu, 2013 and Pandey *et al*., 2015).The high stability of Cu-humate chelate could be attributed to the existence of coordinate covalent bond between the complexing agents and the Cu^{2+} ions. Since, Cu^{2+} being a metal of the transitional series with $3d^9$ electronic configurations can accept the electrons from the complexing agents. Similarly,the low stabilities of Pb,Cd and Mg - complexes could be explained by that Pb^{2+} with $6s^2$, Cd^{2+} with $4d^{10}$ and Mg^{2+} with $2p^6$ their electronic configuration has a completely filled d,p and s orbitals. Moreover, the stabilities of metal ions with hydrolysed humic acid from peat soil were higher than those with unhydrolysed humic acid from peat soil; which is ascribed to the high content of acidity in hydrolysed humic acid than unhydrolysed humic acid.

CONCLUSION

The values of logK for Cu(II) hydrolysed humic acid complex was higher followed by Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes as compared with metal(II) unhydrolysed humic acid complexes . This indicates acid hydrolysis of humic acid can enhance the complexation behavior of humic acid with metal (II) ions. However, the higher values of logβ for Cu(II), Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes indicates more stable stepwise complexes formed as compared with Cu(II), Pb(II), Cd(II) and Mg(II) unhydrolysed humic acid complexes.

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STABILITY CONSTANTS OF COMPLEXES OF METAL IONS WITH PEATSOIL HUMIC ACIDS UNDER NON-ACID-CONDITIONS

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ABSTRACT

Stability constants of complexes of four divalent metal ions viz. Cu^{2+}, Pb^{2+},Mg^{2+} and Cd^{2+} with humic acids (HA) were determined by potentiometric titration of humic acids with the corresponding salt of the divalent metals in aqueous media under non-acid-condition. The log K (logarithm of the stability constant) ranged from 1.0942 to 2.7471 for metal-humic acid complexes were determined using point-wise computational method. The order of stability constants were obtained as follows: Cu >Pb> Cd > Mg for metal -HA complexes respectively, indicating a higher degree of complexation with Cu metal ion.

Keywords: stability constant, humic acid, potentiometric titration, divalent metals, acid hydrolysis.

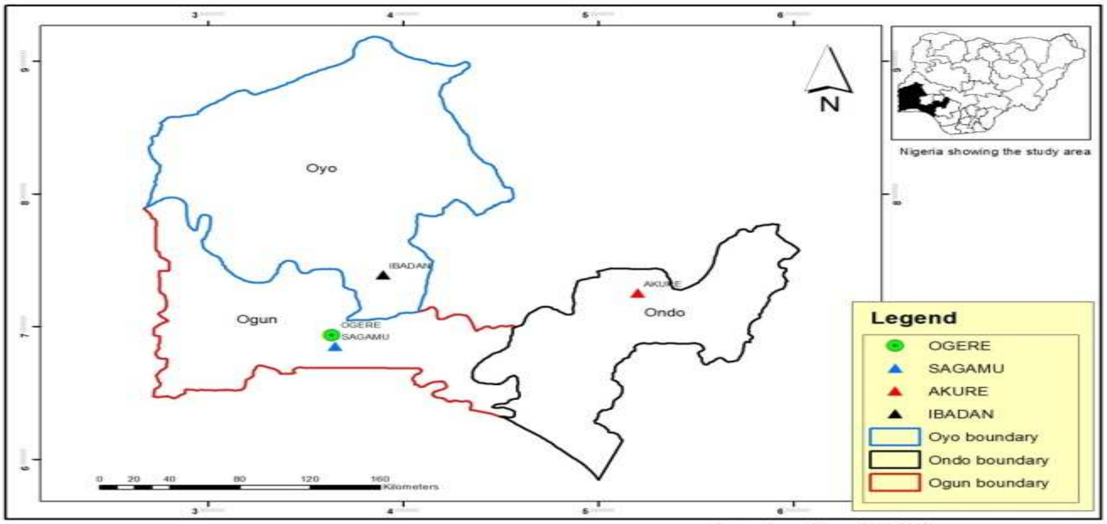
NTRODUCTION

The stability constant of a complex is the numerical expression of its stability and provides a quantitative measure of affinity of the metal ion to the complexing agent. An understanding of the relative stability of metal-complexes helps in predicting the behavior of metal ions in the soil (Ram and Raman, 1982). Extensive researches has been done to determine the stability constants of the complexes formed between humic acid (HA) with a number of metal ions. Ashok *et al.*, (2000) reported that humic acid with hydroxyl, phenoxyl and carboxyl reactive groups can form coordination compound with metal ions at pH 3.5. The stability constants(Log K) for different metal-humic acid complexes indicated the following order of the stabilities of complexes formed between humic acid and metal ion, Cu >Fe >Pb> Ni > Co > Ca > Cd > Zn >Mn> Mg. Andelkovic *et al.*, (2010) investigated the binding of Cd(II) to soil humic acid at pH 6.5 and in 0.1M KNO_3 ionic medium. The stability constant for binding indicating greater stability in the case when carboxyl groups are involved in complexation reaction. Kostic *et al.*,(2012) investigated the complexation of humic acid with certain heavy metal ions (Co(II), Ni(II),Cu(II), Zn(II), and Pb(II). The experiment was performed at 25°C, at pH 4.0 and ionic strength of 0.01M. Stability constant of complex between Pb(II) ions and humic acid is greater than stability constants of other investigated metal-humate complexes. Bogata and Sokolowska (2016) analyses the interaction between humic acids from different soils and Zn (II) ions at wide concentration ranges and at pH 5. Studies have showed significant impact of Zn concentration, pH and some properties of humic acids with zinc.But all of these studies were limited to acidic pH range. Therefore, the present study was carried out to determine and compare the stability constants of complexes of metal ions with hydrolysed peat soil humic acid and unhydrolysed peat soil humic under non-acid conditions.

MATERIALS AND METHODS

Analytical grade chemicals used includes hydrochloric acid (HCl), nitric acid (HNO_3), sodium hydroxide (NaOH), lead nitrate $Pb(NO_3)_2$, copper nitrate $Cu(NO_3)_2.3H_2O$, cadmium nitrate $Cd(NO_3)_2.4H_2O$, magnesium nitrate $Mg(NO_3)_2.6H_2O$, potassium nitrate (KNO_3), calcium chloride ($CaCl_2$), (sigma-Aldrich). Dowex 50WX8, (20-50 mesh) from Fluka.

Area of study



Source: Dept. of Geog. BUK (2016)

Figure 1: Map showing the sampling point at Sagamu Town, Ogun State.

Description of Sampling Area

Sagamu has geographical coordinates between 6°50′ north; 3° 38′ east is located in south western region of Nigeria. The region has tropical wet and dry climate with a lengthy wet season and relatively constant temperatures throughout the course of the year. Wet season runs from March to October, November to December forms the region dry season. The vegetation type of the region is savannah which is really grassland with small bushes and occasional big trees. Grassland soils have substantially higher organic matter content than forest soils (Novackova, 2011).

Sample Collection

The Peatsoil samples were collected from four different sampling points (0-10cm depth) in Sagamu into polyethylene bag with plastic spoons. Samples were taken to the laboratory, extraneous materials were removed; the samples were air-dried, crushed and ground to a fine powder in a mortar passed through a 0.20mm sieve. The samples were kept for analysis.

Isolation and purification of humic acid from peat soil sample

Peatsoil sample (100g) was mixed with 1000 cm^3 of 0.1M NaOH solution, shaken for 3hours and left to stand overnight. Dark-coloured supernatant was obtained and decanted from solid residue. The dark-coloured supernatant was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 6 hours. Yellowish brown supernatant and dark-brown precipitate were obtained. The yellowish brown supernatant was decanted followed by centrifuge and discarded. The dark-brown precipitate was mixed with $500cm^3$of 0.1M NaOH solution followed by passing through dowex resin. The dark-brown solution was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 3 hours. The dark-brown precipitate was washed several times with deionized water. The supernatant was treated with $AgNO_3$ solution until no white precipitate observed. The humic acid was transferred to weighed crucible and dried at 60°C in an oven for 12 hours. The humic acid was cooled and dried in the desiccator, weighed and recorded. The obtained humic acid was dried again at 60°C for additional 6 hours cooled and dried in the desiccator, weighed and recorded constant weight was obtained (Baruah *et al.*, 2015).

FT-IR analysis

FT-IR spectra of humic acid sample was analysed using Carry 630 FT-IR Agilent Technologies.

Unhydrolysed compost humic acid

The unhydrolysed humic acid was obtained after isolation and purification of compost humic acid and kept for investigation.

Acid hydrolysis of Peatsoil acid

Peatsoil humic acid sample (1g) was refluxed for 12 hours at (160°C) with $50cm^3$ of 6M HCl. The mixture was allowed to cool, decanted, and centrifuged after hydrolysis. The insoluble residues were washed with distilled water via centrifugation several times, and the supernatant was treated with $AgNO_3$ solution until no white precipitate was observed. The residue was thoroughly dried over $CaCl_2$ in a desiccator at room temperature (Chefetz *et al.*, 2002). Finally, the obtained hydrolysed humic acid was kept for investigation.

Potentiometric Titrations

Potentiometric measurements were carried out using a pH-meter Jenway (model 3510) with combine electrode, the sensitivity of the pH -meter is 0.01 units. The pH meter was switched on half an hour before starting the titration for initial warm up of the instrument. The instrument was calibrated with an aqueous standard buffer solution of pH 4.00 and 10.0 (borate buffer) prepared from a "Qualigens" buffer tablets.

The following sets of solutions were prepared in a 250cm^3 volumetric flask separately for pH metric titrations.

(i) 5 cm^3 0.1 M HCl + 40 cm^3 deionized water

(ii) 5 cm^3 0.1 M HCl + 39 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid

(iii) 5 cm^3 0.1 M HCl + 37 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid + 2 cm^3 0.01 M Cu(II)

The solutions were titrated against standardized 0.110MNaOH separately. The total volume of each mixture was adjusted to 50 cm^3 and the ionic strength of the solutions was maintained constant at by adding appropriate amount of stock solution of 1M KNO_3 (Gamal, 2015; Omar and Ali, 2015). A magnetic stirrer was used to achieve thorough mixing of the interacting solutions at 550 rpm. The same set of experimental conditions was applied for potentiometric titration of remaining samples.

Evaluation of pKa of Hydrolysed peat soil Humic Acids

The proton-ligand formation number $n_{\mathbf{A}}$ were calculated by Irving and Rossotti expression (Omar and Ali, 2015).

$$nA = Y- \frac{(V2-V1)(No-Eo)}{(Vo+V1)TcL} \quad ....1$$

Where: Y is number of dissociable proton, (V_2-V_1) is the measure of displacement of the ligand curve relative to acid curve, N^o and E^o are the resultant concentration of alkali solution, free acid solution, $T_{cL}{}^o$ is the total ligand concentration, V^o is the total volume of titration solution,V_1 is the volume of alkali added to acid solution,V_2 is the volume of alkali added to acid solution + ligand solution, acid dissociation constants (pKa - values) of ligand were calculated by algebraic method point wise calculation (Tables 1). The dissociation constants (pKa) were calculated according to the following relation:

$$pKa = pH + \log(\frac{nA}{1-nA}) \quad ....2$$

Where: pKa is the acid dissociation constant, $n_A$is the Proton-ligand formation number and pH is the pH-values (Omar and Ali, 2015).

Determination of metal-ligand stability constants (log K) of complexes

The potentiometric measurement for the determination of stability constant of a complex in solution is based on the fact that the redox potential of the couple $\frac{M^{+(m-n)}}{M^{+m}}$ is shifted significantly on complexation of the metal ion with the ligand. This method involves change in hydrogen ion concentration [H$^+$] due to the displacement or association of one or more protons taking place during complexation reaction. This change can be found out by titrating the solutions containing free acid, acid with ligand, and acid with ligand and metal ion, individually against a standard alkali solution at a constant ionic strength or temperature. Either ionic strength or temperature may be varied for different sets of solutions. In all the cases, the change in the pH of the solution is measured after each addition of a known amount of alkali to the reaction cell which contains the reaction mixture. The titration curves are then drawn by plotting the measured pH values against the corresponding volume of alkali added and the stability constants of the complexes are determined from the titration curves by employing pH-metric titration technique given by (Irving and Rossoti).

Metal-ligand stability constants (Log K) were determined by using the following relations:

$$\bar{n} = \frac{(V_3 - V_2)(E^0 + N^0)}{(V^0 + V_2)\bar{n}_A T_m^0} \quad ....3$$

and

$$PL = \log_{10}\{\frac{1 + \beta_n^H \frac{1}{[anti\ \log pH]^n}}{T_L^0 - \bar{n}T_m^0} X \frac{(V^0 + V_3)}{V^0}\} \quad ....4$$

Where $T_{L,}$ T^{o}, E°, and V^{o}havethe same significance as in equation (1) above, T_m denotes the total concentration of metal present in solution, V_3 is the volume of metal ions present in solution and β^H is the overall proton ligand stability constant. The metal-ligand stability constants (log K) were determined by employing point wise computational Method (eq. 5 and 6).

$$\mathrm{Log}K_1 = \log\left(\frac{n}{1-n}\right) + pL \qquad \ldots\ldots\ldots\ldots.5$$

$$\mathrm{Log}K_2 = \log\left(\frac{1-n}{2-n}\right) + pL\ldots\ldots\ldots\ldots\ldots\ldots\ldots.6$$

Where: Log K is the metal-ligand stability constant, pL is the Free ligand exponent function, **n** is the Average number of ligand attached with metal ion (Janrao*et al*., 2014).The results obtained were analyzed by an ORIGIN 2016 program using titration data and then the proton-ligand stability constants (pKa) and Metal-ligand stability constant (LogK) calculated (Omar and Ali, 2015).

RESULTS AND DISCUSSION

Fourier transformed infrared (FT-IR) spectra of isolated humic acid from peat soils Figure 2 had distinct clear absorption bands indicating the presence of major humic acid structural elemental groups such as H bonded OH ($3680cm^{-1}$ peak), C=O of carbonyl ($1721cm^{-1}$ peak), functional groups of aliphatic components CH_2 ($2918cm^{-1}$ peak) and C-O stretching of polysaccharide ($1168cm^{-1}$ peak). The positions of the absorption bands of the spectra fell within typical major absorption bands of humic acid which is at frequencies 3680, 2918, 1721, 1168 cm^{-1}. The first peak centred in the vicinity of 3680 cm^{-1} region is attributed to phenol OH group bounded by intermolecular H bonds. The $2918cm^{-1}$ band usually has absorption maximum at 2918 cm^{-1} which is due to C–H stretching of alkane group (CH_2). The next major absorption band is 1721 cm^{-1}. This band has been commonly ascribed to C=O stretching of mainly carboxyl group (COOH) with trace amount of ketones. The last peak was observed at 1168 cm^{-1} due to C–O stretching of polysaccharides and this peak appeared also in the spectra of humic acid from peat soil. The FTIR spectra of the isolated humic acid contained all major characteristic absorption peaks of humic acid. These absorption peaks indicated the presence of the major structural elements of humic acid namely H bonded OH, C=C of aromatic ring, C=O of carbonyl group (both carboxyl and ketonic), CH_2 group. This strongly supports the presence of humic acid.

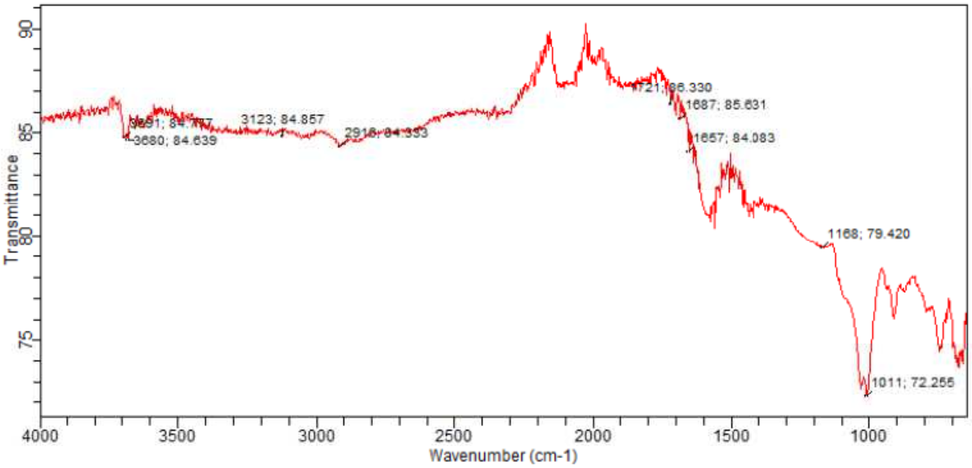


Fig. 2 : FT-IR spectraof peatsoilhumic acid (PSHA)

Evaluation of acid dissociation constant (pka) of acid hydrolysed peat soil humicacid at phenolic group

The value of the dissociation constant of the peat soil humic acid (PSHA) that underwent acidhydrolysis studied was found to be 8.9299 as shown Table 1, which is lower than the literaturevalues reported by Almeida and Szpoganics, (2015), Borges *et al*., (2005); Badr *et al*., (2012)and Fernandes *et al*,.(2009) of 9.73, 9.47 and 10.30. The difference between the obtained valuesand the reported values in this study might be probably as a result of acid hydrolysis of humicacid.

Table 1: PKa of (Hydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	$\log(\frac{nA}{1-nA})$	pKa
8.50	5.30	6.29	0.99	0.3594	-0.2510	8.2490
8.72	5.35	6.37	1.02	0.3400	-0.2880	8.4320
9.00	5.40	6.46	1.06	0.3141	-0.3391	8.6609
9.22	5.45	6.55	1.10	0.2882	-0.3927	8.8273
9.51	5.50	6.66	1.16	0.2494	-0.4786	9.0314
9.73	5.55	6.78	1.23	0.2041	-0.5910	9.1390
10.00	5.60	6.90	1.30	0.1589	-0.7238	9.2762
10.23	5.65	7.05	1.40	0.0941	-0.9835	9.2465
10.49	5.70	7.10	1.40	0.0941	-0.9835	9.5065

Average pKa = 8.9299 ± 0.4186

Table 2: PKa of (Unhydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	$\mathrm{Log}(\frac{nA}{1-n})$	pKa
8.50	5.30	5.81	0.51	0.6619	0.2919	8.7919
8.72	5.35	5.90	0.55	0.6357	0.2418	8.9618
9.00	5.40	6.00	0.60	0.6029	0.1813	9.1813
9.22	5.45	6.10	0.65	0.5701	0.1226	9.3426
9.51	5.50	6.20	0.70	0.5376	0.0654	9.5754
9.73	5.55	6.33	0.78	0.4851	-0.0259	9.7041
10.00	5.60	6.47	0.87	0.4262	-0.1291	9.8709
10.23	5.65	6.62	0.99	0.3609	-0.2481	9.9819
10.49	5.70	6.80	1.10	0.2759	-0.4690	10.0210

Average pKa = 9.4923± 0.4410

Metal-ligand stability constant (Log K)

The stabilityconstants require the accurate values of proton-ligand stability constants (Anil and Maroti, 2008). Metal titration curves crossed over ligand titration curve indicated the formation of complex upon proton release (Santosh, *et al.*, 2011). If the values of n- are within range 0.2-0.8 and 1.2-18 this indicates the formation of 1:1 and 1:2 complexes (Sayyed and Mazahar, 2012).

The metal (II)-humate stepwise stability constants (log k) at phenolic group (Tables 3-18)

Table 3: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$\log(\frac{n}{1-n})$	LogK_1
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

LogK_1 (Average value) = 2.4788± 0.2203

Table 4: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$\mathrm{Log}(\frac{n-1}{2-n})$	LogK_2
9.51	5.50	6.66	6.73	0.07	1.3509	1.70	-0.2671	1.4329
9.73	5.55	6.78	6.85	0.07	1.6383	1.51	0.2467	1.7567
10.00	5.60	6.90	6.98	0.08	2.1783	1.31	-0.2158	1.0942
10.23	5.65	7.05	7.13	0.08	4.1904	1.27		
10.49	5.70	7.10	7.19	0.09	4.6920			

LogK_2(Average value) = 1.4280 ± 0.3312

Table 5:Point-wise method,Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	Log($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430

$LogK_1$ **(Average value)** = 2.3059± 0.6153

Table 6:Point-wise method, Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
9.73	5.55	6.33	6.42	0.09	0.9000	1.69		
10.00	5.60	6.47	6.58	0.11	1.2578	1.44	-0.4592	0.9808
10.23	5.65	6.62	6.84	0.12	1.6137	1.26	-0.2010	1.4610
10.49	5.70	6.80	6.92	0.12	2.1052	1.03		

$LogK_2$ **(Average value)** = 1.2209± 0.3398

Table 7:Point-wise method,Pb (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n}{1-n}$)	$LogK_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.60	0.05	0.8333	1.96	0.6989	2.6589

$LogK_1$ (Average value) = 2.5832 ±0.1614

Table 8:Point-wise method,Pb-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n-1}{2-n}$)	$logK_2$
9.51	5.50	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.83	0.05	1.1702	1.44		
10.00	5.60	6.90	6.90	0.05	1.4864	1.22	-0.0237	1.1963
10.23	5.65	7.05	7.10	0.05	2.0190	1.09		
10.49	5.70	7.10	7.17	0.07	3.6492	1.00		

$LogK_2$(Average value) = 1.1963

Table 9:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log ($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.5477	2.3123
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	0.0272	2.2072
9.51	5.50	6.20	6.26	0.07	0.6417	1.89	0.2530	2.1430
9.73	5.55	6.40	6.40	0.07	0.7000	1.67	0.3680	2.0380

$LogK_1$ **(Average value)** = 2.2364 ± 0.1602

Table 10:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
10.00	5.60	6.47	6.55	0.08	1.9503	1.41		
10.23	5.65	6.62	6.72	0.11	1.4792	1.26	-0.0361	1.2239

$LogK_2$ **(Average value)** = 1.2239

Table 11:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n}{n-1}$)	$LogK_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4290	2.2110
8.72	5.35	6.37	6.39	0.02	0.2858	2.42	-0.3978	2.0222
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

$LogK_1$ (Average value)=2.1382±0.1046

Table 12:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	log($\frac{n-1}{2-n}$)	LogK$_2$
9.51	5.55	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.84	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.93	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.10		
10.49	5.70	7.10	7.18	0.07	3.6492	0.83		

LogK$_2$(Average value) = 1.5453 **±** 0.3450

Table 13:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	V$_3$-V$_2$	n	pL	Log($\frac{n}{n-1}$)	Log K$_1$
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.3477	2.3123
9.00	5.40	6.00	6.04	0.04	0.3236	2.38	-0.3202	2.0598
9.22	5.45	6.10	6.15	0.05	0.4297	2.17	-0.1230	2.0470
9.51	5.50	6.20	6.26	0.06	0.5500	1.89	0.0871	1.9771
9.73	5.55	6.33	6.40	0.07	0.7000	1.67	0.3680	2.0380

LogK$_1$ **(Average value)** = 2.1568 ± 0.2069

Table 14:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	V$_3$-V$_2$	n	pL	Log($\frac{n-1}{2-n}$)	Log K$_2$
10.00	5.60	6.47	6.55	0.08	0.9148	1.41		
10.23	5.65	6.62	6.71	0.09	1.2102	1.20	-0.5749	0.6251
10.49	5.70	6.80	6.92	0.09	1.5968	1.03	0.1703	1.2003

LogK$_2$ **(Average value)** = 0.9127± 0.4070

Table15:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	Log($\frac{n}{1-n}$)	LogK$_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4210	2.2190
8.72	5.35	6.37	6.40	0.03	0.4286	2.42	-0.1249	2.2951
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.96	0.3010	2.2610
9.51	5.55	6.66	6.70	0.04	0.7720	1.67	0.5297	2.1997

LogK$_1$ (Average value) = 2.2108± 0.0825

Table 16:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	Log($\frac{n-1}{2-n}$)	Log K$_2$
9.73	5.55	6.78	6.83	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.95	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.09		
10.49	5.70	7.10	7.16	0.06	3.1429	0.89		

LogK$_2$ **(Average value)** = 1.5453± 0.3450

Table 17:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	V$_3$-V$_2$	n	pL	Log($\frac{n}{n-1}$)	Log K$_1$
8.50	5.30	5.81	5.86	0.05	0.3717	2.88	-0.2280	2.6520
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.06	0.06	0.4853	2.38	-0.0255	2.3545
9.22	5.45	6.10	6.16	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430
9.73	5.55	6.33	6.41	0.08	0.8000	1.69	0.6020	2.2920

LogK$_1$ **(Average value)** = 2.2516± 0.5380

Table 18:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$\text{Log}(\frac{n-1}{2-n})$	Log K_2
10.00	5.60	6.47	6.57	0.10	1.1434	1.43		
10.23	5.65	6.62	6.72	0.10	1.3448	1.23	-0.2788	0.9512
10.49	5.70	6.80	6.90	0.10	1.7742	1.03	0.5351	1.5651

LogK_2 **(Average value)** = 1.2581± 0.4340

Table 19: Stepwise and overall Stability constants of thehydrolysed and unhydrolysed divalent metal (II) complexes

Chelates	**LogK_1**	**LogK_2**	**Logβ**
[Cu (Hydrolysed PSHA-1)$_2$]	2.4788	1.4280	3.9068
[Pb (Hydrolysed PSHA-1)$_2$]	2.5832	1.1963	3.7795
[Cd (Hydrolysed PSHA-1)$_2$]	2.2108	1.5453	3.7561
[Mg (Hydrolysed PSHA-1)$_2$]	2.1382	1.5453	3.6835
[Cu (Unhydrolysed PSHA-1)$_2$]	2.3059	1.2209	3.5268
[Pb (Unhydrolysed PSHA-1)$_2$]	2.2364	1.2239	3.4603
[Cd (Unhydrolysed PSHA-1)$_2$]	2.2516	1.2581	3.5097
[Mg (Unydrolysed PSHA-1)$_2$]	2.1568	0.9127	3.0695

The results obtained (Table19) shows the stepwise and overall stability constants to be not high indicating low stability of the complexes, because the solubility of most metal ions in the basic pH range is minimal due to metal hydroxide precipitation (Karimi, 2017). In general, the stepwise stability constants (K_1 and K_2) follow the order $K_1 > K_2$ for the copper, lead, magnesium and cadmium complexes respectively. The steady decrease of the values with increasing number of ligands is in agreement with the prediction made by researchers (Na'aliya, 2013). The decrease could be attributed to the fact that as the number of the ligands (Humate ions) that enters the coordination zone increases the aqua molecules available for replacement by the ligands become less. Thus, the metal ions become less electron loving with progressive intake of the ligand and this results in the decrease in the values of the constants (Na'aliya, 2013). Also the stability of the complexes is influenced by the size and number of the chelate rings(Mackay and Mackay,2002).All the complexes form rings in their structure as humate, a bidentate ligand, bond the metal ions in the ratio 1:2 (Boguta and Sokolowska, 2016) forming chelate rings. The values of the overall stability constants (logβ) obtained for humate complexes are not high indicating low stability as the values are not high. LogK values for copper-humates (Table 3 to 6) obtained in this study are lower than those reported for the complexes of humic acids (Pandey *et al*., 2015; Dinu, 2013; Kaschl *et al*., 2010 and Gilbeto and Jorg, 2001). The values of LogK(Table 7 to 10) forlead-humates are lower than those reported for the lead in the literature (Dinu, 2013; Gilbeto and Jorg 2001). Log K values(Table 11 to 14) for magnesium-humates obtained in this study are close to those reported by (Pandey *et al*., 2015). Log K values of cadmium-humates (Table 15 to 18) obtained in this work near to the one reported by (Dinu, 2013 and Pandey *et al*., 2015).The difference between the reported values and the values obtained in this study might be probably as a result of acid hydrolysis of humic acid. The values of the overall stability constants (log β) of the copper humates complexes presented in Table 19 is high than that of other metal humate complexes, show relatively high stability of Cu-HA complexes, show the following order of stability: Cu >Pb> Cd > Mg; which are in close agreement to the findings of (Dinu, 2013 and Pandey *et al*., 2015).The high stability of Cu-humate chelate could be attributed to the existence of coordinate covalent bond between the complexing agents and the Cu^{2+} ions. Since, Cu^{2+} being a metal of the transitional series with $3d^9$ electronic configurations can accept the electrons from the complexing agents. Similarly,the low stabilities of Pb,Cd and Mg - complexes could be explained by that Pb^{2+} with $6s^2$, Cd^{2+} with $4d^{10}$ and Mg^{2+} with $2p^6$ their electronic configuration has a completely filled d,p and s orbitals. Moreover, the stabilities of metal ions with hydrolysed humic acid from peat soil were higher than those with unhydrolysed humic acid from peat soil; which is ascribed to the high content of acidity in hydrolysed humic acid than unhydrolysed humic acid.

CONCLUSION

The values of logK for Cu(II) hydrolysed humic acid complex was higher followed by Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes as compared with metal(II) unhydrolysed humic acid complexes . This indicates acid hydrolysis of humic acid can enhance the complexation behavior of humic acid with metal (II) ions. However, the higher values of logβ for Cu(II), Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes indicates more stable stepwise complexes formed as compared with Cu(II), Pb(II), Cd(II) and Mg(II) unhydrolysed humic acid complexes.

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STABILITY CONSTANTS OF COMPLEXES OF METAL IONS WITH PEATSOIL HUMIC ACIDS UNDER NON-ACID-CONDITIONS

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ABSTRACT

Stability constants of complexes of four divalent metal ions viz. Cu^{2+}, Pb^{2+},Mg^{2+} and Cd^{2+} with humic acids (HA) were determined by potentiometric titration of humic acids with the corresponding salt of the divalent metals in aqueous media under non-acid-condition. The log K (logarithm of the stability constant) ranged from 1.0942 to 2.7471 for metal-humic acid complexes were determined using point-wise computational method. The order of stability constants were obtained as follows: Cu >Pb> Cd > Mg for metal -HA complexes respectively, indicating a higher degree of complexation with Cu metal ion.

Keywords: stability constant, humic acid, potentiometric titration, divalent metals, acid hydrolysis.

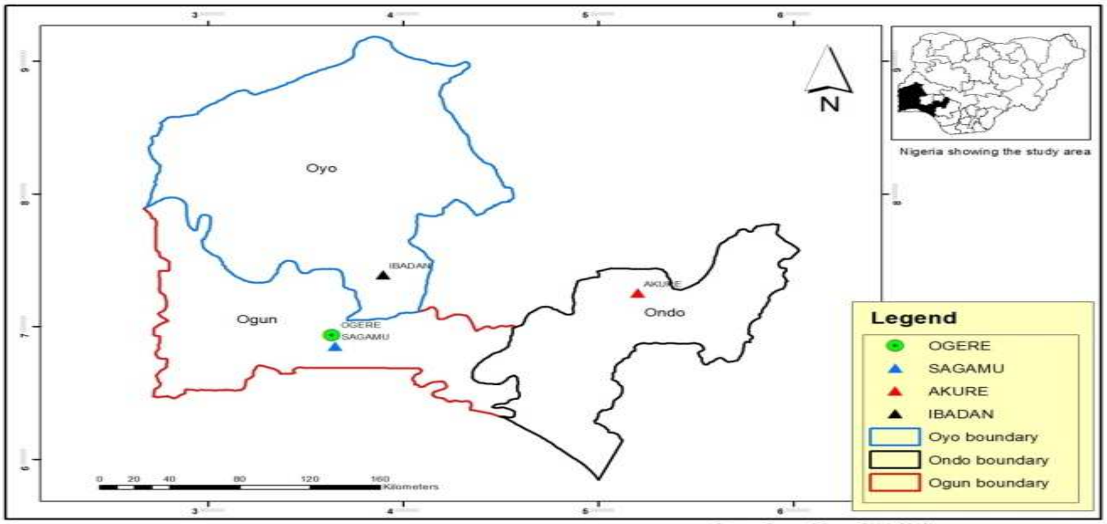
NTRODUCTION

The stability constant of a complex is the numerical expression of its stability and provides a quantitative measure of affinity of the metal ion to the complexing agent. An understanding of the relative stability of metal-complexes helps in predicting the behavior of metal ions in the soil (Ram and Raman, 1982). Extensive researches has been done to determine the stability constants of the complexes formed between humic acid (HA) with a number of metal ions. Ashok *et al.*, (2000) reported that humic acid with hydroxyl, phenoxyl and carboxyl reactive groups can form coordination compound with metal ions at pH 3.5. The stability constants(Log K) for different metal-humic acid complexes indicated the following order of the stabilities of complexes formed between humic acid and metal ion, Cu >Fe >Pb> Ni > Co > Ca > Cd > Zn >Mn> Mg. Andelkovic *et al.*, (2010) investigated the binding of Cd(II) to soil humic acid at pH 6.5 and in 0.1M KNO_3 ionic medium. The stability constant for binding indicating greater stability in the case when carboxyl groups are involved in complexation reaction. Kostic *et al.*,(2012) investigated the complexation of humic acid with certain heavy metal ions (Co(II), Ni(II),Cu(II), Zn(II), and Pb(II). The experiment was performed at 25°C, at pH 4.0 and ionic strength of 0.01M. Stability constant of complex between Pb(II) ions and humic acid is greater than stability constants of other investigated metal-humate complexes. Bogata and Sokolowska (2016) analyses the interaction between humic acids from different soils and Zn (II) ions at wide concentration ranges and at pH 5. Studies have showed significant impact of Zn concentration, pH and some properties of humic acids with zinc.But all of these studies were limited to acidic pH range. Therefore, the present study was carried out to determine and compare the stability constants of complexes of metal ions with hydrolysed peat soil humic acid and unhydrolysed peat soil humic under non-acid conditions.

MATERIALS AND METHODS

Analytical grade chemicals used includes hydrochloric acid (HCl), nitric acid (HNO_3), sodium hydroxide (NaOH), lead nitrate $Pb(NO_3)_2$, copper nitrate $Cu(NO_3)_2.3H_2O$, cadmium nitrate $Cd(NO_3)_2.4H_2O$, magnesium nitrate $Mg(NO_3)_2.6H_2O$, potassium nitrate (KNO_3), calcium chloride ($CaCl_2$), (sigma-Aldrich). Dowex 50WX8, (20-50 mesh) from Fluka.

Area of study



Source: Dept. of Geog. BUK (2016)

Figure 1: Map showing the sampling point at Sagamu Town, Ogun State.

Description of Sampling Area

Sagamu has geographical coordinates between 6°50′ north; 3° 38′ east is located in south western region of Nigeria. The region has tropical wet and dry climate with a lengthy wet season and relatively constant temperatures throughout the course of the year. Wet season runs from March to October, November to December forms the region dry season. The vegetation type of the region is savannah which is really grassland with small bushes and occasional big trees. Grassland soils have substantially higher organic matter content than forest soils (Novackova, 2011).

Sample Collection

The Peatsoil samples were collected from four different sampling points (0-10cm depth) in Sagamu into polyethylene bag with plastic spoons. Samples were taken to the laboratory, extraneous materials were removed; the samples were air-dried, crushed and ground to a fine powder in a mortar passed through a 0.20mm sieve. The samples were kept for analysis.

Isolation and purification of humic acid from peat soil sample

Peatsoil sample (100g) was mixed with 1000 cm^3 of 0.1M NaOH solution, shaken for 3hours and left to stand overnight. Dark-coloured supernatant was obtained and decanted from solid residue. The dark-coloured supernatant was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 6 hours. Yellowish brown supernatant and dark-brown precipitate were obtained. The yellowish brown supernatant was decanted followed by centrifuge and discarded. The dark-brown precipitate was mixed with 500$cm^3$of 0.1M NaOH solution followed by passing through dowex resin. The dark-brown solution was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 3 hours. The dark-brown precipitate was washed several times with deionized water. The supernatant was treated with $AgNO_3$ solution until no white precipitate observed. The humic acid was transferred to weighed crucible and dried at 60°C in an oven for 12 hours. The humic acid was cooled and dried in the desiccator, weighed and recorded. The obtained humic acid was dried again at 60°C for additional 6 hours cooled and dried in the desiccator, weighed and recorded constant weight was obtained (Baruah *et al*., 2015).

FT-IR analysis

FT-IR spectra of humic acid sample was analysed using Carry 630 FT-IR Agilent Technologies.

Unhydrolysed compost humic acid

The unhydrolysed humic acid was obtained after isolation and purification of compost humic acid and kept for investigation.

Acid hydrolysis of Peatsoil acid

Peatsoil humic acid sample (1g) was refluxed for 12 hours at (160°C) with 50cm^3 of 6M HCl. The mixture was allowed to cool, decanted, and centrifuged after hydrolysis. The insoluble residues were washed with distilled water via centrifugation several times, and the supernatant was treated with $AgNO_3$ solution until no white precipitate was observed. The residue was thoroughly dried over $CaCl_2$ in a desiccator at room temperature (Chefetz *et al*., 2002). Finally, the obtained hydrolysed humic acid was kept for investigation.

Potentiometric Titrations

Potentiometric measurements were carried out using a pH-meter Jenway (model 3510) with combine electrode, the sensitivity of the pH - meter is 0.01 units. The pH meter was switched on half an hour before starting the titration for initial warm up of the instrument. The instrument was calibrated with an aqueous standard buffer solution of pH 4.00 and 10.0 (borate buffer) prepared from a "Qualigens" buffer tablets.

The following sets of solutions were prepared in a 250cm^3 volumetric flask separately for pH metric titrations.

(i) 5 cm^3 0.1 M HCl + 40 cm^3 deionized water
(ii) 5 cm^3 0.1 M HCl + 39 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid
(iii) 5 cm^3 0.1 M HCl + 37 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid + 2 cm^3 0.01 M Cu(II)

The solutions were titrated against standardized 0.110MNaOH separately. The total volume of each mixture was adjusted to 50 cm^3 and the ionic strength of the solutions was maintained constant at by adding appropriate amount of stock solution of 1M KNO$_3$ (Gamal, 2015; Omar and Ali, 2015). A magnetic stirrer was used to achieve thorough mixing of the interacting solutions at 550 rpm. The same set of experimental conditions was applied for potentiometric titration of remaining samples.

Evaluation of pKa of Hydrolysed peat soil Humic Acids

The proton-ligand formation number n$_{\mathbf{A}}$ were calculated by Irving and Rossotti expression (Omar and Ali, 2015).

$nA = Y- \frac{(V2-V1)(No-Eo)}{(Vo+V1)TcL}$ ………………………………1

Where: Y is number of dissociable proton, (V_2-V_1) is the measure of displacement of the ligand curve relative to acid curve, N^o and E^o are the resultant concentration of alkali solution, free acid solution, $T_{cL}{}^o$ is the total ligand concentration, V^o is the total volume of titration solution,V_1 is the volume of alkali added to acid solution,V_2 is the volume of alkali added to acid solution + ligand solution, acid dissociation constants (pKa - values) of ligand were calculated by algebraic method point wise calculation (Tables 1). The dissociation constants (pKa) were calculated according to the following relation:

pKa = pH + log$(\frac{nA}{1-nA})$ ………………………..2

Where: pKa is the acid dissociation constant, $n_A$is the Proton-ligand formation number and pH is the pH-values (Omar and Ali, 2015).

Determination of metal-ligand stability constants (log K) of complexes

The potentiometric measurement for the determination of stability constant of a complex in solution is based on the fact that the redox potential of the couple $\frac{M^{+(m-n)}}{M^{+m}}$ is shifted significantly on complexation of the metal ion with the ligand. This method involves change in hydrogen ion concentration [H$^+$] due to the displacement or association of one or more protons taking place during complexation reaction. This change can be found out by titrating the solutions containing free acid, acid with ligand, and acid with ligand and metal ion, individually against a standard alkali solution at a constant ionic strength or temperature. Either ionic strength or temperature may be varied for different sets of solutions. In all the cases, the change in the pH of the solution is measured after each addition of a known amount of alkali to the reaction cell which contains the reaction mixture. The titration curves are then drawn by plotting the measured pH values against the corresponding volume of alkali added and the stability constants of the complexes are determined from the titration curves by employing pH-metric titration technique given by (Irving and Rossoti).

Metal-ligand stability constants (Log K) were determined by using the following relations:

$$\bar{n} = \frac{(V_3 - V_2)(E^0 + N^0)}{(V^0 + V_2)\bar{n}_A T_m^0}$$ ……………………………………………………………………….3

and

$$PL = \log_{10}\{\frac{1+\beta_n^H \frac{1}{[anti\ \log pH]^n}}{T_L^0 - \bar{n}T_m^0} X \frac{(V^0+V_3)}{V^0}\}$$ …………………………………………………….4

Where $T_{L,}$ T^o, E°, and V^ohavethe same significance as in equation (1) above, T_m denotes the total concentration of metal present in solution, V_3 is the volume of metal ions present in solution and β^H is the overall proton ligand stability constant. The metal-ligand stability constants (log K) were determined by employing point wise computational Method (eq. 5 and 6).

$$\text{LogK}_1 = \log\left(\frac{n}{1-n}\right) + \text{pL} \qquad \text{.............}5$$

$$\text{LogK}_2 = \log\left(\frac{1-n}{2-n}\right) + \text{pL.......................}6$$

Where: Log K is the metal-ligand stability constant, pL is the Free ligand exponent function, **n** is the Average number of ligand attached with metal ion (Janrao*et al.*, 2014).The results obtained were analyzed by an ORIGIN 2016 program using titration data and then the proton-ligand stability constants (pKa) and Metal-ligand stability constant (LogK) calculated (Omar and Ali, 2015).

RESULTS AND DISCUSSION

Fourier transformed infrared (FT-IR) spectra of isolated humic acid from peat soils Figure 2 had distinct clear absorption bands indicating the presence of major humic acid structural elemental groups such as H bonded OH ($3680cm^{-1}$ peak), C=O of carbonyl ($1721cm^{-1}$ peak), functional groups of aliphatic components CH_2 ($2918cm^{-1}$ peak) and C-O stretching of polysaccharide ($1168cm^{-1}$ peak). The positions of the absorption bands of the spectra fell within typical major absorption bands of humic acid which is at frequencies 3680, 2918, 1721, 1168 cm^{-1}. The first peak centred in the vicinity of 3680 cm^{-1} region is attributed to phenol OH group bounded by intermolecular H bonds. The $2918cm^{-1}$ band usually has absorption maximum at 2918 cm^{-1} which is due to C–H stretching of alkane group (CH_2). The next major absorption band is 1721 cm^{-1}. This band has been commonly ascribed to C=O stretching of mainly carboxyl group (COOH) with trace amount of ketones. The last peak was observed at 1168 cm^{-1} due to C–O stretching of polysaccharides and this peak appeared also in the spectra of humic acid from peat soil. The FTIR spectra of the isolated humic acid contained all major characteristic absorption peaks of humic acid. These absorption peaks indicated the presence of the major structural elements of humic acid namely H bonded OH, C=C of aromatic ring, C=O of carbonyl group (both carboxyl and ketonic), CH_2 group. This strongly supports the presence of humic acid.

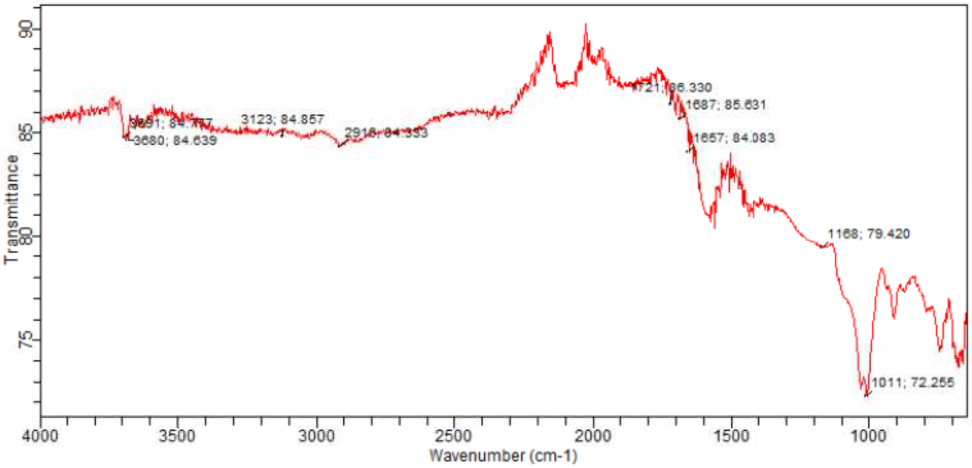


Fig. 2 : FT-IR spectraof peatsoilhumic acid (PSHA)

Evaluation of acid dissociation constant (pka) of acid hydrolysed peat soil humicacid at phenolic group

The value of the dissociation constant of the peat soil humic acid (PSHA) that underwent acidhydrolysis studied was found to be 8.9299 as shown Table 1, which is lower than the literaturevalues reported by Almeida and Szpoganics, (2015), Borges *et al.*, (2005); Badr *et al.*, (2012)and Fernandes *et al*,.(2009) of 9.73, 9.47 and 10.30. The difference between the obtained valuesand the reported values in this study might be probably as a result of acid hydrolysis of humicacid.

Table 1: PKa of (Hydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	log($\frac{nA}{1-nA}$)	pKa
8.50	5.30	6.29	0.99	0.3594	-0.2510	8.2490
8.72	5.35	6.37	1.02	0.3400	-0.2880	8.4320
9.00	5.40	6.46	1.06	0.3141	-0.3391	8.6609
9.22	5.45	6.55	1.10	0.2882	-0.3927	8.8273
9.51	5.50	6.66	1.16	0.2494	-0.4786	9.0314
9.73	5.55	6.78	1.23	0.2041	-0.5910	9.1390
10.00	5.60	6.90	1.30	0.1589	-0.7238	9.2762
10.23	5.65	7.05	1.40	0.0941	-0.9835	9.2465
10.49	5.70	7.10	1.40	0.0941	-0.9835	9.5065

Average pKa = 8.9299 ± 0.4186

Table 2: PKa of (Unhydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	Log($\frac{nA}{1-n}$)	pKa
8.50	5.30	5.81	0.51	0.6619	0.2919	8.7919
8.72	5.35	5.90	0.55	0.6357	0.2418	8.9618
9.00	5.40	6.00	0.60	0.6029	0.1813	9.1813
9.22	5.45	6.10	0.65	0.5701	0.1226	9.3426
9.51	5.50	6.20	0.70	0.5376	0.0654	9.5754
9.73	5.55	6.33	0.78	0.4851	-0.0259	9.7041
10.00	5.60	6.47	0.87	0.4262	-0.1291	9.8709
10.23	5.65	6.62	0.99	0.3609	-0.2481	9.9819
10.49	5.70	6.80	1.10	0.2759	-0.4690	10.0210

Average pKa = 9.4923± 0.4410

Metal-ligand stability constant (Log K)

The stabilityconstants require the accurate values of proton-ligand stability constants (Anil and Maroti, 2008). Metal titration curves crossed over ligand titration curve indicated the formation of complex upon proton release (Santosh, *et al.*, 2011). If the values of n- are within range 0.2-0.8 and 1.2-18 this indicates the formation of 1:1 and 1:2 complexes (Sayyed and Mazahar, 2012).

The metal (II)-humate stepwise stability constants (log k) at phenolic group (Tables 3-18)

Table 3: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n}{1-n}$)	$LogK_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

$LogK_1$ (Average value) = 2.4788± 0.2203

Table 4: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	Log($\frac{n-1}{2-n}$)	$LogK_2$
9.51	5.50	6.66	6.73	0.07	1.3509	1.70	-0.2671	1.4329
9.73	5.55	6.78	6.85	0.07	1.6383	1.51	0.2467	1.7567
10.00	5.60	6.90	6.98	0.08	2.1783	1.31	-0.2158	1.0942
10.23	5.65	7.05	7.13	0.08	4.1904	1.27		
10.49	5.70	7.10	7.19	0.09	4.6920			

$LogK_2$(Average value) = 1.4280 ± 0.3312

Table 5:Point-wise method,Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	Log$(\frac{n}{n-1})$	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430

$LogK_1$ **(Average value)** = 2.3059± 0.6153

Table 6:Point-wise method, Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log$(\frac{n-1}{2-n})$	Log K_2
9.73	5.55	6.33	6.42	0.09	0.9000	1.69		
10.00	5.60	6.47	6.58	0.11	1.2578	1.44	-0.4592	0.9808
10.23	5.65	6.62	6.84	0.12	1.6137	1.26	-0.2010	1.4610
10.49	5.70	6.80	6.92	0.12	2.1052	1.03		

$LogK_2$ **(Average value)** = 1.2209± 0.3398

Table 7:Point-wise method,Pb (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log$(\frac{n}{1-n})$	$LogK_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.60	0.05	0.8333	1.96	0.6989	2.6589

$LogK_1$ (Average value) = 2.5832 ±0.1614

Table 8:Point-wise method,Pb-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log$(\frac{n-1}{2-n})$	$logK_2$
9.51	5.50	6.66	6.71	0.05	0.9650	1.67	-0.0237	1.1963
9.73	5.55	6.78	6.83	0.05	1.1702	1.44		
10.00	5.60	6.90	6.90	0.05	1.4864	1.22		
10.23	5.65	7.05	7.10	0.05	2.0190	1.09		
10.49	5.70	7.10	7.17	0.07	3.6492	1.00		

$LogK_2$(Average value) = 1.1963

Table 9:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log $(\frac{n}{n-1})$	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.5477	2.3123
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	0.0272	2.2072
9.51	5.50	6.20	6.26	0.07	0.6417	1.89	0.2530	2.1430
9.73	5.55	6.40	6.40	0.07	0.7000	1.67	0.3680	2.0380

$LogK_1$ **(Average value)** = 2.2364 ± 0.1602

Table 10:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log$(\frac{n-1}{2-n})$	Log K_2
10.00	5.60	6.47	6.55	0.08	1.9503	1.41		
10.23	5.65	6.62	6.72	0.11	1.4792	1.26	-0.0361	1.2239

$LogK_2$ **(Average value)** = 1.2239

Table 11:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log$(\frac{n}{n-1})$	$LogK_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4290	2.2110
8.72	5.35	6.37	6.39	0.02	0.2858	2.42	-0.3978	2.0222
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

$LogK_1$ (Average value)=2.1382**±**0.1046

Table 12:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$\log(\frac{n-1}{2-n})$	$LogK_2$
9.51	5.55	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.84	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.93	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.10		
10.49	5.70	7.10	7.18	0.07	3.6492	0.83		

$LogK_2$(Average value) = 1.5453 **±** 0.3450

Table 13:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$Log(\frac{n}{n-1})$	$Log\ K_1$
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.3477	2.3123
9.00	5.40	6.00	6.04	0.04	0.3236	2.38	-0.3202	2.0598
9.22	5.45	6.10	6.15	0.05	0.4297	2.17	-0.1230	2.0470
9.51	5.50	6.20	6.26	0.06	0.5500	1.89	0.0871	1.9771
9.73	5.55	6.33	6.40	0.07	0.7000	1.67	0.3680	2.0380

$LogK_1$ **(Average value)** = 2.1568 ± 0.2069

Table 14:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$Log(\frac{n-1}{2-n})$	$Log\ K_2$
10.00	5.60	6.47	6.55	0.08	0.9148	1.41		
10.23	5.65	6.62	6.71	0.09	1.2102	1.20	-0.5749	0.6251
10.49	5.70	6.80	6.92	0.09	1.5968	1.03	0.1703	1.2003

$LogK_2$ **(Average value)** = 0.9127± 0.4070

Table15:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$Log(\frac{n}{1-n})$	$LogK_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4210	2.2190
8.72	5.35	6.37	6.40	0.03	0.4286	2.42	-0.1249	2.2951
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.96	0.3010	2.2610
9.51	5.55	6.66	6.70	0.04	0.7720	1.67	0.5297	2.1997

$LogK_1$ (Average value) = 2.2108± 0.0825

Table 16:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$Log(\frac{n-1}{2-n})$	$Log\ K_2$
9.73	5.55	6.78	6.83	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.95	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.09		
10.49	5.70	7.10	7.16	0.06	3.1429	0.89		

$LogK_2$ **(Average value)** = 1.5453± 0.3450

Table 17:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$Log(\frac{n}{n-1})$	$Log\ K_1$
8.50	5.30	5.81	5.86	0.05	0.3717	2.88	-0.2280	2.6520
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.06	0.06	0.4853	2.38	-0.0255	2.3545
9.22	5.45	6.10	6.16	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430
9.73	5.55	6.33	6.41	0.08	0.8000	1.69	0.6020	2.2920

$LogK_1$ **(Average value)** = 2.2516± 0.5380

Table 18:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$\text{Log}(\frac{n-1}{2-n})$	Log K_2
10.00	5.60	6.47	6.57	0.10	1.1434	1.43		
10.23	5.65	6.62	6.72	0.10	1.3448	1.23	-0.2788	0.9512
10.49	5.70	6.80	6.90	0.10	1.7742	1.03	0.5351	1.5651

LogK_2 **(Average value)** = 1.2581± 0.4340

Table 19: Stepwise and overall Stability constants of thehydrolysed and unhydrolysed divalent metal (II) complexes

Chelates	**LogK_1**	**LogK_2**	**Logβ**
[Cu (Hydrolysed PSHA-1)$_2$]	2.4788	1.4280	3.9068
[Pb (Hydrolysed PSHA-1)$_2$]	2.5832	1.1963	3.7795
[Cd (Hydrolysed PSHA-1)$_2$]	2.2108	1.5453	3.7561
[Mg (Hydrolysed PSHA-1)$_2$]	2.1382	1.5453	3.6835
[Cu (Unhydrolysed PSHA-1)$_2$]	2.3059	1.2209	3.5268
[Pb (Unhydrolysed PSHA-1)$_2$]	2.2364	1.2239	3.4603
[Cd (Unhydrolysed PSHA-1)$_2$]	2.2516	1.2581	3.5097
[Mg (Unydrolysed PSHA-1)$_2$]	2.1568	0.9127	3.0695

The results obtained (Table19) shows the stepwise and overall stability constants to be not high indicating low stability of the complexes, because the solubility of most metal ions in the basic pH range is minimal due to metal hydroxide precipitation (Karimi, 2017). In general, the stepwise stability constants (K_1 and K_2) follow the order $K_1 > K_2$ for the copper, lead, magnesium and cadmium complexes respectively. The steady decrease of the values with increasing number of ligands is in agreement with the prediction made by researchers (Na'aliya, 2013). The decrease could be attributed to the fact that as the number of the ligands (Humate ions) that enters the coordination zone increases the aqua molecules available for replacement by the ligands become less. Thus, the metal ions become less electron loving with progressive intake of the ligand and this results in the decrease in the values of the constants (Na'aliya, 2013). Also the stability of the complexes is influenced by the size and number of the chelate rings(Mackay and Mackay,2002).All the complexes form rings in their structure as humate, a bidentate ligand, bond the metal ions in the ratio 1:2 (Boguta and Sokolowska, 2016) forming chelate rings. The values of the overall stability constants (logβ) obtained for humate complexes are not high indicating low stability as the values are not high. LogK values for copper-humates (Table 3 to 6) obtained in this study are lower than those reported for the complexes of humic acids (Pandey *et al.*, 2015; Dinu, 2013; Kaschl *et al.*, 2010 and Gilbeto and Jorg, 2001). The values of LogK(Table 7 to 10) forlead-humates are lower than those reported for the lead in the literature (Dinu, 2013; Gilbeto and Jorg 2001). Log K values(Table 11 to 14) for magnesium-humates obtained in this study are close to those reported by (Pandey *et al.*, 2015). Log K values of cadmium-humates (Table 15 to 18) obtained in this work near to the one reported by (Dinu, 2013 and Pandey *et al.*, 2015).The difference between the reported values and the values obtained in this study might be probably as a result of acid hydrolysis of humic acid. The values of the overall stability constants (log β) of the copper humates complexes presented in Table 19 is high than that of other metal humate complexes, show relatively high stability of Cu-HA complexes, show the following order of stability: Cu >Pb> Cd > Mg; which are in close agreement to the findings of (Dinu, 2013 and Pandey *et al.*, 2015).The high stability of Cu-humate chelate could be attributed to the existence of coordinate covalent bond between the complexing agents and the Cu^{2+} ions. Since, Cu^{2+} being a metal of the transitional series with $3d^9$ electronic configurations can accept the electrons from the complexing agents. Similarly,the low stabilities of Pb,Cd and Mg - complexes could be explained by that Pb^{2+} with $6s^2$, Cd^{2+} with $4d^{10}$ and Mg^{2+} with $2p^6$ their electronic configuration has a completely filled d,p and s orbitals. Moreover, the stabilities of metal ions with hydrolysed humic acid from peat soil were higher than those with unhydrolysed humic acid from peat soil; which is ascribed to the high content of acidity in hydrolysed humic acid than unhydrolysed humic acid.

CONCLUSION

The values of logK for Cu(II) hydrolysed humic acid complex was higher followed by Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes as compared with metal(II) unhydrolysed humic acid complexes . This indicates acid hydrolysis of humic acid can enhance the complexation behavior of humic acid with metal (II) ions. However, the higher values of logβ for Cu(II), Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes indicates more stable stepwise complexes formed as compared with Cu(II), Pb(II), Cd(II) and Mg(II) unhydrolysed humic acid complexes.

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STABILITY CONSTANTS OF COMPLEXES OF METAL IONS WITH PEATSOIL HUMIC ACIDS UNDER NON-ACID-CONDITIONS

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ABSTRACT

Stability constants of complexes of four divalent metal ions viz. Cu^{2+}, Pb^{2+},Mg^{2+} and Cd^{2+} with humic acids (HA) were determined by potentiometric titration of humic acids with the corresponding salt of the divalent metals in aqueous media under non-acid-condition. The log K (logarithm of the stability constant) ranged from 1.0942 to 2.7471 for metal-humic acid complexes were determined using point-wise computational method. The order of stability constants were obtained as follows: Cu >Pb> Cd > Mg for metal -HA complexes respectively, indicating a higher degree of complexation with Cu metal ion.

Keywords: stability constant, humic acid, potentiometric titration, divalent metals, acid hydrolysis.

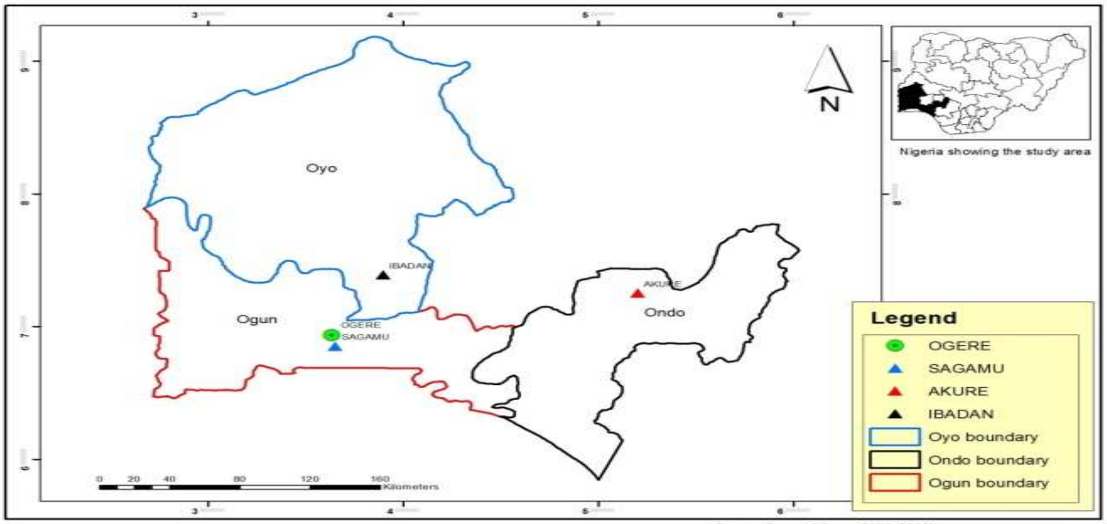
NTRODUCTION

The stability constant of a complex is the numerical expression of its stability and provides a quantitative measure of affinity of the metal ion to the complexing agent. An understanding of the relative stability of metal-complexes helps in predicting the behavior of metal ions in the soil (Ram and Raman, 1982). Extensive researches has been done to determine the stability constants of the complexes formed between humic acid (HA) with a number of metal ions. Ashok *et al*., (2000) reported that humic acid with hydroxyl, phenoxyl and carboxyl reactive groups can form coordination compound with metal ions at pH 3.5. The stability constants(Log K) for different metal-humic acid complexes indicated the following order of the stabilities of complexes formed between humic acid and metal ion, Cu >Fe >Pb> Ni > Co > Ca > Cd > Zn >Mn> Mg. Andelkovic *et al*., (2010) investigated the binding of Cd(II) to soil humic acid at pH 6.5 and in 0.1M KNO_3 ionic medium. The stability constant for binding indicating greater stability in the case when carboxyl groups are involved in complexation reaction. Kostic *et al*.,(2012) investigated the complexation of humic acid with certain heavy metal ions (Co(II), Ni(II),Cu(II), Zn(II), and Pb(II). The experiment was performed at 25°C, at pH 4.0 and ionic strength of 0.01M. Stability constant of complex between Pb(II) ions and humic acid is greater than stability constants of other investigated metal-humate complexes. Bogata and Sokolowska (2016) analyses the interaction between humic acids from different soils and Zn (II) ions at wide concentration ranges and at pH 5. Studies have showed significant impact of Zn concentration, pH and some properties of humic acids with zinc.But all of these studies were limited to acidic pH range. Therefore, the present study was carried out to determine and compare the stability constants of complexes of metal ions with hydrolysed peat soil humic acid and unhydrolysed peat soil humic under non-acid conditions.

MATERIALS AND METHODS

Analytical grade chemicals used includes hydrochloric acid (HCl), nitric acid (HNO_3), sodium hydroxide (NaOH), lead nitrate $Pb(NO_3)_2$, copper nitrate $Cu(NO_3)_2.3H_2O$, cadmium nitrate $Cd(NO_3)_2.4H_2O$, magnesium nitrate $Mg(NO_3)_2.6H_2O$, potassium nitrate (KNO_3), calcium chloride ($CaCl_2$), (sigma-Aldrich). Dowex 50WX8, (20-50 mesh) from Fluka.

Area of study



Source: Dept. of Geog. BUK (2016)

Figure 1: Map showing the sampling point at Sagamu Town, Ogun State.

Description of Sampling Area

Sagamu has geographical coordinates between 6°50′ north; 3° 38′ east is located in south western region of Nigeria. The region has tropical wet and dry climate with a lengthy wet season and relatively constant temperatures throughout the course of the year. Wet season runs from March to October, November to December forms the region dry season. The vegetation type of the region is savannah which is really grassland with small bushes and occasional big trees. Grassland soils have substantially higher organic matter content than forest soils (Novackova, 2011).

Sample Collection

The Peatsoil samples were collected from four different sampling points (0-10cm depth) in Sagamu into polyethylene bag with plastic spoons. Samples were taken to the laboratory, extraneous materials were removed; the samples were air-dried, crushed and ground to a fine powder in a mortar passed through a 0.20mm sieve. The samples were kept for analysis.

Isolation and purification of humic acid from peat soil sample

Peatsoil sample (100g) was mixed with 1000 cm^3 of 0.1M NaOH solution, shaken for 3hours and left to stand overnight. Dark-coloured supernatant was obtained and decanted from solid residue. The dark-coloured supernatant was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 6 hours. Yellowish brown supernatant and dark-brown precipitate were obtained. The yellowish brown supernatant was decanted followed by centrifuge and discarded. The dark-brown precipitate was mixed with 500$cm^3$of 0.1M NaOH solution followed by passing through dowex resin. The dark-brown solution was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 3 hours. The dark-brown precipitate was washed several times with deionized water. The supernatant was treated with $AgNO_3$ solution until no white precipitate observed. The humic acid was transferred to weighed crucible and dried at 60°C in an oven for 12 hours. The humic acid was cooled and dried in the desiccator, weighed and recorded. The obtained humic acid was dried again at 60°C for additional 6 hours cooled and dried in the desiccator, weighed and recorded constant weight was obtained (Baruah *et al.*, 2015).

FT-IR analysis

FT-IR spectra of humic acid sample was analysed using Carry 630 FT-IR Agilent Technologies.

Unhydrolysed compost humic acid

The unhydrolysed humic acid was obtained after isolation and purification of compost humic acid and kept for investigation.

Acid hydrolysis of Peatsoil acid

Peatsoil humic acid sample (1g) was refluxed for 12 hours at (160°C) with 50cm^3 of 6M HCl. The mixture was allowed to cool, decanted, and centrifuged after hydrolysis. The insoluble residues were washed with distilled water via centrifugation several times, and the supernatant was treated with $AgNO_3$ solution until no white precipitate was observed. The residue was thoroughly dried over $CaCl_2$ in a desiccator at room temperature (Chefetz *et al.*, 2002). Finally, the obtained hydrolysed humic acid was kept for investigation.

Potentiometric Titrations

Potentiometric measurements were carried out using a pH-meter Jenway (model 3510) with combine electrode, the sensitivity of the pH -meter is 0.01 units. The pH meter was switched on half an hour before starting the titration for initial warm up of the instrument. The instrument was calibrated with an aqueous standard buffer solution of pH 4.00 and 10.0 (borate buffer) prepared from a "Qualigens" buffer tablets.

The following sets of solutions were prepared in a 250cm^3 volumetric flask separately for pH metric titrations.

- (i) 5 cm^3 0.1 M HCl + 40 cm^3 deionized water
- (ii) 5 cm^3 0.1 M HCl + 39 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid
- (iii) 5 cm^3 0.1 M HCl + 37 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid + 2 cm^3 0.01 M Cu(II)

The solutions were titrated against standardized 0.110MNaOH separately. The total volume of each mixture was adjusted to 50 cm^3 and the ionic strength of the solutions was maintained constant at by adding appropriate amount of stock solution of 1M KNO$_3$ (Gamal, 2015; Omar and Ali, 2015). A magnetic stirrer was used to achieve thorough mixing of the interacting solutions at 550 rpm. The same set of experimental conditions was applied for potentiometric titration of remaining samples.

Evaluation of pKa of Hydrolysed peat soil Humic Acids

The proton-ligand formation number n$_{\mathbf{A}}$ were calculated by Irving and Rossotti expression (Omar and Ali, 2015).

$$nA = Y- \frac{(V2-V1)(No-Eo)}{(Vo+V1)TcL} \quad \text{.................................}1$$

Where: Y is number of dissociable proton, (V$_2$-V$_1$) is the measure of displacement of the ligand curve relative to acid curve, N^o and E^o are the resultant concentration of alkali solution, free acid solution, T$_{cL}$^{o} is the total ligand concentration, V^o is the total volume of titration solution,V$_1$ is the volume of alkali added to acid solution,V$_2$ is the volume of alkali added to acid solution + ligand solution, acid dissociation constants (pKa - values) of ligand were calculated by algebraic method point wise calculation (Tables 1). The dissociation constants (pKa) were calculated according to the following relation:

$$pKa = pH + \log(\frac{nA}{1-nA}) \quad \text{............................}2$$

Where: pKa is the acid dissociation constant, n$_A$is the Proton-ligand formation number and pH is the pH-values (Omar and Ali, 2015).

Determination of metal-ligand stability constants (log K) of complexes

The potentiometric measurement for the determination of stability constant of a complex in solution is based on the fact that the redox potential of the couple $\frac{M^{+(m-n)}}{M^{+m}}$ is shifted significantly on complexation of the metal ion with the ligand. This method involves change in hydrogen ion concentration [H$^+$] due to the displacement or association of one or more protons taking place during complexation reaction. This change can be found out by titrating the solutions containing free acid, acid with ligand, and acid with ligand and metal ion, individually against a standard alkali solution at a constant ionic strength or temperature. Either ionic strength or temperature may be varied for different sets of solutions. In all the cases, the change in the pH of the solution is measured after each addition of a known amount of alkali to the reaction cell which contains the reaction mixture. The titration curves are then drawn by plotting the measured pH values against the corresponding volume of alkali added and the stability constants of the complexes are determined from the titration curves by employing pH-metric titration technique given by (Irving and Rossoti).

Metal-ligand stability constants (Log K) were determined by using the following relations:

$$\bar{n} = \frac{(V_3 - V_2)(E^0 + N^0)}{(V^0 + V_2)\bar{n}_A T_m^0} \quad \text{..}3$$

and

$$PL = \log_{10}\{\frac{1+\beta_n^H \frac{1}{[anti\ \log pH]^n}}{T_L^0 - \bar{n}T_m^0} X \frac{(V^0+V_3)}{V^0}\} \quad \text{...}4$$

Where $T_{L,}$ T^o, E°, and V^ohavethe same significance as in equation (1) above, T_m denotes the total concentration of metal present in solution, V_3 is the volume of metal ions present in solution and β^H is the overall proton ligand stability constant. The metal-ligand stability constants (log K) were determined by employing point wise computational Method (eq. 5 and 6).

$\text{LogK}_1 = \log\left(\frac{n}{1-n}\right) + \text{pL}$ 5

$\text{LogK}_2 = \log\left(\frac{1-n}{2-n}\right) + \text{pL}$.......................6

Where: Log K is the metal-ligand stability constant, pL is the Free ligand exponent function, **n** is the Average number of ligand attached with metal ion (Janrao*et al*., 2014).The results obtained were analyzed by an ORIGIN 2016 program using titration data and then the proton-ligand stability constants (pKa) and Metal-ligand stability constant (LogK) calculated (Omar and Ali, 2015).

RESULTS AND DISCUSSION

Fourier transformed infrared (FT-IR) spectra of isolated humic acid from peat soils Figure 2 had distinct clear absorption bands indicating the presence of major humic acid structural elemental groups such as H bonded OH ($3680cm^{-1}$ peak), C=O of carbonyl ($1721cm^{-1}$ peak), functional groups of aliphatic components CH_2 ($2918cm^{-1}$ peak) and C-O stretching of polysaccharide ($1168cm^{-1}$ peak). The positions of the absorption bands of the spectra fell within typical major absorption bands of humic acid which is at frequencies 3680, 2918, 1721, 1168 cm^{-1}. The first peak centred in the vicinity of 3680 cm^{-1} region is attributed to phenol OH group bounded by intermolecular H bonds. The $2918cm^{-1}$ band usually has absorption maximum at 2918 cm^{-1} which is due to C–H stretching of alkane group (CH_2). The next major absorption band is 1721 cm^{-1}. This band has been commonly ascribed to C=O stretching of mainly carboxyl group (COOH) with trace amount of ketones. The last peak was observed at 1168 cm^{-1} due to C–O stretching of polysaccharides and this peak appeared also in the spectra of humic acid from peat soil. The FTIR spectra of the isolated humic acid contained all major characteristic absorption peaks of humic acid. These absorption peaks indicated the presence of the major structural elements of humic acid namely H bonded OH, C=C of aromatic ring, C=O of carbonyl group (both carboxyl and ketonic), CH_2 group. This strongly supports the presence of humic acid.

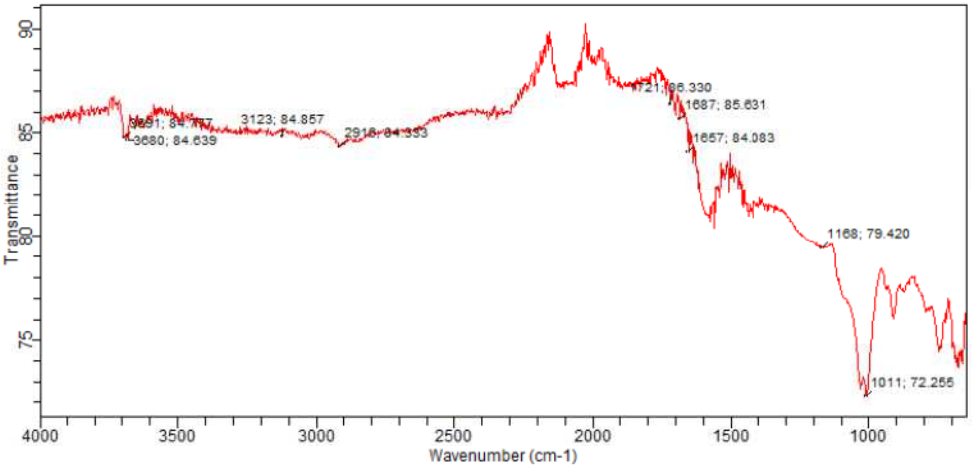


Fig. 2 : FT-IR spectraof peatsoilhumic acid (PSHA)

Evaluation of acid dissociation constant (pka) of acid hydrolysed peat soil humicacid at phenolic group

The value of the dissociation constant of the peat soil humic acid (PSHA) that underwent acidhydrolysis studied was found to be 8.9299 as shown Table 1, which is lower than the literaturevalues reported by Almeida and Szpoganics, (2015), Borges *et al*., (2005); Badr *et al*., (2012)and Fernandes *et al*,.(2009) of 9.73, 9.47 and 10.30. The difference between the obtained valuesand the reported values in this study might be probably as a result of acid hydrolysis of humicacid.

Table 1: PKa of (Hydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	log($\frac{nA}{1-nA}$)	pKa
8.50	5.30	6.29	0.99	0.3594	-0.2510	8.2490
8.72	5.35	6.37	1.02	0.3400	-0.2880	8.4320
9.00	5.40	6.46	1.06	0.3141	-0.3391	8.6609
9.22	5.45	6.55	1.10	0.2882	-0.3927	8.8273
9.51	5.50	6.66	1.16	0.2494	-0.4786	9.0314
9.73	5.55	6.78	1.23	0.2041	-0.5910	9.1390
10.00	5.60	6.90	1.30	0.1589	-0.7238	9.2762
10.23	5.65	7.05	1.40	0.0941	-0.9835	9.2465
10.49	5.70	7.10	1.40	0.0941	-0.9835	9.5065

Average pKa = 8.9299 ± 0.4186

Table 2: PKa of (Unhydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	Log($\frac{nA}{1-n}$)	pKa
8.50	5.30	5.81	0.51	0.6619	0.2919	8.7919
8.72	5.35	5.90	0.55	0.6357	0.2418	8.9618
9.00	5.40	6.00	0.60	0.6029	0.1813	9.1813
9.22	5.45	6.10	0.65	0.5701	0.1226	9.3426
9.51	5.50	6.20	0.70	0.5376	0.0654	9.5754
9.73	5.55	6.33	0.78	0.4851	-0.0259	9.7041
10.00	5.60	6.47	0.87	0.4262	-0.1291	9.8709
10.23	5.65	6.62	0.99	0.3609	-0.2481	9.9819
10.49	5.70	6.80	1.10	0.2759	-0.4690	10.0210

Average pKa = 9.4923± 0.4410

Metal-ligand stability constant (Log K)

The stabilityconstants require the accurate values of proton-ligand stability constants (Anil and Maroti, 2008). Metal titration curves crossed over ligand titration curve indicated the formation of complex upon proton release (Santosh, *et al.*, 2011). If the values of n- are within range 0.2-0.8 and 1.2-18 this indicates the formation of 1:1 and 1:2 complexes (Sayyed and Mazahar, 2012).

The metal (II)-humate stepwise stability constants (log k) at phenolic group (Tables 3-18)

Table 3: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n}{1-n}$)	$LogK_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

$LogK_1$ (Average value) = 2.4788± 0.2203

Table 4: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	Log($\frac{n-1}{2-n}$)	$LogK_2$
9.51	5.50	6.66	6.73	0.07	1.3509	1.70	-0.2671	1.4329
9.73	5.55	6.78	6.85	0.07	1.6383	1.51	0.2467	1.7567
10.00	5.60	6.90	6.98	0.08	2.1783	1.31	-0.2158	1.0942
10.23	5.65	7.05	7.13	0.08	4.1904	1.27		
10.49	5.70	7.10	7.19	0.09	4.6920			

$LogK_2$(Average value) = 1.4280 ± 0.3312

Table 5:Point-wise method,Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	Log($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430

$LogK_1$ **(Average value)** = 2.3059± 0.6153

Table 6:Point-wise method, Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
9.73	5.55	6.33	6.42	0.09	0.9000	1.69		
10.00	5.60	6.47	6.58	0.11	1.2578	1.44	-0.4592	0.9808
10.23	5.65	6.62	6.84	0.12	1.6137	1.26	-0.2010	1.4610
10.49	5.70	6.80	6.92	0.12	2.1052	1.03		

$LogK_2$ **(Average value)** = 1.2209± 0.3398

Table 7:Point-wise method,Pb (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n}{1-n}$)	$LogK_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.60	0.05	0.8333	1.96	0.6989	2.6589

$LogK_1$ (Average value) = 2.5832 ±0.1614

Table 8:Point-wise method,Pb-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n-1}{2-n}$)	$logK_2$
9.51	5.50	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.83	0.05	1.1702	1.44		
10.00	5.60	6.90	6.90	0.05	1.4864	1.22	-0.0237	1.1963
10.23	5.65	7.05	7.10	0.05	2.0190	1.09		
10.49	5.70	7.10	7.17	0.07	3.6492	1.00		

$LogK_2$(Average value) = 1.1963

Table 9:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log ($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.5477	2.3123
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	0.0272	2.2072
9.51	5.50	6.20	6.26	0.07	0.6417	1.89	0.2530	2.1430
9.73	5.55	6.40	6.40	0.07	0.7000	1.67	0.3680	2.0380

$LogK_1$ **(Average value)** = 2.2364 ± 0.1602

Table 10:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
10.00	5.60	6.47	6.55	0.08	1.9503	1.41		
10.23	5.65	6.62	6.72	0.11	1.4792	1.26	-0.0361	1.2239

$LogK_2$ **(Average value)** = 1.2239

Table 11:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n}{n-1}$)	$LogK_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4290	2.2110
8.72	5.35	6.37	6.39	0.02	0.2858	2.42	-0.3978	2.0222
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

$LogK_1$ (Average value)=2.1382**±**0.1046

Table 12:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	log($\frac{n-1}{2-n}$)	LogK$_2$
9.51	5.55	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.84	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.93	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.10		
10.49	5.70	7.10	7.18	0.07	3.6492	0.83		

LogK$_2$(Average value) = 1.5453 **±** 0.3450

Table 13:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	V$_3$-V$_2$	n	pL	Log($\frac{n}{n-1}$)	Log K$_1$
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.3477	2.3123
9.00	5.40	6.00	6.04	0.04	0.3236	2.38	-0.3202	2.0598
9.22	5.45	6.10	6.15	0.05	0.4297	2.17	-0.1230	2.0470
9.51	5.50	6.20	6.26	0.06	0.5500	1.89	0.0871	1.9771
9.73	5.55	6.33	6.40	0.07	0.7000	1.67	0.3680	2.0380

LogK$_1$ **(Average value)** = 2.1568 ± 0.2069

Table 14:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	V$_3$-V$_2$	n	pL	Log($\frac{n-1}{2-n}$)	Log K$_2$
10.00	5.60	6.47	6.55	0.08	0.9148	1.41		
10.23	5.65	6.62	6.71	0.09	1.2102	1.20	-0.5749	0.6251
10.49	5.70	6.80	6.92	0.09	1.5968	1.03	0.1703	1.2003

LogK$_2$ **(Average value)** = 0.9127± 0.4070

Table15:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	Log($\frac{n}{1-n}$)	LogK$_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4210	2.2190
8.72	5.35	6.37	6.40	0.03	0.4286	2.42	-0.1249	2.2951
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.96	0.3010	2.2610
9.51	5.55	6.66	6.70	0.04	0.7720	1.67	0.5297	2.1997

LogK$_1$ (Average value) = 2.2108± 0.0825

Table 16:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	Log($\frac{n-1}{2-n}$)	Log K$_2$
9.73	5.55	6.78	6.83	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.95	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.09		
10.49	5.70	7.10	7.16	0.06	3.1429	0.89		

LogK$_2$ **(Average value)** = 1.5453± 0.3450

Table 17:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	V$_3$-V$_2$	n	pL	Log($\frac{n}{n-1}$)	Log K$_1$
8.50	5.30	5.81	5.86	0.05	0.3717	2.88	-0.2280	2.6520
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.06	0.06	0.4853	2.38	-0.0255	2.3545
9.22	5.45	6.10	6.16	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430
9.73	5.55	6.33	6.41	0.08	0.8000	1.69	0.6020	2.2920

LogK$_1$ **(Average value)** = 2.2516± 0.5380

Table 18:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log$(\frac{n-1}{2-n})$	Log K_2
10.00	5.60	6.47	6.57	0.10	1.1434	1.43		
10.23	5.65	6.62	6.72	0.10	1.3448	1.23	-0.2788	0.9512
10.49	5.70	6.80	6.90	0.10	1.7742	1.03	0.5351	1.5651

LogK_2 **(Average value)** = 1.2581± 0.4340

Table 19: Stepwise and overall Stability constants of thehydrolysed and unhydrolysed divalent metal (II) complexes

Chelates	**LogK_1**	**LogK_2**	**Logβ**
[Cu (Hydrolysed PSHA-1)$_2$]	2.4788	1.4280	3.9068
[Pb (Hydrolysed PSHA-1)$_2$]	2.5832	1.1963	3.7795
[Cd (Hydrolysed PSHA-1)$_2$]	2.2108	1.5453	3.7561
[Mg (Hydrolysed PSHA-1)$_2$]	2.1382	1.5453	3.6835
[Cu (Unhydrolysed PSHA-1)$_2$]	2.3059	1.2209	3.5268
[Pb (Unhydrolysed PSHA-1)$_2$]	2.2364	1.2239	3.4603
[Cd (Unhydrolysed PSHA-1)$_2$]	2.2516	1.2581	3.5097
[Mg (Unydrolysed PSHA-1)$_2$]	2.1568	0.9127	3.0695

The results obtained (Table19) shows the stepwise and overall stability constants to be not high indicating low stability of the complexes, because the solubility of most metal ions in the basic pH range is minimal due to metal hydroxide precipitation (Karimi, 2017). In general, the stepwise stability constants (K_1 and K_2) follow the order $K_1 > K_2$ for the copper, lead, magnesium and cadmium complexes respectively. The steady decrease of the values with increasing number of ligands is in agreement with the prediction made by researchers (Na'aliya, 2013). The decrease could be attributed to the fact that as the number of the ligands (Humate ions) that enters the coordination zone increases the aqua molecules available for replacement by the ligands become less. Thus, the metal ions become less electron loving with progressive intake of the ligand and this results in the decrease in the values of the constants (Na'aliya, 2013). Also the stability of the complexes is influenced by the size and number of the chelate rings(Mackay and Mackay,2002).All the complexes form rings in their structure as humate, a bidentate ligand, bond the metal ions in the ratio 1:2 (Boguta and Sokolowska, 2016) forming chelate rings. The values of the overall stability constants (logβ) obtained for humate complexes are not high indicating low stability as the values are not high. LogK values for copper-humates (Table 3 to 6) obtained in this study are lower than those reported for the complexes of humic acids (Pandey *et al.*, 2015; Dinu, 2013; Kaschl *et al.*, 2010 and Gilbeto and Jorg, 2001). The values of LogK(Table 7 to 10) forlead-humates are lower than those reported for the lead in the literature (Dinu, 2013; Gilbeto and Jorg 2001). Log K values(Table 11 to 14) for magnesium-humates obtained in this study are close to those reported by (Pandey *et al.*, 2015). Log K values of cadmium-humates (Table 15 to 18) obtained in this work near to the one reported by (Dinu, 2013 and Pandey *et al.*, 2015).The difference between the reported values and the values obtained in this study might be probably as a result of acid hydrolysis of humic acid. The values of the overall stability constants (log β) of the copper humates complexes presented in Table 19 is high than that of other metal humate complexes, show relatively high stability of Cu-HA complexes, show the following order of stability: Cu >Pb> Cd > Mg; which are in close agreement to the findings of (Dinu, 2013 and Pandey *et al.*, 2015).The high stability of Cu-humate chelate could be attributed to the existence of coordinate covalent bond between the complexing agents and the Cu^{2+} ions. Since, Cu^{2+} being a metal of the transitional series with $3d^9$ electronic configurations can accept the electrons from the complexing agents. Similarly,the low stabilities of Pb,Cd and Mg - complexes could be explained by that Pb^{2+} with $6s^2$, Cd^{2+} with $4d^{10}$ and Mg^{2+} with $2p^6$ their electronic configuration has a completely filled d,p and s orbitals. Moreover, the stabilities of metal ions with hydrolysed humic acid from peat soil were higher than those with unhydrolysed humic acid from peat soil; which is ascribed to the high content of acidity in hydrolysed humic acid than unhydrolysed humic acid.

CONCLUSION

The values of logK for Cu(II) hydrolysed humic acid complex was higher followed by Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes as compared with metal(II) unhydrolysed humic acid complexes . This indicates acid hydrolysis of humic acid can enhance the complexation behavior of humic acid with metal (II) ions. However, the higher values of logβ for Cu(II), Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes indicates more stable stepwise complexes formed as compared with Cu(II), Pb(II), Cd(II) and Mg(II) unhydrolysed humic acid complexes.

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STABILITY CONSTANTS OF COMPLEXES OF METAL IONS WITH PEATSOIL HUMIC ACIDS UNDER NON-ACID-CONDITIONS

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ABSTRACT
Stability constants of complexes of four divalent metal ions viz. Cu^{2+}, Pb^{2+},Mg^{2+} and Cd^{2+} with humic acids (HA) were determined by potentiometric titration of humic acids with the corresponding salt of the divalent metals in aqueous media under non-acid-condition. The log K (logarithm of the stability constant) ranged from 1.0942 to 2.7471 for metal-humic acid complexes were determined using point-wise computational method. The order of stability constants were obtained as follows: Cu >Pb> Cd > Mg for metal -HA complexes respectively, indicating a higher degree of complexation with Cu metal ion.
Keywords: stability constant, humic acid, potentiometric titration, divalent metals, acid hydrolysis.

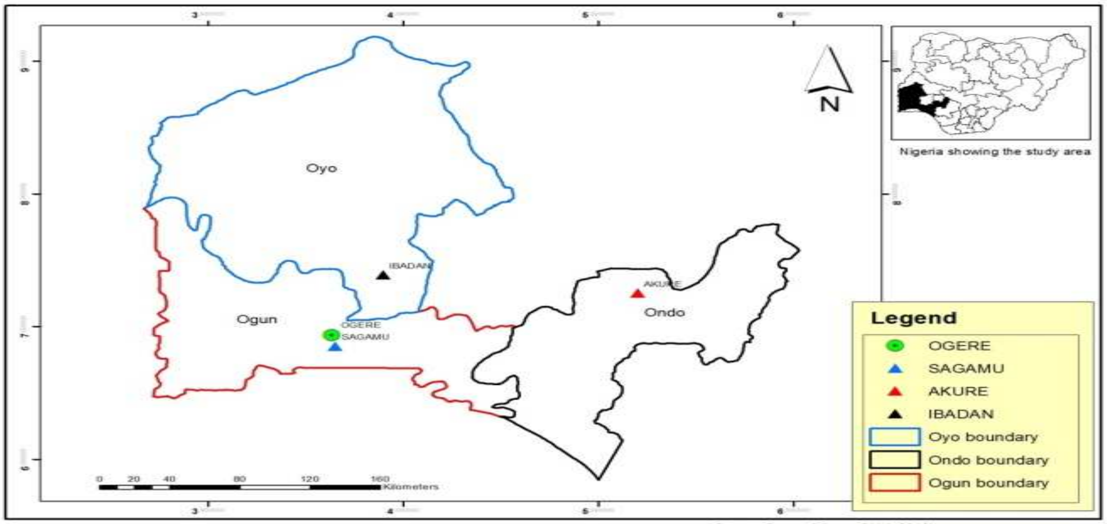
NTRODUCTION

The stability constant of a complex is the numerical expression of its stability and provides a quantitative measure of affinity of the metal ion to the complexing agent. An understanding of the relative stability of metal-complexes helps in predicting the behavior of metal ions in the soil (Ram and Raman, 1982). Extensive researches has been done to determine the stability constants of the complexes formed between humic acid (HA) with a number of metal ions. Ashok *et al*., (2000) reported that humic acid with hydroxyl, phenoxyl and carboxyl reactive groups can form coordination compound with metal ions at pH 3.5. The stability constants(Log K) for different metal-humic acid complexes indicated the following order of the stabilities of complexes formed between humic acid and metal ion, Cu >Fe >Pb> Ni > Co > Ca > Cd > Zn >Mn> Mg. Andelkovic *et al*., (2010) investigated the binding of Cd(II) to soil humic acid at pH 6.5 and in 0.1M KNO_3 ionic medium. The stability constant for binding indicating greater stability in the case when carboxyl groups are involved in complexation reaction. Kostic *et al*.,(2012) investigated the complexation of humic acid with certain heavy metal ions (Co(II), Ni(II),Cu(II), Zn(II), and Pb(II). The experiment was performed at 25°C, at pH 4.0 and ionic strength of 0.01M. Stability constant of complex between Pb(II) ions and humic acid is greater than stability constants of other investigated metal-humate complexes. Bogata and Sokolowska (2016) analyses the interaction between humic acids from different soils and Zn (II) ions at wide concentration ranges and at pH 5. Studies have showed significant impact of Zn concentration, pH and some properties of humic acids with zinc.But all of these studies were limited to acidic pH range. Therefore, the present study was carried out to determine and compare the stability constants of complexes of metal ions with hydrolysed peat soil humic acid and unhydrolysed peat soil humic under non-acid conditions.

MATERIALS AND METHODS

Analytical grade chemicals used includes hydrochloric acid (HCl), nitric acid (HNO_3), sodium hydroxide (NaOH), lead nitrate $Pb(NO_3)_2$, copper nitrate $Cu(NO_3)_2.3H_2O$, cadmium nitrate $Cd(NO_3)_2.4H_2O$, magnesium nitrate $Mg(NO_3)_2.6H_2O$, potassium nitrate (KNO_3), calcium chloride ($CaCl_2$), (sigma-Aldrich). Dowex 50WX8, (20-50 mesh) from Fluka.

Area of study



Source: Dept. of Geog. BUK (2016)

Figure 1: Map showing the sampling point at Sagamu Town, Ogun State.

Description of Sampling Area

Sagamu has geographical coordinates between 6°50′ north; 3° 38′ east is located in south western region of Nigeria. The region has tropical wet and dry climate with a lengthy wet season and relatively constant temperatures throughout the course of the year. Wet season runs from March to October, November to December forms the region dry season. The vegetation type of the region is savannah which is really grassland with small bushes and occasional big trees. Grassland soils have substantially higher organic matter content than forest soils (Novackova, 2011).

Sample Collection

The Peatsoil samples were collected from four different sampling points (0-10cm depth) in Sagamu into polyethylene bag with plastic spoons. Samples were taken to the laboratory, extraneous materials were removed; the samples were air-dried, crushed and ground to a fine powder in a mortar passed through a 0.20mm sieve. The samples were kept for analysis.

Isolation and purification of humic acid from peat soil sample

Peatsoil sample (100g) was mixed with 1000 cm^3 of 0.1M NaOH solution, shaken for 3hours and left to stand overnight. Dark-coloured supernatant was obtained and decanted from solid residue. The dark-coloured supernatant was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 6 hours. Yellowish brown supernatant and dark-brown precipitate were obtained. The yellowish brown supernatant was decanted followed by centrifuge and discarded. The dark-brown precipitate was mixed with 500$cm^3$of 0.1M NaOH solution followed by passing through dowex resin. The dark-brown solution was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 3 hours. The dark-brown precipitate was washed several times with deionized water. The supernatant was treated with $AgNO_3$ solution until no white precipitate observed. The humic acid was transferred to weighed crucible and dried at 60°C in an oven for 12 hours. The humic acid was cooled and dried in the desiccator, weighed and recorded. The obtained humic acid was dried again at 60°C for additional 6 hours cooled and dried in the desiccator, weighed and recorded constant weight was obtained (Baruah *et al*., 2015).

FT-IR analysis

FT-IR spectra of humic acid sample was analysed using Carry 630 FT-IR Agilent Technologies.

Unhydrolysed compost humic acid

The unhydrolysed humic acid was obtained after isolation and purification of compost humic acid and kept for investigation.

Acid hydrolysis of Peatsoil acid

Peatsoil humic acid sample (1g) was refluxed for 12 hours at (160°C) with 50cm^3 of 6M HCl. The mixture was allowed to cool, decanted, and centrifuged after hydrolysis. The insoluble residues were washed with distilled water via centrifugation several times, and the supernatant was treated with $AgNO_3$ solution until no white precipitate was observed. The residue was thoroughly dried over $CaCl_2$ in a desiccator at room temperature (Chefetz *et al*., 2002). Finally, the obtained hydrolysed humic acid was kept for investigation.

Potentiometric Titrations

Potentiometric measurements were carried out using a pH-meter Jenway (model 3510) with combine electrode, the sensitivity of the pH - meter is 0.01 units. The pH meter was switched on half an hour before starting the titration for initial warm up of the instrument. The instrument was calibrated with an aqueous standard buffer solution of pH 4.00 and 10.0 (borate buffer) prepared from a "Qualigens" buffer tablets.

The following sets of solutions were prepared in a 250cm^3 volumetric flask separately for pH metric titrations.

(i) 5 cm^3 0.1 M HCl + 40 cm^3 deionized water

(ii) 5 cm^3 0.1 M HCl + 39 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid

(iii) 5 cm^3 0.1 M HCl + 37 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid + 2 cm^3 0.01 M Cu(II)

The solutions were titrated against standardized 0.110MNaOH separately. The total volume of each mixture was adjusted to 50 cm^3 and the ionic strength of the solutions was maintained constant at by adding appropriate amount of stock solution of 1M KNO_3 (Gamal, 2015; Omar and Ali, 2015). A magnetic stirrer was used to achieve thorough mixing of the interacting solutions at 550 rpm. The same set of experimental conditions was applied for potentiometric titration of remaining samples.

Evaluation of pKa of Hydrolysed peat soil Humic Acids

The proton-ligand formation number $n_{\mathbf{A}}$ were calculated by Irving and Rossotti expression (Omar and Ali, 2015).

$$nA = Y - \frac{(V2-V1)(No-Eo)}{(Vo+V1)TcL} \text{ ....1}$$

Where: Y is number of dissociable proton, (V_2-V_1) is the measure of displacement of the ligand curve relative to acid curve, N^o and E^o are the resultant concentration of alkali solution, free acid solution, $T_{cL}{}^o$ is the total ligand concentration, V^o is the total volume of titration solution,V_1 is the volume of alkali added to acid solution,V_2 is the volume of alkali added to acid solution + ligand solution, acid dissociation constants (pKa - values) of ligand were calculated by algebraic method point wise calculation (Tables 1). The dissociation constants (pKa) were calculated according to the following relation:

$$\text{pKa} = \text{pH} + \log(\frac{nA}{1-nA}) \text{ ....2}$$

Where: pKa is the acid dissociation constant, $n_A$is the Proton-ligand formation number and pH is the pH-values (Omar and Ali, 2015).

Determination of metal-ligand stability constants (log K) of complexes

The potentiometric measurement for the determination of stability constant of a complex in solution is based on the fact that the redox potential of the couple $\frac{M^{+(m-n)}}{M^{+m}}$ is shifted significantly on complexation of the metal ion with the ligand. This method involves change in hydrogen ion concentration [H$^+$] due to the displacement or association of one or more protons taking place during complexation reaction. This change can be found out by titrating the solutions containing free acid, acid with ligand, and acid with ligand and metal ion, individually against a standard alkali solution at a constant ionic strength or temperature. Either ionic strength or temperature may be varied for different sets of solutions. In all the cases, the change in the pH of the solution is measured after each addition of a known amount of alkali to the reaction cell which contains the reaction mixture. The titration curves are then drawn by plotting the measured pH values against the corresponding volume of alkali added and the stability constants of the complexes are determined from the titration curves by employing pH-metric titration technique given by (Irving and Rossoti).

Metal-ligand stability constants (Log K) were determined by using the following relations:

$$\bar{n} = \frac{(V_3 - V_2)(E^0 + N^0)}{(V^0 + V_2)\bar{n}_A T_m^0} \text{ ....3}$$

and

$$PL = \log_{10}\{\frac{1 + \beta_n^H \frac{1}{[anti\ \log \text{pH}]^n}}{T_L^0 - \bar{n} T_m^0} X \frac{(V^0 + V_3)}{V^0}\} \text{ ....4}$$

Where $T_{L,}$ T^{o}, E°, and V^{o}havethe same significance as in equation (1) above, T_m denotes the total concentration of metal present in solution, V_3 is the volume of metal ions present in solution and β^H is the overall proton ligand stability constant. The metal-ligand stability constants (log K) were determined by employing point wise computational Method (eq. 5 and 6).

$$\text{LogK}_1 = \log\left(\frac{n}{1-n}\right) + \text{pL} \qquad \ldots\ldots\ldots\ldots.5$$

$$\text{LogK}_2 = \log\left(\frac{1-n}{2-n}\right) + \text{pL}\ldots\ldots\ldots\ldots\ldots\ldots..6$$

Where: Log K is the metal-ligand stability constant, pL is the Free ligand exponent function, **n** is the Average number of ligand attached with metal ion (Janrao*et al.*, 2014).The results obtained were analyzed by an ORIGIN 2016 program using titration data and then the proton-ligand stability constants (pKa) and Metal-ligand stability constant (LogK) calculated (Omar and Ali, 2015).

RESULTS AND DISCUSSION

Fourier transformed infrared (FT-IR) spectra of isolated humic acid from peat soils Figure 2 had distinct clear absorption bands indicating the presence of major humic acid structural elemental groups such as H bonded OH ($3680cm^{-1}$ peak), C=O of carbonyl ($1721cm^{-1}$ peak), functional groups of aliphatic components CH_2 ($2918cm^{-1}$ peak) and C-O stretching of polysaccharide ($1168cm^{-1}$ peak). The positions of the absorption bands of the spectra fell within typical major absorption bands of humic acid which is at frequencies 3680, 2918, 1721, 1168 cm^{-1}. The first peak centred in the vicinity of 3680 cm^{-1} region is attributed to phenol OH group bounded by intermolecular H bonds. The $2918cm^{-1}$ band usually has absorption maximum at 2918 cm^{-1} which is due to C–H stretching of alkane group (CH_2). The next major absorption band is 1721 cm^{-1}. This band has been commonly ascribed to C=O stretching of mainly carboxyl group (COOH) with trace amount of ketones. The last peak was observed at 1168 cm^{-1} due to C–O stretching of polysaccharides and this peak appeared also in the spectra of humic acid from peat soil. The FTIR spectra of the isolated humic acid contained all major characteristic absorption peaks of humic acid. These absorption peaks indicated the presence of the major structural elements of humic acid namely H bonded OH, C=C of aromatic ring, C=O of carbonyl group (both carboxyl and ketonic), CH_2 group. This strongly supports the presence of humic acid.

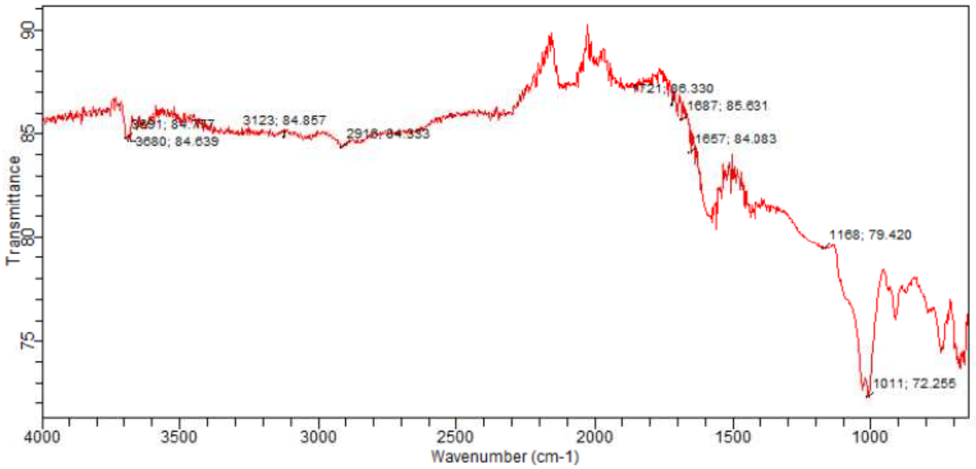


Fig. 2 : FT-IR spectraof peatsoilhumic acid (PSHA)

Evaluation of acid dissociation constant (pka) of acid hydrolysed peat soil humicacid at phenolic group

The value of the dissociation constant of the peat soil humic acid (PSHA) that underwent acidhydrolysis studied was found to be 8.9299 as shown Table 1, which is lower than the literaturevalues reported by Almeida and Szpoganics, (2015), Borges *et al.*, (2005); Badr *et al.*, (2012)and Fernandes *et al*,.(2009) of 9.73, 9.47 and 10.30. The difference between the obtained valuesand the reported values in this study might be probably as a result of acid hydrolysis of humicacid.

Table 1: PKa of (Hydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	$\log(\frac{nA}{1-nA})$	pKa
8.50	5.30	6.29	0.99	0.3594	-0.2510	8.2490
8.72	5.35	6.37	1.02	0.3400	-0.2880	8.4320
9.00	5.40	6.46	1.06	0.3141	-0.3391	8.6609
9.22	5.45	6.55	1.10	0.2882	-0.3927	8.8273
9.51	5.50	6.66	1.16	0.2494	-0.4786	9.0314
9.73	5.55	6.78	1.23	0.2041	-0.5910	9.1390
10.00	5.60	6.90	1.30	0.1589	-0.7238	9.2762
10.23	5.65	7.05	1.40	0.0941	-0.9835	9.2465
10.49	5.70	7.10	1.40	0.0941	-0.9835	9.5065

Average pKa = 8.9299 ± 0.4186

Table 2: PKa of (Unhydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	$\mathrm{Log}(\frac{nA}{1-n})$	pKa
8.50	5.30	5.81	0.51	0.6619	0.2919	8.7919
8.72	5.35	5.90	0.55	0.6357	0.2418	8.9618
9.00	5.40	6.00	0.60	0.6029	0.1813	9.1813
9.22	5.45	6.10	0.65	0.5701	0.1226	9.3426
9.51	5.50	6.20	0.70	0.5376	0.0654	9.5754
9.73	5.55	6.33	0.78	0.4851	-0.0259	9.7041
10.00	5.60	6.47	0.87	0.4262	-0.1291	9.8709
10.23	5.65	6.62	0.99	0.3609	-0.2481	9.9819
10.49	5.70	6.80	1.10	0.2759	-0.4690	10.0210

Average pKa = 9.4923± 0.4410

Metal-ligand stability constant (Log K)

The stabilityconstants require the accurate values of proton-ligand stability constants (Anil and Maroti, 2008). Metal titration curves crossed over ligand titration curve indicated the formation of complex upon proton release (Santosh, *et al.*, 2011). If the values of n- are within range 0.2-0.8 and 1.2-18 this indicates the formation of 1:1 and 1:2 complexes (Sayyed and Mazahar, 2012).

The metal (II)-humate stepwise stability constants (log k) at phenolic group (Tables 3-18)

Table 3: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$\log(\frac{n}{1-n})$	$\mathrm{Log}K_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

LogK_1 (Average value) = 2.4788± 0.2203

Table 4: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$\mathrm{Log}(\frac{n-1}{2-n})$	$\mathrm{Log}K_2$
9.51	5.50	6.66	6.73	0.07	1.3509	1.70	-0.2671	1.4329
9.73	5.55	6.78	6.85	0.07	1.6383	1.51	0.2467	1.7567
10.00	5.60	6.90	6.98	0.08	2.1783	1.31	-0.2158	1.0942
10.23	5.65	7.05	7.13	0.08	4.1904	1.27		
10.49	5.70	7.10	7.19	0.09	4.6920			

LogK_2(Average value) = 1.4280 ± 0.3312

Table 5:Point-wise method,Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	$\text{Log}(\frac{n}{n-1})$	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430

LogK_1 **(Average value)** = 2.3059± 0.6153

Table 6:Point-wise method, Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$V_3\text{-}V_2$	n	pL	$\text{Log}(\frac{n-1}{2-n})$	Log K_2
9.73	5.55	6.33	6.42	0.09	0.9000	1.69		
10.00	5.60	6.47	6.58	0.11	1.2578	1.44	-0.4592	0.9808
10.23	5.65	6.62	6.84	0.12	1.6137	1.26	-0.2010	1.4610
10.49	5.70	6.80	6.92	0.12	2.1052	1.03		

LogK_2 **(Average value)** = 1.2209± 0.3398

Table 7:Point-wise method,Pb (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	$\log(\frac{n}{1-n})$	LogK_1
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.60	0.05	0.8333	1.96	0.6989	2.6589

LogK_1 (Average value) = 2.5832 ±0.1614

Table 8:Point-wise method,Pb-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	$\log(\frac{n-1}{2-n})$	$\log K_2$
9.51	5.50	6.66	6.71	0.05	0.9650	1.67	-0.0237	1.1963
9.73	5.55	6.78	6.83	0.05	1.1702	1.44		
10.00	5.60	6.90	6.90	0.05	1.4864	1.22		
10.23	5.65	7.05	7.10	0.05	2.0190	1.09		
10.49	5.70	7.10	7.17	0.07	3.6492	1.00		

LogK_2(Average value) = 1.1963

Table 9:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$V_3\text{-}V_2$	n	pL	Log $(\frac{n}{n-1})$	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.5477	2.3123
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	0.0272	2.2072
9.51	5.50	6.20	6.26	0.07	0.6417	1.89	0.2530	2.1430
9.73	5.55	6.40	6.40	0.07	0.7000	1.67	0.3680	2.0380

LogK_1 **(Average value)** = 2.2364 ± 0.1602

Table 10:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$V_3\text{-}V_2$	n	pL	$\text{Log}(\frac{n-1}{2-n})$	Log K_2
10.00	5.60	6.47	6.55	0.08	1.9503	1.41		
10.23	5.65	6.62	6.72	0.11	1.4792	1.26	-0.0361	1.2239

LogK_2 **(Average value)** = 1.2239

Table 11:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	$\log(\frac{n}{n-1})$	LogK_1
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4290	2.2110
8.72	5.35	6.37	6.39	0.02	0.2858	2.42	-0.3978	2.0222
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

LogK_1 (Average value)=2.1382**±**0.1046

Table 12:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$\log(\frac{n-1}{2-n})$	$LogK_2$
9.51	5.55	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.84	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.93	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.10		
10.49	5.70	7.10	7.18	0.07	3.6492	0.83		

$LogK_2$(Average value) = 1.5453 **±** 0.3450

Table 13:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$Log(\frac{n}{n-1})$	$Log\ K_1$
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.3477	2.3123
9.00	5.40	6.00	6.04	0.04	0.3236	2.38	-0.3202	2.0598
9.22	5.45	6.10	6.15	0.05	0.4297	2.17	-0.1230	2.0470
9.51	5.50	6.20	6.26	0.06	0.5500	1.89	0.0871	1.9771
9.73	5.55	6.33	6.40	0.07	0.7000	1.67	0.3680	2.0380

$LogK_1$ **(Average value)** = 2.1568 ± 0.2069

Table 14:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$Log(\frac{n-1}{2-n})$	$Log\ K_2$
10.00	5.60	6.47	6.55	0.08	0.9148	1.41		
10.23	5.65	6.62	6.71	0.09	1.2102	1.20	-0.5749	0.6251
10.49	5.70	6.80	6.92	0.09	1.5968	1.03	0.1703	1.2003

$LogK_2$ **(Average value)** = 0.9127± 0.4070

Table15:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$Log(\frac{n}{1-n})$	$LogK_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4210	2.2190
8.72	5.35	6.37	6.40	0.03	0.4286	2.42	-0.1249	2.2951
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.96	0.3010	2.2610
9.51	5.55	6.66	6.70	0.04	0.7720	1.67	0.5297	2.1997

$LogK_1$ (Average value) = 2.2108± 0.0825

Table 16:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$Log(\frac{n-1}{2-n})$	$Log\ K_2$
9.73	5.55	6.78	6.83	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.95	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.09		
10.49	5.70	7.10	7.16	0.06	3.1429	0.89		

$LogK_2$ **(Average value)** = 1.5453± 0.3450

Table 17:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$Log(\frac{n}{n-1})$	$Log\ K_1$
8.50	5.30	5.81	5.86	0.05	0.3717	2.88	-0.2280	2.6520
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.06	0.06	0.4853	2.38	-0.0255	2.3545
9.22	5.45	6.10	6.16	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430
9.73	5.55	6.33	6.41	0.08	0.8000	1.69	0.6020	2.2920

$LogK_1$ **(Average value)** = 2.2516± 0.5380

Table 18:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$\text{Log}(\frac{n-1}{2-n})$	Log K_2
10.00	5.60	6.47	6.57	0.10	1.1434	1.43		
10.23	5.65	6.62	6.72	0.10	1.3448	1.23	-0.2788	0.9512
10.49	5.70	6.80	6.90	0.10	1.7742	1.03	0.5351	1.5651

LogK_2 **(Average value)** = 1.2581± 0.4340

Table 19: Stepwise and overall Stability constants of thehydrolysed and unhydrolysed divalent metal (II) complexes

Chelates	**LogK$_1$**	**LogK$_2$**	**Logβ**
[Cu (Hydrolysed PSHA-1)$_2$]	2.4788	1.4280	3.9068
[Pb (Hydrolysed PSHA-1)$_2$]	2.5832	1.1963	3.7795
[Cd (Hydrolysed PSHA-1)$_2$]	2.2108	1.5453	3.7561
[Mg (Hydrolysed PSHA-1)$_2$]	2.1382	1.5453	3.6835
[Cu (Unhydrolysed PSHA-1)$_2$]	2.3059	1.2209	3.5268
[Pb (Unhydrolysed PSHA-1)$_2$]	2.2364	1.2239	3.4603
[Cd (Unhydrolysed PSHA-1)$_2$]	2.2516	1.2581	3.5097
[Mg (Unydrolysed PSHA-1)$_2$]	2.1568	0.9127	3.0695

The results obtained (Table19) shows the stepwise and overall stability constants to be not high indicating low stability of the complexes, because the solubility of most metal ions in the basic pH range is minimal due to metal hydroxide precipitation (Karimi, 2017). In general, the stepwise stability constants (K_1 and K_2) follow the order K_1> K_2 for the copper, lead, magnesium and cadmium complexes respectively. The steady decrease of the values with increasing number of ligands is in agreement with the prediction made by researchers (Na'aliya, 2013). The decrease could be attributed to the fact that as the number of the ligands (Humate ions) that enters the coordination zone increases the aqua molecules available for replacement by the ligands become less. Thus, the metal ions become less electron loving with progressive intake of the ligand and this results in the decrease in the values of the constants (Na'aliya, 2013). Also the stability of the complexes is influenced by the size and number of the chelate rings(Mackay and Mackay,2002).All the complexes form rings in their structure as humate, a bidentate ligand, bond the metal ions in the ratio 1:2 (Boguta and Sokolowska, 2016) forming chelate rings. The values of the overall stability constants (logβ) obtained for humate complexes are not high indicating low stability as the values are not high. LogK values for copper-humates (Table 3 to 6) obtained in this study are lower than those reported for the complexes of humic acids (Pandey *et al.*, 2015; Dinu, 2013; Kaschl *et al.*, 2010 and Gilbeto and Jorg, 2001). The values of LogK(Table 7 to 10) forlead-humates are lower than those reported for the lead in the literature (Dinu, 2013; Gilbeto and Jorg 2001). Log K values(Table 11 to 14) for magnesium-humates obtained in this study are close to those reported by (Pandey *et al.*, 2015). Log K values of cadmium-humates (Table 15 to 18) obtained in this work near to the one reported by (Dinu, 2013 and Pandey *et al.*, 2015).The difference between the reported values and the values obtained in this study might be probably as a result of acid hydrolysis of humic acid. The values of the overall stability constants (log β) of the copper humates complexes presented in Table 19 is high than that of other metal humate complexes, show relatively high stability of Cu-HA complexes, show the following order of stability: Cu >Pb> Cd > Mg; which are in close agreement to the findings of (Dinu, 2013 and Pandey *et al.*, 2015).The high stability of Cu-humate chelate could be attributed to the existence of coordinate covalent bond between the complexing agents and the Cu^{2+} ions. Since, Cu^{2+} being a metal of the transitional series with $3d^9$ electronic configurations can accept the electrons from the complexing agents. Similarly,the low stabilities of Pb,Cd and Mg -complexes could be explained by that Pb^{2+} with $6s^2$, Cd^{2+} with $4d^{10}$ and Mg^{2+} with $2p^6$ their electronic configuration has a completely filled d,p and s orbitals. Moreover, the stabilities of metal ions with hydrolysed humic acid from peat soil were higher than those with unhydrolysed humic acid from peat soil; which is ascribed to the high content of acidity in hydrolysed humic acid than unhydrolysed humic acid.

CONCLUSION

The values of logK for Cu(II) hydrolysed humic acid complex was higher followed by Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes as compared with metal(II) unhydrolysed humic acid complexes . This indicates acid hydrolysis of humic acid can enhance the complexation behavior of humic acid with metal (II) ions. However, the higher values of logβ for Cu(II), Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes indicates more stable stepwise complexes formed as compared with Cu(II), Pb(II), Cd(II) and Mg(II) unhydrolysed humic acid complexes.

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STABILITY CONSTANTS OF COMPLEXES OF METAL IONS WITH PEATSOIL HUMIC ACIDS UNDER NON-ACID-CONDITIONS

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ABSTRACT

Stability constants of complexes of four divalent metal ions viz. Cu^{2+}, Pb^{2+},Mg^{2+} and Cd^{2+} with humic acids (HA) were determined by potentiometric titration of humic acids with the corresponding salt of the divalent metals in aqueous media under non-acid-condition. The log K (logarithm of the stability constant) ranged from 1.0942 to 2.7471 for metal-humic acid complexes were determined using point-wise computational method. The order of stability constants were obtained as follows: Cu >Pb> Cd > Mg for metal -HA complexes respectively, indicating a higher degree of complexation with Cu metal ion.

Keywords: stability constant, humic acid, potentiometric titration, divalent metals, acid hydrolysis.

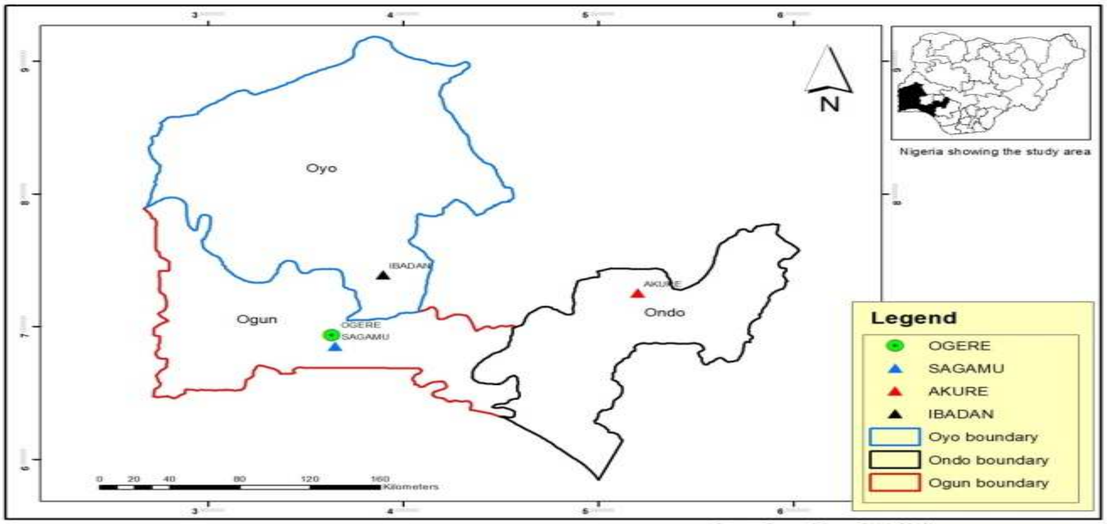
NTRODUCTION

The stability constant of a complex is the numerical expression of its stability and provides a quantitative measure of affinity of the metal ion to the complexing agent. An understanding of the relative stability of metal-complexes helps in predicting the behavior of metal ions in the soil (Ram and Raman, 1982). Extensive researches has been done to determine the stability constants of the complexes formed between humic acid (HA) with a number of metal ions. Ashok *et al*., (2000) reported that humic acid with hydroxyl, phenoxyl and carboxyl reactive groups can form coordination compound with metal ions at pH 3.5. The stability constants(Log K) for different metal-humic acid complexes indicated the following order of the stabilities of complexes formed between humic acid and metal ion, Cu >Fe >Pb> Ni > Co > Ca > Cd > Zn >Mn> Mg. Andelkovic *et al*., (2010) investigated the binding of Cd(II) to soil humic acid at pH 6.5 and in 0.1M KNO_3 ionic medium. The stability constant for binding indicating greater stability in the case when carboxyl groups are involved in complexation reaction. Kostic *et al*.,(2012) investigated the complexation of humic acid with certain heavy metal ions (Co(II), Ni(II),Cu(II), Zn(II), and Pb(II). The experiment was performed at 25°C, at pH 4.0 and ionic strength of 0.01M. Stability constant of complex between Pb(II) ions and humic acid is greater than stability constants of other investigated metal-humate complexes. Bogata and Sokolowska (2016) analyses the interaction between humic acids from different soils and Zn (II) ions at wide concentration ranges and at pH 5. Studies have showed significant impact of Zn concentration, pH and some properties of humic acids with zinc.But all of these studies were limited to acidic pH range. Therefore, the present study was carried out to determine and compare the stability constants of complexes of metal ions with hydrolysed peat soil humic acid and unhydrolysed peat soil humic under non-acid conditions.

MATERIALS AND METHODS

Analytical grade chemicals used includes hydrochloric acid (HCl), nitric acid (HNO_3), sodium hydroxide (NaOH), lead nitrate $Pb(NO_3)_2$, copper nitrate $Cu(NO_3)_2.3H_2O$, cadmium nitrate $Cd(NO_3)_2.4H_2O$, magnesium nitrate $Mg(NO_3)_2.6H_2O$, potassium nitrate (KNO_3), calcium chloride ($CaCl_2$), (sigma-Aldrich). Dowex 50WX8, (20-50 mesh) from Fluka.

Area of study



Source: Dept. of Geog. BUK (2016)

Figure 1: Map showing the sampling point at Sagamu Town, Ogun State.

Description of Sampling Area

Sagamu has geographical coordinates between 6°50′ north; 3° 38′ east is located in south western region of Nigeria. The region has tropical wet and dry climate with a lengthy wet season and relatively constant temperatures throughout the course of the year. Wet season runs from March to October, November to December forms the region dry season. The vegetation type of the region is savannah which is really grassland with small bushes and occasional big trees. Grassland soils have substantially higher organic matter content than forest soils (Novackova, 2011).

Sample Collection

The Peatsoil samples were collected from four different sampling points (0-10cm depth) in Sagamu into polyethylene bag with plastic spoons. Samples were taken to the laboratory, extraneous materials were removed; the samples were air-dried, crushed and ground to a fine powder in a mortar passed through a 0.20mm sieve. The samples were kept for analysis.

Isolation and purification of humic acid from peat soil sample

Peatsoil sample (100g) was mixed with 1000 cm^3 of 0.1M NaOH solution, shaken for 3hours and left to stand overnight. Dark-coloured supernatant was obtained and decanted from solid residue. The dark-coloured supernatant was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 6 hours. Yellowish brown supernatant and dark-brown precipitate were obtained. The yellowish brown supernatant was decanted followed by centrifuge and discarded. The dark-brown precipitate was mixed with $500cm^3$of 0.1M NaOH solution followed by passing through dowex resin. The dark-brown solution was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 3 hours. The dark-brown precipitate was washed several times with deionized water. The supernatant was treated with $AgNO_3$ solution until no white precipitate observed. The humic acid was transferred to weighed crucible and dried at 60°C in an oven for 12 hours. The humic acid was cooled and dried in the desiccator, weighed and recorded. The obtained humic acid was dried again at 60°C for additional 6 hours cooled and dried in the desiccator, weighed and recorded constant weight was obtained (Baruah *et al*., 2015).

FT-IR analysis

FT-IR spectra of humic acid sample was analysed using Carry 630 FT-IR Agilent Technologies.

Unhydrolysed compost humic acid

The unhydrolysed humic acid was obtained after isolation and purification of compost humic acid and kept for investigation.

Acid hydrolysis of Peatsoil acid

Peatsoil humic acid sample (1g) was refluxed for 12 hours at (160°C) with $50cm^3$ of 6M HCl. The mixture was allowed to cool, decanted, and centrifuged after hydrolysis. The insoluble residues were washed with distilled water via centrifugation several times, and the supernatant was treated with $AgNO_3$ solution until no white precipitate was observed. The residue was thoroughly dried over $CaCl_2$ in a desiccator at room temperature (Chefetz *et al*., 2002). Finally, the obtained hydrolysed humic acid was kept for investigation.

Potentiometric Titrations

Potentiometric measurements were carried out using a pH-meter Jenway (model 3510) with combine electrode, the sensitivity of the pH -meter is 0.01 units. The pH meter was switched on half an hour before starting the titration for initial warm up of the instrument. The instrument was calibrated with an aqueous standard buffer solution of pH 4.00 and 10.0 (borate buffer) prepared from a "Qualigens" buffer tablets.

The following sets of solutions were prepared in a 250cm^3 volumetric flask separately for pH metric titrations.

(i) 5 cm^3 0.1 M HCl + 40 cm^3 deionized water
(ii) 5 cm^3 0.1 M HCl + 39 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid
(iii) 5 cm^3 0.1 M HCl + 37 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid + 2 cm^3 0.01 M Cu(II)

The solutions were titrated against standardized 0.110MNaOH separately. The total volume of each mixture was adjusted to 50 cm^3 and the ionic strength of the solutions was maintained constant at by adding appropriate amount of stock solution of 1M KNO$_3$ (Gamal, 2015; Omar and Ali, 2015). A magnetic stirrer was used to achieve thorough mixing of the interacting solutions at 550 rpm. The same set of experimental conditions was applied for potentiometric titration of remaining samples.

Evaluation of pKa of Hydrolysed peat soil Humic Acids

The proton-ligand formation number n$_{\mathbf{A}}$ were calculated by Irving and Rossotti expression (Omar and Ali, 2015).

$$nA = Y- \frac{(V2-V1)(No-Eo)}{(Vo+V1)TcL} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots1$$

Where: Y is number of dissociable proton, (V_2-V_1) is the measure of displacement of the ligand curve relative to acid curve, N^o and E^o are the resultant concentration of alkali solution, free acid solution, $T_{cL}{}^o$ is the total ligand concentration, V^o is the total volume of titration solution,V_1 is the volume of alkali added to acid solution,V_2 is the volume of alkali added to acid solution + ligand solution, acid dissociation constants (pKa - values) of ligand were calculated by algebraic method point wise calculation (Tables 1). The dissociation constants (pKa) were calculated according to the following relation:

$$pKa = pH + \log(\frac{nA}{1-nA}) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots2$$

Where: pKa is the acid dissociation constant, $n_A$is the Proton-ligand formation number and pH is the pH-values (Omar and Ali, 2015).

Determination of metal-ligand stability constants (log K) of complexes

The potentiometric measurement for the determination of stability constant of a complex in solution is based on the fact that the redox potential of the couple $\frac{M^{+(m-n)}}{M^{+m}}$ is shifted significantly on complexation of the metal ion with the ligand. This method involves change in hydrogen ion concentration [H$^+$] due to the displacement or association of one or more protons taking place during complexation reaction. This change can be found out by titrating the solutions containing free acid, acid with ligand, and acid with ligand and metal ion, individually against a standard alkali solution at a constant ionic strength or temperature. Either ionic strength or temperature may be varied for different sets of solutions. In all the cases, the change in the pH of the solution is measured after each addition of a known amount of alkali to the reaction cell which contains the reaction mixture. The titration curves are then drawn by plotting the measured pH values against the corresponding volume of alkali added and the stability constants of the complexes are determined from the titration curves by employing pH-metric titration technique given by (Irving and Rossoti).

Metal-ligand stability constants (Log K) were determined by using the following relations:

$$\bar{n} = \frac{(V_3 - V_2)(E^0 + N^0)}{(V^0 + V_2)\bar{n}_A T_m^0} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots3$$

and

$$PL = \log_{10}\{\frac{1 + \beta_n^H \frac{1}{[anti\ \log pH]^n}}{T_L^0 - \bar{n}T_m^0} X \frac{(V^0 + V_3)}{V^0}\} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots4$$

Where $T_{L,}$ T^{o}, E°, and V^{o}havethe same significance as in equation (1) above, T_m denotes the total concentration of metal present in solution, V_3 is the volume of metal ions present in solution and β^H is the overall proton ligand stability constant. The metal-ligand stability constants (log K) were determined by employing point wise computational Method (eq. 5 and 6).

$$\text{Log}K_1 = \log\left(\frac{n}{1-n}\right) + pL \qquad \ldots\ldots\ldots\ldots.5$$

$$\text{Log}K_2 = \log\left(\frac{1-n}{2-n}\right) + pL\ldots\ldots\ldots\ldots\ldots\ldots\ldots.6$$

Where: Log K is the metal-ligand stability constant, pL is the Free ligand exponent function, **n** is the Average number of ligand attached with metal ion (Janrao*et al.*, 2014).The results obtained were analyzed by an ORIGIN 2016 program using titration data and then the proton-ligand stability constants (pKa) and Metal-ligand stability constant (LogK) calculated (Omar and Ali, 2015).

RESULTS AND DISCUSSION

Fourier transformed infrared (FT-IR) spectra of isolated humic acid from peat soils Figure 2 had distinct clear absorption bands indicating the presence of major humic acid structural elemental groups such as H bonded OH ($3680cm^{-1}$ peak), C=O of carbonyl ($1721cm^{-1}$ peak), functional groups of aliphatic components CH_2 ($2918cm^{-1}$ peak) and C-O stretching of polysaccharide ($1168cm^{-1}$ peak). The positions of the absorption bands of the spectra fell within typical major absorption bands of humic acid which is at frequencies 3680, 2918, 1721, 1168 cm^{-1}. The first peak centred in the vicinity of 3680 cm^{-1} region is attributed to phenol OH group bounded by intermolecular H bonds. The $2918cm^{-1}$ band usually has absorption maximum at 2918 cm^{-1} which is due to C–H stretching of alkane group (CH_2). The next major absorption band is 1721 cm^{-1}. This band has been commonly ascribed to C=O stretching of mainly carboxyl group (COOH) with trace amount of ketones. The last peak was observed at 1168 cm^{-1} due to C–O stretching of polysaccharides and this peak appeared also in the spectra of humic acid from peat soil. The FTIR spectra of the isolated humic acid contained all major characteristic absorption peaks of humic acid. These absorption peaks indicated the presence of the major structural elements of humic acid namely H bonded OH, C=C of aromatic ring, C=O of carbonyl group (both carboxyl and ketonic), CH_2 group. This strongly supports the presence of humic acid.

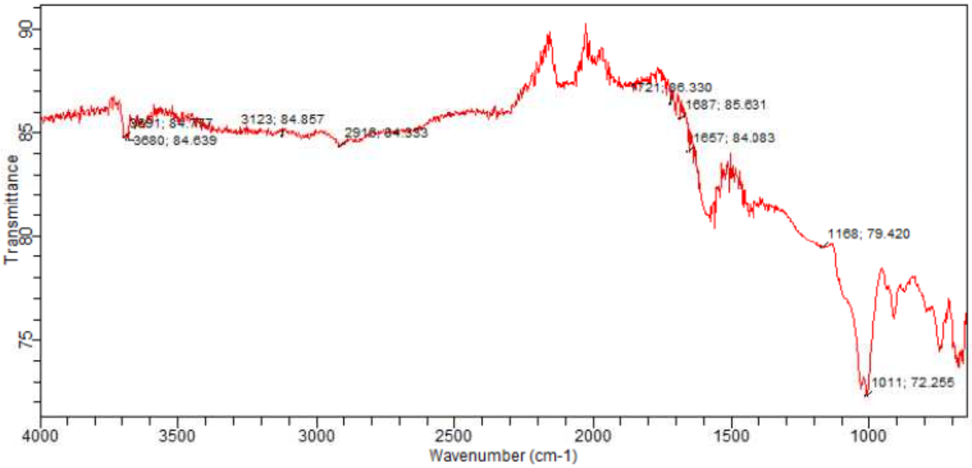


Fig. 2 : FT-IR spectraof peatsoilhumic acid (PSHA)

Evaluation of acid dissociation constant (pka) of acid hydrolysed peat soil humicacid at phenolic group

The value of the dissociation constant of the peat soil humic acid (PSHA) that underwent acidhydrolysis studied was found to be 8.9299 as shown Table 1, which is lower than the literaturevalues reported by Almeida and Szpoganics, (2015), Borges *et al.*, (2005); Badr *et al.*, (2012)and Fernandes *et al*,.(2009) of 9.73, 9.47 and 10.30. The difference between the obtained valuesand the reported values in this study might be probably as a result of acid hydrolysis of humicacid.

Table 1: PKa of (Hydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	$\log(\frac{nA}{1-nA})$	pKa
8.50	5.30	6.29	0.99	0.3594	-0.2510	8.2490
8.72	5.35	6.37	1.02	0.3400	-0.2880	8.4320
9.00	5.40	6.46	1.06	0.3141	-0.3391	8.6609
9.22	5.45	6.55	1.10	0.2882	-0.3927	8.8273
9.51	5.50	6.66	1.16	0.2494	-0.4786	9.0314
9.73	5.55	6.78	1.23	0.2041	-0.5910	9.1390
10.00	5.60	6.90	1.30	0.1589	-0.7238	9.2762
10.23	5.65	7.05	1.40	0.0941	-0.9835	9.2465
10.49	5.70	7.10	1.40	0.0941	-0.9835	9.5065

Average pKa = 8.9299 ± 0.4186

Table 2: PKa of (Unhydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	$\text{Log}(\frac{nA}{1-n})$	pKa
8.50	5.30	5.81	0.51	0.6619	0.2919	8.7919
8.72	5.35	5.90	0.55	0.6357	0.2418	8.9618
9.00	5.40	6.00	0.60	0.6029	0.1813	9.1813
9.22	5.45	6.10	0.65	0.5701	0.1226	9.3426
9.51	5.50	6.20	0.70	0.5376	0.0654	9.5754
9.73	5.55	6.33	0.78	0.4851	-0.0259	9.7041
10.00	5.60	6.47	0.87	0.4262	-0.1291	9.8709
10.23	5.65	6.62	0.99	0.3609	-0.2481	9.9819
10.49	5.70	6.80	1.10	0.2759	-0.4690	10.0210

Average pKa = 9.4923± 0.4410

Metal-ligand stability constant (Log K)

The stabilityconstants require the accurate values of proton-ligand stability constants (Anil and Maroti, 2008). Metal titration curves crossed over ligand titration curve indicated the formation of complex upon proton release (Santosh, *et al.*, 2011). If the values of n- are within range 0.2-0.8 and 1.2-18 this indicates the formation of 1:1 and 1:2 complexes (Sayyed and Mazahar, 2012).

The metal (II)-humate stepwise stability constants (log k) at phenolic group (Tables 3-18)

Table 3: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$\log(\frac{n}{1-n})$	LogK_1
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

LogK_1 (Average value) = 2.4788± 0.2203

Table 4: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$\text{Log}(\frac{n-1}{2-n})$	LogK_2
9.51	5.50	6.66	6.73	0.07	1.3509	1.70	-0.2671	1.4329
9.73	5.55	6.78	6.85	0.07	1.6383	1.51	0.2467	1.7567
10.00	5.60	6.90	6.98	0.08	2.1783	1.31	-0.2158	1.0942
10.23	5.65	7.05	7.13	0.08	4.1904	1.27		
10.49	5.70	7.10	7.19	0.09	4.6920			

LogK_2(Average value) = 1.4280 ± 0.3312

Table 5:Point-wise method,Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	Log($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430

$LogK_1$ **(Average value)** = 2.3059± 0.6153

Table 6:Point-wise method, Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
9.73	5.55	6.33	6.42	0.09	0.9000	1.69		
10.00	5.60	6.47	6.58	0.11	1.2578	1.44	-0.4592	0.9808
10.23	5.65	6.62	6.84	0.12	1.6137	1.26	-0.2010	1.4610
10.49	5.70	6.80	6.92	0.12	2.1052	1.03		

$LogK_2$ **(Average value)** = 1.2209± 0.3398

Table 7:Point-wise method,Pb (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n}{1-n}$)	$LogK_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.60	0.05	0.8333	1.96	0.6989	2.6589

$\mathbf{LogK_1}$ **(Average value)** = 2.5832 ±0.1614

Table 8:Point-wise method,Pb-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n-1}{2-n}$)	$logK_2$
9.51	5.50	6.66	6.71	0.05	0.9650	1.67	-0.0237	1.1963
9.73	5.55	6.78	6.83	0.05	1.1702	1.44		
10.00	5.60	6.90	6.90	0.05	1.4864	1.22		
10.23	5.65	7.05	7.10	0.05	2.0190	1.09		
10.49	5.70	7.10	7.17	0.07	3.6492	1.00		

$\mathbf{LogK_2}$**(Average value)** = 1.1963

Table 9:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log ($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.5477	2.3123
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	0.0272	2.2072
9.51	5.50	6.20	6.26	0.07	0.6417	1.89	0.2530	2.1430
9.73	5.55	6.40	6.40	0.07	0.7000	1.67	0.3680	2.0380

$LogK_1$ **(Average value)** = 2.2364 ± 0.1602

Table 10:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
10.00	5.60	6.47	6.55	0.08	1.9503	1.41		
10.23	5.65	6.62	6.72	0.11	1.4792	1.26	-0.0361	1.2239

$LogK_2$ **(Average value)** = 1.2239

Table 11:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n}{n-1}$)	$LogK_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4290	2.2110
8.72	5.35	6.37	6.39	0.02	0.2858	2.42	-0.3978	2.0222
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

$\mathbf{LogK_1}$ **(Average value)=**2.1382**±**0.1046

Table 12:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n-1}{2-n}$)	$LogK_2$
9.51	5.55	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.84	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.93	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.10		
10.49	5.70	7.10	7.18	0.07	3.6492	0.83		

$LogK_2$(Average value) = 1.5453 **±** 0.3450

Table 13:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.3477	2.3123
9.00	5.40	6.00	6.04	0.04	0.3236	2.38	-0.3202	2.0598
9.22	5.45	6.10	6.15	0.05	0.4297	2.17	-0.1230	2.0470
9.51	5.50	6.20	6.26	0.06	0.5500	1.89	0.0871	1.9771
9.73	5.55	6.33	6.40	0.07	0.7000	1.67	0.3680	2.0380

$LogK_1$ **(Average value)** = 2.1568 ± 0.2069

Table 14:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
10.00	5.60	6.47	6.55	0.08	0.9148	1.41		
10.23	5.65	6.62	6.71	0.09	1.2102	1.20	-0.5749	0.6251
10.49	5.70	6.80	6.92	0.09	1.5968	1.03	0.1703	1.2003

$LogK_2$ **(Average value)** = 0.9127± 0.4070

Table15:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	Log($\frac{n}{1-n}$)	$LogK_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4210	2.2190
8.72	5.35	6.37	6.40	0.03	0.4286	2.42	-0.1249	2.2951
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.96	0.3010	2.2610
9.51	5.55	6.66	6.70	0.04	0.7720	1.67	0.5297	2.1997

$LogK_1$ (Average value) = 2.2108± 0.0825

Table 16:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
9.73	5.55	6.78	6.83	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.95	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.09		
10.49	5.70	7.10	7.16	0.06	3.1429	0.89		

$LogK_2$ **(Average value)** = 1.5453± 0.3450

Table 17:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.86	0.05	0.3717	2.88	-0.2280	2.6520
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.06	0.06	0.4853	2.38	-0.0255	2.3545
9.22	5.45	6.10	6.16	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430
9.73	5.55	6.33	6.41	0.08	0.8000	1.69	0.6020	2.2920

$LogK_1$ **(Average value)** = 2.2516± 0.5380

Table 18:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$\text{Log}(\frac{n-1}{2-n})$	Log K_2
10.00	5.60	6.47	6.57	0.10	1.1434	1.43		
10.23	5.65	6.62	6.72	0.10	1.3448	1.23	-0.2788	0.9512
10.49	5.70	6.80	6.90	0.10	1.7742	1.03	0.5351	1.5651

LogK_2 **(Average value)** = 1.2581± 0.4340

Table 19: Stepwise and overall Stability constants of thehydrolysed and unhydrolysed divalent metal (II) complexes

Chelates	**LogK₁**	**LogK₂**	**Logβ**
[Cu (Hydrolysed PSHA-1)$_2$]	2.4788	1.4280	3.9068
[Pb (Hydrolysed PSHA-1)$_2$]	2.5832	1.1963	3.7795
[Cd (Hydrolysed PSHA-1)$_2$]	2.2108	1.5453	3.7561
[Mg (Hydrolysed PSHA-1)$_2$]	2.1382	1.5453	3.6835
[Cu (Unhydrolysed PSHA-1)$_2$]	2.3059	1.2209	3.5268
[Pb (Unhydrolysed PSHA-1)$_2$]	2.2364	1.2239	3.4603
[Cd (Unhydrolysed PSHA-1)$_2$]	2.2516	1.2581	3.5097
[Mg (Unydrolysed PSHA-1)$_2$]	2.1568	0.9127	3.0695

The results obtained (Table19) shows the stepwise and overall stability constants to be not high indicating low stability of the complexes, because the solubility of most metal ions in the basic pH range is minimal due to metal hydroxide precipitation (Karimi, 2017). In general, the stepwise stability constants (K_1 and K_2) follow the order $K_1 > K_2$ for the copper, lead, magnesium and cadmium complexes respectively. The steady decrease of the values with increasing number of ligands is in agreement with the prediction made by researchers (Na'aliya, 2013). The decrease could be attributed to the fact that as the number of the ligands (Humate ions) that enters the coordination zone increases the aqua molecules available for replacement by the ligands become less. Thus, the metal ions become less electron loving with progressive intake of the ligand and this results in the decrease in the values of the constants (Na'aliya, 2013). Also the stability of the complexes is influenced by the size and number of the chelate rings(Mackay and Mackay,2002).All the complexes form rings in their structure as humate, a bidentate ligand, bond the metal ions in the ratio 1:2 (Boguta and Sokolowska, 2016) forming chelate rings. The values of the overall stability constants (logβ) obtained for humate complexes are not high indicating low stability as the values are not high. LogK values for copper-humates (Table 3 to 6) obtained in this study are lower than those reported for the complexes of humic acids (Pandey *et al*., 2015; Dinu, 2013; Kaschl *et al*., 2010 and Gilbeto and Jorg, 2001). The values of LogK(Table 7 to 10) forlead-humates are lower than those reported for the lead in the literature (Dinu, 2013; Gilbeto and Jorg 2001). Log K values(Table 11 to 14) for magnesium-humates obtained in this study are close to those reported by (Pandey *et al*., 2015). Log K values of cadmium-humates (Table 15 to 18) obtained in this work near to the one reported by (Dinu, 2013 and Pandey *et al*., 2015).The difference between the reported values and the values obtained in this study might be probably as a result of acid hydrolysis of humic acid. The values of the overall stability constants (log β) of the copper humates complexes presented in Table 19 is high than that of other metal humate complexes, show relatively high stability of Cu-HA complexes, show the following order of stability: Cu >Pb> Cd > Mg; which are in close agreement to the findings of (Dinu, 2013 and Pandey *et al*., 2015).The high stability of Cu-humate chelate could be attributed to the existence of coordinate covalent bond between the complexing agents and the Cu^{2+} ions. Since, Cu^{2+} being a metal of the transitional series with $3d^9$ electronic configurations can accept the electrons from the complexing agents. Similarly,the low stabilities of Pb,Cd and Mg -complexes could be explained by that Pb^{2+} with $6s^2$, Cd^{2+} with $4d^{10}$ and Mg^{2+} with $2p^6$ their electronic configuration has a completely filled d,p and s orbitals. Moreover, the stabilities of metal ions with hydrolysed humic acid from peat soil were higher than those with unhydrolysed humic acid from peat soil; which is ascribed to the high content of acidity in hydrolysed humic acid than unhydrolysed humic acid.

CONCLUSION

The values of logK for Cu(II) hydrolysed humic acid complex was higher followed by Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes as compared with metal(II) unhydrolysed humic acid complexes . This indicates acid hydrolysis of humic acid can enhance the complexation behavior of humic acid with metal (II) ions. However, the higher values of logβ for Cu(II), Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes indicates more stable stepwise complexes formed as compared with Cu(II), Pb(II), Cd(II) and Mg(II) unhydrolysed humic acid complexes.

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STABILITY CONSTANTS OF COMPLEXES OF METAL IONS WITH PEATSOIL HUMIC ACIDS UNDER NON-ACID-CONDITIONS

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ABSTRACT

Stability constants of complexes of four divalent metal ions viz. Cu^{2+}, Pb^{2+},Mg^{2+} and Cd^{2+} with humic acids (HA) were determined by potentiometric titration of humic acids with the corresponding salt of the divalent metals in aqueous media under non-acid-condition. The log K (logarithm of the stability constant) ranged from 1.0942 to 2.7471 for metal-humic acid complexes were determined using point-wise computational method. The order of stability constants were obtained as follows: Cu >Pb> Cd > Mg for metal -HA complexes respectively, indicating a higher degree of complexation with Cu metal ion.
Keywords: stability constant, humic acid, potentiometric titration, divalent metals, acid hydrolysis.

NTRODUCTION

The stability constant of a complex is the numerical expression of its stability and provides a quantitative measure of affinity of the metal ion to the complexing agent. An understanding of the relative stability of metal-complexes helps in predicting the behavior of metal ions in the soil (Ram and Raman, 1982). Extensive researches has been done to determine the stability constants of the complexes formed between humic acid (HA) with a number of metal ions. Ashok *et al*., (2000) reported that humic acid with hydroxyl, phenoxyl and carboxyl reactive groups can form coordination compound with metal ions at pH 3.5. The stability constants(Log K) for different metal-humic acid complexes indicated the following order of the stabilities of complexes formed between humic acid and metal ion, Cu >Fe >Pb> Ni > Co > Ca > Cd > Zn >Mn> Mg. Andelkovic *et al*., (2010) investigated the binding of Cd(II) to soil humic acid at pH 6.5 and in 0.1M KNO_3 ionic medium. The stability constant for binding indicating greater stability in the case when carboxyl groups are involved in complexation reaction. Kostic *et al*.,(2012) investigated the complexation of humic acid with certain heavy metal ions (Co(II), Ni(II),Cu(II), Zn(II), and Pb(II). The experiment was performed at 25°C, at pH 4.0 and ionic strength of 0.01M. Stability constant of complex between Pb(II) ions and humic acid is greater than stability constants of other investigated metal-humate complexes. Bogata and Sokolowska (2016) analyses the interaction between humic acids from different soils and Zn (II) ions at wide concentration ranges and at pH 5. Studies have showed significant impact of Zn concentration, pH and some properties of humic acids with zinc.But all of these studies were limited to acidic pH range. Therefore, the present study was carried out to determine and compare the stability constants of complexes of metal ions with hydrolysed peat soil humic acid and unhydrolysed peat soil humic under non-acid conditions.

MATERIALS AND METHODS

Analytical grade chemicals used includes hydrochloric acid (HCl), nitric acid (HNO_3), sodium hydroxide (NaOH), lead nitrate $Pb(NO_3)_2$, copper nitrate $Cu(NO_3)_2.3H_2O$, cadmium nitrate $Cd(NO_3)_2.4H_2O$, magnesium nitrate $Mg(NO_3)_2.6H_2O$, potassium nitrate (KNO_3), calcium chloride ($CaCl_2$), (sigma-Aldrich). Dowex 50WX8, (20-50 mesh) from Fluka.

Area of study

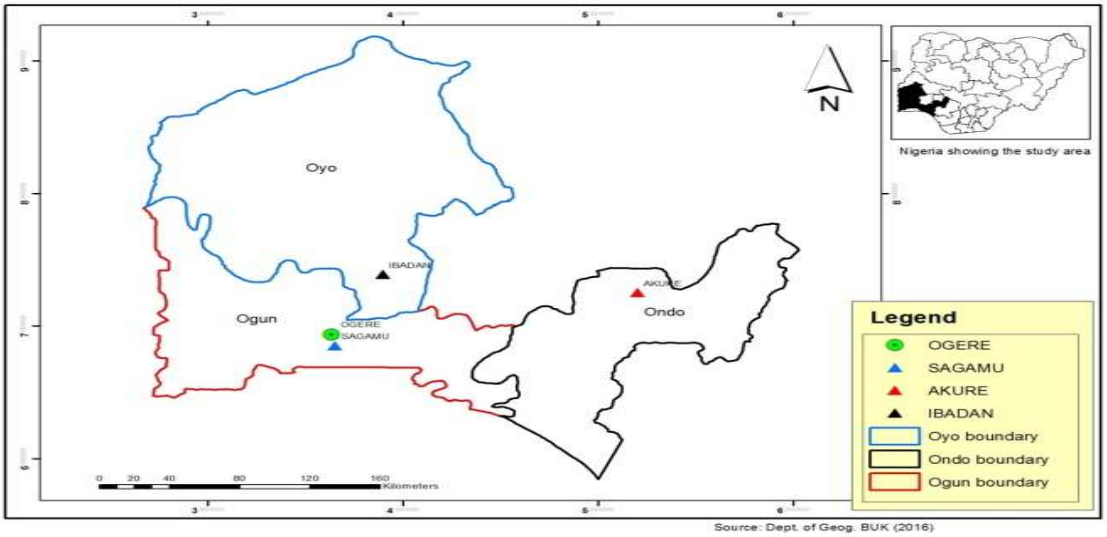

Figure 1: Map showing the sampling point at Sagamu Town, Ogun State.

Description of Sampling Area

Sagamu has geographical coordinates between 6°50′ north; 3° 38′ east is located in south western region of Nigeria. The region has tropical wet and dry climate with a lengthy wet season and relatively constant temperatures throughout the course of the year. Wet season runs from March to October, November to December forms the region dry season. The vegetation type of the region is savannah which is really grassland with small bushes and occasional big trees. Grassland soils have substantially higher organic matter content than forest soils (Novackova, 2011).

Sample Collection

The Peatsoil samples were collected from four different sampling points (0-10cm depth) in Sagamu into polyethylene bag with plastic spoons. Samples were taken to the laboratory, extraneous materials were removed; the samples were air-dried, crushed and ground to a fine powder in a mortar passed through a 0.20mm sieve. The samples were kept for analysis.

Isolation and purification of humic acid from peat soil sample

Peatsoil sample (100g) was mixed with 1000 cm^3 of 0.1M NaOH solution, shaken for 3hours and left to stand overnight. Dark-coloured supernatant was obtained and decanted from solid residue. The dark-coloured supernatant was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 6 hours. Yellowish brown supernatant and dark-brown precipitate were obtained. The yellowish brown supernatant was decanted followed by centrifuge and discarded. The dark-brown precipitate was mixed with $500cm^3$of 0.1M NaOH solution followed by passing through dowex resin. The dark-brown solution was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 3 hours. The dark-brown precipitate was washed several times with deionized water. The supernatant was treated with $AgNO_3$ solution until no white precipitate observed. The humic acid was transferred to weighed crucible and dried at 60°C in an oven for 12 hours. The humic acid was cooled and dried in the desiccator, weighed and recorded. The obtained humic acid was dried again at 60°C for additional 6 hours cooled and dried in the desiccator, weighed and recorded constant weight was obtained (Baruah *et al*., 2015).

FT-IR analysis

FT-IR spectra of humic acid sample was analysed using Carry 630 FT-IR Agilent Technologies.

Unhydrolysed compost humic acid

The unhydrolysed humic acid was obtained after isolation and purification of compost humic acid and kept for investigation.

Acid hydrolysis of Peatsoil acid

Peatsoil humic acid sample (1g) was refluxed for 12 hours at (160°C) with $50cm^3$ of 6M HCl. The mixture was allowed to cool, decanted, and centrifuged after hydrolysis. The insoluble residues were washed with distilled water via centrifugation several times, and the supernatant was treated with $AgNO_3$ solution until no white precipitate was observed. The residue was thoroughly dried over $CaCl_2$ in a desiccator at room temperature (Chefetz *et al*., 2002). Finally, the obtained hydrolysed humic acid was kept for investigation.

Potentiometric Titrations

Potentiometric measurements were carried out using a pH-meter Jenway (model 3510) with combine electrode, the sensitivity of the pH - meter is 0.01 units. The pH meter was switched on half an hour before starting the titration for initial warm up of the instrument. The instrument was calibrated with an aqueous standard buffer solution of pH 4.00 and 10.0 (borate buffer) prepared from a "Qualigens" buffer tablets.

The following sets of solutions were prepared in a 250cm^3 volumetric flask separately for pH metric titrations.

(i) 5 cm^3 0.1 M HCl + 40 cm^3 deionized water
(ii) 5 cm^3 0.1 M HCl + 39 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid
(iii) 5 cm^3 0.1 M HCl + 37 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid + 2 cm^3 0.01 M Cu(II)

The solutions were titrated against standardized 0.110MNaOH separately. The total volume of each mixture was adjusted to 50 cm^3 and the ionic strength of the solutions was maintained constant at by adding appropriate amount of stock solution of 1M KNO$_3$ (Gamal, 2015; Omar and Ali, 2015). A magnetic stirrer was used to achieve thorough mixing of the interacting solutions at 550 rpm. The same set of experimental conditions was applied for potentiometric titration of remaining samples.

Evaluation of pKa of Hydrolysed peat soil Humic Acids

The proton-ligand formation number n$_{\mathbf{A}}$ were calculated by Irving and Rossotti expression (Omar and Ali, 2015).

$$nA = Y - \frac{(V2-V1)(No-Eo)}{(Vo+V1)TcL} \quad \text{..................................1}$$

Where: Y is number of dissociable proton, (V$_2$-V$_1$) is the measure of displacement of the ligand curve relative to acid curve, N^o and E^o are the resultant concentration of alkali solution, free acid solution, T$_{cL}{}^o$ is the total ligand concentration, V^o is the total volume of titration solution,V$_1$ is the volume of alkali added to acid solution,V$_2$ is the volume of alkali added to acid solution + ligand solution, acid dissociation constants (pKa - values) of ligand were calculated by algebraic method point wise calculation (Tables 1). The dissociation constants (pKa) were calculated according to the following relation:

$$pKa = pH + \log\left(\frac{nA}{1-nA}\right) \quad \text{.............................2}$$

Where: pKa is the acid dissociation constant, n$_A$is the Proton-ligand formation number and pH is the pH-values (Omar and Ali, 2015).

Determination of metal-ligand stability constants (log K) of complexes

The potentiometric measurement for the determination of stability constant of a complex in solution is based on the fact that the redox potential of the couple $\frac{M^{+(m-n)}}{M^{+m}}$ is shifted significantly on complexation of the metal ion with the ligand. This method involves change in hydrogen ion concentration [H$^+$] due to the displacement or association of one or more protons taking place during complexation reaction. This change can be found out by titrating the solutions containing free acid, acid with ligand, and acid with ligand and metal ion, individually against a standard alkali solution at a constant ionic strength or temperature. Either ionic strength or temperature may be varied for different sets of solutions. In all the cases, the change in the pH of the solution is measured after each addition of a known amount of alkali to the reaction cell which contains the reaction mixture. The titration curves are then drawn by plotting the measured pH values against the corresponding volume of alkali added and the stability constants of the complexes are determined from the titration curves by employing pH-metric titration technique given by (Irving and Rossoti).

Metal-ligand stability constants (Log K) were determined by using the following relations:

$$\bar{n} = \frac{(V_3 - V_2)(E^0 + N^0)}{(V^0 + V_2)\bar{n}_A T_m^0} \quad \text{...3}$$

and

$$PL = \log_{10}\left\{\frac{1 + \beta_n^H \frac{1}{[anti\ \log pH]^n}}{T_L^0 - \bar{n}T_m^0} X \frac{(V^0 + V_3)}{V^0}\right\} \quad \text{..4}$$

Where $T_{L,}$ T^o, E°, and V^ohavethe same significance as in equation (1) above, T_m denotes the total concentration of metal present in solution, V_3 is the volume of metal ions present in solution and β^H is the overall proton ligand stability constant. The metal-ligand stability constants (log K) were determined by employing point wise computational Method (eq. 5 and 6).

$$\text{LogK}_1 = \log\left(\frac{n}{1-n}\right) + \text{pL} \qquad \ldots\ldots\ldots\ldots.5$$

$$\text{LogK}_2 = \log\left(\frac{1-n}{2-n}\right) + \text{pL}\ldots\ldots\ldots\ldots\ldots\ldots\ldots.6$$

Where: Log K is the metal-ligand stability constant, pL is the Free ligand exponent function, **n** is the Average number of ligand attached with metal ion (Janrao*et al*., 2014).The results obtained were analyzed by an ORIGIN 2016 program using titration data and then the proton-ligand stability constants (pKa) and Metal-ligand stability constant (LogK) calculated (Omar and Ali, 2015).

RESULTS AND DISCUSSION

Fourier transformed infrared (FT-IR) spectra of isolated humic acid from peat soils Figure 2 had distinct clear absorption bands indicating the presence of major humic acid structural elemental groups such as H bonded OH (3680cm^{-1} peak), C=O of carbonyl (1721cm^{-1} peak), functional groups of aliphatic components CH_2 (2918cm^{-1} peak) and C-O stretching of polysaccharide (1168cm^{-1} peak). The positions of the absorption bands of the spectra fell within typical major absorption bands of humic acid which is at frequencies 3680, 2918, 1721, 1168 cm^{-1}. The first peak centred in the vicinity of 3680 cm^{-1} region is attributed to phenol OH group bounded by intermolecular H bonds. The 2918cm^{-1} band usually has absorption maximum at 2918 cm^{-1} which is due to C–H stretching of alkane group (CH_2). The next major absorption band is 1721 cm^{-1}. This band has been commonly ascribed to C=O stretching of mainly carboxyl group (COOH) with trace amount of ketones. The last peak was observed at 1168 cm^{-1} due to C–O stretching of polysaccharides and this peak appeared also in the spectra of humic acid from peat soil. The FTIR spectra of the isolated humic acid contained all major characteristic absorption peaks of humic acid. These absorption peaks indicated the presence of the major structural elements of humic acid namely H bonded OH, C=C of aromatic ring, C=O of carbonyl group (both carboxyl and ketonic), CH_2 group. This strongly supports the presence of humic acid.

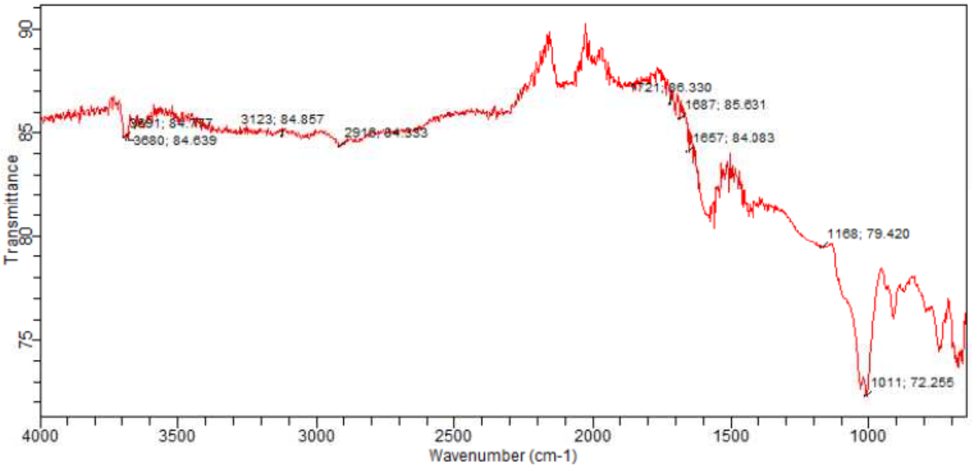

Fig. 2 : FT-IR spectraof peatsoilhumic acid (PSHA)

Evaluation of acid dissociation constant (pka) of acid hydrolysed peat soil humicacid at phenolic group

The value of the dissociation constant of the peat soil humic acid (PSHA) that underwent acidhydrolysis studied was found to be 8.9299 as shown Table 1, which is lower than the literaturevalues reported by Almeida and Szpoganics, (2015), Borges *et al*., (2005); Badr *et al*., (2012)and Fernandes *et al*,.(2009) of 9.73, 9.47 and 10.30. The difference between the obtained valuesand the reported values in this study might be probably as a result of acid hydrolysis of humicacid.

Table 1: PKa of (Hydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	$\log(\frac{nA}{1-nA})$	pKa
8.50	5.30	6.29	0.99	0.3594	-0.2510	8.2490
8.72	5.35	6.37	1.02	0.3400	-0.2880	8.4320
9.00	5.40	6.46	1.06	0.3141	-0.3391	8.6609
9.22	5.45	6.55	1.10	0.2882	-0.3927	8.8273
9.51	5.50	6.66	1.16	0.2494	-0.4786	9.0314
9.73	5.55	6.78	1.23	0.2041	-0.5910	9.1390
10.00	5.60	6.90	1.30	0.1589	-0.7238	9.2762
10.23	5.65	7.05	1.40	0.0941	-0.9835	9.2465
10.49	5.70	7.10	1.40	0.0941	-0.9835	9.5065

Average pKa = 8.9299 ± 0.4186

Table 2: PKa of (Unhydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	$\text{Log}(\frac{\boldsymbol{nA}}{\boldsymbol{1-n}})$	pKa
8.50	5.30	5.81	0.51	0.6619	0.2919	8.7919
8.72	5.35	5.90	0.55	0.6357	0.2418	8.9618
9.00	5.40	6.00	0.60	0.6029	0.1813	9.1813
9.22	5.45	6.10	0.65	0.5701	0.1226	9.3426
9.51	5.50	6.20	0.70	0.5376	0.0654	9.5754
9.73	5.55	6.33	0.78	0.4851	-0.0259	9.7041
10.00	5.60	6.47	0.87	0.4262	-0.1291	9.8709
10.23	5.65	6.62	0.99	0.3609	-0.2481	9.9819
10.49	5.70	6.80	1.10	0.2759	-0.4690	10.0210

Average pKa = 9.4923± 0.4410

Metal-ligand stability constant (Log K)

The stabilityconstants require the accurate values of proton-ligand stability constants (Anil and Maroti, 2008). Metal titration curves crossed over ligand titration curve indicated the formation of complex upon proton release (Santosh, *et al.*, 2011). If the values of n- are within range 0.2-0.8 and 1.2-18 this indicates the formation of 1:1 and 1:2 complexes (Sayyed and Mazahar, 2012).

The metal (II)-humate stepwise stability constants (log k) at phenolic group (Tables 3-18)

Table 3: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$\log(\frac{n}{1-n})$	LogK_1
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

LogK_1 (Average value) = 2.4788± 0.2203

Table 4: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$\text{Log}(\frac{n-1}{2-n})$	LogK_2
9.51	5.50	6.66	6.73	0.07	1.3509	1.70	-0.2671	1.4329
9.73	5.55	6.78	6.85	0.07	1.6383	1.51	0.2467	1.7567
10.00	5.60	6.90	6.98	0.08	2.1783	1.31	-0.2158	1.0942
10.23	5.65	7.05	7.13	0.08	4.1904	1.27		
10.49	5.70	7.10	7.19	0.09	4.6920			

LogK_2(Average value) = 1.4280 ± 0.3312

Table 5:Point-wise method,Cu (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	Log($\frac{n}{n-1}$)	Log K$_1$
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430

LogK$_1$ **(Average value)** = 2.3059± 0.6153

Table 6:Point-wise method, Cu (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	V$_3$-V$_2$	n	pL	Log($\frac{n-1}{2-n}$)	Log K$_2$
9.73	5.55	6.33	6.42	0.09	0.9000	1.69		
10.00	5.60	6.47	6.58	0.11	1.2578	1.44	-0.4592	0.9808
10.23	5.65	6.62	6.84	0.12	1.6137	1.26	-0.2010	1.4610
10.49	5.70	6.80	6.92	0.12	2.1052	1.03		

LogK$_2$ **(Average value)** = 1.2209± 0.3398

Table 7:Point-wise method,Pb (Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	log($\frac{n}{1-n}$)	LogK$_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.60	0.05	0.8333	1.96	0.6989	2.6589

LogK$_1$ (Average value) = 2.5832 ±0.1614

Table 8:Point-wise method,Pb-(Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	log($\frac{n-1}{2-n}$)	logK$_2$
9.51	5.50	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.83	0.05	1.1702	1.44		
10.00	5.60	6.90	6.90	0.05	1.4864	1.22	-0.0237	1.1963
10.23	5.65	7.05	7.10	0.05	2.0190	1.09		
10.49	5.70	7.10	7.17	0.07	3.6492	1.00		

LogK$_2$(Average value) = 1.1963

Table 9:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	V$_3$-V$_2$	n	pL	Log ($\frac{n}{n-1}$)	Log K$_1$
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.5477	2.3123
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	0.0272	2.2072
9.51	5.50	6.20	6.26	0.07	0.6417	1.89	0.2530	2.1430
9.73	5.55	6.40	6.40	0.07	0.7000	1.67	0.3680	2.0380

LogK$_1$ **(Average value)** = 2.2364 ± 0.1602

Table 10:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	V$_3$-V$_2$	n	pL	Log($\frac{n-1}{2-n}$)	Log K$_2$
10.00	5.60	6.47	6.55	0.08	1.9503	1.41		
10.23	5.65	6.62	6.72	0.11	1.4792	1.26	-0.0361	1.2239

LogK$_2$ **(Average value)** = 1.2239

Table 11:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	log($\frac{n}{n-1}$)	LogK$_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4290	2.2110
8.72	5.35	6.37	6.39	0.02	0.2858	2.42	-0.3978	2.0222
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

LogK$_1$ (Average value)=2.1382**±**0.1046

Table 12:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$\log(\frac{n-1}{2-n})$	$LogK_2$
9.51	5.55	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.84	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.93	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.10		
10.49	5.70	7.10	7.18	0.07	3.6492	0.83		

$LogK_2$(Average value) = 1.5453 **±** 0.3450

Table 13:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$Log(\frac{n}{n-1})$	$Log K_1$
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.3477	2.3123
9.00	5.40	6.00	6.04	0.04	0.3236	2.38	-0.3202	2.0598
9.22	5.45	6.10	6.15	0.05	0.4297	2.17	-0.1230	2.0470
9.51	5.50	6.20	6.26	0.06	0.5500	1.89	0.0871	1.9771
9.73	5.55	6.33	6.40	0.07	0.7000	1.67	0.3680	2.0380

$LogK_1$ **(Average value)** = 2.1568 ± 0.2069

Table 14:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$Log(\frac{n-1}{2-n})$	$Log K_2$
10.00	5.60	6.47	6.55	0.08	0.9148	1.41		
10.23	5.65	6.62	6.71	0.09	1.2102	1.20	-0.5749	0.6251
10.49	5.70	6.80	6.92	0.09	1.5968	1.03	0.1703	1.2003

$LogK_2$ **(Average value)** = 0.9127± 0.4070

Table15:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$Log(\frac{n}{1-n})$	$LogK_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4210	2.2190
8.72	5.35	6.37	6.40	0.03	0.4286	2.42	-0.1249	2.2951
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.96	0.3010	2.2610
9.51	5.55	6.66	6.70	0.04	0.7720	1.67	0.5297	2.1997

$LogK_1$ (Average value) = 2.2108± 0.0825

Table 16:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$Log(\frac{n-1}{2-n})$	$Log K_2$
9.73	5.55	6.78	6.83	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.95	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.09		
10.49	5.70	7.10	7.16	0.06	3.1429	0.89		

$LogK_2$ **(Average value)** = 1.5453± 0.3450

Table 17:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$Log(\frac{n}{n-1})$	$Log K_1$
8.50	5.30	5.81	5.86	0.05	0.3717	2.88	-0.2280	2.6520
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.06	0.06	0.4853	2.38	-0.0255	2.3545
9.22	5.45	6.10	6.16	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430
9.73	5.55	6.33	6.41	0.08	0.8000	1.69	0.6020	2.2920

$LogK_1$ **(Average value)** = 2.2516± 0.5380

Table 18:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$\text{Log}(\frac{n-1}{2-n})$	Log K_2
10.00	5.60	6.47	6.57	0.10	1.1434	1.43		
10.23	5.65	6.62	6.72	0.10	1.3448	1.23	-0.2788	0.9512
10.49	5.70	6.80	6.90	0.10	1.7742	1.03	0.5351	1.5651

LogK_2 **(Average value)** = 1.2581± 0.4340

Table 19: Stepwise and overall Stability constants of thehydrolysed and unhydrolysed divalent metal (II) complexes

Chelates	**LogK_1**	**LogK_2**	**Logβ**
[Cu (Hydrolysed PSHA-1)$_2$]	2.4788	1.4280	3.9068
[Pb (Hydrolysed PSHA-1)$_2$]	2.5832	1.1963	3.7795
[Cd (Hydrolysed PSHA-1)$_2$]	2.2108	1.5453	3.7561
[Mg (Hydrolysed PSHA-1)$_2$]	2.1382	1.5453	3.6835
[Cu (Unhydrolysed PSHA-1)$_2$]	2.3059	1.2209	3.5268
[Pb (Unhydrolysed PSHA-1)$_2$]	2.2364	1.2239	3.4603
[Cd (Unhydrolysed PSHA-1)$_2$]	2.2516	1.2581	3.5097
[Mg (Unydrolysed PSHA-1)$_2$]	2.1568	0.9127	3.0695

The results obtained (Table19) shows the stepwise and overall stability constants to be not high indicating low stability of the complexes, because the solubility of most metal ions in the basic pH range is minimal due to metal hydroxide precipitation (Karimi, 2017). In general, the stepwise stability constants (K_1 and K_2) follow the order $K_1 > K_2$ for the copper, lead, magnesium and cadmium complexes respectively. The steady decrease of the values with increasing number of ligands is in agreement with the prediction made by researchers (Na'aliya, 2013). The decrease could be attributed to the fact that as the number of the ligands (Humate ions) that enters the coordination zone increases the aqua molecules available for replacement by the ligands become less. Thus, the metal ions become less electron loving with progressive intake of the ligand and this results in the decrease in the values of the constants (Na'aliya, 2013). Also the stability of the complexes is influenced by the size and number of the chelate rings(Mackay and Mackay,2002).All the complexes form rings in their structure as humate, a bidentate ligand, bond the metal ions in the ratio 1:2 (Boguta and Sokolowska, 2016) forming chelate rings. The values of the overall stability constants (logβ) obtained for humate complexes are not high indicating low stability as the values are not high. LogK values for copper-humates (Table 3 to 6) obtained in this study are lower than those reported for the complexes of humic acids (Pandey *et al.*, 2015; Dinu, 2013; Kaschl *et al.*, 2010 and Gilbeto and Jorg, 2001). The values of LogK(Table 7 to 10) forlead-humates are lower than those reported for the lead in the literature (Dinu, 2013; Gilbeto and Jorg 2001). Log K values(Table 11 to 14) for magnesium-humates obtained in this study are close to those reported by (Pandey *et al.*, 2015). Log K values of cadmium-humates (Table 15 to 18) obtained in this work near to the one reported by (Dinu, 2013 and Pandey *et al.*, 2015).The difference between the reported values and the values obtained in this study might be probably as a result of acid hydrolysis of humic acid. The values of the overall stability constants (log β) of the copper humates complexes presented in Table 19 is high than that of other metal humate complexes, show relatively high stability of Cu-HA complexes, show the following order of stability: Cu >Pb> Cd > Mg; which are in close agreement to the findings of (Dinu, 2013 and Pandey *et al.*, 2015).The high stability of Cu-humate chelate could be attributed to the existence of coordinate covalent bond between the complexing agents and the Cu^{2+} ions. Since, Cu^{2+} being a metal of the transitional series with $3d^9$ electronic configurations can accept the electrons from the complexing agents. Similarly,the low stabilities of Pb,Cd and Mg - complexes could be explained by that Pb^{2+} with $6s^2$, Cd^{2+} with $4d^{10}$ and Mg^{2+} with $2p^6$ their electronic configuration has a completely filled d,p and s orbitals. Moreover, the stabilities of metal ions with hydrolysed humic acid from peat soil were higher than those with unhydrolysed humic acid from peat soil; which is ascribed to the high content of acidity in hydrolysed humic acid than unhydrolysed humic acid.

CONCLUSION

The values of logK for Cu(II) hydrolysed humic acid complex was higher followed by Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes as compared with metal(II) unhydrolysed humic acid complexes . This indicates acid hydrolysis of humic acid can enhance the complexation behavior of humic acid with metal (II) ions. However, the higher values of logβ for Cu(II), Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes indicates more stable stepwise complexes formed as compared with Cu(II), Pb(II), Cd(II) and Mg(II) unhydrolysed humic acid complexes.

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STABILITY CONSTANTS OF COMPLEXES OF METAL IONS WITH PEATSOIL HUMIC ACIDS UNDER NON-ACID-CONDITIONS

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ABSTRACT

Stability constants of complexes of four divalent metal ions viz. Cu^{2+}, Pb^{2+},Mg^{2+} and Cd^{2+} with humic acids (HA) were determined by potentiometric titration of humic acids with the corresponding salt of the divalent metals in aqueous media under non-acid-condition. The log K (logarithm of the stability constant) ranged from 1.0942 to 2.7471 for metal-humic acid complexes were determined using point-wise computational method. The order of stability constants were obtained as follows: Cu >Pb> Cd > Mg for metal -HA complexes respectively, indicating a higher degree of complexation with Cu metal ion.

Keywords: stability constant, humic acid, potentiometric titration, divalent metals, acid hydrolysis.

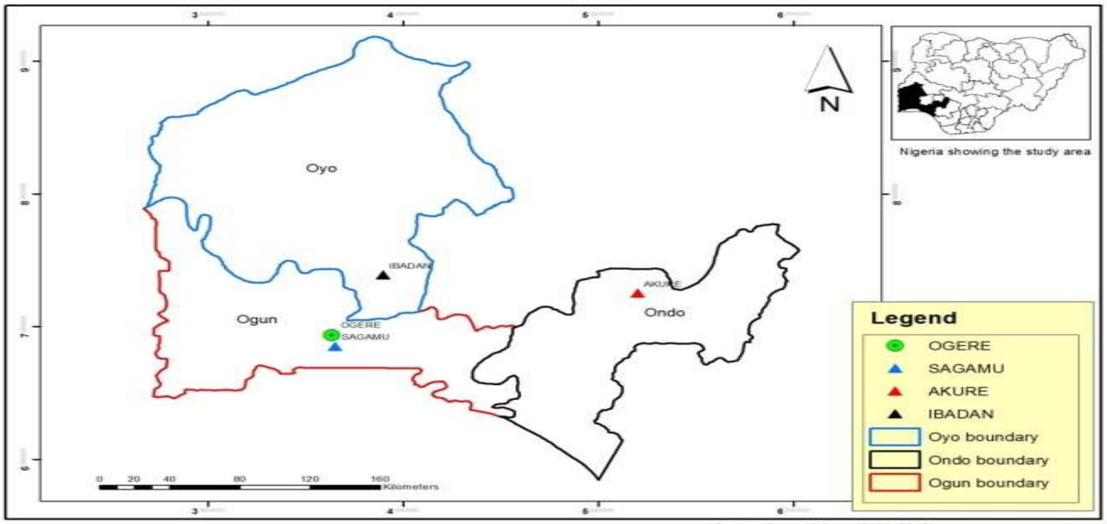
NTRODUCTION

The stability constant of a complex is the numerical expression of its stability and provides a quantitative measure of affinity of the metal ion to the complexing agent. An understanding of the relative stability of metal-complexes helps in predicting the behavior of metal ions in the soil (Ram and Raman, 1982). Extensive researches has been done to determine the stability constants of the complexes formed between humic acid (HA) with a number of metal ions. Ashok *et al.*, (2000) reported that humic acid with hydroxyl, phenoxyl and carboxyl reactive groups can form coordination compound with metal ions at pH 3.5. The stability constants(Log K) for different metal-humic acid complexes indicated the following order of the stabilities of complexes formed between humic acid and metal ion, Cu >Fe >Pb> Ni > Co > Ca > Cd > Zn >Mn> Mg. Andelkovic *et al.*, (2010) investigated the binding of Cd(II) to soil humic acid at pH 6.5 and in 0.1M KNO_3 ionic medium. The stability constant for binding indicating greater stability in the case when carboxyl groups are involved in complexation reaction. Kostic *et al.*,(2012) investigated the complexation of humic acid with certain heavy metal ions (Co(II), Ni(II),Cu(II), Zn(II), and Pb(II). The experiment was performed at 25°C, at pH 4.0 and ionic strength of 0.01M. Stability constant of complex between Pb(II) ions and humic acid is greater than stability constants of other investigated metal-humate complexes. Bogata and Sokolowska (2016) analyses the interaction between humic acids from different soils and Zn (II) ions at wide concentration ranges and at pH 5. Studies have showed significant impact of Zn concentration, pH and some properties of humic acids with zinc.But all of these studies were limited to acidic pH range. Therefore, the present study was carried out to determine and compare the stability constants of complexes of metal ions with hydrolysed peat soil humic acid and unhydrolysed peat soil humic under non-acid conditions.

MATERIALS AND METHODS

Analytical grade chemicals used includes hydrochloric acid (HCl), nitric acid (HNO_3), sodium hydroxide (NaOH), lead nitrate $Pb(NO_3)_2$, copper nitrate $Cu(NO_3)_2.3H_2O$, cadmium nitrate $Cd(NO_3)_2.4H_2O$, magnesium nitrate $Mg(NO_3)_2.6H_2O$, potassium nitrate (KNO_3), calcium chloride ($CaCl_2$), (sigma-Aldrich). Dowex 50WX8, (20-50 mesh) from Fluka.

Area of study



Source: Dept. of Geog. BUK (2016)

Figure 1: Map showing the sampling point at Sagamu Town, Ogun State.

Description of Sampling Area

Sagamu has geographical coordinates between 6°50′ north; 3° 38′ east is located in south western region of Nigeria. The region has tropical wet and dry climate with a lengthy wet season and relatively constant temperatures throughout the course of the year. Wet season runs from March to October, November to December forms the region dry season. The vegetation type of the region is savannah which is really grassland with small bushes and occasional big trees. Grassland soils have substantially higher organic matter content than forest soils (Novackova, 2011).

Sample Collection

The Peatsoil samples were collected from four different sampling points (0-10cm depth) in Sagamu into polyethylene bag with plastic spoons. Samples were taken to the laboratory, extraneous materials were removed; the samples were air-dried, crushed and ground to a fine powder in a mortar passed through a 0.20mm sieve. The samples were kept for analysis.

Isolation and purification of humic acid from peat soil sample

Peatsoil sample (100g) was mixed with 1000 cm^3 of 0.1M NaOH solution, shaken for 3hours and left to stand overnight. Dark-coloured supernatant was obtained and decanted from solid residue. The dark-coloured supernatant was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 6 hours. Yellowish brown supernatant and dark-brown precipitate were obtained. The yellowish brown supernatant was decanted followed by centrifuge and discarded. The dark-brown precipitate was mixed with $500cm^3$of 0.1M NaOH solution followed by passing through dowex resin. The dark-brown solution was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 3 hours. The dark-brown precipitate was washed several times with deionized water. The supernatant was treated with $AgNO_3$ solution until no white precipitate observed. The humic acid was transferred to weighed crucible and dried at 60°C in an oven for 12 hours. The humic acid was cooled and dried in the desiccator, weighed and recorded. The obtained humic acid was dried again at 60°C for additional 6 hours cooled and dried in the desiccator, weighed and recorded constant weight was obtained (Baruah *et al.*, 2015).

FT-IR analysis

FT-IR spectra of humic acid sample was analysed using Carry 630 FT-IR Agilent Technologies.

Unhydrolysed compost humic acid

The unhydrolysed humic acid was obtained after isolation and purification of compost humic acid and kept for investigation.

Acid hydrolysis of Peatsoil acid

Peatsoil humic acid sample (1g) was refluxed for 12 hours at (160°C) with $50cm^3$ of 6M HCl. The mixture was allowed to cool, decanted, and centrifuged after hydrolysis. The insoluble residues were washed with distilled water via centrifugation several times, and the supernatant was treated with $AgNO_3$ solution until no white precipitate was observed. The residue was thoroughly dried over $CaCl_2$ in a desiccator at room temperature (Chefetz *et al.*, 2002). Finally, the obtained hydrolysed humic acid was kept for investigation.

Potentiometric Titrations

Potentiometric measurements were carried out using a pH-meter Jenway (model 3510) with combine electrode, the sensitivity of the pH - meter is 0.01 units. The pH meter was switched on half an hour before starting the titration for initial warm up of the instrument. The instrument was calibrated with an aqueous standard buffer solution of pH 4.00 and 10.0 (borate buffer) prepared from a "Qualigens" buffer tablets.

The following sets of solutions were prepared in a 250cm^3 volumetric flask separately for pH metric titrations.

(i) 5 cm^3 0.1 M HCl + 40 cm^3 deionized water

(ii) 5 cm^3 0.1 M HCl + 39 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid

(iii) 5 cm^3 0.1 M HCl + 37 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid + 2 cm^3 0.01 M Cu(II)

The solutions were titrated against standardized 0.110MNaOH separately. The total volume of each mixture was adjusted to 50 cm^3 and the ionic strength of the solutions was maintained constant at by adding appropriate amount of stock solution of 1M KNO$_3$ (Gamal, 2015; Omar and Ali, 2015). A magnetic stirrer was used to achieve thorough mixing of the interacting solutions at 550 rpm. The same set of experimental conditions was applied for potentiometric titration of remaining samples.

Evaluation of pKa of Hydrolysed peat soil Humic Acids

The proton-ligand formation number n$_{\mathbf{A}}$ were calculated by Irving and Rossotti expression (Omar and Ali, 2015).

$$nA = Y - \frac{(V2-V1)(No-Eo)}{(Vo+V1)TcL} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 1$$

Where: Y is number of dissociable proton, (V$_2$-V$_1$) is the measure of displacement of the ligand curve relative to acid curve, N^o and E^o are the resultant concentration of alkali solution, free acid solution, T$_{cL}$^{o} is the total ligand concentration, V^o is the total volume of titration solution,V$_1$ is the volume of alkali added to acid solution,V$_2$ is the volume of alkali added to acid solution + ligand solution, acid dissociation constants (pKa - values) of ligand were calculated by algebraic method point wise calculation (Tables 1). The dissociation constants (pKa) were calculated according to the following relation:

$$pKa = pH + \log\left(\frac{nA}{1-nA}\right) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 2$$

Where: pKa is the acid dissociation constant, n$_A$is the Proton-ligand formation number and pH is the pH-values (Omar and Ali, 2015).

Determination of metal-ligand stability constants (log K) of complexes

The potentiometric measurement for the determination of stability constant of a complex in solution is based on the fact that the redox potential of the couple $\frac{M^{+(m-n)}}{M^{+m}}$ is shifted significantly on complexation of the metal ion with the ligand. This method involves change in hydrogen ion concentration [H$^+$] due to the displacement or association of one or more protons taking place during complexation reaction. This change can be found out by titrating the solutions containing free acid, acid with ligand, and acid with ligand and metal ion, individually against a standard alkali solution at a constant ionic strength or temperature. Either ionic strength or temperature may be varied for different sets of solutions. In all the cases, the change in the pH of the solution is measured after each addition of a known amount of alkali to the reaction cell which contains the reaction mixture. The titration curves are then drawn by plotting the measured pH values against the corresponding volume of alkali added and the stability constants of the complexes are determined from the titration curves by employing pH-metric titration technique given by (Irving and Rossoti).

Metal-ligand stability constants (Log K) were determined by using the following relations:

$$\bar{n} = \frac{(V_3 - V_2)(E^0 + N^0)}{(V^0 + V_2)\bar{n}_A T_m^0} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 3$$

and

$$PL = \log_{10}\left\{\frac{1 + \beta_n^H \dfrac{1}{[anti\ \log pH]^n}}{T_L^0 - \bar{n}T_m^0} X \frac{(V^0 + V_3)}{V^0}\right\} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 4$$

Where $T_{L,}$ T^{o}, E°, and V^{o}havethe same significance as in equation (1) above, T_m denotes the total concentration of metal present in solution, V_3 is the volume of metal ions present in solution and β^{H} is the overall proton ligand stability constant. The metal-ligand stability constants (log K) were determined by employing point wise computational Method (eq. 5 and 6).

$$\mathrm{LogK}_1 = \log\left(\frac{n}{1-n}\right) + \mathrm{pL} \qquad \ldots\ldots\ldots\ldots.5$$

$$\mathrm{LogK}_2 = \log\left(\frac{1-n}{2-n}\right) + \mathrm{pL}\ldots\ldots\ldots\ldots\ldots\ldots\ldots.6$$

Where: Log K is the metal-ligand stability constant, pL is the Free ligand exponent function, **n** is the Average number of ligand attached with metal ion (Janrao*et al.*, 2014).The results obtained were analyzed by an ORIGIN 2016 program using titration data and then the proton-ligand stability constants (pKa) and Metal-ligand stability constant (LogK) calculated (Omar and Ali, 2015).

RESULTS AND DISCUSSION

Fourier transformed infrared (FT-IR) spectra of isolated humic acid from peat soils Figure 2 had distinct clear absorption bands indicating the presence of major humic acid structural elemental groups such as H bonded OH ($3680cm^{-1}$ peak), C=O of carbonyl ($1721cm^{-1}$ peak), functional groups of aliphatic components CH_2 ($2918cm^{-1}$ peak) and C-O stretching of polysaccharide ($1168cm^{-1}$ peak). The positions of the absorption bands of the spectra fell within typical major absorption bands of humic acid which is at frequencies 3680, 2918, 1721, 1168 cm^{-1}. The first peak centred in the vicinity of 3680 cm^{-1} region is attributed to phenol OH group bounded by intermolecular H bonds. The $2918cm^{-1}$ band usually has absorption maximum at 2918 cm^{-1} which is due to C–H stretching of alkane group (CH_2). The next major absorption band is 1721 cm^{-1}. This band has been commonly ascribed to C=O stretching of mainly carboxyl group (COOH) with trace amount of ketones. The last peak was observed at 1168 cm^{-1} due to C–O stretching of polysaccharides and this peak appeared also in the spectra of humic acid from peat soil. The FTIR spectra of the isolated humic acid contained all major characteristic absorption peaks of humic acid. These absorption peaks indicated the presence of the major structural elements of humic acid namely H bonded OH, C=C of aromatic ring, C=O of carbonyl group (both carboxyl and ketonic), CH_2 group. This strongly supports the presence of humic acid.

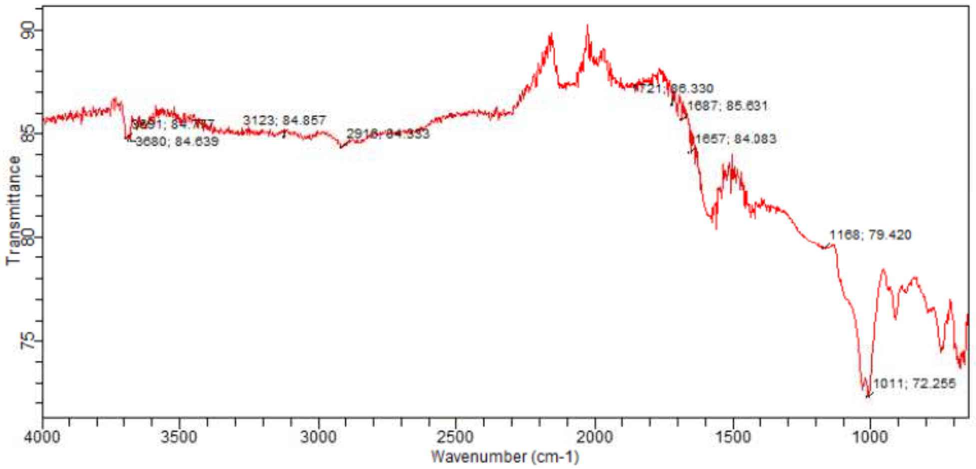


Fig. 2 : FT-IR spectraof peatsoilhumic acid (PSHA)

Evaluation of acid dissociation constant (pka) of acid hydrolysed peat soil humicacid at phenolic group

The value of the dissociation constant of the peat soil humic acid (PSHA) that underwent acidhydrolysis studied was found to be 8.9299 as shown Table 1, which is lower than the literaturevalues reported by Almeida and Szpoganics, (2015), Borges *et al.*, (2005); Badr *et al.*, (2012)and Fernandes *et al*,.(2009) of 9.73, 9.47 and 10.30. The difference between the obtained valuesand the reported values in this study might be probably as a result of acid hydrolysis of humicacid.

Table 1: PKa of (Hydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	$\log(\frac{nA}{1-nA})$	pKa
8.50	5.30	6.29	0.99	0.3594	-0.2510	8.2490
8.72	5.35	6.37	1.02	0.3400	-0.2880	8.4320
9.00	5.40	6.46	1.06	0.3141	-0.3391	8.6609
9.22	5.45	6.55	1.10	0.2882	-0.3927	8.8273
9.51	5.50	6.66	1.16	0.2494	-0.4786	9.0314
9.73	5.55	6.78	1.23	0.2041	-0.5910	9.1390
10.00	5.60	6.90	1.30	0.1589	-0.7238	9.2762
10.23	5.65	7.05	1.40	0.0941	-0.9835	9.2465
10.49	5.70	7.10	1.40	0.0941	-0.9835	9.5065

Average pKa = 8.9299 ± 0.4186

Table 2: PKa of (Unhydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	$\text{Log}(\frac{nA}{1-n})$	pKa
8.50	5.30	5.81	0.51	0.6619	0.2919	8.7919
8.72	5.35	5.90	0.55	0.6357	0.2418	8.9618
9.00	5.40	6.00	0.60	0.6029	0.1813	9.1813
9.22	5.45	6.10	0.65	0.5701	0.1226	9.3426
9.51	5.50	6.20	0.70	0.5376	0.0654	9.5754
9.73	5.55	6.33	0.78	0.4851	-0.0259	9.7041
10.00	5.60	6.47	0.87	0.4262	-0.1291	9.8709
10.23	5.65	6.62	0.99	0.3609	-0.2481	9.9819
10.49	5.70	6.80	1.10	0.2759	-0.4690	10.0210

Average pKa = 9.4923± 0.4410

Metal-ligand stability constant (Log K)

The stabilityconstants require the accurate values of proton-ligand stability constants (Anil and Maroti, 2008). Metal titration curves crossed over ligand titration curve indicated the formation of complex upon proton release (Santosh, *et al.*, 2011). If the values of n- are within range 0.2-0.8 and 1.2-18 this indicates the formation of 1:1 and 1:2 complexes (Sayyed and Mazahar, 2012).

The metal (II)-humate stepwise stability constants (log k) at phenolic group (Tables 3-18)

Table 3: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$\log(\frac{n}{1-n})$	$\text{Log}K_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

LogK_1 (Average value) = 2.4788± 0.2203

Table 4: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$\text{Log}(\frac{n-1}{2-n})$	$\text{Log}K_2$
9.51	5.50	6.66	6.73	0.07	1.3509	1.70	-0.2671	1.4329
9.73	5.55	6.78	6.85	0.07	1.6383	1.51	0.2467	1.7567
10.00	5.60	6.90	6.98	0.08	2.1783	1.31	-0.2158	1.0942
10.23	5.65	7.05	7.13	0.08	4.1904	1.27		
10.49	5.70	7.10	7.19	0.09	4.6920			

LogK_2(Average value) = 1.4280 ± 0.3312

Table 5:Point-wise method,Cu (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V_3-V_2)	n	pL	Log($\frac{n}{n-1}$)	Log K$_1$
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430

LogK$_1$ **(Average value)** = 2.3059± 0.6153

Table 6:Point-wise method, Cu (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	V_3-V_2	n	pL	Log($\frac{n-1}{2-n}$)	Log K$_2$
9.73	5.55	6.33	6.42	0.09	0.9000	1.69		
10.00	5.60	6.47	6.58	0.11	1.2578	1.44	-0.4592	0.9808
10.23	5.65	6.62	6.84	0.12	1.6137	1.26	-0.2010	1.4610
10.49	5.70	6.80	6.92	0.12	2.1052	1.03		

LogK$_2$ **(Average value)** = 1.2209± 0.3398

Table 7:Point-wise method,Pb (Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V_3-V_2)	n	pL	log($\frac{n}{1-n}$)	LogK$_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.60	0.05	0.8333	1.96	0.6989	2.6589

LogK$_1$ (Average value) = 2.5832 ±0.1614

Table 8:Point-wise method,Pb-(Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V_3-V_2)	n	pL	log($\frac{n-1}{2-n}$)	logK$_2$
9.51	5.50	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.83	0.05	1.1702	1.44		
10.00	5.60	6.90	6.90	0.05	1.4864	1.22	-0.0237	1.1963
10.23	5.65	7.05	7.10	0.05	2.0190	1.09		
10.49	5.70	7.10	7.17	0.07	3.6492	1.00		

LogK$_2$(Average value) = 1.1963

Table 9:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	V_3-V_2	n	pL	Log ($\frac{n}{n-1}$)	Log K$_1$
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.5477	2.3123
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	0.0272	2.2072
9.51	5.50	6.20	6.26	0.07	0.6417	1.89	0.2530	2.1430
9.73	5.55	6.40	6.40	0.07	0.7000	1.67	0.3680	2.0380

LogK$_1$ **(Average value)** = 2.2364 ± 0.1602

Table 10:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	V_3-V_2	n	pL	Log($\frac{n-1}{2-n}$)	Log K$_2$
10.00	5.60	6.47	6.55	0.08	1.9503	1.41		
10.23	5.65	6.62	6.72	0.11	1.4792	1.26	-0.0361	1.2239

LogK$_2$ **(Average value)** = 1.2239

Table 11:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V_3-V_2)	n	pL	log($\frac{n}{n-1}$)	LogK$_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4290	2.2110
8.72	5.35	6.37	6.39	0.02	0.2858	2.42	-0.3978	2.0222
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

LogK$_1$ (Average value)=2.1382**±**0.1046

Table 12:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$\log(\frac{n-1}{2-n})$	$LogK_2$
9.51	5.55	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.84	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.93	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.10		
10.49	5.70	7.10	7.18	0.07	3.6492	0.83		

$LogK_2$(Average value) = 1.5453 **±** 0.3450

Table 13:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$Log(\frac{n}{n-1})$	$Log\ K_1$
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.3477	2.3123
9.00	5.40	6.00	6.04	0.04	0.3236	2.38	-0.3202	2.0598
9.22	5.45	6.10	6.15	0.05	0.4297	2.17	-0.1230	2.0470
9.51	5.50	6.20	6.26	0.06	0.5500	1.89	0.0871	1.9771
9.73	5.55	6.33	6.40	0.07	0.7000	1.67	0.3680	2.0380

$LogK_1$ **(Average value)** = 2.1568 ± 0.2069

Table 14:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$Log(\frac{n-1}{2-n})$	$Log\ K_2$
10.00	5.60	6.47	6.55	0.08	0.9148	1.41		
10.23	5.65	6.62	6.71	0.09	1.2102	1.20	-0.5749	0.6251
10.49	5.70	6.80	6.92	0.09	1.5968	1.03	0.1703	1.2003

$LogK_2$ **(Average value)** = 0.9127± 0.4070

Table15:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$Log(\frac{n}{1-n})$	$LogK_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4210	2.2190
8.72	5.35	6.37	6.40	0.03	0.4286	2.42	-0.1249	2.2951
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.96	0.3010	2.2610
9.51	5.55	6.66	6.70	0.04	0.7720	1.67	0.5297	2.1997

$LogK_1$ (Average value) = 2.2108± 0.0825

Table 16:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$Log(\frac{n-1}{2-n})$	$Log\ K_2$
9.73	5.55	6.78	6.83	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.95	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.09		
10.49	5.70	7.10	7.16	0.06	3.1429	0.89		

$LogK_2$ **(Average value)** = 1.5453± 0.3450

Table 17:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$Log(\frac{n}{n-1})$	$Log\ K_1$
8.50	5.30	5.81	5.86	0.05	0.3717	2.88	-0.2280	2.6520
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.06	0.06	0.4853	2.38	-0.0255	2.3545
9.22	5.45	6.10	6.16	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430
9.73	5.55	6.33	6.41	0.08	0.8000	1.69	0.6020	2.2920

$LogK_1$ **(Average value)** = 2.2516± 0.5380

Table 18:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$\text{Log}(\frac{n-1}{2-n})$	Log K_2
10.00	5.60	6.47	6.57	0.10	1.1434	1.43		
10.23	5.65	6.62	6.72	0.10	1.3448	1.23	-0.2788	0.9512
10.49	5.70	6.80	6.90	0.10	1.7742	1.03	0.5351	1.5651

LogK_2 **(Average value)** = 1.2581± 0.4340

Table 19: Stepwise and overall Stability constants of thehydrolysed and unhydrolysed divalent metal (II) complexes

Chelates	**LogK_1**	**LogK_2**	**Logβ**
[Cu (Hydrolysed PSHA-1)$_2$]	2.4788	1.4280	3.9068
[Pb (Hydrolysed PSHA-1)$_2$]	2.5832	1.1963	3.7795
[Cd (Hydrolysed PSHA-1)$_2$]	2.2108	1.5453	3.7561
[Mg (Hydrolysed PSHA-1)$_2$]	2.1382	1.5453	3.6835
[Cu (Unhydrolysed PSHA-1)$_2$]	2.3059	1.2209	3.5268
[Pb (Unhydrolysed PSHA-1)$_2$]	2.2364	1.2239	3.4603
[Cd (Unhydrolysed PSHA-1)$_2$]	2.2516	1.2581	3.5097
[Mg (Unydrolysed PSHA-1)$_2$]	2.1568	0.9127	3.0695

The results obtained (Table19) shows the stepwise and overall stability constants to be not high indicating low stability of the complexes, because the solubility of most metal ions in the basic pH range is minimal due to metal hydroxide precipitation (Karimi, 2017). In general, the stepwise stability constants (K_1 and K_2) follow the order $K_1 > K_2$ for the copper, lead, magnesium and cadmium complexes respectively. The steady decrease of the values with increasing number of ligands is in agreement with the prediction made by researchers (Na'aliya, 2013). The decrease could be attributed to the fact that as the number of the ligands (Humate ions) that enters the coordination zone increases the aqua molecules available for replacement by the ligands become less. Thus, the metal ions become less electron loving with progressive intake of the ligand and this results in the decrease in the values of the constants (Na'aliya, 2013). Also the stability of the complexes is influenced by the size and number of the chelate rings(Mackay and Mackay,2002).All the complexes form rings in their structure as humate, a bidentate ligand, bond the metal ions in the ratio 1:2 (Boguta and Sokolowska, 2016) forming chelate rings. The values of the overall stability constants (logβ) obtained for humate complexes are not high indicating low stability as the values are not high. LogK values for copper-humates (Table 3 to 6) obtained in this study are lower than those reported for the complexes of humic acids (Pandey *et al.*, 2015; Dinu, 2013; Kaschl *et al.*, 2010 and Gilbeto and Jorg, 2001). The values of LogK(Table 7 to 10) forlead-humates are lower than those reported for the lead in the literature (Dinu, 2013; Gilbeto and Jorg 2001). Log K values(Table 11 to 14) for magnesium-humates obtained in this study are close to those reported by (Pandey *et al.*, 2015). Log K values of cadmium-humates (Table 15 to 18) obtained in this work near to the one reported by (Dinu, 2013 and Pandey *et al.*, 2015).The difference between the reported values and the values obtained in this study might be probably as a result of acid hydrolysis of humic acid. The values of the overall stability constants (log β) of the copper humates complexes presented in Table 19 is high than that of other metal humate complexes, show relatively high stability of Cu-HA complexes, show the following order of stability: Cu >Pb> Cd > Mg; which are in close agreement to the findings of (Dinu, 2013 and Pandey *et al.*, 2015).The high stability of Cu-humate chelate could be attributed to the existence of coordinate covalent bond between the complexing agents and the Cu^{2+} ions. Since, Cu^{2+} being a metal of the transitional series with $3d^9$ electronic configurations can accept the electrons from the complexing agents. Similarly,the low stabilities of Pb,Cd and Mg -complexes could be explained by that Pb^{2+} with $6s^2$, Cd^{2+} with $4d^{10}$ and Mg^{2+} with $2p^6$ their electronic configuration has a completely filled d,p and s orbitals. Moreover, the stabilities of metal ions with hydrolysed humic acid from peat soil were higher than those with unhydrolysed humic acid from peat soil; which is ascribed to the high content of acidity in hydrolysed humic acid than unhydrolysed humic acid.

CONCLUSION

The values of logK for Cu(II) hydrolysed humic acid complex was higher followed by Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes as compared with metal(II) unhydrolysed humic acid complexes . This indicates acid hydrolysis of humic acid can enhance the complexation behavior of humic acid with metal (II) ions. However, the higher values of logβ for Cu(II), Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes indicates more stable stepwise complexes formed as compared with Cu(II), Pb(II), Cd(II) and Mg(II) unhydrolysed humic acid complexes.

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STABILITY CONSTANTS OF COMPLEXES OF METAL IONS WITH PEATSOIL HUMIC ACIDS UNDER NON-ACID-CONDITIONS

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ABSTRACT

Stability constants of complexes of four divalent metal ions viz. Cu^{2+}, Pb^{2+},Mg^{2+} and Cd^{2+} with humic acids (HA) were determined by potentiometric titration of humic acids with the corresponding salt of the divalent metals in aqueous media under non-acid-condition. The log K (logarithm of the stability constant) ranged from 1.0942 to 2.7471 for metal-humic acid complexes were determined using point-wise computational method. The order of stability constants were obtained as follows: Cu >Pb> Cd > Mg for metal -HA complexes respectively, indicating a higher degree of complexation with Cu metal ion.

Keywords: stability constant, humic acid, potentiometric titration, divalent metals, acid hydrolysis.

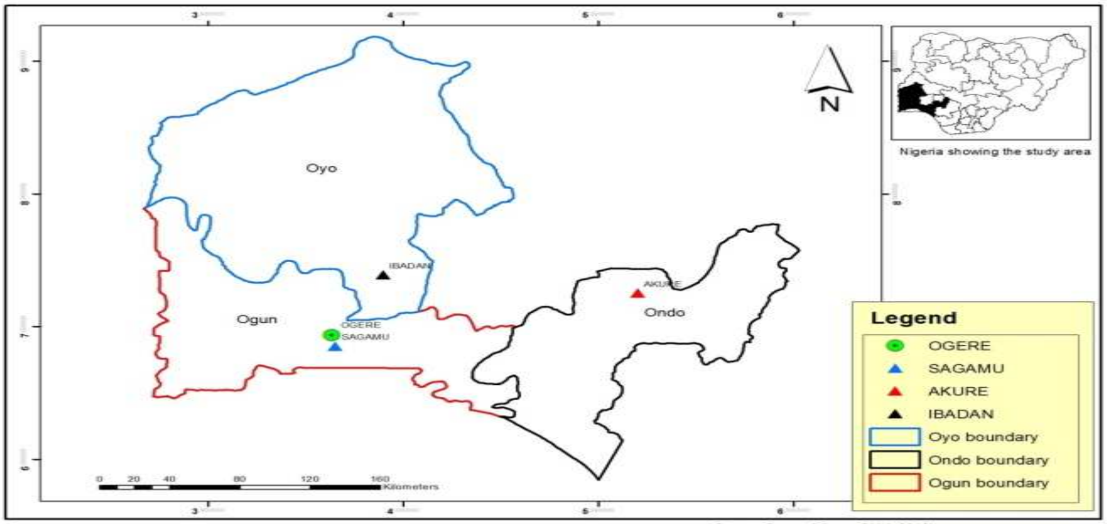
NTRODUCTION

The stability constant of a complex is the numerical expression of its stability and provides a quantitative measure of affinity of the metal ion to the complexing agent. An understanding of the relative stability of metal-complexes helps in predicting the behavior of metal ions in the soil (Ram and Raman, 1982). Extensive researches has been done to determine the stability constants of the complexes formed between humic acid (HA) with a number of metal ions. Ashok *et al.*, (2000) reported that humic acid with hydroxyl, phenoxyl and carboxyl reactive groups can form coordination compound with metal ions at pH 3.5. The stability constants(Log K) for different metal-humic acid complexes indicated the following order of the stabilities of complexes formed between humic acid and metal ion, Cu >Fe >Pb> Ni > Co > Ca > Cd > Zn >Mn> Mg. Andelkovic *et al.*, (2010) investigated the binding of Cd(II) to soil humic acid at pH 6.5 and in 0.1M KNO_3 ionic medium. The stability constant for binding indicating greater stability in the case when carboxyl groups are involved in complexation reaction. Kostic *et al.*,(2012) investigated the complexation of humic acid with certain heavy metal ions (Co(II), Ni(II),Cu(II), Zn(II), and Pb(II). The experiment was performed at 25°C, at pH 4.0 and ionic strength of 0.01M. Stability constant of complex between Pb(II) ions and humic acid is greater than stability constants of other investigated metal-humate complexes. Bogata and Sokolowska (2016) analyses the interaction between humic acids from different soils and Zn (II) ions at wide concentration ranges and at pH 5. Studies have showed significant impact of Zn concentration, pH and some properties of humic acids with zinc.But all of these studies were limited to acidic pH range. Therefore, the present study was carried out to determine and compare the stability constants of complexes of metal ions with hydrolysed peat soil humic acid and unhydrolysed peat soil humic under non-acid conditions.

MATERIALS AND METHODS

Analytical grade chemicals used includes hydrochloric acid (HCl), nitric acid (HNO_3), sodium hydroxide (NaOH), lead nitrate $Pb(NO_3)_2$, copper nitrate $Cu(NO_3)_2.3H_2O$, cadmium nitrate $Cd(NO_3)_2.4H_2O$, magnesium nitrate $Mg(NO_3)_2.6H_2O$, potassium nitrate (KNO_3), calcium chloride ($CaCl_2$), (sigma-Aldrich). Dowex 50WX8, (20-50 mesh) from Fluka.

Area of study



Source: Dept. of Geog. BUK (2016)

Figure 1: Map showing the sampling point at Sagamu Town, Ogun State.

Description of Sampling Area

Sagamu has geographical coordinates between 6°50′ north; 3° 38′ east is located in south western region of Nigeria. The region has tropical wet and dry climate with a lengthy wet season and relatively constant temperatures throughout the course of the year. Wet season runs from March to October, November to December forms the region dry season. The vegetation type of the region is savannah which is really grassland with small bushes and occasional big trees. Grassland soils have substantially higher organic matter content than forest soils (Novackova, 2011).

Sample Collection

The Peatsoil samples were collected from four different sampling points (0-10cm depth) in Sagamu into polyethylene bag with plastic spoons. Samples were taken to the laboratory, extraneous materials were removed; the samples were air-dried, crushed and ground to a fine powder in a mortar passed through a 0.20mm sieve. The samples were kept for analysis.

Isolation and purification of humic acid from peat soil sample

Peatsoil sample (100g) was mixed with 1000 cm^3 of 0.1M NaOH solution, shaken for 3hours and left to stand overnight. Dark-coloured supernatant was obtained and decanted from solid residue. The dark-coloured supernatant was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 6 hours. Yellowish brown supernatant and dark-brown precipitate were obtained. The yellowish brown supernatant was decanted followed by centrifuge and discarded. The dark-brown precipitate was mixed with $500cm^3$of 0.1M NaOH solution followed by passing through dowex resin. The dark-brown solution was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 3 hours. The dark-brown precipitate was washed several times with deionized water. The supernatant was treated with $AgNO_3$ solution until no white precipitate observed. The humic acid was transferred to weighed crucible and dried at 60°C in an oven for 12 hours. The humic acid was cooled and dried in the desiccator, weighed and recorded. The obtained humic acid was dried again at 60°C for additional 6 hours cooled and dried in the desiccator, weighed and recorded constant weight was obtained (Baruah *et al*., 2015).

FT-IR analysis

FT-IR spectra of humic acid sample was analysed using Carry 630 FT-IR Agilent Technologies.

Unhydrolysed compost humic acid

The unhydrolysed humic acid was obtained after isolation and purification of compost humic acid and kept for investigation.

Acid hydrolysis of Peatsoil acid

Peatsoil humic acid sample (1g) was refluxed for 12 hours at (160°C) with $50cm^3$ of 6M HCl. The mixture was allowed to cool, decanted, and centrifuged after hydrolysis. The insoluble residues were washed with distilled water via centrifugation several times, and the supernatant was treated with $AgNO_3$ solution until no white precipitate was observed. The residue was thoroughly dried over $CaCl_2$ in a desiccator at room temperature (Chefetz *et al*., 2002). Finally, the obtained hydrolysed humic acid was kept for investigation.

Potentiometric Titrations

Potentiometric measurements were carried out using a pH-meter Jenway (model 3510) with combine electrode, the sensitivity of the pH - meter is 0.01 units. The pH meter was switched on half an hour before starting the titration for initial warm up of the instrument. The instrument was calibrated with an aqueous standard buffer solution of pH 4.00 and 10.0 (borate buffer) prepared from a "Qualigens" buffer tablets.

The following sets of solutions were prepared in a 250cm^3 volumetric flask separately for pH metric titrations.

(i) 5 cm^3 0.1 M HCl + 40 cm^3 deionized water
(ii) 5 cm^3 0.1 M HCl + 39 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid
(iii) 5 cm^3 0.1 M HCl + 37 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid + 2 cm^3 0.01 M Cu(II)

The solutions were titrated against standardized 0.110MNaOH separately. The total volume of each mixture was adjusted to 50 cm^3 and the ionic strength of the solutions was maintained constant at by adding appropriate amount of stock solution of 1M KNO$_3$ (Gamal, 2015; Omar and Ali, 2015). A magnetic stirrer was used to achieve thorough mixing of the interacting solutions at 550 rpm. The same set of experimental conditions was applied for potentiometric titration of remaining samples.

Evaluation of pKa of Hydrolysed peat soil Humic Acids

The proton-ligand formation number n_A were calculated by Irving and Rossotti expression (Omar and Ali, 2015).

$$nA = Y - \frac{(V2-V1)(No-Eo)}{(Vo+V1)TcL} \quad \text{..................................1}$$

Where: Y is number of dissociable proton, (V_2-V_1) is the measure of displacement of the ligand curve relative to acid curve, N^o and E^o are the resultant concentration of alkali solution, free acid solution, T_{cL}^o is the total ligand concentration, V^o is the total volume of titration solution,V_1 is the volume of alkali added to acid solution,V_2 is the volume of alkali added to acid solution + ligand solution, acid dissociation constants (pKa - values) of ligand were calculated by algebraic method point wise calculation (Tables 1). The dissociation constants (pKa) were calculated according to the following relation:

$$pKa = pH + \log(\frac{nA}{1-nA}) \quad \text{..............................2}$$

Where: pKa is the acid dissociation constant, $n_A$is the Proton-ligand formation number and pH is the pH-values (Omar and Ali, 2015).

Determination of metal-ligand stability constants (log K) of complexes

The potentiometric measurement for the determination of stability constant of a complex in solution is based on the fact that the redox potential of the couple $\frac{M^{+(m-n)}}{M^{+m}}$ is shifted significantly on complexation of the metal ion with the ligand. This method involves change in hydrogen ion concentration [H$^+$] due to the displacement or association of one or more protons taking place during complexation reaction. This change can be found out by titrating the solutions containing free acid, acid with ligand, and acid with ligand and metal ion, individually against a standard alkali solution at a constant ionic strength or temperature. Either ionic strength or temperature may be varied for different sets of solutions. In all the cases, the change in the pH of the solution is measured after each addition of a known amount of alkali to the reaction cell which contains the reaction mixture. The titration curves are then drawn by plotting the measured pH values against the corresponding volume of alkali added and the stability constants of the complexes are determined from the titration curves by employing pH-metric titration technique given by (Irving and Rossoti).

Metal-ligand stability constants (Log K) were determined by using the following relations:

$$\bar{n} = \frac{(V_3 - V_2)(E^0 + N^0)}{(V^0 + V_2)\bar{n}_A T_m^0} \quad \text{..3}$$

and

$$PL = \log_{10}\{\frac{1+\beta_n^H \frac{1}{[anti\ \log pH]^n}}{T_L^0 - \bar{n}T_m^0} X \frac{(V^0+V_3)}{V^0}\} \quad \text{..4}$$

Where $T_{L,}$ T^{o}, E°, and V^{o}havethe same significance as in equation (1) above, T_m denotes the total concentration of metal present in solution, V_3 is the volume of metal ions present in solution and β^H is the overall proton ligand stability constant. The metal-ligand stability constants (log K) were determined by employing point wise computational Method (eq. 5 and 6).

$\text{Log}K_1 = \log\left(\frac{n}{1-n}\right) + pL$ 5

$\text{Log}K_2 = \log\left(\frac{1-n}{2-n}\right) + pL$........................6

Where: Log K is the metal-ligand stability constant, pL is the Free ligand exponent function, **n** is the Average number of ligand attached with metal ion (Janrao*et al.*, 2014).The results obtained were analyzed by an ORIGIN 2016 program using titration data and then the proton-ligand stability constants (pKa) and Metal-ligand stability constant (LogK) calculated (Omar and Ali, 2015).

RESULTS AND DISCUSSION

Fourier transformed infrared (FT-IR) spectra of isolated humic acid from peat soils Figure 2 had distinct clear absorption bands indicating the presence of major humic acid structural elemental groups such as H bonded OH ($3680cm^{-1}$ peak), C=O of carbonyl ($1721cm^{-1}$ peak), functional groups of aliphatic components CH_2 ($2918cm^{-1}$ peak) and C-O stretching of polysaccharide ($1168cm^{-1}$ peak). The positions of the absorption bands of the spectra fell within typical major absorption bands of humic acid which is at frequencies 3680, 2918, 1721, 1168 cm^{-1}. The first peak centred in the vicinity of 3680 cm^{-1} region is attributed to phenol OH group bounded by intermolecular H bonds. The $2918cm^{-1}$ band usually has absorption maximum at 2918 cm^{-1} which is due to C–H stretching of alkane group (CH_2). The next major absorption band is 1721 cm^{-1}. This band has been commonly ascribed to C=O stretching of mainly carboxyl group (COOH) with trace amount of ketones. The last peak was observed at 1168 cm^{-1} due to C–O stretching of polysaccharides and this peak appeared also in the spectra of humic acid from peat soil. The FTIR spectra of the isolated humic acid contained all major characteristic absorption peaks of humic acid. These absorption peaks indicated the presence of the major structural elements of humic acid namely H bonded OH, C=C of aromatic ring, C=O of carbonyl group (both carboxyl and ketonic), CH_2 group. This strongly supports the presence of humic acid.

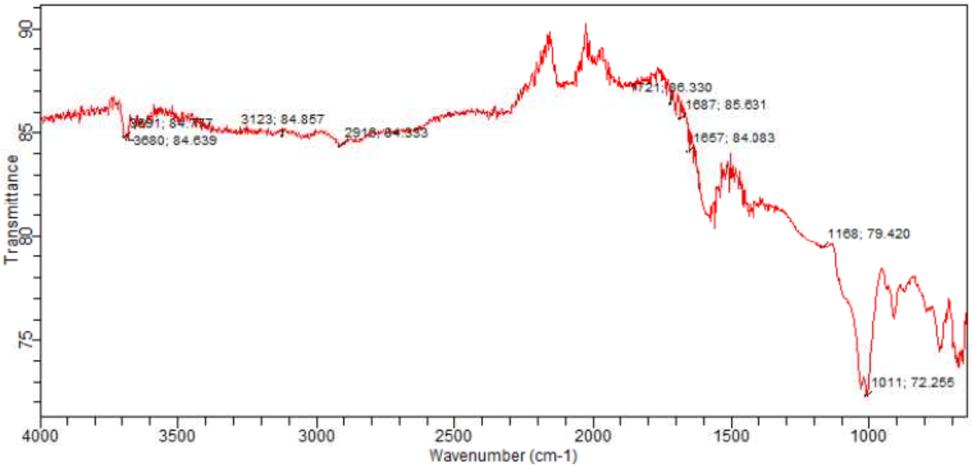


Fig. 2 : FT-IR spectraof peatsoilhumic acid (PSHA)

Evaluation of acid dissociation constant (pka) of acid hydrolysed peat soil humicacid at phenolic group

The value of the dissociation constant of the peat soil humic acid (PSHA) that underwent acidhydrolysis studied was found to be 8.9299 as shown Table 1, which is lower than the literaturevalues reported by Almeida and Szpoganics, (2015), Borges *et al.*, (2005); Badr *et al.*, (2012)and Fernandes *et al*,.(2009) of 9.73, 9.47 and 10.30. The difference between the obtained valuesand the reported values in this study might be probably as a result of acid hydrolysis of humicacid.

Table 1: PKa of (Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	V$_2$-V$_1$	nA	log($\frac{nA}{1-nA}$)	pKa
8.50	5.30	6.29	0.99	0.3594	-0.2510	8.2490
8.72	5.35	6.37	1.02	0.3400	-0.2880	8.4320
9.00	5.40	6.46	1.06	0.3141	-0.3391	8.6609
9.22	5.45	6.55	1.10	0.2882	-0.3927	8.8273
9.51	5.50	6.66	1.16	0.2494	-0.4786	9.0314
9.73	5.55	6.78	1.23	0.2041	-0.5910	9.1390
10.00	5.60	6.90	1.30	0.1589	-0.7238	9.2762
10.23	5.65	7.05	1.40	0.0941	-0.9835	9.2465
10.49	5.70	7.10	1.40	0.0941	-0.9835	9.5065

Average pKa = 8.9299 ± 0.4186

Table 2: PKa of (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	V$_2$-V$_1$	nA	Log($\frac{nA}{1-n}$)	pKa
8.50	5.30	5.81	0.51	0.6619	0.2919	8.7919
8.72	5.35	5.90	0.55	0.6357	0.2418	8.9618
9.00	5.40	6.00	0.60	0.6029	0.1813	9.1813
9.22	5.45	6.10	0.65	0.5701	0.1226	9.3426
9.51	5.50	6.20	0.70	0.5376	0.0654	9.5754
9.73	5.55	6.33	0.78	0.4851	-0.0259	9.7041
10.00	5.60	6.47	0.87	0.4262	-0.1291	9.8709
10.23	5.65	6.62	0.99	0.3609	-0.2481	9.9819
10.49	5.70	6.80	1.10	0.2759	-0.4690	10.0210

Average pKa = 9.4923± 0.4410

Metal-ligand stability constant (Log K)

The stabilityconstants require the accurate values of proton-ligand stability constants (Anil and Maroti, 2008). Metal titration curves crossed over ligand titration curve indicated the formation of complex upon proton release (Santosh, *et al.*, 2011). If the values of n- are within range 0.2-0.8 and 1.2-18 this indicates the formation of 1:1 and 1:2 complexes (Sayyed and Mazahar, 2012).

The metal (II)-humate stepwise stability constants (log k) at phenolic group (Tables 3-18)

Table 3: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	log($\frac{n}{1-n}$)	LogK$_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

LogK$_1$ (Average value) = 2.4788± 0.2203

Table 4: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	Log($\frac{n-1}{2-n}$)	LogK$_2$
9.51	5.50	6.66	6.73	0.07	1.3509	1.70	-0.2671	1.4329
9.73	5.55	6.78	6.85	0.07	1.6383	1.51	0.2467	1.7567
10.00	5.60	6.90	6.98	0.08	2.1783	1.31	-0.2158	1.0942
10.23	5.65	7.05	7.13	0.08	4.1904	1.27		
10.49	5.70	7.10	7.19	0.09	4.6920			

LogK$_2$(Average value) = 1.4280 ± 0.3312

Table 5:Point-wise method,Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	Log($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430

$LogK_1$ **(Average value)** = 2.3059± 0.6153

Table 6:Point-wise method, Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
9.73	5.55	6.33	6.42	0.09	0.9000	1.69		
10.00	5.60	6.47	6.58	0.11	1.2578	1.44	-0.4592	0.9808
10.23	5.65	6.62	6.84	0.12	1.6137	1.26	-0.2010	1.4610
10.49	5.70	6.80	6.92	0.12	2.1052	1.03		

$LogK_2$ **(Average value)** = 1.2209± 0.3398

Table 7:Point-wise method,Pb (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n}{1-n}$)	$LogK_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.60	0.05	0.8333	1.96	0.6989	2.6589

$LogK_1$ (Average value) = 2.5832 ±0.1614

Table 8:Point-wise method,Pb-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n-1}{2-n}$)	$logK_2$
9.51	5.50	6.66	6.71	0.05	0.9650	1.67	-0.0237	1.1963
9.73	5.55	6.78	6.83	0.05	1.1702	1.44		
10.00	5.60	6.90	6.90	0.05	1.4864	1.22		
10.23	5.65	7.05	7.10	0.05	2.0190	1.09		
10.49	5.70	7.10	7.17	0.07	3.6492	1.00		

$LogK_2$(Average value) = 1.1963

Table 9:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log ($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.5477	2.3123
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	0.0272	2.2072
9.51	5.50	6.20	6.26	0.07	0.6417	1.89	0.2530	2.1430
9.73	5.55	6.40	6.40	0.07	0.7000	1.67	0.3680	2.0380

$LogK_1$ **(Average value)** = 2.2364 ± 0.1602

Table 10:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
10.00	5.60	6.47	6.55	0.08	1.9503	1.41		
10.23	5.65	6.62	6.72	0.11	1.4792	1.26	-0.0361	1.2239

$LogK_2$ **(Average value)** = 1.2239

Table 11:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n}{n-1}$)	$LogK_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4290	2.2110
8.72	5.35	6.37	6.39	0.02	0.2858	2.42	-0.3978	2.0222
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

$LogK_1$ (Average value)=2.1382±0.1046

Table 12:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	log($\frac{n-1}{2-n}$)	LogK$_2$
9.51	5.55	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.84	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.93	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.10		
10.49	5.70	7.10	7.18	0.07	3.6492	0.83		

LogK$_2$(Average value) = 1.5453 **±** 0.3450

Table 13:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	V$_3$-V$_2$	n	pL	Log($\frac{n}{n-1}$)	Log K$_1$
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.3477	2.3123
9.00	5.40	6.00	6.04	0.04	0.3236	2.38	-0.3202	2.0598
9.22	5.45	6.10	6.15	0.05	0.4297	2.17	-0.1230	2.0470
9.51	5.50	6.20	6.26	0.06	0.5500	1.89	0.0871	1.9771
9.73	5.55	6.33	6.40	0.07	0.7000	1.67	0.3680	2.0380

LogK$_1$ **(Average value)** = 2.1568 ± 0.2069

Table 14:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	V$_3$-V$_2$	n	pL	Log($\frac{n-1}{2-n}$)	Log K$_2$
10.00	5.60	6.47	6.55	0.08	0.9148	1.41		
10.23	5.65	6.62	6.71	0.09	1.2102	1.20	-0.5749	0.6251
10.49	5.70	6.80	6.92	0.09	1.5968	1.03	0.1703	1.2003

LogK$_2$ **(Average value)** = 0.9127± 0.4070

Table15:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	Log($\frac{n}{1-n}$)	LogK$_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4210	2.2190
8.72	5.35	6.37	6.40	0.03	0.4286	2.42	-0.1249	2.2951
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.96	0.3010	2.2610
9.51	5.55	6.66	6.70	0.04	0.7720	1.67	0.5297	2.1997

LogK$_1$ (Average value) = 2.2108± 0.0825

Table 16:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	Log($\frac{n-1}{2-n}$)	Log K$_2$
9.73	5.55	6.78	6.83	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.95	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.09		
10.49	5.70	7.10	7.16	0.06	3.1429	0.89		

LogK$_2$ **(Average value)** = 1.5453± 0.3450

Table 17:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	V$_3$-V$_2$	n	pL	Log($\frac{n}{n-1}$)	Log K$_1$
8.50	5.30	5.81	5.86	0.05	0.3717	2.88	-0.2280	2.6520
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.06	0.06	0.4853	2.38	-0.0255	2.3545
9.22	5.45	6.10	6.16	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430
9.73	5.55	6.33	6.41	0.08	0.8000	1.69	0.6020	2.2920

LogK$_1$ **(Average value)** = 2.2516± 0.5380

Table 18:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$\text{Log}(\frac{n-1}{2-n})$	Log K_2
10.00	5.60	6.47	6.57	0.10	1.1434	1.43		
10.23	5.65	6.62	6.72	0.10	1.3448	1.23	-0.2788	0.9512
10.49	5.70	6.80	6.90	0.10	1.7742	1.03	0.5351	1.5651

LogK_2 **(Average value)** = 1.2581± 0.4340

Table 19: Stepwise and overall Stability constants of thehydrolysed and unhydrolysed divalent metal (II) complexes

Chelates	**LogK_1**	**LogK_2**	**Logβ**
[Cu (Hydrolysed PSHA-1)$_2$]	2.4788	1.4280	3.9068
[Pb (Hydrolysed PSHA-1)$_2$]	2.5832	1.1963	3.7795
[Cd (Hydrolysed PSHA-1)$_2$]	2.2108	1.5453	3.7561
[Mg (Hydrolysed PSHA-1)$_2$]	2.1382	1.5453	3.6835
[Cu (Unhydrolysed PSHA-1)$_2$]	2.3059	1.2209	3.5268
[Pb (Unhydrolysed PSHA-1)$_2$]	2.2364	1.2239	3.4603
[Cd (Unhydrolysed PSHA-1)$_2$]	2.2516	1.2581	3.5097
[Mg (Unydrolysed PSHA-1)$_2$]	2.1568	0.9127	3.0695

The results obtained (Table19) shows the stepwise and overall stability constants to be not high indicating low stability of the complexes, because the solubility of most metal ions in the basic pH range is minimal due to metal hydroxide precipitation (Karimi, 2017). In general, the stepwise stability constants (K_1 and K_2) follow the order $K_1 > K_2$ for the copper, lead, magnesium and cadmium complexes respectively. The steady decrease of the values with increasing number of ligands is in agreement with the prediction made by researchers (Na'aliya, 2013). The decrease could be attributed to the fact that as the number of the ligands (Humate ions) that enters the coordination zone increases the aqua molecules available for replacement by the ligands become less. Thus, the metal ions become less electron loving with progressive intake of the ligand and this results in the decrease in the values of the constants (Na'aliya, 2013). Also the stability of the complexes is influenced by the size and number of the chelate rings(Mackay and Mackay,2002).All the complexes form rings in their structure as humate, a bidentate ligand, bond the metal ions in the ratio 1:2 (Boguta and Sokolowska, 2016) forming chelate rings. The values of the overall stability constants (logβ) obtained for humate complexes are not high indicating low stability as the values are not high. LogK values for copper-humates (Table 3 to 6) obtained in this study are lower than those reported for the complexes of humic acids (Pandey *et al.*, 2015; Dinu, 2013; Kaschl *et al.*, 2010 and Gilbeto and Jorg, 2001). The values of LogK(Table 7 to 10) forlead-humates are lower than those reported for the lead in the literature (Dinu, 2013; Gilbeto and Jorg 2001). Log K values(Table 11 to 14) for magnesium-humates obtained in this study are close to those reported by (Pandey *et al.*, 2015). Log K values of cadmium-humates (Table 15 to 18) obtained in this work near to the one reported by (Dinu, 2013 and Pandey *et al.*, 2015).The difference between the reported values and the values obtained in this study might be probably as a result of acid hydrolysis of humic acid. The values of the overall stability constants (log β) of the copper humates complexes presented in Table 19 is high than that of other metal humate complexes, show relatively high stability of Cu-HA complexes, show the following order of stability: Cu >Pb> Cd > Mg; which are in close agreement to the findings of (Dinu, 2013 and Pandey *et al.*, 2015).The high stability of Cu-humate chelate could be attributed to the existence of coordinate covalent bond between the complexing agents and the Cu^{2+} ions. Since, Cu^{2+} being a metal of the transitional series with $3d^9$ electronic configurations can accept the electrons from the complexing agents. Similarly,the low stabilities of Pb,Cd and Mg -complexes could be explained by that Pb^{2+} with $6s^2$, Cd^{2+} with $4d^{10}$ and Mg^{2+} with $2p^6$ their electronic configuration has a completely filled d,p and s orbitals. Moreover, the stabilities of metal ions with hydrolysed humic acid from peat soil were higher than those with unhydrolysed humic acid from peat soil; which is ascribed to the high content of acidity in hydrolysed humic acid than unhydrolysed humic acid.

CONCLUSION

The values of logK for Cu(II) hydrolysed humic acid complex was higher followed by Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes as compared with metal(II) unhydrolysed humic acid complexes . This indicates acid hydrolysis of humic acid can enhance the complexation behavior of humic acid with metal (II) ions. However, the higher values of logβ for Cu(II), Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes indicates more stable stepwise complexes formed as compared with Cu(II), Pb(II), Cd(II) and Mg(II) unhydrolysed humic acid complexes.

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STABILITY CONSTANTS OF COMPLEXES OF METAL IONS WITH PEATSOIL HUMIC ACIDS UNDER NON-ACID-CONDITIONS

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ABSTRACT

Stability constants of complexes of four divalent metal ions viz. Cu^{2+}, Pb^{2+},Mg^{2+} and Cd^{2+} with humic acids (HA) were determined by potentiometric titration of humic acids with the corresponding salt of the divalent metals in aqueous media under non-acid-condition. The log K (logarithm of the stability constant) ranged from 1.0942 to 2.7471 for metal-humic acid complexes were determined using point-wise computational method. The order of stability constants were obtained as follows: Cu >Pb> Cd > Mg for metal -HA complexes respectively, indicating a higher degree of complexation with Cu metal ion.

Keywords: stability constant, humic acid, potentiometric titration, divalent metals, acid hydrolysis.

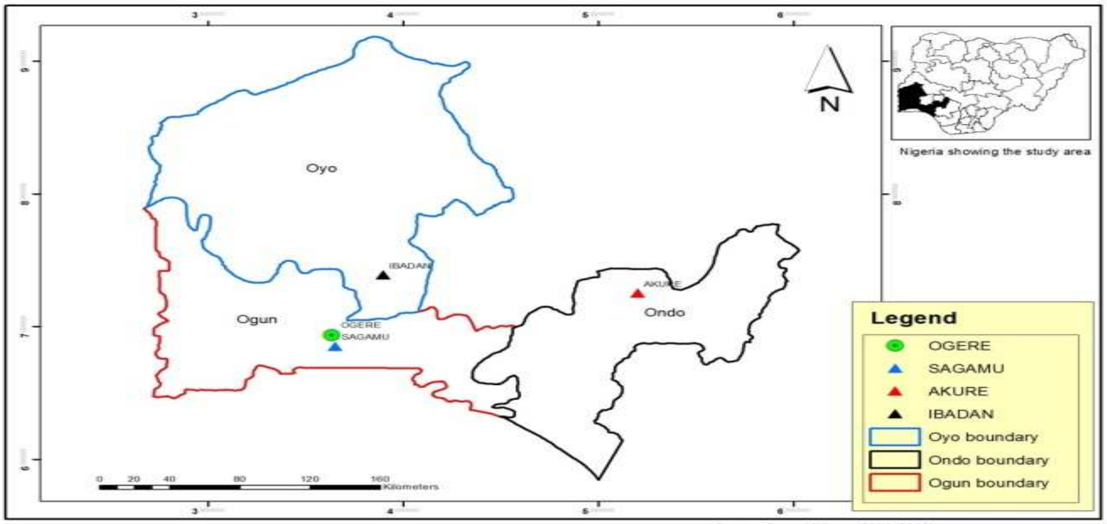
NTRODUCTION

The stability constant of a complex is the numerical expression of its stability and provides a quantitative measure of affinity of the metal ion to the complexing agent. An understanding of the relative stability of metal-complexes helps in predicting the behavior of metal ions in the soil (Ram and Raman, 1982). Extensive researches has been done to determine the stability constants of the complexes formed between humic acid (HA) with a number of metal ions. Ashok *et al*., (2000) reported that humic acid with hydroxyl, phenoxyl and carboxyl reactive groups can form coordination compound with metal ions at pH 3.5. The stability constants(Log K) for different metal-humic acid complexes indicated the following order of the stabilities of complexes formed between humic acid and metal ion, Cu >Fe >Pb> Ni > Co > Ca > Cd > Zn >Mn> Mg. Andelkovic *et al*., (2010) investigated the binding of Cd(II) to soil humic acid at pH 6.5 and in 0.1M KNO_3 ionic medium. The stability constant for binding indicating greater stability in the case when carboxyl groups are involved in complexation reaction. Kostic *et al*.,(2012) investigated the complexation of humic acid with certain heavy metal ions (Co(II), Ni(II),Cu(II), Zn(II), and Pb(II). The experiment was performed at 25°C, at pH 4.0 and ionic strength of 0.01M. Stability constant of complex between Pb(II) ions and humic acid is greater than stability constants of other investigated metal-humate complexes. Bogata and Sokolowska (2016) analyses the interaction between humic acids from different soils and Zn (II) ions at wide concentration ranges and at pH 5. Studies have showed significant impact of Zn concentration, pH and some properties of humic acids with zinc.But all of these studies were limited to acidic pH range. Therefore, the present study was carried out to determine and compare the stability constants of complexes of metal ions with hydrolysed peat soil humic acid and unhydrolysed peat soil humic under non-acid conditions.

MATERIALS AND METHODS

Analytical grade chemicals used includes hydrochloric acid (HCl), nitric acid (HNO_3), sodium hydroxide (NaOH), lead nitrate $Pb(NO_3)_2$, copper nitrate $Cu(NO_3)_2.3H_2O$, cadmium nitrate $Cd(NO_3)_2.4H_2O$, magnesium nitrate $Mg(NO_3)_2.6H_2O$, potassium nitrate (KNO_3), calcium chloride ($CaCl_2$), (sigma-Aldrich). Dowex 50WX8, (20-50 mesh) from Fluka.

Area of study



Source: Dept. of Geog. BUK (2016)

Figure 1: Map showing the sampling point at Sagamu Town, Ogun State.

Description of Sampling Area

Sagamu has geographical coordinates between 6°50′ north; 3° 38′ east is located in south western region of Nigeria. The region has tropical wet and dry climate with a lengthy wet season and relatively constant temperatures throughout the course of the year. Wet season runs from March to October, November to December forms the region dry season. The vegetation type of the region is savannah which is really grassland with small bushes and occasional big trees. Grassland soils have substantially higher organic matter content than forest soils (Novackova, 2011).

Sample Collection

The Peatsoil samples were collected from four different sampling points (0-10cm depth) in Sagamu into polyethylene bag with plastic spoons. Samples were taken to the laboratory, extraneous materials were removed; the samples were air-dried, crushed and ground to a fine powder in a mortar passed through a 0.20mm sieve. The samples were kept for analysis.

Isolation and purification of humic acid from peat soil sample

Peatsoil sample (100g) was mixed with 1000 cm^3 of 0.1M NaOH solution, shaken for 3hours and left to stand overnight. Dark-coloured supernatant was obtained and decanted from solid residue. The dark-coloured supernatant was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 6 hours. Yellowish brown supernatant and dark-brown precipitate were obtained. The yellowish brown supernatant was decanted followed by centrifuge and discarded. The dark-brown precipitate was mixed with $500cm^3$of 0.1M NaOH solution followed by passing through dowex resin. The dark-brown solution was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 3 hours. The dark-brown precipitate was washed several times with deionized water. The supernatant was treated with $AgNO_3$ solution until no white precipitate observed. The humic acid was transferred to weighed crucible and dried at 60^oC in an oven for 12 hours. The humic acid was cooled and dried in the desiccator, weighed and recorded. The obtained humic acid was dried again at 60^oC for additional 6 hours cooled and dried in the desiccator, weighed and recorded constant weight was obtained (Baruah *et al*., 2015).

FT-IR analysis

FT-IR spectra of humic acid sample was analysed using Carry 630 FT-IR Agilent Technologies.

Unhydrolysed compost humic acid

The unhydrolysed humic acid was obtained after isolation and purification of compost humic acid and kept for investigation.

Acid hydrolysis of Peatsoil acid

Peatsoil humic acid sample (1g) was refluxed for 12 hours at (160^oC) with $50cm^3$ of 6M HCl. The mixture was allowed to cool, decanted, and centrifuged after hydrolysis. The insoluble residues were washed with distilled water via centrifugation several times, and the supernatant was treated with $AgNO_3$ solution until no white precipitate was observed. The residue was thoroughly dried over $CaCl_2$ in a desiccator at room temperature (Chefetz *et al*., 2002). Finally, the obtained hydrolysed humic acid was kept for investigation.

Potentiometric Titrations

Potentiometric measurements were carried out using a pH-meter Jenway (model 3510) with combine electrode, the sensitivity of the pH - meter is 0.01 units. The pH meter was switched on half an hour before starting the titration for initial warm up of the instrument. The instrument was calibrated with an aqueous standard buffer solution of pH 4.00 and 10.0 (borate buffer) prepared from a "Qualigens" buffer tablets.

The following sets of solutions were prepared in a 250cm^3 volumetric flask separately for pH metric titrations.

(i) 5 cm^3 0.1 M HCl + 40 cm^3 deionized water

(ii) 5 cm^3 0.1 M HCl + 39 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid

(iii) 5 cm^3 0.1 M HCl + 37 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid + 2 cm^3 0.01 M Cu(II)

The solutions were titrated against standardized 0.110MNaOH separately. The total volume of each mixture was adjusted to 50 cm^3 and the ionic strength of the solutions was maintained constant at by adding appropriate amount of stock solution of 1M KNO$_3$ (Gamal, 2015; Omar and Ali, 2015). A magnetic stirrer was used to achieve thorough mixing of the interacting solutions at 550 rpm. The same set of experimental conditions was applied for potentiometric titration of remaining samples.

Evaluation of pKa of Hydrolysed peat soil Humic Acids

The proton-ligand formation number n$_{\mathbf{A}}$ were calculated by Irving and Rossotti expression (Omar and Ali, 2015).

$$nA = Y- \frac{(V2-V1)(No-Eo)}{(Vo+V1)TcL} \quad ....1$$

Where: Y is number of dissociable proton, (V$_2$-V$_1$) is the measure of displacement of the ligand curve relative to acid curve, N^o and E^o are the resultant concentration of alkali solution, free acid solution, T$_{cL}$^{o} is the total ligand concentration, V^o is the total volume of titration solution,V$_1$ is the volume of alkali added to acid solution,V$_2$ is the volume of alkali added to acid solution + ligand solution, acid dissociation constants (pKa - values) of ligand were calculated by algebraic method point wise calculation (Tables 1). The dissociation constants (pKa) were calculated according to the following relation:

$$pKa = pH + \log(\frac{nA}{1-nA}) \quad ....2$$

Where: pKa is the acid dissociation constant, n$_A$is the Proton-ligand formation number and pH is the pH-values (Omar and Ali, 2015).

Determination of metal-ligand stability constants (log K) of complexes

The potentiometric measurement for the determination of stability constant of a complex in solution is based on the fact that the redox potential of the couple $\frac{M^{+(m-n)}}{M^{+m}}$ is shifted significantly on complexation of the metal ion with the ligand. This method involves change in hydrogen ion concentration [H$^+$] due to the displacement or association of one or more protons taking place during complexation reaction. This change can be found out by titrating the solutions containing free acid, acid with ligand, and acid with ligand and metal ion, individually against a standard alkali solution at a constant ionic strength or temperature. Either ionic strength or temperature may be varied for different sets of solutions. In all the cases, the change in the pH of the solution is measured after each addition of a known amount of alkali to the reaction cell which contains the reaction mixture. The titration curves are then drawn by plotting the measured pH values against the corresponding volume of alkali added and the stability constants of the complexes are determined from the titration curves by employing pH-metric titration technique given by (Irving and Rossoti).

Metal-ligand stability constants (Log K) were determined by using the following relations:

$$\bar{n} = \frac{(V_3 - V_2)(E^0 + N^0)}{(V^0 + V_2)\bar{n}_A T_m^0} \quad ....3$$

and

$$PL = \log_{10}\{\frac{1+\beta_n^H \frac{1}{[anti\ \log pH]^n}}{T_L^0 - \bar{n}T_m^0} X \frac{(V^0+V_3)}{V^0}\} \quad ....4$$

Where $T_{L,}$ T^o, E°, and V^ohavethe same significance as in equation (1) above, T_m denotes the total concentration of metal present in solution, V_3 is the volume of metal ions present in solution and β^H is the overall proton ligand stability constant. The metal-ligand stability constants (log K) were determined by employing point wise computational Method (eq. 5 and 6).

$$\text{Log}K_1 = \log\left(\frac{n}{1-n}\right) + pL \qquad \text{.............5}$$

$$\text{Log}K_2 = \log\left(\frac{1-n}{2-n}\right) + pL\text{.......................6}$$

Where: Log K is the metal-ligand stability constant, pL is the Free ligand exponent function, **n** is the Average number of ligand attached with metal ion (Janrao*et al*., 2014).The results obtained were analyzed by an ORIGIN 2016 program using titration data and then the proton-ligand stability constants (pKa) and Metal-ligand stability constant (LogK) calculated (Omar and Ali, 2015).

RESULTS AND DISCUSSION

Fourier transformed infrared (FT-IR) spectra of isolated humic acid from peat soils Figure 2 had distinct clear absorption bands indicating the presence of major humic acid structural elemental groups such as H bonded OH (3680cm^{-1} peak), C=O of carbonyl (1721cm^{-1} peak), functional groups of aliphatic components CH_2 (2918cm^{-1} peak) and C-O stretching of polysaccharide (1168cm^{-1} peak). The positions of the absorption bands of the spectra fell within typical major absorption bands of humic acid which is at frequencies 3680, 2918, 1721, 1168 cm^{-1}. The first peak centred in the vicinity of 3680 cm^{-1} region is attributed to phenol OH group bounded by intermolecular H bonds. The 2918cm^{-1} band usually has absorption maximum at 2918 cm^{-1} which is due to C–H stretching of alkane group (CH_2). The next major absorption band is 1721 cm^{-1}. This band has been commonly ascribed to C=O stretching of mainly carboxyl group (COOH) with trace amount of ketones. The last peak was observed at 1168 cm^{-1} due to C–O stretching of polysaccharides and this peak appeared also in the spectra of humic acid from peat soil. The FTIR spectra of the isolated humic acid contained all major characteristic absorption peaks of humic acid. These absorption peaks indicated the presence of the major structural elements of humic acid namely H bonded OH, C=C of aromatic ring, C=O of carbonyl group (both carboxyl and ketonic), CH_2 group. This strongly supports the presence of humic acid.

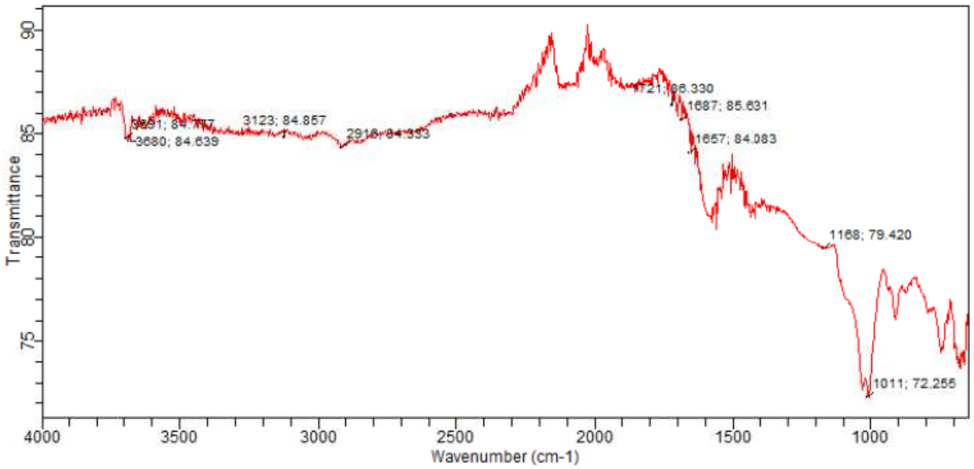


Fig. 2 : FT-IR spectraof peatsoilhumic acid (PSHA)

Evaluation of acid dissociation constant (pka) of acid hydrolysed peat soil humicacid at phenolic group

The value of the dissociation constant of the peat soil humic acid (PSHA) that underwent acidhydrolysis studied was found to be 8.9299 as shown Table 1, which is lower than the literaturevalues reported by Almeida and Szpoganics, (2015), Borges *et al*., (2005); Badr *et al*., (2012)and Fernandes *et al*,.(2009) of 9.73, 9.47 and 10.30. The difference between the obtained valuesand the reported values in this study might be probably as a result of acid hydrolysis of humicacid.

Table 1: PKa of (Hydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	log($\frac{nA}{1-nA}$)	pKa
8.50	5.30	6.29	0.99	0.3594	-0.2510	8.2490
8.72	5.35	6.37	1.02	0.3400	-0.2880	8.4320
9.00	5.40	6.46	1.06	0.3141	-0.3391	8.6609
9.22	5.45	6.55	1.10	0.2882	-0.3927	8.8273
9.51	5.50	6.66	1.16	0.2494	-0.4786	9.0314
9.73	5.55	6.78	1.23	0.2041	-0.5910	9.1390
10.00	5.60	6.90	1.30	0.1589	-0.7238	9.2762
10.23	5.65	7.05	1.40	0.0941	-0.9835	9.2465
10.49	5.70	7.10	1.40	0.0941	-0.9835	9.5065

Average pKa = 8.9299 ± 0.4186

Table 2: PKa of (Unhydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	Log($\frac{nA}{1-n}$)	pKa
8.50	5.30	5.81	0.51	0.6619	0.2919	8.7919
8.72	5.35	5.90	0.55	0.6357	0.2418	8.9618
9.00	5.40	6.00	0.60	0.6029	0.1813	9.1813
9.22	5.45	6.10	0.65	0.5701	0.1226	9.3426
9.51	5.50	6.20	0.70	0.5376	0.0654	9.5754
9.73	5.55	6.33	0.78	0.4851	-0.0259	9.7041
10.00	5.60	6.47	0.87	0.4262	-0.1291	9.8709
10.23	5.65	6.62	0.99	0.3609	-0.2481	9.9819
10.49	5.70	6.80	1.10	0.2759	-0.4690	10.0210

Average pKa = 9.4923± 0.4410

Metal-ligand stability constant (Log K)

The stabilityconstants require the accurate values of proton-ligand stability constants (Anil and Maroti, 2008). Metal titration curves crossed over ligand titration curve indicated the formation of complex upon proton release (Santosh, *et al.*, 2011). If the values of n- are within range 0.2-0.8 and 1.2-18 this indicates the formation of 1:1 and 1:2 complexes (Sayyed and Mazahar, 2012).

The metal (II)-humate stepwise stability constants (log k) at phenolic group (Tables 3-18)

Table 3: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n}{1-n}$)	$LogK_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

$LogK_1$ (Average value) = 2.4788± 0.2203

Table 4: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	Log($\frac{n-1}{2-n}$)	$LogK_2$
9.51	5.50	6.66	6.73	0.07	1.3509	1.70	-0.2671	1.4329
9.73	5.55	6.78	6.85	0.07	1.6383	1.51	0.2467	1.7567
10.00	5.60	6.90	6.98	0.08	2.1783	1.31	-0.2158	1.0942
10.23	5.65	7.05	7.13	0.08	4.1904	1.27		
10.49	5.70	7.10	7.19	0.09	4.6920			

$LogK_2$(Average value) = 1.4280 ± 0.3312

Table 5:Point-wise method,Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	Log$(\frac{n}{n-1})$	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430

$LogK_1$ **(Average value)** = 2.3059± 0.6153

Table 6:Point-wise method, Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log$(\frac{n-1}{2-n})$	Log K_2
9.73	5.55	6.33	6.42	0.09	0.9000	1.69		
10.00	5.60	6.47	6.58	0.11	1.2578	1.44	-0.4592	0.9808
10.23	5.65	6.62	6.84	0.12	1.6137	1.26	-0.2010	1.4610
10.49	5.70	6.80	6.92	0.12	2.1052	1.03		

$LogK_2$ **(Average value)** = 1.2209± 0.3398

Table 7:Point-wise method,Pb (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log$(\frac{n}{1-n})$	$LogK_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.60	0.05	0.8333	1.96	0.6989	2.6589

$LogK_1$ (Average value) = 2.5832 ±0.1614

Table 8:Point-wise method,Pb-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log$(\frac{n-1}{2-n})$	$logK_2$
9.51	5.50	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.83	0.05	1.1702	1.44		
10.00	5.60	6.90	6.90	0.05	1.4864	1.22	-0.0237	1.1963
10.23	5.65	7.05	7.10	0.05	2.0190	1.09		
10.49	5.70	7.10	7.17	0.07	3.6492	1.00		

$LogK_2$(Average value) = 1.1963

Table 9:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log $(\frac{n}{n-1})$	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.5477	2.3123
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	0.0272	2.2072
9.51	5.50	6.20	6.26	0.07	0.6417	1.89	0.2530	2.1430
9.73	5.55	6.40	6.40	0.07	0.7000	1.67	0.3680	2.0380

$LogK_1$ **(Average value)** = 2.2364 ± 0.1602

Table 10:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log$(\frac{n-1}{2-n})$	Log K_2
10.00	5.60	6.47	6.55	0.08	1.9503	1.41		
10.23	5.65	6.62	6.72	0.11	1.4792	1.26	-0.0361	1.2239

$LogK_2$ **(Average value)** = 1.2239

Table 11:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log$(\frac{n}{n-1})$	$LogK_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4290	2.2110
8.72	5.35	6.37	6.39	0.02	0.2858	2.42	-0.3978	2.0222
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

$LogK_1$ (Average value)=2.1382**±**0.1046

Table 12:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$\log(\frac{n-1}{2-n})$	$LogK_2$
9.51	5.55	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.84	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.93	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.10		
10.49	5.70	7.10	7.18	0.07	3.6492	0.83		

$LogK_2$(Average value) = 1.5453 **±** 0.3450

Table 13:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$Log(\frac{n}{n-1})$	$Log\ K_1$
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.3477	2.3123
9.00	5.40	6.00	6.04	0.04	0.3236	2.38	-0.3202	2.0598
9.22	5.45	6.10	6.15	0.05	0.4297	2.17	-0.1230	2.0470
9.51	5.50	6.20	6.26	0.06	0.5500	1.89	0.0871	1.9771
9.73	5.55	6.33	6.40	0.07	0.7000	1.67	0.3680	2.0380

$LogK_1$ **(Average value)** = 2.1568 ± 0.2069

Table 14:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$Log(\frac{n-1}{2-n})$	$Log\ K_2$
10.00	5.60	6.47	6.55	0.08	0.9148	1.41		
10.23	5.65	6.62	6.71	0.09	1.2102	1.20	-0.5749	0.6251
10.49	5.70	6.80	6.92	0.09	1.5968	1.03	0.1703	1.2003

$LogK_2$ **(Average value)** = 0.9127± 0.4070

Table15:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$Log(\frac{n}{1-n})$	$LogK_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4210	2.2190
8.72	5.35	6.37	6.40	0.03	0.4286	2.42	-0.1249	2.2951
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.96	0.3010	2.2610
9.51	5.55	6.66	6.70	0.04	0.7720	1.67	0.5297	2.1997

$LogK_1$ (Average value) = 2.2108± 0.0825

Table 16:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$Log(\frac{n-1}{2-n})$	$Log\ K_2$
9.73	5.55	6.78	6.83	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.95	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.09		
10.49	5.70	7.10	7.16	0.06	3.1429	0.89		

$LogK_2$ **(Average value)** = 1.5453± 0.3450

Table 17:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$Log(\frac{n}{n-1})$	$Log\ K_1$
8.50	5.30	5.81	5.86	0.05	0.3717	2.88	-0.2280	2.6520
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.06	0.06	0.4853	2.38	-0.0255	2.3545
9.22	5.45	6.10	6.16	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430
9.73	5.55	6.33	6.41	0.08	0.8000	1.69	0.6020	2.2920

$LogK_1$ **(Average value)** = 2.2516± 0.5380

Table 18:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$\text{Log}(\frac{n-1}{2-n})$	Log K_2
10.00	5.60	6.47	6.57	0.10	1.1434	1.43		
10.23	5.65	6.62	6.72	0.10	1.3448	1.23	-0.2788	0.9512
10.49	5.70	6.80	6.90	0.10	1.7742	1.03	0.5351	1.5651

LogK_2 **(Average value)** = 1.2581± 0.4340

Table 19: Stepwise and overall Stability constants of thehydrolysed and unhydrolysed divalent metal (II) complexes

Chelates	**LogK_1**	**LogK_2**	**Logβ**
[Cu (Hydrolysed PSHA-1)$_2$]	2.4788	1.4280	3.9068
[Pb (Hydrolysed PSHA-1)$_2$]	2.5832	1.1963	3.7795
[Cd (Hydrolysed PSHA-1)$_2$]	2.2108	1.5453	3.7561
[Mg (Hydrolysed PSHA-1)$_2$]	2.1382	1.5453	3.6835
[Cu (Unhydrolysed PSHA-1)$_2$]	2.3059	1.2209	3.5268
[Pb (Unhydrolysed PSHA-1)$_2$]	2.2364	1.2239	3.4603
[Cd (Unhydrolysed PSHA-1)$_2$]	2.2516	1.2581	3.5097
[Mg (Unydrolysed PSHA-1)$_2$]	2.1568	0.9127	3.0695

The results obtained (Table19) shows the stepwise and overall stability constants to be not high indicating low stability of the complexes, because the solubility of most metal ions in the basic pH range is minimal due to metal hydroxide precipitation (Karimi, 2017). In general, the stepwise stability constants (K_1 and K_2) follow the order $K_1 > K_2$ for the copper, lead, magnesium and cadmium complexes respectively. The steady decrease of the values with increasing number of ligands is in agreement with the prediction made by researchers (Na'aliya, 2013). The decrease could be attributed to the fact that as the number of the ligands (Humate ions) that enters the coordination zone increases the aqua molecules available for replacement by the ligands become less. Thus, the metal ions become less electron loving with progressive intake of the ligand and this results in the decrease in the values of the constants (Na'aliya, 2013). Also the stability of the complexes is influenced by the size and number of the chelate rings(Mackay and Mackay,2002).All the complexes form rings in their structure as humate, a bidentate ligand, bond the metal ions in the ratio 1:2 (Boguta and Sokolowska, 2016) forming chelate rings. The values of the overall stability constants (logβ) obtained for humate complexes are not high indicating low stability as the values are not high. LogK values for copper-humates (Table 3 to 6) obtained in this study are lower than those reported for the complexes of humic acids (Pandey *et al.*, 2015; Dinu, 2013; Kaschl *et al.*, 2010 and Gilbeto and Jorg, 2001). The values of LogK(Table 7 to 10) forlead-humates are lower than those reported for the lead in the literature (Dinu, 2013; Gilbeto and Jorg 2001). Log K values(Table 11 to 14) for magnesium-humates obtained in this study are close to those reported by (Pandey *et al.*, 2015). Log K values of cadmium-humates (Table 15 to 18) obtained in this work near to the one reported by (Dinu, 2013 and Pandey *et al.*, 2015).The difference between the reported values and the values obtained in this study might be probably as a result of acid hydrolysis of humic acid. The values of the overall stability constants (log β) of the copper humates complexes presented in Table 19 is high than that of other metal humate complexes, show relatively high stability of Cu-HA complexes, show the following order of stability: Cu >Pb> Cd > Mg; which are in close agreement to the findings of (Dinu, 2013 and Pandey *et al.*, 2015).The high stability of Cu-humate chelate could be attributed to the existence of coordinate covalent bond between the complexing agents and the Cu^{2+} ions. Since, Cu^{2+} being a metal of the transitional series with $3d^9$ electronic configurations can accept the electrons from the complexing agents. Similarly,the low stabilities of Pb,Cd and Mg -complexes could be explained by that Pb^{2+} with $6s^2$, Cd^{2+} with $4d^{10}$ and Mg^{2+} with $2p^6$ their electronic configuration has a completely filled d,p and s orbitals. Moreover, the stabilities of metal ions with hydrolysed humic acid from peat soil were higher than those with unhydrolysed humic acid from peat soil; which is ascribed to the high content of acidity in hydrolysed humic acid than unhydrolysed humic acid.

CONCLUSION

The values of logK for Cu(II) hydrolysed humic acid complex was higher followed by Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes as compared with metal(II) unhydrolysed humic acid complexes . This indicates acid hydrolysis of humic acid can enhance the complexation behavior of humic acid with metal (II) ions. However, the higher values of logβ for Cu(II), Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes indicates more stable stepwise complexes formed as compared with Cu(II), Pb(II), Cd(II) and Mg(II) unhydrolysed humic acid complexes.

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STABILITY CONSTANTS OF COMPLEXES OF METAL IONS WITH PEATSOIL HUMIC ACIDS UNDER NON-ACID-CONDITIONS

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ABSTRACT

Stability constants of complexes of four divalent metal ions viz. Cu^{2+}, Pb^{2+},Mg^{2+} and Cd^{2+} with humic acids (HA) were determined by potentiometric titration of humic acids with the corresponding salt of the divalent metals in aqueous media under non-acid-condition. The log K (logarithm of the stability constant) ranged from 1.0942 to 2.7471 for metal-humic acid complexes were determined using point-wise computational method. The order of stability constants were obtained as follows: Cu >Pb> Cd > Mg for metal -HA complexes respectively, indicating a higher degree of complexation with Cu metal ion.

Keywords: stability constant, humic acid, potentiometric titration, divalent metals, acid hydrolysis.

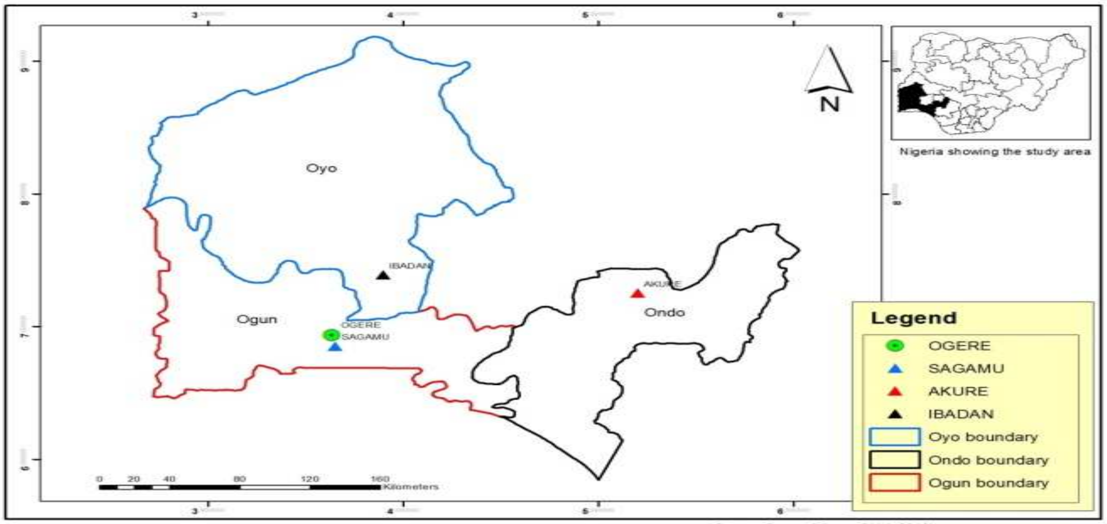
NTRODUCTION

The stability constant of a complex is the numerical expression of its stability and provides a quantitative measure of affinity of the metal ion to the complexing agent. An understanding of the relative stability of metal-complexes helps in predicting the behavior of metal ions in the soil (Ram and Raman, 1982). Extensive researches has been done to determine the stability constants of the complexes formed between humic acid (HA) with a number of metal ions. Ashok *et al.*, (2000) reported that humic acid with hydroxyl, phenoxyl and carboxyl reactive groups can form coordination compound with metal ions at pH 3.5. The stability constants(Log K) for different metal-humic acid complexes indicated the following order of the stabilities of complexes formed between humic acid and metal ion, Cu >Fe >Pb> Ni > Co > Ca > Cd > Zn >Mn> Mg. Andelkovic *et al.*, (2010) investigated the binding of Cd(II) to soil humic acid at pH 6.5 and in 0.1M KNO_3 ionic medium. The stability constant for binding indicating greater stability in the case when carboxyl groups are involved in complexation reaction. Kostic *et al.*,(2012) investigated the complexation of humic acid with certain heavy metal ions (Co(II), Ni(II),Cu(II), Zn(II), and Pb(II). The experiment was performed at 25°C, at pH 4.0 and ionic strength of 0.01M. Stability constant of complex between Pb(II) ions and humic acid is greater than stability constants of other investigated metal-humate complexes. Bogata and Sokolowska (2016) analyses the interaction between humic acids from different soils and Zn (II) ions at wide concentration ranges and at pH 5. Studies have showed significant impact of Zn concentration, pH and some properties of humic acids with zinc.But all of these studies were limited to acidic pH range. Therefore, the present study was carried out to determine and compare the stability constants of complexes of metal ions with hydrolysed peat soil humic acid and unhydrolysed peat soil humic under non-acid conditions.

MATERIALS AND METHODS

Analytical grade chemicals used includes hydrochloric acid (HCl), nitric acid (HNO_3), sodium hydroxide (NaOH), lead nitrate $Pb(NO_3)_2$, copper nitrate $Cu(NO_3)_2.3H_2O$, cadmium nitrate $Cd(NO_3)_2.4H_2O$, magnesium nitrate $Mg(NO_3)_2.6H_2O$, potassium nitrate (KNO_3), calcium chloride ($CaCl_2$), (sigma-Aldrich). Dowex 50WX8, (20-50 mesh) from Fluka.

Area of study



Source: Dept. of Geog. BUK (2016)

Figure 1: Map showing the sampling point at Sagamu Town, Ogun State.

Description of Sampling Area

Sagamu has geographical coordinates between 6°50′ north; 3° 38′ east is located in south western region of Nigeria. The region has tropical wet and dry climate with a lengthy wet season and relatively constant temperatures throughout the course of the year. Wet season runs from March to October, November to December forms the region dry season. The vegetation type of the region is savannah which is really grassland with small bushes and occasional big trees. Grassland soils have substantially higher organic matter content than forest soils (Novackova, 2011).

Sample Collection

The Peatsoil samples were collected from four different sampling points (0-10cm depth) in Sagamu into polyethylene bag with plastic spoons. Samples were taken to the laboratory, extraneous materials were removed; the samples were air-dried, crushed and ground to a fine powder in a mortar passed through a 0.20mm sieve. The samples were kept for analysis.

Isolation and purification of humic acid from peat soil sample

Peatsoil sample (100g) was mixed with 1000 cm^3 of 0.1M NaOH solution, shaken for 3hours and left to stand overnight. Dark-coloured supernatant was obtained and decanted from solid residue. The dark-coloured supernatant was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 6 hours. Yellowish brown supernatant and dark-brown precipitate were obtained. The yellowish brown supernatant was decanted followed by centrifuge and discarded. The dark-brown precipitate was mixed with 500$cm^3$of 0.1M NaOH solution followed by passing through dowex resin. The dark-brown solution was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 3 hours. The dark-brown precipitate was washed several times with deionized water. The supernatant was treated with $AgNO_3$ solution until no white precipitate observed. The humic acid was transferred to weighed crucible and dried at 60°C in an oven for 12 hours. The humic acid was cooled and dried in the desiccator, weighed and recorded. The obtained humic acid was dried again at 60°C for additional 6 hours cooled and dried in the desiccator, weighed and recorded constant weight was obtained (Baruah *et al*., 2015).

FT-IR analysis

FT-IR spectra of humic acid sample was analysed using Carry 630 FT-IR Agilent Technologies.

Unhydrolysed compost humic acid

The unhydrolysed humic acid was obtained after isolation and purification of compost humic acid and kept for investigation.

Acid hydrolysis of Peatsoil acid

Peatsoil humic acid sample (1g) was refluxed for 12 hours at (160°C) with 50cm^3 of 6M HCl. The mixture was allowed to cool, decanted, and centrifuged after hydrolysis. The insoluble residues were washed with distilled water via centrifugation several times, and the supernatant was treated with $AgNO_3$ solution until no white precipitate was observed. The residue was thoroughly dried over $CaCl_2$ in a desiccator at room temperature (Chefetz *et al*., 2002). Finally, the obtained hydrolysed humic acid was kept for investigation.

Potentiometric Titrations

Potentiometric measurements were carried out using a pH-meter Jenway (model 3510) with combine electrode, the sensitivity of the pH - meter is 0.01 units. The pH meter was switched on half an hour before starting the titration for initial warm up of the instrument. The instrument was calibrated with an aqueous standard buffer solution of pH 4.00 and 10.0 (borate buffer) prepared from a "Qualigens" buffer tablets.

The following sets of solutions were prepared in a 250cm^3 volumetric flask separately for pH metric titrations.

(i) 5 cm^3 0.1 M HCl + 40 cm^3 deionized water

(ii) 5 cm^3 0.1 M HCl + 39 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid

(iii) 5 cm^3 0.1 M HCl + 37 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid + 2 cm^3 0.01 M Cu(II)

The solutions were titrated against standardized 0.110MNaOH separately. The total volume of each mixture was adjusted to 50 cm^3 and the ionic strength of the solutions was maintained constant at by adding appropriate amount of stock solution of 1M KNO_3 (Gamal, 2015; Omar and Ali, 2015). A magnetic stirrer was used to achieve thorough mixing of the interacting solutions at 550 rpm. The same set of experimental conditions was applied for potentiometric titration of remaining samples.

Evaluation of pKa of Hydrolysed peat soil Humic Acids

The proton-ligand formation number $n_{\mathbf{A}}$ were calculated by Irving and Rossotti expression (Omar and Ali, 2015).

$$nA = Y- \frac{(V2-V1)(No-Eo)}{(Vo+V1)TcL} \text{ ………………………………1}$$

Where: Y is number of dissociable proton, (V_2-V_1) is the measure of displacement of the ligand curve relative to acid curve, N^o and E^o are the resultant concentration of alkali solution, free acid solution, $T_{cL}{}^o$ is the total ligand concentration, V^o is the total volume of titration solution,V_1 is the volume of alkali added to acid solution,V_2 is the volume of alkali added to acid solution + ligand solution, acid dissociation constants (pKa - values) of ligand were calculated by algebraic method point wise calculation (Tables 1). The dissociation constants (pKa) were calculated according to the following relation:

$$pKa = pH + \log(\frac{nA}{1-nA}) \text{ …………………………2}$$

Where: pKa is the acid dissociation constant, $n_A$is the Proton-ligand formation number and pH is the pH-values (Omar and Ali, 2015).

Determination of metal-ligand stability constants (log K) of complexes

The potentiometric measurement for the determination of stability constant of a complex in solution is based on the fact that the redox potential of the couple $\frac{M^{+(m-n)}}{M^{+m}}$ is shifted significantly on complexation of the metal ion with the ligand. This method involves change in hydrogen ion concentration [H$^+$] due to the displacement or association of one or more protons taking place during complexation reaction. This change can be found out by titrating the solutions containing free acid, acid with ligand, and acid with ligand and metal ion, individually against a standard alkali solution at a constant ionic strength or temperature. Either ionic strength or temperature may be varied for different sets of solutions. In all the cases, the change in the pH of the solution is measured after each addition of a known amount of alkali to the reaction cell which contains the reaction mixture. The titration curves are then drawn by plotting the measured pH values against the corresponding volume of alkali added and the stability constants of the complexes are determined from the titration curves by employing pH-metric titration technique given by (Irving and Rossoti).

Metal-ligand stability constants (Log K) were determined by using the following relations:

$$\bar{n} = \frac{(V_3 - V_2)(E^0 + N^0)}{(V^0 + V_2)\bar{n}_A T_m^0} \text{ ……………………………………………………………………3}$$

and

$$PL = \log_{10}\{\frac{1 + \beta_n^H \frac{1}{[anti\ \log pH]^n}}{T_L^0 - \bar{n}T_m^0} X \frac{(V^0 + V_3)}{V^0}\} \text{ ……………………………………………………4}$$

Where $T_{L,}$ T^o, E°, and V^ohavethe same significance as in equation (1) above, T_m denotes the total concentration of metal present in solution, V_3 is the volume of metal ions present in solution and β^H is the overall proton ligand stability constant. The metal-ligand stability constants (log K) were determined by employing point wise computational Method (eq. 5 and 6).

$$\text{Log}K_1 = \log\left(\frac{n}{1-n}\right) + pL \qquad \ldots\ldots\ldots\ldots.5$$

$$\text{Log}K_2 = \log\left(\frac{1-n}{2-n}\right) + pL\ldots\ldots\ldots\ldots\ldots\ldots\ldots.6$$

Where: Log K is the metal-ligand stability constant, pL is the Free ligand exponent function, **n** is the Average number of ligand attached with metal ion (Janrao*et al.*, 2014).The results obtained were analyzed by an ORIGIN 2016 program using titration data and then the proton-ligand stability constants (pKa) and Metal-ligand stability constant (LogK) calculated (Omar and Ali, 2015).

RESULTS AND DISCUSSION

Fourier transformed infrared (FT-IR) spectra of isolated humic acid from peat soils Figure 2 had distinct clear absorption bands indicating the presence of major humic acid structural elemental groups such as H bonded OH ($3680cm^{-1}$ peak), C=O of carbonyl ($1721cm^{-1}$ peak), functional groups of aliphatic components CH_2 ($2918cm^{-1}$ peak) and C-O stretching of polysaccharide ($1168cm^{-1}$ peak). The positions of the absorption bands of the spectra fell within typical major absorption bands of humic acid which is at frequencies 3680, 2918, 1721, 1168 cm^{-1}. The first peak centred in the vicinity of 3680 cm^{-1} region is attributed to phenol OH group bounded by intermolecular H bonds. The $2918cm^{-1}$ band usually has absorption maximum at 2918 cm^{-1} which is due to C–H stretching of alkane group (CH_2). The next major absorption band is 1721 cm^{-1}. This band has been commonly ascribed to C=O stretching of mainly carboxyl group (COOH) with trace amount of ketones. The last peak was observed at 1168 cm^{-1} due to C–O stretching of polysaccharides and this peak appeared also in the spectra of humic acid from peat soil. The FTIR spectra of the isolated humic acid contained all major characteristic absorption peaks of humic acid. These absorption peaks indicated the presence of the major structural elements of humic acid namely H bonded OH, C=C of aromatic ring, C=O of carbonyl group (both carboxyl and ketonic), CH_2 group. This strongly supports the presence of humic acid.

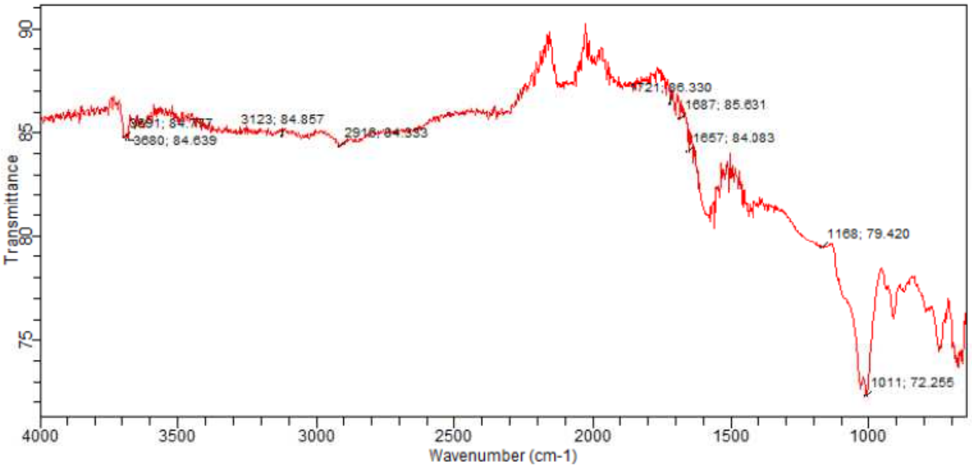


Fig. 2 : FT-IR spectraof peatsoilhumic acid (PSHA)

Evaluation of acid dissociation constant (pka) of acid hydrolysed peat soil humicacid at phenolic group

The value of the dissociation constant of the peat soil humic acid (PSHA) that underwent acidhydrolysis studied was found to be 8.9299 as shown Table 1, which is lower than the literaturevalues reported by Almeida and Szpoganics, (2015), Borges *et al.*, (2005); Badr *et al.*, (2012)and Fernandes *et al*,.(2009) of 9.73, 9.47 and 10.30. The difference between the obtained valuesand the reported values in this study might be probably as a result of acid hydrolysis of humicacid.

Table 1: PKa of (Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	V$_2$-V$_1$	nA	log($\frac{nA}{1-nA}$)	pKa
8.50	5.30	6.29	0.99	0.3594	-0.2510	8.2490
8.72	5.35	6.37	1.02	0.3400	-0.2880	8.4320
9.00	5.40	6.46	1.06	0.3141	-0.3391	8.6609
9.22	5.45	6.55	1.10	0.2882	-0.3927	8.8273
9.51	5.50	6.66	1.16	0.2494	-0.4786	9.0314
9.73	5.55	6.78	1.23	0.2041	-0.5910	9.1390
10.00	5.60	6.90	1.30	0.1589	-0.7238	9.2762
10.23	5.65	7.05	1.40	0.0941	-0.9835	9.2465
10.49	5.70	7.10	1.40	0.0941	-0.9835	9.5065

Average pKa = 8.9299 ± 0.4186

Table 2: PKa of (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	V$_2$-V$_1$	nA	Log($\frac{nA}{1-n}$)	pKa
8.50	5.30	5.81	0.51	0.6619	0.2919	8.7919
8.72	5.35	5.90	0.55	0.6357	0.2418	8.9618
9.00	5.40	6.00	0.60	0.6029	0.1813	9.1813
9.22	5.45	6.10	0.65	0.5701	0.1226	9.3426
9.51	5.50	6.20	0.70	0.5376	0.0654	9.5754
9.73	5.55	6.33	0.78	0.4851	-0.0259	9.7041
10.00	5.60	6.47	0.87	0.4262	-0.1291	9.8709
10.23	5.65	6.62	0.99	0.3609	-0.2481	9.9819
10.49	5.70	6.80	1.10	0.2759	-0.4690	10.0210

Average pKa = 9.4923± 0.4410

Metal-ligand stability constant (Log K)

The stabilityconstants require the accurate values of proton-ligand stability constants (Anil and Maroti, 2008). Metal titration curves crossed over ligand titration curve indicated the formation of complex upon proton release (Santosh, *et al.*, 2011). If the values of n- are within range 0.2-0.8 and 1.2-18 this indicates the formation of 1:1 and 1:2 complexes (Sayyed and Mazahar, 2012).

The metal (II)-humate stepwise stability constants (log k) at phenolic group (Tables 3-18)

Table 3: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	log($\frac{n}{1-n}$)	LogK$_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

LogK$_1$ (Average value) = 2.4788± 0.2203

Table 4: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	Log($\frac{n-1}{2-n}$)	LogK$_2$
9.51	5.50	6.66	6.73	0.07	1.3509	1.70	-0.2671	1.4329
9.73	5.55	6.78	6.85	0.07	1.6383	1.51	0.2467	1.7567
10.00	5.60	6.90	6.98	0.08	2.1783	1.31	-0.2158	1.0942
10.23	5.65	7.05	7.13	0.08	4.1904	1.27		
10.49	5.70	7.10	7.19	0.09	4.6920			

LogK$_2$(Average value) = 1.4280 ± 0.3312

Table 5:Point-wise method,Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	Log($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430

$LogK_1$ **(Average value)** = 2.3059± 0.6153

Table 6:Point-wise method, Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
9.73	5.55	6.33	6.42	0.09	0.9000	1.69		
10.00	5.60	6.47	6.58	0.11	1.2578	1.44	-0.4592	0.9808
10.23	5.65	6.62	6.84	0.12	1.6137	1.26	-0.2010	1.4610
10.49	5.70	6.80	6.92	0.12	2.1052	1.03		

$LogK_2$ **(Average value)** = 1.2209± 0.3398

Table 7:Point-wise method,Pb (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n}{1-n}$)	$LogK_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.60	0.05	0.8333	1.96	0.6989	2.6589

$LogK_1$ (Average value) = 2.5832 ±0.1614

Table 8:Point-wise method,Pb-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n-1}{2-n}$)	$logK_2$
9.51	5.50	6.66	6.71	0.05	0.9650	1.67	-0.0237	1.1963
9.73	5.55	6.78	6.83	0.05	1.1702	1.44		
10.00	5.60	6.90	6.90	0.05	1.4864	1.22		
10.23	5.65	7.05	7.10	0.05	2.0190	1.09		
10.49	5.70	7.10	7.17	0.07	3.6492	1.00		

$LogK_2$(Average value) = 1.1963

Table 9:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log ($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.5477	2.3123
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	0.0272	2.2072
9.51	5.50	6.20	6.26	0.07	0.6417	1.89	0.2530	2.1430
9.73	5.55	6.40	6.40	0.07	0.7000	1.67	0.3680	2.0380

$LogK_1$ **(Average value)** = 2.2364 ± 0.1602

Table 10:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
10.00	5.60	6.47	6.55	0.08	1.9503	1.41		
10.23	5.65	6.62	6.72	0.11	1.4792	1.26	-0.0361	1.2239

$LogK_2$ **(Average value)** = 1.2239

Table 11:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n}{n-1}$)	$LogK_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4290	2.2110
8.72	5.35	6.37	6.39	0.02	0.2858	2.42	-0.3978	2.0222
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

$LogK_1$ (Average value)=2.1382**±**0.1046

Table 12:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	log$(\frac{n-1}{2-n})$	LogK$_2$
9.51	5.55	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.84	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.93	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.10		
10.49	5.70	7.10	7.18	0.07	3.6492	0.83		

LogK$_2$(Average value) = 1.5453 **±** 0.3450

Table 13:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	V$_3$-V$_2$	n	pL	Log$(\frac{n}{n-1})$	Log K$_1$
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.3477	2.3123
9.00	5.40	6.00	6.04	0.04	0.3236	2.38	-0.3202	2.0598
9.22	5.45	6.10	6.15	0.05	0.4297	2.17	-0.1230	2.0470
9.51	5.50	6.20	6.26	0.06	0.5500	1.89	0.0871	1.9771
9.73	5.55	6.33	6.40	0.07	0.7000	1.67	0.3680	2.0380

LogK$_1$ **(Average value)** = 2.1568 ± 0.2069

Table 14:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	V$_3$-V$_2$	n	pL	Log$(\frac{n-1}{2-n})$	Log K$_2$
10.00	5.60	6.47	6.55	0.08	0.9148	1.41		
10.23	5.65	6.62	6.71	0.09	1.2102	1.20	-0.5749	0.6251
10.49	5.70	6.80	6.92	0.09	1.5968	1.03	0.1703	1.2003

LogK$_2$ **(Average value)** = 0.9127± 0.4070

Table15:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	Log$(\frac{n}{1-n})$	LogK$_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4210	2.2190
8.72	5.35	6.37	6.40	0.03	0.4286	2.42	-0.1249	2.2951
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.96	0.3010	2.2610
9.51	5.55	6.66	6.70	0.04	0.7720	1.67	0.5297	2.1997

LogK$_1$ (Average value) = 2.2108± 0.0825

Table 16:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	Log$(\frac{n-1}{2-n})$	Log K$_2$
9.73	5.55	6.78	6.83	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.95	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.09		
10.49	5.70	7.10	7.16	0.06	3.1429	0.89		

LogK$_2$ **(Average value)** = 1.5453± 0.3450

Table 17:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	V$_3$-V$_2$	n	pL	Log$(\frac{n}{n-1})$	Log K$_1$
8.50	5.30	5.81	5.86	0.05	0.3717	2.88	-0.2280	2.6520
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.06	0.06	0.4853	2.38	-0.0255	2.3545
9.22	5.45	6.10	6.16	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430
9.73	5.55	6.33	6.41	0.08	0.8000	1.69	0.6020	2.2920

LogK$_1$ **(Average value)** = 2.2516± 0.5380

Table 18:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$\text{Log}(\frac{n-1}{2-n})$	Log K_2
10.00	5.60	6.47	6.57	0.10	1.1434	1.43		
10.23	5.65	6.62	6.72	0.10	1.3448	1.23	-0.2788	0.9512
10.49	5.70	6.80	6.90	0.10	1.7742	1.03	0.5351	1.5651

LogK_2 **(Average value)** = 1.2581± 0.4340

Table 19: Stepwise and overall Stability constants of thehydrolysed and unhydrolysed divalent metal (II) complexes

Chelates	**LogK_1**	**LogK_2**	**Logβ**
[Cu (Hydrolysed PSHA-1)$_2$]	2.4788	1.4280	3.9068
[Pb (Hydrolysed PSHA-1)$_2$]	2.5832	1.1963	3.7795
[Cd (Hydrolysed PSHA-1)$_2$]	2.2108	1.5453	3.7561
[Mg (Hydrolysed PSHA-1)$_2$]	2.1382	1.5453	3.6835
[Cu (Unhydrolysed PSHA-1)$_2$]	2.3059	1.2209	3.5268
[Pb (Unhydrolysed PSHA-1)$_2$]	2.2364	1.2239	3.4603
[Cd (Unhydrolysed PSHA-1)$_2$]	2.2516	1.2581	3.5097
[Mg (Unydrolysed PSHA-1)$_2$]	2.1568	0.9127	3.0695

The results obtained (Table19) shows the stepwise and overall stability constants to be not high indicating low stability of the complexes, because the solubility of most metal ions in the basic pH range is minimal due to metal hydroxide precipitation (Karimi, 2017). In general, the stepwise stability constants (K_1 and K_2) follow the order $K_1 > K_2$ for the copper, lead, magnesium and cadmium complexes respectively. The steady decrease of the values with increasing number of ligands is in agreement with the prediction made by researchers (Na'aliya, 2013). The decrease could be attributed to the fact that as the number of the ligands (Humate ions) that enters the coordination zone increases the aqua molecules available for replacement by the ligands become less. Thus, the metal ions become less electron loving with progressive intake of the ligand and this results in the decrease in the values of the constants (Na'aliya, 2013). Also the stability of the complexes is influenced by the size and number of the chelate rings(Mackay and Mackay,2002).All the complexes form rings in their structure as humate, a bidentate ligand, bond the metal ions in the ratio 1:2 (Boguta and Sokolowska, 2016) forming chelate rings. The values of the overall stability constants (logβ) obtained for humate complexes are not high indicating low stability as the values are not high. LogK values for copper-humates (Table 3 to 6) obtained in this study are lower than those reported for the complexes of humic acids (Pandey *et al*., 2015; Dinu, 2013; Kaschl *et al*., 2010 and Gilbeto and Jorg, 2001). The values of LogK(Table 7 to 10) forlead-humates are lower than those reported for the lead in the literature (Dinu, 2013; Gilbeto and Jorg 2001). Log K values(Table 11 to 14) for magnesium-humates obtained in this study are close to those reported by (Pandey *et al*., 2015). Log K values of cadmium-humates (Table 15 to 18) obtained in this work near to the one reported by (Dinu, 2013 and Pandey *et al*., 2015).The difference between the reported values and the values obtained in this study might be probably as a result of acid hydrolysis of humic acid. The values of the overall stability constants (log β) of the copper humates complexes presented in Table 19 is high than that of other metal humate complexes, show relatively high stability of Cu-HA complexes, show the following order of stability: Cu >Pb> Cd > Mg; which are in close agreement to the findings of (Dinu, 2013 and Pandey *et al*., 2015).The high stability of Cu-humate chelate could be attributed to the existence of coordinate covalent bond between the complexing agents and the Cu^{2+} ions. Since, Cu^{2+} being a metal of the transitional series with $3d^9$ electronic configurations can accept the electrons from the complexing agents. Similarly,the low stabilities of Pb,Cd and Mg - complexes could be explained by that Pb^{2+} with $6s^2$, Cd^{2+} with $4d^{10}$ and Mg^{2+} with $2p^6$ their electronic configuration has a completely filled d,p and s orbitals. Moreover, the stabilities of metal ions with hydrolysed humic acid from peat soil were higher than those with unhydrolysed humic acid from peat soil; which is ascribed to the high content of acidity in hydrolysed humic acid than unhydrolysed humic acid.

CONCLUSION

The values of logK for Cu(II) hydrolysed humic acid complex was higher followed by Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes as compared with metal(II) unhydrolysed humic acid complexes . This indicates acid hydrolysis of humic acid can enhance the complexation behavior of humic acid with metal (II) ions. However, the higher values of logβ for Cu(II), Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes indicates more stable stepwise complexes formed as compared with Cu(II), Pb(II), Cd(II) and Mg(II) unhydrolysed humic acid complexes.

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STABILITY CONSTANTS OF COMPLEXES OF METAL IONS WITH PEATSOIL HUMIC ACIDS UNDER NON-ACID-CONDITIONS

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ABSTRACT

Stability constants of complexes of four divalent metal ions viz. Cu^{2+}, Pb^{2+},Mg^{2+} and Cd^{2+} with humic acids (HA) were determined by potentiometric titration of humic acids with the corresponding salt of the divalent metals in aqueous media under non-acid-condition. The log K (logarithm of the stability constant) ranged from 1.0942 to 2.7471 for metal-humic acid complexes were determined using point-wise computational method. The order of stability constants were obtained as follows: Cu >Pb> Cd > Mg for metal -HA complexes respectively, indicating a higher degree of complexation with Cu metal ion.

Keywords: stability constant, humic acid, potentiometric titration, divalent metals, acid hydrolysis.

NTRODUCTION

The stability constant of a complex is the numerical expression of its stability and provides a quantitative measure of affinity of the metal ion to the complexing agent. An understanding of the relative stability of metal-complexes helps in predicting the behavior of metal ions in the soil (Ram and Raman, 1982). Extensive researches has been done to determine the stability constants of the complexes formed between humic acid (HA) with a number of metal ions. Ashok *et al.*, (2000) reported that humic acid with hydroxyl, phenoxyl and carboxyl reactive groups can form coordination compound with metal ions at pH 3.5. The stability constants(Log K) for different metal-humic acid complexes indicated the following order of the stabilities of complexes formed between humic acid and metal ion, Cu >Fe >Pb> Ni > Co > Ca > Cd > Zn >Mn> Mg. Andelkovic *et al.*, (2010) investigated the binding of Cd(II) to soil humic acid at pH 6.5 and in 0.1M KNO_3 ionic medium. The stability constant for binding indicating greater stability in the case when carboxyl groups are involved in complexation reaction. Kostic *et al.*,(2012) investigated the complexation of humic acid with certain heavy metal ions (Co(II), Ni(II),Cu(II), Zn(II), and Pb(II). The experiment was performed at 25^{o}C, at pH 4.0 and ionic strength of 0.01M. Stability constant of complex between Pb(II) ions and humic acid is greater than stability constants of other investigated metal-humate complexes. Bogata and Sokolowska (2016) analyses the interaction between humic acids from different soils and Zn (II) ions at wide concentration ranges and at pH 5. Studies have showed significant impact of Zn concentration, pH and some properties of humic acids with zinc.But all of these studies were limited to acidic pH range. Therefore, the present study was carried out to determine and compare the stability constants of complexes of metal ions with hydrolysed peat soil humic acid and unhydrolysed peat soil humic under non-acid conditions.

MATERIALS AND METHODS

Analytical grade chemicals used includes hydrochloric acid (HCl), nitric acid (HNO_3), sodium hydroxide (NaOH), lead nitrate $Pb(NO_3)_2$, copper nitrate $Cu(NO_3)_2.3H_2O$, cadmium nitrate $Cd(NO_3)_2.4H_2O$, magnesium nitrate $Mg(NO_3)_2.6H_2O$, potassium nitrate (KNO_3), calcium chloride ($CaCl_2$), (sigma-Aldrich). Dowex 50WX8, (20-50 mesh) from Fluka.

Area of study

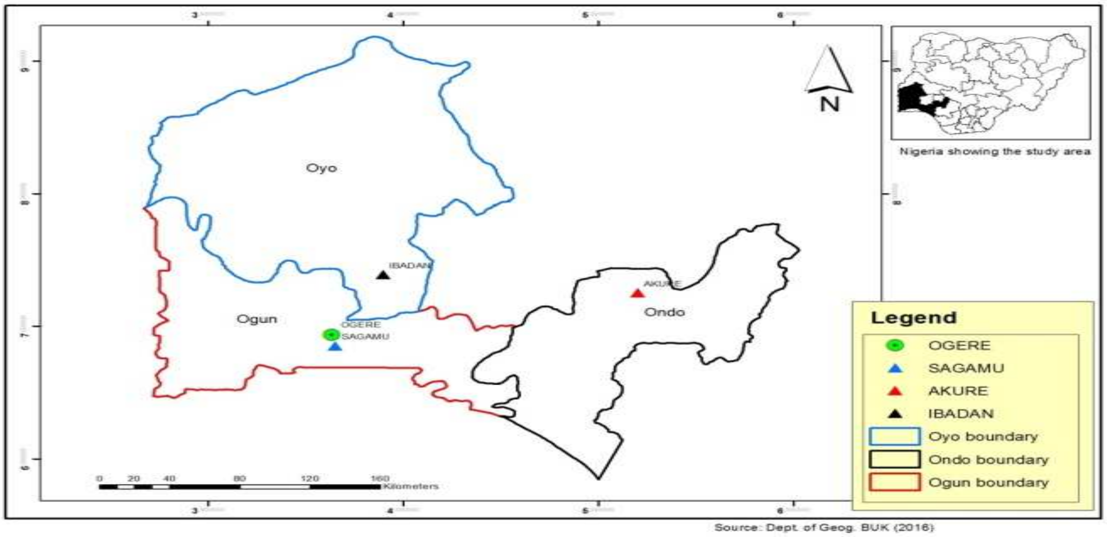

Figure 1: Map showing the sampling point at Sagamu Town, Ogun State.

Description of Sampling Area

Sagamu has geographical coordinates between 6°50′ north; 3° 38′ east is located in south western region of Nigeria. The region has tropical wet and dry climate with a lengthy wet season and relatively constant temperatures throughout the course of the year. Wet season runs from March to October, November to December forms the region dry season. The vegetation type of the region is savannah which is really grassland with small bushes and occasional big trees. Grassland soils have substantially higher organic matter content than forest soils (Novackova, 2011).

Sample Collection

The Peatsoil samples were collected from four different sampling points (0-10cm depth) in Sagamu into polyethylene bag with plastic spoons. Samples were taken to the laboratory, extraneous materials were removed; the samples were air-dried, crushed and ground to a fine powder in a mortar passed through a 0.20mm sieve. The samples were kept for analysis.

Isolation and purification of humic acid from peat soil sample

Peatsoil sample (100g) was mixed with 1000 cm^3 of 0.1M NaOH solution, shaken for 3hours and left to stand overnight. Dark-coloured supernatant was obtained and decanted from solid residue. The dark-coloured supernatant was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 6 hours. Yellowish brown supernatant and dark-brown precipitate were obtained. The yellowish brown supernatant was decanted followed by centrifuge and discarded. The dark-brown precipitate was mixed with 500$cm^3$of 0.1M NaOH solution followed by passing through dowex resin. The dark-brown solution was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 3 hours. The dark-brown precipitate was washed several times with deionized water. The supernatant was treated with $AgNO_3$ solution until no white precipitate observed. The humic acid was transferred to weighed crucible and dried at 60°C in an oven for 12 hours. The humic acid was cooled and dried in the desiccator, weighed and recorded. The obtained humic acid was dried again at 60°C for additional 6 hours cooled and dried in the desiccator, weighed and recorded constant weight was obtained (Baruah *et al*., 2015).

FT-IR analysis

FT-IR spectra of humic acid sample was analysed using Carry 630 FT-IR Agilent Technologies.

Unhydrolysed compost humic acid

The unhydrolysed humic acid was obtained after isolation and purification of compost humic acid and kept for investigation.

Acid hydrolysis of Peatsoil acid

Peatsoil humic acid sample (1g) was refluxed for 12 hours at (160°C) with 50cm^3 of 6M HCl. The mixture was allowed to cool, decanted, and centrifuged after hydrolysis. The insoluble residues were washed with distilled water via centrifugation several times, and the supernatant was treated with $AgNO_3$ solution until no white precipitate was observed. The residue was thoroughly dried over $CaCl_2$ in a desiccator at room temperature (Chefetz *et al*., 2002). Finally, the obtained hydrolysed humic acid was kept for investigation.

Potentiometric Titrations

Potentiometric measurements were carried out using a pH-meter Jenway (model 3510) with combine electrode, the sensitivity of the pH - meter is 0.01 units. The pH meter was switched on half an hour before starting the titration for initial warm up of the instrument. The instrument was calibrated with an aqueous standard buffer solution of pH 4.00 and 10.0 (borate buffer) prepared from a "Qualigens" buffer tablets.

The following sets of solutions were prepared in a 250cm^3 volumetric flask separately for pH metric titrations.

(i) 5 cm^3 0.1 M HCl + 40 cm^3 deionized water

(ii) 5 cm^3 0.1 M HCl + 39 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid

(iii) 5 cm^3 0.1 M HCl + 37 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid + 2 cm^3 0.01 M Cu(II)

The solutions were titrated against standardized 0.110MNaOH separately. The total volume of each mixture was adjusted to 50 cm^3 and the ionic strength of the solutions was maintained constant at by adding appropriate amount of stock solution of 1M KNO_3 (Gamal, 2015; Omar and Ali, 2015). A magnetic stirrer was used to achieve thorough mixing of the interacting solutions at 550 rpm. The same set of experimental conditions was applied for potentiometric titration of remaining samples.

Evaluation of pKa of Hydrolysed peat soil Humic Acids

The proton-ligand formation number $n_{\mathbf{A}}$ were calculated by Irving and Rossotti expression (Omar and Ali, 2015).

$$nA = Y- \frac{(V2-V1)(No-Eo)}{(Vo+V1)TcL} \text{ ....1}$$

Where: Y is number of dissociable proton, (V_2-V_1) is the measure of displacement of the ligand curve relative to acid curve, N^o and E^o are the resultant concentration of alkali solution, free acid solution, $T_{cL}{}^o$ is the total ligand concentration, V^o is the total volume of titration solution,V_1 is the volume of alkali added to acid solution,V_2 is the volume of alkali added to acid solution + ligand solution, acid dissociation constants (pKa - values) of ligand were calculated by algebraic method point wise calculation (Tables 1). The dissociation constants (pKa) were calculated according to the following relation:

$$pKa = pH + \log(\frac{nA}{1-nA}) \text{ ....2}$$

Where: pKa is the acid dissociation constant, $n_A$is the Proton-ligand formation number and pH is the pH-values (Omar and Ali, 2015).

Determination of metal-ligand stability constants (log K) of complexes

The potentiometric measurement for the determination of stability constant of a complex in solution is based on the fact that the redox potential of the couple $\frac{M^{+(m-n)}}{M^{+m}}$ is shifted significantly on complexation of the metal ion with the ligand. This method involves change in hydrogen ion concentration [H$^+$] due to the displacement or association of one or more protons taking place during complexation reaction. This change can be found out by titrating the solutions containing free acid, acid with ligand, and acid with ligand and metal ion, individually against a standard alkali solution at a constant ionic strength or temperature. Either ionic strength or temperature may be varied for different sets of solutions. In all the cases, the change in the pH of the solution is measured after each addition of a known amount of alkali to the reaction cell which contains the reaction mixture. The titration curves are then drawn by plotting the measured pH values against the corresponding volume of alkali added and the stability constants of the complexes are determined from the titration curves by employing pH-metric titration technique given by (Irving and Rossoti).

Metal-ligand stability constants (Log K) were determined by using the following relations:

$$\bar{n} = \frac{(V_3 - V_2)(E^0 + N^0)}{(V^0 + V_2)\bar{n}_A T_m^0} \text{ ....3}$$

and

$$PL = \log_{10}\{\frac{1 + \beta_n^H \frac{1}{[anti\ \log pH]^n}}{T_L^0 - \bar{n}T_m^0} X \frac{(V^0 + V_3)}{V^0}\} \text{ ....4}$$

Where $T_{L,}$ T^{o}, E°, and V^{o}havethe same significance as in equation (1) above, T_m denotes the total concentration of metal present in solution, V_3 is the volume of metal ions present in solution and β^H is the overall proton ligand stability constant. The metal-ligand stability constants (log K) were determined by employing point wise computational Method (eq. 5 and 6).

$$\text{Log}K_1 = \log\left(\frac{n}{1-n}\right) + pL \qquad \ldots\ldots\ldots\ldots.5$$

$$\text{Log}K_2 = \log\left(\frac{1-n}{2-n}\right) + pL\ldots\ldots\ldots\ldots\ldots\ldots\ldots.6$$

Where: Log K is the metal-ligand stability constant, pL is the Free ligand exponent function, **n** is the Average number of ligand attached with metal ion (Janrao*et al.*, 2014).The results obtained were analyzed by an ORIGIN 2016 program using titration data and then the proton-ligand stability constants (pKa) and Metal-ligand stability constant (LogK) calculated (Omar and Ali, 2015).

RESULTS AND DISCUSSION

Fourier transformed infrared (FT-IR) spectra of isolated humic acid from peat soils Figure 2 had distinct clear absorption bands indicating the presence of major humic acid structural elemental groups such as H bonded OH ($3680cm^{-1}$ peak), C=O of carbonyl ($1721cm^{-1}$ peak), functional groups of aliphatic components CH_2 ($2918cm^{-1}$ peak) and C-O stretching of polysaccharide ($1168cm^{-1}$ peak). The positions of the absorption bands of the spectra fell within typical major absorption bands of humic acid which is at frequencies 3680, 2918, 1721, 1168 cm^{-1}. The first peak centred in the vicinity of 3680 cm^{-1} region is attributed to phenol OH group bounded by intermolecular H bonds. The $2918cm^{-1}$ band usually has absorption maximum at 2918 cm^{-1} which is due to C–H stretching of alkane group (CH_2). The next major absorption band is 1721 cm^{-1}. This band has been commonly ascribed to C=O stretching of mainly carboxyl group (COOH) with trace amount of ketones. The last peak was observed at 1168 cm^{-1} due to C–O stretching of polysaccharides and this peak appeared also in the spectra of humic acid from peat soil. The FTIR spectra of the isolated humic acid contained all major characteristic absorption peaks of humic acid. These absorption peaks indicated the presence of the major structural elements of humic acid namely H bonded OH, C=C of aromatic ring, C=O of carbonyl group (both carboxyl and ketonic), CH_2 group. This strongly supports the presence of humic acid.

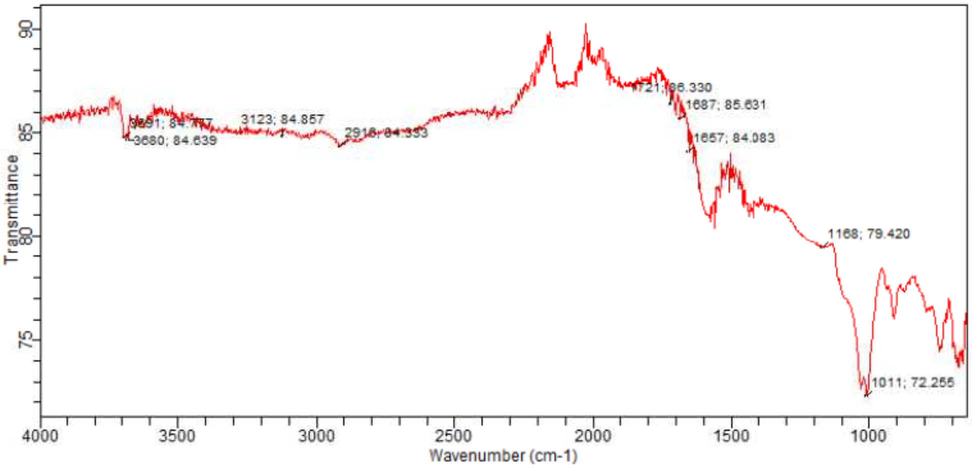

Fig. 2 : FT-IR spectraof peatsoilhumic acid (PSHA)

Evaluation of acid dissociation constant (pka) of acid hydrolysed peat soil humicacid at phenolic group

The value of the dissociation constant of the peat soil humic acid (PSHA) that underwent acidhydrolysis studied was found to be 8.9299 as shown Table 1, which is lower than the literaturevalues reported by Almeida and Szpoganics, (2015), Borges *et al.*, (2005); Badr *et al.*, (2012)and Fernandes *et al*,.(2009) of 9.73, 9.47 and 10.30. The difference between the obtained valuesand the reported values in this study might be probably as a result of acid hydrolysis of humicacid.

Table 1: PKa of (Hydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	log($\frac{nA}{1-nA}$)	pKa
8.50	5.30	6.29	0.99	0.3594	-0.2510	8.2490
8.72	5.35	6.37	1.02	0.3400	-0.2880	8.4320
9.00	5.40	6.46	1.06	0.3141	-0.3391	8.6609
9.22	5.45	6.55	1.10	0.2882	-0.3927	8.8273
9.51	5.50	6.66	1.16	0.2494	-0.4786	9.0314
9.73	5.55	6.78	1.23	0.2041	-0.5910	9.1390
10.00	5.60	6.90	1.30	0.1589	-0.7238	9.2762
10.23	5.65	7.05	1.40	0.0941	-0.9835	9.2465
10.49	5.70	7.10	1.40	0.0941	-0.9835	9.5065

Average pKa = 8.9299 ± 0.4186

Table 2: PKa of (Unhydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	Log($\frac{nA}{1-n}$)	pKa
8.50	5.30	5.81	0.51	0.6619	0.2919	8.7919
8.72	5.35	5.90	0.55	0.6357	0.2418	8.9618
9.00	5.40	6.00	0.60	0.6029	0.1813	9.1813
9.22	5.45	6.10	0.65	0.5701	0.1226	9.3426
9.51	5.50	6.20	0.70	0.5376	0.0654	9.5754
9.73	5.55	6.33	0.78	0.4851	-0.0259	9.7041
10.00	5.60	6.47	0.87	0.4262	-0.1291	9.8709
10.23	5.65	6.62	0.99	0.3609	-0.2481	9.9819
10.49	5.70	6.80	1.10	0.2759	-0.4690	10.0210

Average pKa = 9.4923± 0.4410

Metal-ligand stability constant (Log K)

The stabilityconstants require the accurate values of proton-ligand stability constants (Anil and Maroti, 2008). Metal titration curves crossed over ligand titration curve indicated the formation of complex upon proton release (Santosh, *et al.*, 2011). If the values of n- are within range 0.2-0.8 and 1.2-18 this indicates the formation of 1:1 and 1:2 complexes (Sayyed and Mazahar, 2012).

The metal (II)-humate stepwise stability constants (log k) at phenolic group (Tables 3-18)

Table 3: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n}{1-n}$)	$LogK_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

$LogK_1$ (Average value) = 2.4788± 0.2203

Table 4: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	Log($\frac{n-1}{2-n}$)	$LogK_2$
9.51	5.50	6.66	6.73	0.07	1.3509	1.70	-0.2671	1.4329
9.73	5.55	6.78	6.85	0.07	1.6383	1.51	0.2467	1.7567
10.00	5.60	6.90	6.98	0.08	2.1783	1.31	-0.2158	1.0942
10.23	5.65	7.05	7.13	0.08	4.1904	1.27		
10.49	5.70	7.10	7.19	0.09	4.6920			

$LogK_2$(Average value) = 1.4280 ± 0.3312

Table 5:Point-wise method,Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	Log($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430

$LogK_1$ **(Average value)** = 2.3059± 0.6153

Table 6:Point-wise method, Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
9.73	5.55	6.33	6.42	0.09	0.9000	1.69		
10.00	5.60	6.47	6.58	0.11	1.2578	1.44	-0.4592	0.9808
10.23	5.65	6.62	6.84	0.12	1.6137	1.26	-0.2010	1.4610
10.49	5.70	6.80	6.92	0.12	2.1052	1.03		

$LogK_2$ **(Average value)** = 1.2209± 0.3398

Table 7:Point-wise method,Pb (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n}{1-n}$)	$LogK_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.60	0.05	0.8333	1.96	0.6989	2.6589

$LogK_1$ (Average value) = 2.5832 ±0.1614

Table 8:Point-wise method,Pb-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n-1}{2-n}$)	$logK_2$
9.51	5.50	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.83	0.05	1.1702	1.44		
10.00	5.60	6.90	6.90	0.05	1.4864	1.22	-0.0237	1.1963
10.23	5.65	7.05	7.10	0.05	2.0190	1.09		
10.49	5.70	7.10	7.17	0.07	3.6492	1.00		

$LogK_2$(Average value) = 1.1963

Table 9:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log ($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.5477	2.3123
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	0.0272	2.2072
9.51	5.50	6.20	6.26	0.07	0.6417	1.89	0.2530	2.1430
9.73	5.55	6.40	6.40	0.07	0.7000	1.67	0.3680	2.0380

$LogK_1$ **(Average value)** = 2.2364 ± 0.1602

Table 10:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
10.00	5.60	6.47	6.55	0.08	1.9503	1.41		
10.23	5.65	6.62	6.72	0.11	1.4792	1.26	-0.0361	1.2239

$LogK_2$ **(Average value)** = 1.2239

Table 11:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n}{n-1}$)	$LogK_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4290	2.2110
8.72	5.35	6.37	6.39	0.02	0.2858	2.42	-0.3978	2.0222
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

$LogK_1$ (Average value)=2.1382**±**0.1046

Table 12:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n-1}{2-n}$)	$LogK_2$
9.51	5.55	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.84	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.93	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.10		
10.49	5.70	7.10	7.18	0.07	3.6492	0.83		

$LogK_2$(Average value) = 1.5453 **±** 0.3450

Table 13:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.3477	2.3123
9.00	5.40	6.00	6.04	0.04	0.3236	2.38	-0.3202	2.0598
9.22	5.45	6.10	6.15	0.05	0.4297	2.17	-0.1230	2.0470
9.51	5.50	6.20	6.26	0.06	0.5500	1.89	0.0871	1.9771
9.73	5.55	6.33	6.40	0.07	0.7000	1.67	0.3680	2.0380

$LogK_1$ **(Average value)** = 2.1568 ± 0.2069

Table 14:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
10.00	5.60	6.47	6.55	0.08	0.9148	1.41		
10.23	5.65	6.62	6.71	0.09	1.2102	1.20	-0.5749	0.6251
10.49	5.70	6.80	6.92	0.09	1.5968	1.03	0.1703	1.2003

$LogK_2$ **(Average value)** = 0.9127± 0.4070

Table15:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	Log($\frac{n}{1-n}$)	$LogK_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4210	2.2190
8.72	5.35	6.37	6.40	0.03	0.4286	2.42	-0.1249	2.2951
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.96	0.3010	2.2610
9.51	5.55	6.66	6.70	0.04	0.7720	1.67	0.5297	2.1997

$LogK_1$ (Average value) = 2.2108± 0.0825

Table 16:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
9.73	5.55	6.78	6.83	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.95	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.09		
10.49	5.70	7.10	7.16	0.06	3.1429	0.89		

$LogK_2$ **(Average value)** = 1.5453± 0.3450

Table 17:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.86	0.05	0.3717	2.88	-0.2280	2.6520
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.06	0.06	0.4853	2.38	-0.0255	2.3545
9.22	5.45	6.10	6.16	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430
9.73	5.55	6.33	6.41	0.08	0.8000	1.69	0.6020	2.2920

$LogK_1$ **(Average value)** = 2.2516± 0.5380

Table 18:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$\mathrm{Log}(\frac{n-1}{2-n})$	Log K_2
10.00	5.60	6.47	6.57	0.10	1.1434	1.43		
10.23	5.65	6.62	6.72	0.10	1.3448	1.23	-0.2788	0.9512
10.49	5.70	6.80	6.90	0.10	1.7742	1.03	0.5351	1.5651

LogK_2 **(Average value)** = 1.2581± 0.4340

Table 19: Stepwise and overall Stability constants of thehydrolysed and unhydrolysed divalent metal (II) complexes

Chelates	**LogK_1**	**LogK_2**	**Logβ**
[Cu (Hydrolysed PSHA-1)$_2$]	2.4788	1.4280	3.9068
[Pb (Hydrolysed PSHA-1)$_2$]	2.5832	1.1963	3.7795
[Cd (Hydrolysed PSHA-1)$_2$]	2.2108	1.5453	3.7561
[Mg (Hydrolysed PSHA-1)$_2$]	2.1382	1.5453	3.6835
[Cu (Unhydrolysed PSHA-1)$_2$]	2.3059	1.2209	3.5268
[Pb (Unhydrolysed PSHA-1)$_2$]	2.2364	1.2239	3.4603
[Cd (Unhydrolysed PSHA-1)$_2$]	2.2516	1.2581	3.5097
[Mg (Unydrolysed PSHA-1)$_2$]	2.1568	0.9127	3.0695

The results obtained (Table19) shows the stepwise and overall stability constants to be not high indicating low stability of the complexes, because the solubility of most metal ions in the basic pH range is minimal due to metal hydroxide precipitation (Karimi, 2017). In general, the stepwise stability constants (K_1 and K_2) follow the order $K_1 > K_2$ for the copper, lead, magnesium and cadmium complexes respectively. The steady decrease of the values with increasing number of ligands is in agreement with the prediction made by researchers (Na'aliya, 2013). The decrease could be attributed to the fact that as the number of the ligands (Humate ions) that enters the coordination zone increases the aqua molecules available for replacement by the ligands become less. Thus, the metal ions become less electron loving with progressive intake of the ligand and this results in the decrease in the values of the constants (Na'aliya, 2013). Also the stability of the complexes is influenced by the size and number of the chelate rings(Mackay and Mackay,2002).All the complexes form rings in their structure as humate, a bidentate ligand, bond the metal ions in the ratio 1:2 (Boguta and Sokolowska, 2016) forming chelate rings. The values of the overall stability constants (logβ) obtained for humate complexes are not high indicating low stability as the values are not high. LogK values for copper-humates (Table 3 to 6) obtained in this study are lower than those reported for the complexes of humic acids (Pandey *et al.*, 2015; Dinu, 2013; Kaschl *et al.*, 2010 and Gilbeto and Jorg, 2001). The values of LogK(Table 7 to 10) forlead-humates are lower than those reported for the lead in the literature (Dinu, 2013; Gilbeto and Jorg 2001). Log K values(Table 11 to 14) for magnesium-humates obtained in this study are close to those reported by (Pandey *et al.*, 2015). Log K values of cadmium-humates (Table 15 to 18) obtained in this work near to the one reported by (Dinu, 2013 and Pandey *et al.*, 2015).The difference between the reported values and the values obtained in this study might be probably as a result of acid hydrolysis of humic acid. The values of the overall stability constants (log β) of the copper humates complexes presented in Table 19 is high than that of other metal humate complexes, show relatively high stability of Cu-HA complexes, show the following order of stability: Cu >Pb> Cd > Mg; which are in close agreement to the findings of (Dinu, 2013 and Pandey *et al.*, 2015).The high stability of Cu-humate chelate could be attributed to the existence of coordinate covalent bond between the complexing agents and the Cu^{2+} ions. Since, Cu^{2+} being a metal of the transitional series with $3d^9$ electronic configurations can accept the electrons from the complexing agents. Similarly,the low stabilities of Pb,Cd and Mg -complexes could be explained by that Pb^{2+} with $6s^2$, Cd^{2+} with $4d^{10}$ and Mg^{2+} with $2p^6$ their electronic configuration has a completely filled d,p and s orbitals. Moreover, the stabilities of metal ions with hydrolysed humic acid from peat soil were higher than those with unhydrolysed humic acid from peat soil; which is ascribed to the high content of acidity in hydrolysed humic acid than unhydrolysed humic acid.

CONCLUSION

The values of logK for Cu(II) hydrolysed humic acid complex was higher followed by Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes as compared with metal(II) unhydrolysed humic acid complexes . This indicates acid hydrolysis of humic acid can enhance the complexation behavior of humic acid with metal (II) ions. However, the higher values of logβ for Cu(II), Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes indicates more stable stepwise complexes formed as compared with Cu(II), Pb(II), Cd(II) and Mg(II) unhydrolysed humic acid complexes.

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STABILITY CONSTANTS OF COMPLEXES OF METAL IONS WITH PEATSOIL HUMIC ACIDS UNDER NON-ACID-CONDITIONS

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ABSTRACT

Stability constants of complexes of four divalent metal ions viz. Cu^{2+}, Pb^{2+},Mg^{2+} and Cd^{2+} with humic acids (HA) were determined by potentiometric titration of humic acids with the corresponding salt of the divalent metals in aqueous media under non-acid-condition. The log K (logarithm of the stability constant) ranged from 1.0942 to 2.7471 for metal-humic acid complexes were determined using point-wise computational method. The order of stability constants were obtained as follows: Cu >Pb> Cd > Mg for metal -HA complexes respectively, indicating a higher degree of complexation with Cu metal ion.

Keywords: stability constant, humic acid, potentiometric titration, divalent metals, acid hydrolysis.

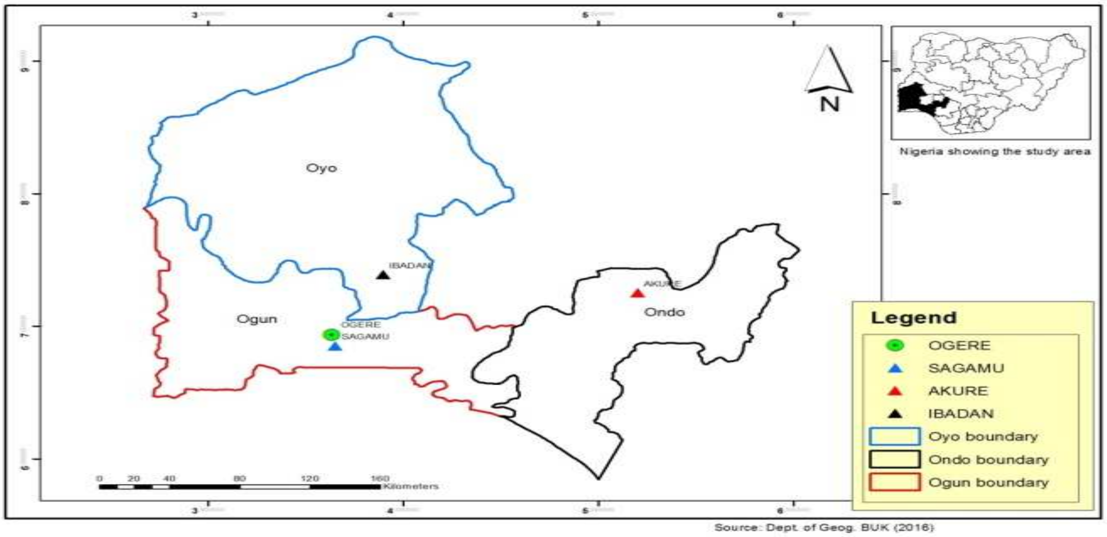
NTRODUCTION

The stability constant of a complex is the numerical expression of its stability and provides a quantitative measure of affinity of the metal ion to the complexing agent. An understanding of the relative stability of metal-complexes helps in predicting the behavior of metal ions in the soil (Ram and Raman, 1982). Extensive researches has been done to determine the stability constants of the complexes formed between humic acid (HA) with a number of metal ions. Ashok *et al*., (2000) reported that humic acid with hydroxyl, phenoxyl and carboxyl reactive groups can form coordination compound with metal ions at pH 3.5. The stability constants(Log K) for different metal-humic acid complexes indicated the following order of the stabilities of complexes formed between humic acid and metal ion, Cu >Fe >Pb> Ni > Co > Ca > Cd > Zn >Mn> Mg. Andelkovic *et al*., (2010) investigated the binding of Cd(II) to soil humic acid at pH 6.5 and in 0.1M KNO_3 ionic medium. The stability constant for binding indicating greater stability in the case when carboxyl groups are involved in complexation reaction. Kostic *et al*.,(2012) investigated the complexation of humic acid with certain heavy metal ions (Co(II), Ni(II),Cu(II), Zn(II), and Pb(II). The experiment was performed at 25°C, at pH 4.0 and ionic strength of 0.01M. Stability constant of complex between Pb(II) ions and humic acid is greater than stability constants of other investigated metal-humate complexes. Bogata and Sokolowska (2016) analyses the interaction between humic acids from different soils and Zn (II) ions at wide concentration ranges and at pH 5. Studies have showed significant impact of Zn concentration, pH and some properties of humic acids with zinc.But all of these studies were limited to acidic pH range. Therefore, the present study was carried out to determine and compare the stability constants of complexes of metal ions with hydrolysed peat soil humic acid and unhydrolysed peat soil humic under non-acid conditions.

MATERIALS AND METHODS

Analytical grade chemicals used includes hydrochloric acid (HCl), nitric acid (HNO_3), sodium hydroxide (NaOH), lead nitrate $Pb(NO_3)_2$, copper nitrate $Cu(NO_3)_2.3H_2O$, cadmium nitrate $Cd(NO_3)_2.4H_2O$, magnesium nitrate $Mg(NO_3)_2.6H_2O$, potassium nitrate (KNO_3), calcium chloride ($CaCl_2$), (sigma-Aldrich). Dowex 50WX8, (20-50 mesh) from Fluka.

Area of study



Source: Dept. of Geog. BUK (2016)

Figure 1: Map showing the sampling point at Sagamu Town, Ogun State.

Description of Sampling Area

Sagamu has geographical coordinates between 6°50′ north; 3° 38′ east is located in south western region of Nigeria. The region has tropical wet and dry climate with a lengthy wet season and relatively constant temperatures throughout the course of the year. Wet season runs from March to October, November to December forms the region dry season. The vegetation type of the region is savannah which is really grassland with small bushes and occasional big trees. Grassland soils have substantially higher organic matter content than forest soils (Novackova, 2011).

Sample Collection

The Peatsoil samples were collected from four different sampling points (0-10cm depth) in Sagamu into polyethylene bag with plastic spoons. Samples were taken to the laboratory, extraneous materials were removed; the samples were air-dried, crushed and ground to a fine powder in a mortar passed through a 0.20mm sieve. The samples were kept for analysis.

Isolation and purification of humic acid from peat soil sample

Peatsoil sample (100g) was mixed with 1000 cm^3 of 0.1M NaOH solution, shaken for 3hours and left to stand overnight. Dark-coloured supernatant was obtained and decanted from solid residue. The dark-coloured supernatant was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 6 hours. Yellowish brown supernatant and dark-brown precipitate were obtained. The yellowish brown supernatant was decanted followed by centrifuge and discarded. The dark-brown precipitate was mixed with $500cm^3$of 0.1M NaOH solution followed by passing through dowex resin. The dark-brown solution was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 3 hours. The dark-brown precipitate was washed several times with deionized water. The supernatant was treated with $AgNO_3$ solution until no white precipitate observed. The humic acid was transferred to weighed crucible and dried at 60°C in an oven for 12 hours. The humic acid was cooled and dried in the desiccator, weighed and recorded. The obtained humic acid was dried again at 60°C for additional 6 hours cooled and dried in the desiccator, weighed and recorded constant weight was obtained (Baruah *et al*., 2015).

FT-IR analysis

FT-IR spectra of humic acid sample was analysed using Carry 630 FT-IR Agilent Technologies.

Unhydrolysed compost humic acid

The unhydrolysed humic acid was obtained after isolation and purification of compost humic acid and kept for investigation.

Acid hydrolysis of Peatsoil acid

Peatsoil humic acid sample (1g) was refluxed for 12 hours at (160°C) with $50cm^3$ of 6M HCl. The mixture was allowed to cool, decanted, and centrifuged after hydrolysis. The insoluble residues were washed with distilled water via centrifugation several times, and the supernatant was treated with $AgNO_3$ solution until no white precipitate was observed. The residue was thoroughly dried over $CaCl_2$ in a desiccator at room temperature (Chefetz *et al*., 2002). Finally, the obtained hydrolysed humic acid was kept for investigation.

Potentiometric Titrations

Potentiometric measurements were carried out using a pH-meter Jenway (model 3510) with combine electrode, the sensitivity of the pH - meter is 0.01 units. The pH meter was switched on half an hour before starting the titration for initial warm up of the instrument. The instrument was calibrated with an aqueous standard buffer solution of pH 4.00 and 10.0 (borate buffer) prepared from a "Qualigens" buffer tablets.

The following sets of solutions were prepared in a 250cm^3 volumetric flask separately for pH metric titrations.

(i) 5 cm^3 0.1 M HCl + 40 cm^3 deionized water
(ii) 5 cm^3 0.1 M HCl + 39 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid
(iii) 5 cm^3 0.1 M HCl + 37 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid + 2 cm^3 0.01 M Cu(II)

The solutions were titrated against standardized 0.110MNaOH separately. The total volume of each mixture was adjusted to 50 cm^3 and the ionic strength of the solutions was maintained constant at by adding appropriate amount of stock solution of 1M KNO$_3$ (Gamal, 2015; Omar and Ali, 2015). A magnetic stirrer was used to achieve thorough mixing of the interacting solutions at 550 rpm. The same set of experimental conditions was applied for potentiometric titration of remaining samples.

Evaluation of pKa of Hydrolysed peat soil Humic Acids

The proton-ligand formation number n$_{\mathbf{A}}$ were calculated by Irving and Rossotti expression (Omar and Ali, 2015).

$$nA = Y - \frac{(V2-V1)(No-Eo)}{(Vo+V1)TcL} \quad ....1$$

Where: Y is number of dissociable proton, (V$_2$-V$_1$) is the measure of displacement of the ligand curve relative to acid curve, N^o and E^o are the resultant concentration of alkali solution, free acid solution, T$_{cL}^{o}$ is the total ligand concentration, V^o is the total volume of titration solution,V$_1$ is the volume of alkali added to acid solution,V$_2$ is the volume of alkali added to acid solution + ligand solution, acid dissociation constants (pKa - values) of ligand were calculated by algebraic method point wise calculation (Tables 1). The dissociation constants (pKa) were calculated according to the following relation:

$$pKa = pH + \log(\frac{nA}{1-nA}) \quad ....2$$

Where: pKa is the acid dissociation constant, n$_A$is the Proton-ligand formation number and pH is the pH-values (Omar and Ali, 2015).

Determination of metal-ligand stability constants (log K) of complexes

The potentiometric measurement for the determination of stability constant of a complex in solution is based on the fact that the redox potential of the couple $\frac{M^{+(m-n)}}{M^{+m}}$ is shifted significantly on complexation of the metal ion with the ligand. This method involves change in hydrogen ion concentration [H$^+$] due to the displacement or association of one or more protons taking place during complexation reaction. This change can be found out by titrating the solutions containing free acid, acid with ligand, and acid with ligand and metal ion, individually against a standard alkali solution at a constant ionic strength or temperature. Either ionic strength or temperature may be varied for different sets of solutions. In all the cases, the change in the pH of the solution is measured after each addition of a known amount of alkali to the reaction cell which contains the reaction mixture. The titration curves are then drawn by plotting the measured pH values against the corresponding volume of alkali added and the stability constants of the complexes are determined from the titration curves by employing pH-metric titration technique given by (Irving and Rossoti).

Metal-ligand stability constants (Log K) were determined by using the following relations:

$$\bar{n} = \frac{(V_3 - V_2)(E^0 + N^0)}{(V^0 + V_2)\bar{n}_A T_m^0} \quad ....3$$

and

$$PL = \log_{10}\{\frac{1+\beta_n^H \frac{1}{[anti\ \log pH]^n}}{T_L^0 - \bar{n}T_m^0} X \frac{(V^0 + V_3)}{V^0}\} \quad ....4$$

Where $T_{L,}$ T^{o}, E°, and V^{o}havethe same significance as in equation (1) above, T_m denotes the total concentration of metal present in solution, V_3 is the volume of metal ions present in solution and β^H is the overall proton ligand stability constant. The metal-ligand stability constants (log K) were determined by employing point wise computational Method (eq. 5 and 6).

$\text{LogK}_1 = \log\left(\frac{n}{1-n}\right) + \text{pL}$ 5

$\text{LogK}_2 = \log\left(\frac{1-n}{2-n}\right) + \text{pL}$.......................6

Where: Log K is the metal-ligand stability constant, pL is the Free ligand exponent function, **n** is the Average number of ligand attached with metal ion (Janrao*et al.*, 2014).The results obtained were analyzed by an ORIGIN 2016 program using titration data and then the proton-ligand stability constants (pKa) and Metal-ligand stability constant (LogK) calculated (Omar and Ali, 2015).

RESULTS AND DISCUSSION

Fourier transformed infrared (FT-IR) spectra of isolated humic acid from peat soils Figure 2 had distinct clear absorption bands indicating the presence of major humic acid structural elemental groups such as H bonded OH ($3680cm^{-1}$ peak), C=O of carbonyl ($1721cm^{-1}$ peak), functional groups of aliphatic components CH_2 ($2918cm^{-1}$ peak) and C-O stretching of polysaccharide ($1168cm^{-1}$ peak). The positions of the absorption bands of the spectra fell within typical major absorption bands of humic acid which is at frequencies 3680, 2918, 1721, 1168 cm^{-1}. The first peak centred in the vicinity of 3680 cm^{-1} region is attributed to phenol OH group bounded by intermolecular H bonds. The $2918cm^{-1}$ band usually has absorption maximum at 2918 cm^{-1} which is due to C–H stretching of alkane group (CH_2). The next major absorption band is 1721 cm^{-1}. This band has been commonly ascribed to C=O stretching of mainly carboxyl group (COOH) with trace amount of ketones. The last peak was observed at 1168 cm^{-1} due to C–O stretching of polysaccharides and this peak appeared also in the spectra of humic acid from peat soil. The FTIR spectra of the isolated humic acid contained all major characteristic absorption peaks of humic acid. These absorption peaks indicated the presence of the major structural elements of humic acid namely H bonded OH, C=C of aromatic ring, C=O of carbonyl group (both carboxyl and ketonic), CH_2 group. This strongly supports the presence of humic acid.

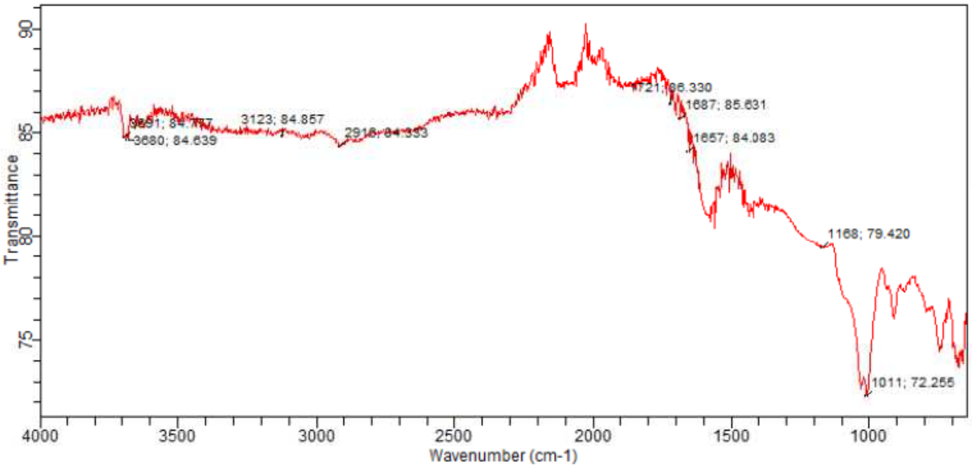


Fig. 2 : FT-IR spectraof peatsoilhumic acid (PSHA)

Evaluation of acid dissociation constant (pka) of acid hydrolysed peat soil humicacid at phenolic group

The value of the dissociation constant of the peat soil humic acid (PSHA) that underwent acidhydrolysis studied was found to be 8.9299 as shown Table 1, which is lower than the literaturevalues reported by Almeida and Szpoganics, (2015), Borges *et al.*, (2005); Badr *et al.*, (2012)and Fernandes *et al*,.(2009) of 9.73, 9.47 and 10.30. The difference between the obtained valuesand the reported values in this study might be probably as a result of acid hydrolysis of humicacid.

Table 1: PKa of (Hydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	log($\frac{nA}{1-nA}$)	pKa
8.50	5.30	6.29	0.99	0.3594	-0.2510	8.2490
8.72	5.35	6.37	1.02	0.3400	-0.2880	8.4320
9.00	5.40	6.46	1.06	0.3141	-0.3391	8.6609
9.22	5.45	6.55	1.10	0.2882	-0.3927	8.8273
9.51	5.50	6.66	1.16	0.2494	-0.4786	9.0314
9.73	5.55	6.78	1.23	0.2041	-0.5910	9.1390
10.00	5.60	6.90	1.30	0.1589	-0.7238	9.2762
10.23	5.65	7.05	1.40	0.0941	-0.9835	9.2465
10.49	5.70	7.10	1.40	0.0941	-0.9835	9.5065

Average pKa = 8.9299 ± 0.4186

Table 2: PKa of (Unhydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	Log($\frac{nA}{1-n}$)	pKa
8.50	5.30	5.81	0.51	0.6619	0.2919	8.7919
8.72	5.35	5.90	0.55	0.6357	0.2418	8.9618
9.00	5.40	6.00	0.60	0.6029	0.1813	9.1813
9.22	5.45	6.10	0.65	0.5701	0.1226	9.3426
9.51	5.50	6.20	0.70	0.5376	0.0654	9.5754
9.73	5.55	6.33	0.78	0.4851	-0.0259	9.7041
10.00	5.60	6.47	0.87	0.4262	-0.1291	9.8709
10.23	5.65	6.62	0.99	0.3609	-0.2481	9.9819
10.49	5.70	6.80	1.10	0.2759	-0.4690	10.0210

Average pKa = 9.4923± 0.4410

Metal-ligand stability constant (Log K)

The stabilityconstants require the accurate values of proton-ligand stability constants (Anil and Maroti, 2008). Metal titration curves crossed over ligand titration curve indicated the formation of complex upon proton release (Santosh, *et al.*, 2011). If the values of n- are within range 0.2-0.8 and 1.2-18 this indicates the formation of 1:1 and 1:2 complexes (Sayyed and Mazahar, 2012).

The metal (II)-humate stepwise stability constants (log k) at phenolic group (Tables 3-18)

Table 3: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n}{1-n}$)	$LogK_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

$LogK_1$ (Average value) = 2.4788± 0.2203

Table 4: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	Log($\frac{n-1}{2-n}$)	$LogK_2$
9.51	5.50	6.66	6.73	0.07	1.3509	1.70	-0.2671	1.4329
9.73	5.55	6.78	6.85	0.07	1.6383	1.51	0.2467	1.7567
10.00	5.60	6.90	6.98	0.08	2.1783	1.31	-0.2158	1.0942
10.23	5.65	7.05	7.13	0.08	4.1904	1.27		
10.49	5.70	7.10	7.19	0.09	4.6920			

$LogK_2$(Average value) = 1.4280 ± 0.3312

Table 5:Point-wise method,Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	Log($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430

$LogK_1$ **(Average value)** = 2.3059± 0.6153

Table 6:Point-wise method, Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
9.73	5.55	6.33	6.42	0.09	0.9000	1.69		
10.00	5.60	6.47	6.58	0.11	1.2578	1.44	-0.4592	0.9808
10.23	5.65	6.62	6.84	0.12	1.6137	1.26	-0.2010	1.4610
10.49	5.70	6.80	6.92	0.12	2.1052	1.03		

$LogK_2$ **(Average value)** = 1.2209± 0.3398

Table 7:Point-wise method,Pb (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n}{1-n}$)	$LogK_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.60	0.05	0.8333	1.96	0.6989	2.6589

$LogK_1$ (Average value) = 2.5832 ±0.1614

Table 8:Point-wise method,Pb-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n-1}{2-n}$)	$logK_2$
9.51	5.50	6.66	6.71	0.05	0.9650	1.67	-0.0237	1.1963
9.73	5.55	6.78	6.83	0.05	1.1702	1.44		
10.00	5.60	6.90	6.90	0.05	1.4864	1.22		
10.23	5.65	7.05	7.10	0.05	2.0190	1.09		
10.49	5.70	7.10	7.17	0.07	3.6492	1.00		

$LogK_2$(Average value) = 1.1963

Table 9:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log ($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.5477	2.3123
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	0.0272	2.2072
9.51	5.50	6.20	6.26	0.07	0.6417	1.89	0.2530	2.1430
9.73	5.55	6.40	6.40	0.07	0.7000	1.67	0.3680	2.0380

$LogK_1$ **(Average value)** = 2.2364 ± 0.1602

Table 10:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
10.00	5.60	6.47	6.55	0.08	1.9503	1.41		
10.23	5.65	6.62	6.72	0.11	1.4792	1.26	-0.0361	1.2239

$LogK_2$ **(Average value)** = 1.2239

Table 11:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n}{n-1}$)	$LogK_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4290	2.2110
8.72	5.35	6.37	6.39	0.02	0.2858	2.42	-0.3978	2.0222
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

$LogK_1$ (Average value)=2.1382**±**0.1046

Table 12:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	log($\frac{n-1}{2-n}$)	LogK$_2$
9.51	5.55	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.84	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.93	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.10		
10.49	5.70	7.10	7.18	0.07	3.6492	0.83		

LogK$_2$(Average value) = 1.5453 **±** 0.3450

Table 13:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	V$_3$-V$_2$	n	pL	Log($\frac{n}{n-1}$)	Log K$_1$
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.3477	2.3123
9.00	5.40	6.00	6.04	0.04	0.3236	2.38	-0.3202	2.0598
9.22	5.45	6.10	6.15	0.05	0.4297	2.17	-0.1230	2.0470
9.51	5.50	6.20	6.26	0.06	0.5500	1.89	0.0871	1.9771
9.73	5.55	6.33	6.40	0.07	0.7000	1.67	0.3680	2.0380

LogK$_1$ **(Average value)** = 2.1568 ± 0.2069

Table 14:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	V$_3$-V$_2$	n	pL	Log($\frac{n-1}{2-n}$)	Log K$_2$
10.00	5.60	6.47	6.55	0.08	0.9148	1.41		
10.23	5.65	6.62	6.71	0.09	1.2102	1.20	-0.5749	0.6251
10.49	5.70	6.80	6.92	0.09	1.5968	1.03	0.1703	1.2003

LogK$_2$ **(Average value)** = 0.9127± 0.4070

Table15:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	Log($\frac{n}{1-n}$)	LogK$_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4210	2.2190
8.72	5.35	6.37	6.40	0.03	0.4286	2.42	-0.1249	2.2951
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.96	0.3010	2.2610
9.51	5.55	6.66	6.70	0.04	0.7720	1.67	0.5297	2.1997

LogK$_1$ (Average value) = 2.2108± 0.0825

Table 16:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	Log($\frac{n-1}{2-n}$)	Log K$_2$
9.73	5.55	6.78	6.83	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.95	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.09		
10.49	5.70	7.10	7.16	0.06	3.1429	0.89		

LogK$_2$ **(Average value)** = 1.5453± 0.3450

Table 17:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	V$_3$-V$_2$	n	pL	Log($\frac{n}{n-1}$)	Log K$_1$
8.50	5.30	5.81	5.86	0.05	0.3717	2.88	-0.2280	2.6520
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.06	0.06	0.4853	2.38	-0.0255	2.3545
9.22	5.45	6.10	6.16	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430
9.73	5.55	6.33	6.41	0.08	0.8000	1.69	0.6020	2.2920

LogK$_1$ **(Average value)** = 2.2516± 0.5380

Table 18:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$\mathrm{Log}(\frac{n-1}{2-n})$	Log K_2
10.00	5.60	6.47	6.57	0.10	1.1434	1.43		
10.23	5.65	6.62	6.72	0.10	1.3448	1.23	-0.2788	0.9512
10.49	5.70	6.80	6.90	0.10	1.7742	1.03	0.5351	1.5651

LogK_2 **(Average value)** = 1.2581± 0.4340

Table 19: Stepwise and overall Stability constants of thehydrolysed and unhydrolysed divalent metal (II) complexes

Chelates	**LogK_1**	**LogK_2**	**Logβ**
[Cu (Hydrolysed PSHA-1)$_2$]	2.4788	1.4280	3.9068
[Pb (Hydrolysed PSHA-1)$_2$]	2.5832	1.1963	3.7795
[Cd (Hydrolysed PSHA-1)$_2$]	2.2108	1.5453	3.7561
[Mg (Hydrolysed PSHA-1)$_2$]	2.1382	1.5453	3.6835
[Cu (Unhydrolysed PSHA-1)$_2$]	2.3059	1.2209	3.5268
[Pb (Unhydrolysed PSHA-1)$_2$]	2.2364	1.2239	3.4603
[Cd (Unhydrolysed PSHA-1)$_2$]	2.2516	1.2581	3.5097
[Mg (Unydrolysed PSHA-1)$_2$]	2.1568	0.9127	3.0695

The results obtained (Table19) shows the stepwise and overall stability constants to be not high indicating low stability of the complexes, because the solubility of most metal ions in the basic pH range is minimal due to metal hydroxide precipitation (Karimi, 2017). In general, the stepwise stability constants (K_1 and K_2) follow the order $K_1 > K_2$ for the copper, lead, magnesium and cadmium complexes respectively. The steady decrease of the values with increasing number of ligands is in agreement with the prediction made by researchers (Na'aliya, 2013). The decrease could be attributed to the fact that as the number of the ligands (Humate ions) that enters the coordination zone increases the aqua molecules available for replacement by the ligands become less. Thus, the metal ions become less electron loving with progressive intake of the ligand and this results in the decrease in the values of the constants (Na'aliya, 2013). Also the stability of the complexes is influenced by the size and number of the chelate rings(Mackay and Mackay,2002).All the complexes form rings in their structure as humate, a bidentate ligand, bond the metal ions in the ratio 1:2 (Boguta and Sokolowska, 2016) forming chelate rings. The values of the overall stability constants (logβ) obtained for humate complexes are not high indicating low stability as the values are not high. LogK values for copper-humates (Table 3 to 6) obtained in this study are lower than those reported for the complexes of humic acids (Pandey *et al*., 2015; Dinu, 2013; Kaschl *et al*., 2010 and Gilbeto and Jorg, 2001). The values of LogK(Table 7 to 10) forlead-humates are lower than those reported for the lead in the literature (Dinu, 2013; Gilbeto and Jorg 2001). Log K values(Table 11 to 14) for magnesium-humates obtained in this study are close to those reported by (Pandey *et al*., 2015). Log K values of cadmium-humates (Table 15 to 18) obtained in this work near to the one reported by (Dinu, 2013 and Pandey *et al*., 2015).The difference between the reported values and the values obtained in this study might be probably as a result of acid hydrolysis of humic acid. The values of the overall stability constants (log β) of the copper humates complexes presented in Table 19 is high than that of other metal humate complexes, show relatively high stability of Cu-HA complexes, show the following order of stability: Cu >Pb> Cd > Mg; which are in close agreement to the findings of (Dinu, 2013 and Pandey *et al*., 2015).The high stability of Cu-humate chelate could be attributed to the existence of coordinate covalent bond between the complexing agents and the Cu^{2+} ions. Since, Cu^{2+} being a metal of the transitional series with $3d^9$ electronic configurations can accept the electrons from the complexing agents. Similarly,the low stabilities of Pb,Cd and Mg -complexes could be explained by that Pb^{2+} with $6s^2$, Cd^{2+} with $4d^{10}$ and Mg^{2+} with $2p^6$ their electronic configuration has a completely filled d,p and s orbitals. Moreover, the stabilities of metal ions with hydrolysed humic acid from peat soil were higher than those with unhydrolysed humic acid from peat soil; which is ascribed to the high content of acidity in hydrolysed humic acid than unhydrolysed humic acid.

CONCLUSION

The values of logK for Cu(II) hydrolysed humic acid complex was higher followed by Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes as compared with metal(II) unhydrolysed humic acid complexes . This indicates acid hydrolysis of humic acid can enhance the complexation behavior of humic acid with metal (II) ions. However, the higher values of logβ for Cu(II), Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes indicates more stable stepwise complexes formed as compared with Cu(II), Pb(II), Cd(II) and Mg(II) unhydrolysed humic acid complexes.

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STABILITY CONSTANTS OF COMPLEXES OF METAL IONS WITH PEATSOIL HUMIC ACIDS UNDER NON-ACID-CONDITIONS

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ABSTRACT

Stability constants of complexes of four divalent metal ions viz. Cu^{2+}, Pb^{2+},Mg^{2+} and Cd^{2+} with humic acids (HA) were determined by potentiometric titration of humic acids with the corresponding salt of the divalent metals in aqueous media under non-acid-condition. The log K (logarithm of the stability constant) ranged from 1.0942 to 2.7471 for metal-humic acid complexes were determined using point-wise computational method. The order of stability constants were obtained as follows: Cu >Pb> Cd > Mg for metal -HA complexes respectively, indicating a higher degree of complexation with Cu metal ion.

Keywords: stability constant, humic acid, potentiometric titration, divalent metals, acid hydrolysis.

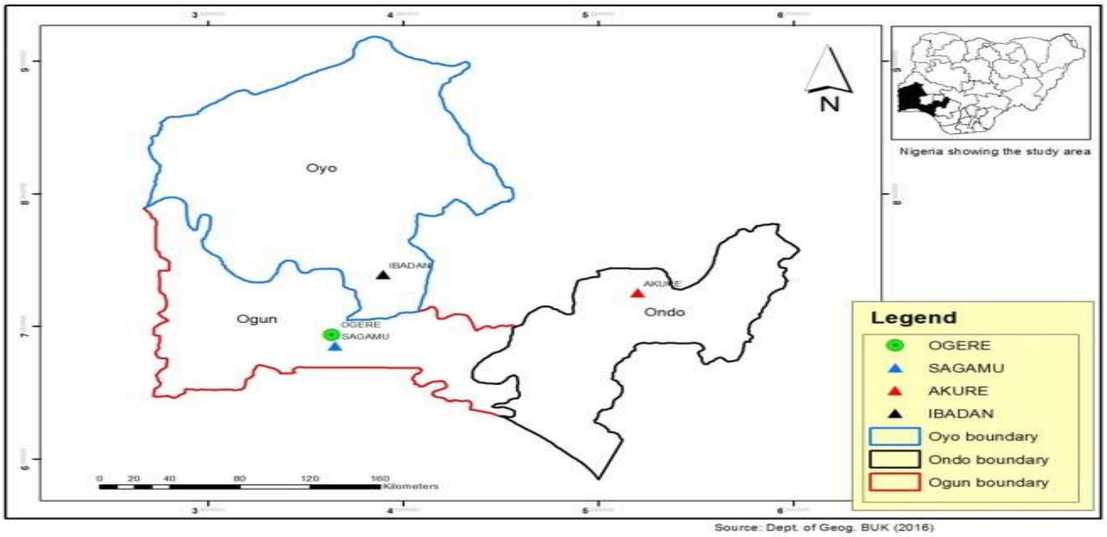
NTRODUCTION

The stability constant of a complex is the numerical expression of its stability and provides a quantitative measure of affinity of the metal ion to the complexing agent. An understanding of the relative stability of metal-complexes helps in predicting the behavior of metal ions in the soil (Ram and Raman, 1982). Extensive researches has been done to determine the stability constants of the complexes formed between humic acid (HA) with a number of metal ions. Ashok *et al*., (2000) reported that humic acid with hydroxyl, phenoxyl and carboxyl reactive groups can form coordination compound with metal ions at pH 3.5. The stability constants(Log K) for different metal-humic acid complexes indicated the following order of the stabilities of complexes formed between humic acid and metal ion, Cu >Fe >Pb> Ni > Co > Ca > Cd > Zn >Mn> Mg. Andelkovic *et al*., (2010) investigated the binding of Cd(II) to soil humic acid at pH 6.5 and in 0.1M KNO_3 ionic medium. The stability constant for binding indicating greater stability in the case when carboxyl groups are involved in complexation reaction. Kostic *et al*.,(2012) investigated the complexation of humic acid with certain heavy metal ions (Co(II), Ni(II),Cu(II), Zn(II), and Pb(II). The experiment was performed at 25°C, at pH 4.0 and ionic strength of 0.01M. Stability constant of complex between Pb(II) ions and humic acid is greater than stability constants of other investigated metal-humate complexes. Bogata and Sokolowska (2016) analyses the interaction between humic acids from different soils and Zn (II) ions at wide concentration ranges and at pH 5. Studies have showed significant impact of Zn concentration, pH and some properties of humic acids with zinc.But all of these studies were limited to acidic pH range. Therefore, the present study was carried out to determine and compare the stability constants of complexes of metal ions with hydrolysed peat soil humic acid and unhydrolysed peat soil humic under non-acid conditions.

MATERIALS AND METHODS

Analytical grade chemicals used includes hydrochloric acid (HCl), nitric acid (HNO_3), sodium hydroxide (NaOH), lead nitrate $Pb(NO_3)_2$, copper nitrate $Cu(NO_3)_2.3H_2O$, cadmium nitrate $Cd(NO_3)_2.4H_2O$, magnesium nitrate $Mg(NO_3)_2.6H_2O$, potassium nitrate (KNO_3), calcium chloride ($CaCl_2$), (sigma-Aldrich). Dowex 50WX8, (20-50 mesh) from Fluka.

Area of study



Source: Dept. of Geog. BUK (2016)

Figure 1: Map showing the sampling point at Sagamu Town, Ogun State.

Description of Sampling Area

Sagamu has geographical coordinates between 6°50′ north; 3° 38′ east is located in south western region of Nigeria. The region has tropical wet and dry climate with a lengthy wet season and relatively constant temperatures throughout the course of the year. Wet season runs from March to October, November to December forms the region dry season. The vegetation type of the region is savannah which is really grassland with small bushes and occasional big trees. Grassland soils have substantially higher organic matter content than forest soils (Novackova, 2011).

Sample Collection

The Peatsoil samples were collected from four different sampling points (0-10cm depth) in Sagamu into polyethylene bag with plastic spoons. Samples were taken to the laboratory, extraneous materials were removed; the samples were air-dried, crushed and ground to a fine powder in a mortar passed through a 0.20mm sieve. The samples were kept for analysis.

Isolation and purification of humic acid from peat soil sample

Peatsoil sample (100g) was mixed with 1000 cm^3 of 0.1M NaOH solution, shaken for 3hours and left to stand overnight. Dark-coloured supernatant was obtained and decanted from solid residue. The dark-coloured supernatant was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 6 hours. Yellowish brown supernatant and dark-brown precipitate were obtained. The yellowish brown supernatant was decanted followed by centrifuge and discarded. The dark-brown precipitate was mixed with 500$cm^3$of 0.1M NaOH solution followed by passing through dowex resin. The dark-brown solution was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 3 hours. The dark-brown precipitate was washed several times with deionized water. The supernatant was treated with $AgNO_3$ solution until no white precipitate observed. The humic acid was transferred to weighed crucible and dried at 60°C in an oven for 12 hours. The humic acid was cooled and dried in the desiccator, weighed and recorded. The obtained humic acid was dried again at 60°C for additional 6 hours cooled and dried in the desiccator, weighed and recorded constant weight was obtained (Baruah *et al.*, 2015).

FT-IR analysis

FT-IR spectra of humic acid sample was analysed using Carry 630 FT-IR Agilent Technologies.

Unhydrolysed compost humic acid

The unhydrolysed humic acid was obtained after isolation and purification of compost humic acid and kept for investigation.

Acid hydrolysis of Peatsoil acid

Peatsoil humic acid sample (1g) was refluxed for 12 hours at (160°C) with 50cm^3 of 6M HCl. The mixture was allowed to cool, decanted, and centrifuged after hydrolysis. The insoluble residues were washed with distilled water via centrifugation several times, and the supernatant was treated with $AgNO_3$ solution until no white precipitate was observed. The residue was thoroughly dried over $CaCl_2$ in a desiccator at room temperature (Chefetz *et al.*, 2002). Finally, the obtained hydrolysed humic acid was kept for investigation.

Potentiometric Titrations

Potentiometric measurements were carried out using a pH-meter Jenway (model 3510) with combine electrode, the sensitivity of the pH - meter is 0.01 units. The pH meter was switched on half an hour before starting the titration for initial warm up of the instrument. The instrument was calibrated with an aqueous standard buffer solution of pH 4.00 and 10.0 (borate buffer) prepared from a "Qualigens" buffer tablets.

The following sets of solutions were prepared in a 250cm^3 volumetric flask separately for pH metric titrations.

(i) 5 cm^3 0.1 M HCl + 40 cm^3 deionized water

(ii) 5 cm^3 0.1 M HCl + 39 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid

(iii) 5 cm^3 0.1 M HCl + 37 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid + 2 cm^3 0.01 M Cu(II)

The solutions were titrated against standardized 0.110MNaOH separately. The total volume of each mixture was adjusted to 50 cm^3 and the ionic strength of the solutions was maintained constant at by adding appropriate amount of stock solution of 1M KNO$_3$ (Gamal, 2015; Omar and Ali, 2015). A magnetic stirrer was used to achieve thorough mixing of the interacting solutions at 550 rpm. The same set of experimental conditions was applied for potentiometric titration of remaining samples.

Evaluation of pKa of Hydrolysed peat soil Humic Acids

The proton-ligand formation number n_A were calculated by Irving and Rossotti expression (Omar and Ali, 2015).

$$nA = Y- \frac{(V2-V1)(No-Eo)}{(Vo+V1)TcL} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 1$$

Where: Y is number of dissociable proton, (V_2-V_1) is the measure of displacement of the ligand curve relative to acid curve, N^o and E^o are the resultant concentration of alkali solution, free acid solution, T_{cL}^o is the total ligand concentration, V^o is the total volume of titration solution,V_1 is the volume of alkali added to acid solution,V_2 is the volume of alkali added to acid solution + ligand solution, acid dissociation constants (pKa - values) of ligand were calculated by algebraic method point wise calculation (Tables 1). The dissociation constants (pKa) were calculated according to the following relation:

$$pKa = pH + \log(\frac{nA}{1-nA}) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 2$$

Where: pKa is the acid dissociation constant, $n_A$is the Proton-ligand formation number and pH is the pH-values (Omar and Ali, 2015).

Determination of metal-ligand stability constants (log K) of complexes

The potentiometric measurement for the determination of stability constant of a complex in solution is based on the fact that the redox potential of the couple $\frac{M^{+(m-n)}}{M^{+m}}$ is shifted significantly on complexation of the metal ion with the ligand. This method involves change in hydrogen ion concentration [H$^+$] due to the displacement or association of one or more protons taking place during complexation reaction. This change can be found out by titrating the solutions containing free acid, acid with ligand, and acid with ligand and metal ion, individually against a standard alkali solution at a constant ionic strength or temperature. Either ionic strength or temperature may be varied for different sets of solutions. In all the cases, the change in the pH of the solution is measured after each addition of a known amount of alkali to the reaction cell which contains the reaction mixture. The titration curves are then drawn by plotting the measured pH values against the corresponding volume of alkali added and the stability constants of the complexes are determined from the titration curves by employing pH-metric titration technique given by (Irving and Rossoti).

Metal-ligand stability constants (Log K) were determined by using the following relations:

$$\bar{n} = \frac{(V_3 - V_2)(E^0 + N^0)}{(V^0 + V_2)\bar{n}_A T_m^0} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 3$$

and

$$PL = \log_{10}\{\frac{1+\beta_n^H \frac{1}{[anti\ \log pH]^n}}{T_L^0 - \bar{n}T_m^0} X \frac{(V^0 + V_3)}{V^0}\} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 4$$

Where $T_{L,}$ T^o, E°, and V^ohavethe same significance as in equation (1) above, T_m denotes the total concentration of metal present in solution, V_3 is the volume of metal ions present in solution and β^H is the overall proton ligand stability constant. The metal-ligand stability constants (log K) were determined by employing point wise computational Method (eq. 5 and 6).

$\mathrm{LogK}_1 = \log\left(\frac{n}{1-n}\right) + \mathrm{pL}$ 5

$\mathrm{LogK}_2 = \log\left(\frac{1-n}{2-n}\right) + \mathrm{pL}$........................6

Where: Log K is the metal-ligand stability constant, pL is the Free ligand exponent function, **n** is the Average number of ligand attached with metal ion (Janrao*et al.*, 2014).The results obtained were analyzed by an ORIGIN 2016 program using titration data and then the proton-ligand stability constants (pKa) and Metal-ligand stability constant (LogK) calculated (Omar and Ali, 2015).

RESULTS AND DISCUSSION

Fourier transformed infrared (FT-IR) spectra of isolated humic acid from peat soils Figure 2 had distinct clear absorption bands indicating the presence of major humic acid structural elemental groups such as H bonded OH ($3680cm^{-1}$ peak), C=O of carbonyl ($1721cm^{-1}$ peak), functional groups of aliphatic components CH_2 ($2918cm^{-1}$ peak) and C-O stretching of polysaccharide ($1168cm^{-1}$ peak). The positions of the absorption bands of the spectra fell within typical major absorption bands of humic acid which is at frequencies 3680, 2918, 1721, 1168 cm^{-1}. The first peak centred in the vicinity of 3680 cm^{-1} region is attributed to phenol OH group bounded by intermolecular H bonds. The $2918cm^{-1}$ band usually has absorption maximum at 2918 cm^{-1} which is due to C–H stretching of alkane group (CH_2). The next major absorption band is 1721 cm^{-1}. This band has been commonly ascribed to C=O stretching of mainly carboxyl group (COOH) with trace amount of ketones. The last peak was observed at 1168 cm^{-1} due to C–O stretching of polysaccharides and this peak appeared also in the spectra of humic acid from peat soil. The FTIR spectra of the isolated humic acid contained all major characteristic absorption peaks of humic acid. These absorption peaks indicated the presence of the major structural elements of humic acid namely H bonded OH, C=C of aromatic ring, C=O of carbonyl group (both carboxyl and ketonic), CH_2 group. This strongly supports the presence of humic acid.

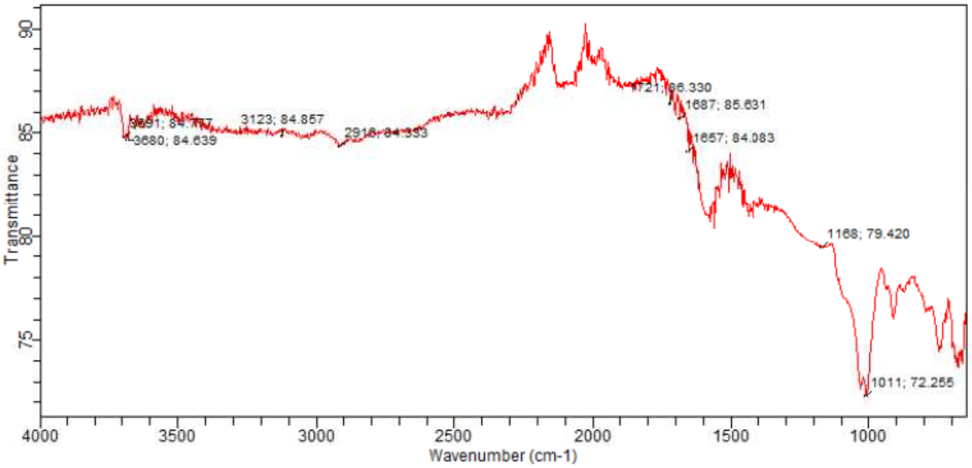


Fig. 2 : FT-IR spectraof peatsoilhumic acid (PSHA)

Evaluation of acid dissociation constant (pka) of acid hydrolysed peat soil humicacid at phenolic group

The value of the dissociation constant of the peat soil humic acid (PSHA) that underwent acidhydrolysis studied was found to be 8.9299 as shown Table 1, which is lower than the literaturevalues reported by Almeida and Szpoganics, (2015), Borges *et al.*, (2005); Badr *et al.*, (2012)and Fernandes *et al*,.(2009) of 9.73, 9.47 and 10.30. The difference between the obtained valuesand the reported values in this study might be probably as a result of acid hydrolysis of humicacid.

Table 1: PKa of (Hydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	$\log(\frac{nA}{1-nA})$	pKa
8.50	5.30	6.29	0.99	0.3594	-0.2510	8.2490
8.72	5.35	6.37	1.02	0.3400	-0.2880	8.4320
9.00	5.40	6.46	1.06	0.3141	-0.3391	8.6609
9.22	5.45	6.55	1.10	0.2882	-0.3927	8.8273
9.51	5.50	6.66	1.16	0.2494	-0.4786	9.0314
9.73	5.55	6.78	1.23	0.2041	-0.5910	9.1390
10.00	5.60	6.90	1.30	0.1589	-0.7238	9.2762
10.23	5.65	7.05	1.40	0.0941	-0.9835	9.2465
10.49	5.70	7.10	1.40	0.0941	-0.9835	9.5065

Average pKa = 8.9299 ± 0.4186

Table 2: PKa of (Unhydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	$\text{Log}(\frac{nA}{1-n})$	pKa
8.50	5.30	5.81	0.51	0.6619	0.2919	8.7919
8.72	5.35	5.90	0.55	0.6357	0.2418	8.9618
9.00	5.40	6.00	0.60	0.6029	0.1813	9.1813
9.22	5.45	6.10	0.65	0.5701	0.1226	9.3426
9.51	5.50	6.20	0.70	0.5376	0.0654	9.5754
9.73	5.55	6.33	0.78	0.4851	-0.0259	9.7041
10.00	5.60	6.47	0.87	0.4262	-0.1291	9.8709
10.23	5.65	6.62	0.99	0.3609	-0.2481	9.9819
10.49	5.70	6.80	1.10	0.2759	-0.4690	10.0210

Average pKa = 9.4923± 0.4410

Metal-ligand stability constant (Log K)

The stabilityconstants require the accurate values of proton-ligand stability constants (Anil and Maroti, 2008). Metal titration curves crossed over ligand titration curve indicated the formation of complex upon proton release (Santosh, *et al.*, 2011). If the values of n- are within range 0.2-0.8 and 1.2-18 this indicates the formation of 1:1 and 1:2 complexes (Sayyed and Mazahar, 2012).

The metal (II)-humate stepwise stability constants (log k) at phenolic group (Tables 3-18)

Table 3: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$\log(\frac{n}{1-n})$	LogK_1
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

LogK_1 (Average value) = 2.4788± 0.2203

Table 4: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$\text{Log}(\frac{n-1}{2-n})$	LogK_2
9.51	5.50	6.66	6.73	0.07	1.3509	1.70	-0.2671	1.4329
9.73	5.55	6.78	6.85	0.07	1.6383	1.51	0.2467	1.7567
10.00	5.60	6.90	6.98	0.08	2.1783	1.31	-0.2158	1.0942
10.23	5.65	7.05	7.13	0.08	4.1904	1.27		
10.49	5.70	7.10	7.19	0.09	4.6920			

LogK_2(Average value) = 1.4280 ± 0.3312

Table 5:Point-wise method,Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	Log($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430

LogK_1 **(Average value)** = 2.3059± 0.6153

Table 6:Point-wise method, Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$V_3\text{-}V_2$	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
9.73	5.55	6.33	6.42	0.09	0.9000	1.69		
10.00	5.60	6.47	6.58	0.11	1.2578	1.44	-0.4592	0.9808
10.23	5.65	6.62	6.84	0.12	1.6137	1.26	-0.2010	1.4610
10.49	5.70	6.80	6.92	0.12	2.1052	1.03		

LogK_2 **(Average value)** = 1.2209± 0.3398

Table 7:Point-wise method,Pb (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	log($\frac{n}{1-n}$)	LogK_1
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.60	0.05	0.8333	1.96	0.6989	2.6589

LogK_1 (Average value) = 2.5832 ±0.1614

Table 8:Point-wise method,Pb-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	log($\frac{n-1}{2-n}$)	logK_2
9.51	5.50	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.83	0.05	1.1702	1.44		
10.00	5.60	6.90	6.90	0.05	1.4864	1.22	-0.0237	1.1963
10.23	5.65	7.05	7.10	0.05	2.0190	1.09		
10.49	5.70	7.10	7.17	0.07	3.6492	1.00		

LogK_2(Average value) = 1.1963

Table 9:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$V_3\text{-}V_2$	n	pL	Log ($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.5477	2.3123
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	0.0272	2.2072
9.51	5.50	6.20	6.26	0.07	0.6417	1.89	0.2530	2.1430
9.73	5.55	6.40	6.40	0.07	0.7000	1.67	0.3680	2.0380

LogK_1 **(Average value)** = 2.2364 ± 0.1602

Table 10:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$V_3\text{-}V_2$	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
10.00	5.60	6.47	6.55	0.08	1.9503	1.41		
10.23	5.65	6.62	6.72	0.11	1.4792	1.26	-0.0361	1.2239

LogK_2 **(Average value)** = 1.2239

Table 11:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	log($\frac{n}{n-1}$)	LogK_1
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4290	2.2110
8.72	5.35	6.37	6.39	0.02	0.2858	2.42	-0.3978	2.0222
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

LogK_1 (Average value)=2.1382**±**0.1046

Table 12:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	log($\frac{n-1}{2-n}$)	LogK$_2$
9.51	5.55	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.84	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.93	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.10		
10.49	5.70	7.10	7.18	0.07	3.6492	0.83		

LogK$_2$(Average value) = 1.5453 **±** 0.3450

Table 13:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	V$_3$-V$_2$	n	pL	Log($\frac{n}{n-1}$)	Log K$_1$
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.3477	2.3123
9.00	5.40	6.00	6.04	0.04	0.3236	2.38	-0.3202	2.0598
9.22	5.45	6.10	6.15	0.05	0.4297	2.17	-0.1230	2.0470
9.51	5.50	6.20	6.26	0.06	0.5500	1.89	0.0871	1.9771
9.73	5.55	6.33	6.40	0.07	0.7000	1.67	0.3680	2.0380

LogK$_1$ **(Average value)** = 2.1568 ± 0.2069

Table 14:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	V$_3$-V$_2$	n	pL	Log($\frac{n-1}{2-n}$)	Log K$_2$
10.00	5.60	6.47	6.55	0.08	0.9148	1.41		
10.23	5.65	6.62	6.71	0.09	1.2102	1.20	-0.5749	0.6251
10.49	5.70	6.80	6.92	0.09	1.5968	1.03	0.1703	1.2003

LogK$_2$ **(Average value)** = 0.9127± 0.4070

Table15:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	Log($\frac{n}{1-n}$)	LogK$_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4210	2.2190
8.72	5.35	6.37	6.40	0.03	0.4286	2.42	-0.1249	2.2951
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.96	0.3010	2.2610
9.51	5.55	6.66	6.70	0.04	0.7720	1.67	0.5297	2.1997

LogK$_1$ (Average value) = 2.2108± 0.0825

Table 16:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	Log($\frac{n-1}{2-n}$)	Log K$_2$
9.73	5.55	6.78	6.83	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.95	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.09		
10.49	5.70	7.10	7.16	0.06	3.1429	0.89		

LogK$_2$ **(Average value)** = 1.5453± 0.3450

Table 17:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	V$_3$-V$_2$	n	pL	Log($\frac{n}{n-1}$)	Log K$_1$
8.50	5.30	5.81	5.86	0.05	0.3717	2.88	-0.2280	2.6520
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.06	0.06	0.4853	2.38	-0.0255	2.3545
9.22	5.45	6.10	6.16	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430
9.73	5.55	6.33	6.41	0.08	0.8000	1.69	0.6020	2.2920

LogK$_1$ **(Average value)** = 2.2516± 0.5380

Table 18:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$\mathrm{Log}(\frac{n-1}{2-n})$	Log K_2
10.00	5.60	6.47	6.57	0.10	1.1434	1.43		
10.23	5.65	6.62	6.72	0.10	1.3448	1.23	-0.2788	0.9512
10.49	5.70	6.80	6.90	0.10	1.7742	1.03	0.5351	1.5651

LogK_2 **(Average value)** = 1.2581± 0.4340

Table 19: Stepwise and overall Stability constants of thehydrolysed and unhydrolysed divalent metal (II) complexes

Chelates	**LogK_1**	**LogK_2**	**Logβ**
[Cu (Hydrolysed PSHA-1)$_2$]	2.4788	1.4280	3.9068
[Pb (Hydrolysed PSHA-1)$_2$]	2.5832	1.1963	3.7795
[Cd (Hydrolysed PSHA-1)$_2$]	2.2108	1.5453	3.7561
[Mg (Hydrolysed PSHA-1)$_2$]	2.1382	1.5453	3.6835
[Cu (Unhydrolysed PSHA-1)$_2$]	2.3059	1.2209	3.5268
[Pb (Unhydrolysed PSHA-1)$_2$]	2.2364	1.2239	3.4603
[Cd (Unhydrolysed PSHA-1)$_2$]	2.2516	1.2581	3.5097
[Mg (Unydrolysed PSHA-1)$_2$]	2.1568	0.9127	3.0695

The results obtained (Table19) shows the stepwise and overall stability constants to be not high indicating low stability of the complexes, because the solubility of most metal ions in the basic pH range is minimal due to metal hydroxide precipitation (Karimi, 2017). In general, the stepwise stability constants (K_1 and K_2) follow the order $K_1 > K_2$ for the copper, lead, magnesium and cadmium complexes respectively. The steady decrease of the values with increasing number of ligands is in agreement with the prediction made by researchers (Na'aliya, 2013). The decrease could be attributed to the fact that as the number of the ligands (Humate ions) that enters the coordination zone increases the aqua molecules available for replacement by the ligands become less. Thus, the metal ions become less electron loving with progressive intake of the ligand and this results in the decrease in the values of the constants (Na'aliya, 2013). Also the stability of the complexes is influenced by the size and number of the chelate rings(Mackay and Mackay,2002).All the complexes form rings in their structure as humate, a bidentate ligand, bond the metal ions in the ratio 1:2 (Boguta and Sokolowska, 2016) forming chelate rings. The values of the overall stability constants (logβ) obtained for humate complexes are not high indicating low stability as the values are not high. LogK values for copper-humates (Table 3 to 6) obtained in this study are lower than those reported for the complexes of humic acids (Pandey *et al*., 2015; Dinu, 2013; Kaschl *et al*., 2010 and Gilbeto and Jorg, 2001). The values of LogK(Table 7 to 10) forlead-humates are lower than those reported for the lead in the literature (Dinu, 2013; Gilbeto and Jorg 2001). Log K values(Table 11 to 14) for magnesium-humates obtained in this study are close to those reported by (Pandey *et al*., 2015). Log K values of cadmium-humates (Table 15 to 18) obtained in this work near to the one reported by (Dinu, 2013 and Pandey *et al*., 2015).The difference between the reported values and the values obtained in this study might be probably as a result of acid hydrolysis of humic acid. The values of the overall stability constants (log β) of the copper humates complexes presented in Table 19 is high than that of other metal humate complexes, show relatively high stability of Cu-HA complexes, show the following order of stability: Cu >Pb> Cd > Mg; which are in close agreement to the findings of (Dinu, 2013 and Pandey *et al*., 2015).The high stability of Cu-humate chelate could be attributed to the existence of coordinate covalent bond between the complexing agents and the Cu^{2+} ions. Since, Cu^{2+} being a metal of the transitional series with $3d^9$ electronic configurations can accept the electrons from the complexing agents. Similarly,the low stabilities of Pb,Cd and Mg - complexes could be explained by that Pb^{2+} with $6s^2$, Cd^{2+} with $4d^{10}$ and Mg^{2+} with $2p^6$ their electronic configuration has a completely filled d,p and s orbitals. Moreover, the stabilities of metal ions with hydrolysed humic acid from peat soil were higher than those with unhydrolysed humic acid from peat soil; which is ascribed to the high content of acidity in hydrolysed humic acid than unhydrolysed humic acid.

CONCLUSION

The values of logK for Cu(II) hydrolysed humic acid complex was higher followed by Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes as compared with metal(II) unhydrolysed humic acid complexes . This indicates acid hydrolysis of humic acid can enhance the complexation behavior of humic acid with metal (II) ions. However, the higher values of logβ for Cu(II), Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes indicates more stable stepwise complexes formed as compared with Cu(II), Pb(II), Cd(II) and Mg(II) unhydrolysed humic acid complexes.

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STABILITY CONSTANTS OF COMPLEXES OF METAL IONS WITH PEATSOIL HUMIC ACIDS UNDER NON-ACID-CONDITIONS

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ABSTRACT

Stability constants of complexes of four divalent metal ions viz. Cu^{2+}, Pb^{2+},Mg^{2+} and Cd^{2+} with humic acids (HA) were determined by potentiometric titration of humic acids with the corresponding salt of the divalent metals in aqueous media under non-acid-condition. The log K (logarithm of the stability constant) ranged from 1.0942 to 2.7471 for metal-humic acid complexes were determined using point-wise computational method. The order of stability constants were obtained as follows: Cu >Pb> Cd > Mg for metal -HA complexes respectively, indicating a higher degree of complexation with Cu metal ion.

Keywords: stability constant, humic acid, potentiometric titration, divalent metals, acid hydrolysis.

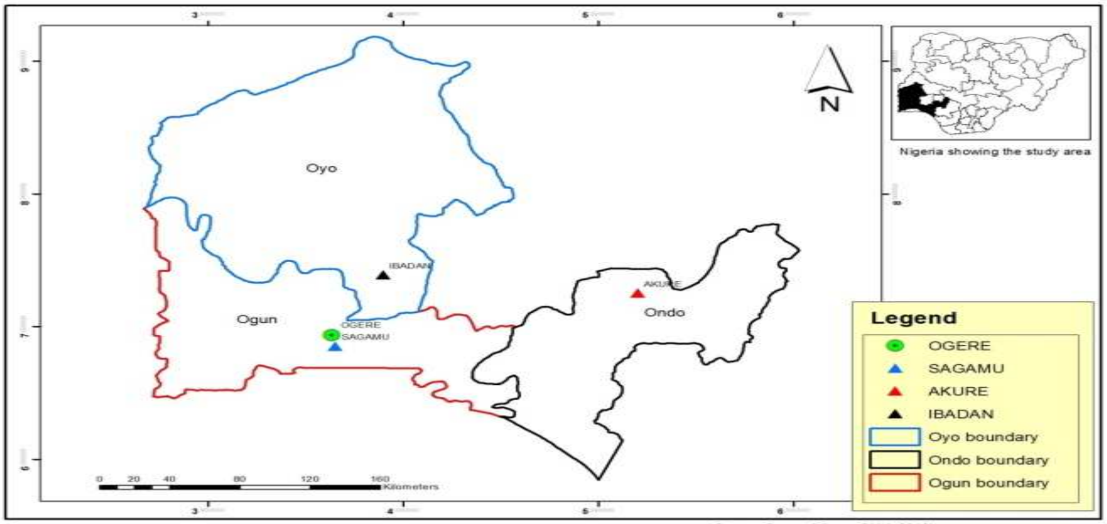
NTRODUCTION

The stability constant of a complex is the numerical expression of its stability and provides a quantitative measure of affinity of the metal ion to the complexing agent. An understanding of the relative stability of metal-complexes helps in predicting the behavior of metal ions in the soil (Ram and Raman, 1982). Extensive researches has been done to determine the stability constants of the complexes formed between humic acid (HA) with a number of metal ions. Ashok *et al*., (2000) reported that humic acid with hydroxyl, phenoxyl and carboxyl reactive groups can form coordination compound with metal ions at pH 3.5. The stability constants(Log K) for different metal-humic acid complexes indicated the following order of the stabilities of complexes formed between humic acid and metal ion, Cu >Fe >Pb> Ni > Co > Ca > Cd > Zn >Mn> Mg. Andelkovic *et al*., (2010) investigated the binding of Cd(II) to soil humic acid at pH 6.5 and in 0.1M KNO_3 ionic medium. The stability constant for binding indicating greater stability in the case when carboxyl groups are involved in complexation reaction. Kostic *et al*.,(2012) investigated the complexation of humic acid with certain heavy metal ions (Co(II), Ni(II),Cu(II), Zn(II), and Pb(II). The experiment was performed at 25°C, at pH 4.0 and ionic strength of 0.01M. Stability constant of complex between Pb(II) ions and humic acid is greater than stability constants of other investigated metal-humate complexes. Bogata and Sokolowska (2016) analyses the interaction between humic acids from different soils and Zn (II) ions at wide concentration ranges and at pH 5. Studies have showed significant impact of Zn concentration, pH and some properties of humic acids with zinc.But all of these studies were limited to acidic pH range. Therefore, the present study was carried out to determine and compare the stability constants of complexes of metal ions with hydrolysed peat soil humic acid and unhydrolysed peat soil humic under non-acid conditions.

MATERIALS AND METHODS

Analytical grade chemicals used includes hydrochloric acid (HCl), nitric acid (HNO_3), sodium hydroxide (NaOH), lead nitrate $Pb(NO_3)_2$, copper nitrate $Cu(NO_3)_2.3H_2O$, cadmium nitrate $Cd(NO_3)_2.4H_2O$, magnesium nitrate $Mg(NO_3)_2.6H_2O$, potassium nitrate (KNO_3), calcium chloride ($CaCl_2$), (sigma-Aldrich). Dowex 50WX8, (20-50 mesh) from Fluka.

Area of study



Source: Dept. of Geog. BUK (2016)

Figure 1: Map showing the sampling point at Sagamu Town, Ogun State.

Description of Sampling Area

Sagamu has geographical coordinates between 6°50′ north; 3° 38′ east is located in south western region of Nigeria. The region has tropical wet and dry climate with a lengthy wet season and relatively constant temperatures throughout the course of the year. Wet season runs from March to October, November to December forms the region dry season. The vegetation type of the region is savannah which is really grassland with small bushes and occasional big trees. Grassland soils have substantially higher organic matter content than forest soils (Novackova, 2011).

Sample Collection

The Peatsoil samples were collected from four different sampling points (0-10cm depth) in Sagamu into polyethylene bag with plastic spoons. Samples were taken to the laboratory, extraneous materials were removed; the samples were air-dried, crushed and ground to a fine powder in a mortar passed through a 0.20mm sieve. The samples were kept for analysis.

Isolation and purification of humic acid from peat soil sample

Peatsoil sample (100g) was mixed with 1000 cm^3 of 0.1M NaOH solution, shaken for 3hours and left to stand overnight. Dark-coloured supernatant was obtained and decanted from solid residue. The dark-coloured supernatant was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 6 hours. Yellowish brown supernatant and dark-brown precipitate were obtained. The yellowish brown supernatant was decanted followed by centrifuge and discarded. The dark-brown precipitate was mixed with 500$cm^3$of 0.1M NaOH solution followed by passing through dowex resin. The dark-brown solution was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 3 hours. The dark-brown precipitate was washed several times with deionized water. The supernatant was treated with $AgNO_3$ solution until no white precipitate observed. The humic acid was transferred to weighed crucible and dried at 60°C in an oven for 12 hours. The humic acid was cooled and dried in the desiccator, weighed and recorded. The obtained humic acid was dried again at 60°C for additional 6 hours cooled and dried in the desiccator, weighed and recorded constant weight was obtained (Baruah *et al*., 2015).

FT-IR analysis

FT-IR spectra of humic acid sample was analysed using Carry 630 FT-IR Agilent Technologies.

Unhydrolysed compost humic acid

The unhydrolysed humic acid was obtained after isolation and purification of compost humic acid and kept for investigation.

Acid hydrolysis of Peatsoil acid

Peatsoil humic acid sample (1g) was refluxed for 12 hours at (160°C) with 50cm^3 of 6M HCl. The mixture was allowed to cool, decanted, and centrifuged after hydrolysis. The insoluble residues were washed with distilled water via centrifugation several times, and the supernatant was treated with $AgNO_3$ solution until no white precipitate was observed. The residue was thoroughly dried over $CaCl_2$ in a desiccator at room temperature (Chefetz *et al*., 2002). Finally, the obtained hydrolysed humic acid was kept for investigation.

Potentiometric Titrations

Potentiometric measurements were carried out using a pH-meter Jenway (model 3510) with combine electrode, the sensitivity of the pH -meter is 0.01 units. The pH meter was switched on half an hour before starting the titration for initial warm up of the instrument. The instrument was calibrated with an aqueous standard buffer solution of pH 4.00 and 10.0 (borate buffer) prepared from a "Qualigens" buffer tablets.

The following sets of solutions were prepared in a 250cm^3 volumetric flask separately for pH metric titrations.

(i) 5 cm^3 0.1 M HCl + 40 cm^3 deionized water
(ii) 5 cm^3 0.1 M HCl + 39 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid
(iii) 5 cm^3 0.1 M HCl + 37 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid + 2 cm^3 0.01 M Cu(II)

The solutions were titrated against standardized 0.110MNaOH separately. The total volume of each mixture was adjusted to 50 cm^3 and the ionic strength of the solutions was maintained constant at by adding appropriate amount of stock solution of 1M KNO$_3$ (Gamal, 2015; Omar and Ali, 2015). A magnetic stirrer was used to achieve thorough mixing of the interacting solutions at 550 rpm. The same set of experimental conditions was applied for potentiometric titration of remaining samples.

Evaluation of pKa of Hydrolysed peat soil Humic Acids

The proton-ligand formation number n$_{\mathbf{A}}$ were calculated by Irving and Rossotti expression (Omar and Ali, 2015).

$$nA = Y- \frac{(V2-V1)(No-Eo)}{(Vo+V1)TcL} \quad ....1$$

Where: Y is number of dissociable proton, (V$_2$-V$_1$) is the measure of displacement of the ligand curve relative to acid curve, N^o and E^o are the resultant concentration of alkali solution, free acid solution, T$_{cL}$^{o} is the total ligand concentration, V^o is the total volume of titration solution,V$_1$ is the volume of alkali added to acid solution,V$_2$ is the volume of alkali added to acid solution + ligand solution, acid dissociation constants (pKa - values) of ligand were calculated by algebraic method point wise calculation (Tables 1). The dissociation constants (pKa) were calculated according to the following relation:

$$pKa = pH + \log(\frac{nA}{1-nA}) \quad ....2$$

Where: pKa is the acid dissociation constant, n$_A$is the Proton-ligand formation number and pH is the pH-values (Omar and Ali, 2015).

Determination of metal-ligand stability constants (log K) of complexes

The potentiometric measurement for the determination of stability constant of a complex in solution is based on the fact that the redox potential of the couple $\frac{M^{+(m-n)}}{M^{+m}}$ is shifted significantly on complexation of the metal ion with the ligand. This method involves change in hydrogen ion concentration [H$^+$] due to the displacement or association of one or more protons taking place during complexation reaction. This change can be found out by titrating the solutions containing free acid, acid with ligand, and acid with ligand and metal ion, individually against a standard alkali solution at a constant ionic strength or temperature. Either ionic strength or temperature may be varied for different sets of solutions. In all the cases, the change in the pH of the solution is measured after each addition of a known amount of alkali to the reaction cell which contains the reaction mixture. The titration curves are then drawn by plotting the measured pH values against the corresponding volume of alkali added and the stability constants of the complexes are determined from the titration curves by employing pH-metric titration technique given by (Irving and Rossoti).

Metal-ligand stability constants (Log K) were determined by using the following relations:

$$\bar{n} = \frac{(V_3 - V_2)(E^0 + N^0)}{(V^0 + V_2)\bar{n}_A T_m^0} \quad ....3$$

and

$$PL = \log_{10}\{\frac{1 + \beta_n^H \frac{1}{[anti\ \log pH]^n}}{T_L^0 - \bar{n} T_m^0} X \frac{(V^0 + V_3)}{V^0}\} \quad ....4$$

Where $T_{L,}$ T^{o}, E°, and V^{o}havethe same significance as in equation (1) above, T_m denotes the total concentration of metal present in solution, V_3 is the volume of metal ions present in solution and β^{H} is the overall proton ligand stability constant. The metal-ligand stability constants (log K) were determined by employing point wise computational Method (eq. 5 and 6).

$\mathrm{Log}K_1 = \log\left(\frac{n}{1-n}\right) + pL$ 5

$\mathrm{Log}K_2 = \log\left(\frac{1-n}{2-n}\right) + pL$.......................6

Where: Log K is the metal-ligand stability constant, pL is the Free ligand exponent function, **n** is the Average number of ligand attached with metal ion (Janrao*et al*., 2014).The results obtained were analyzed by an ORIGIN 2016 program using titration data and then the proton-ligand stability constants (pKa) and Metal-ligand stability constant (LogK) calculated (Omar and Ali, 2015).

RESULTS AND DISCUSSION

Fourier transformed infrared (FT-IR) spectra of isolated humic acid from peat soils Figure 2 had distinct clear absorption bands indicating the presence of major humic acid structural elemental groups such as H bonded OH ($3680cm^{-1}$ peak), C=O of carbonyl ($1721cm^{-1}$ peak), functional groups of aliphatic components CH_2 ($2918cm^{-1}$ peak) and C-O stretching of polysaccharide ($1168cm^{-1}$ peak). The positions of the absorption bands of the spectra fell within typical major absorption bands of humic acid which is at frequencies 3680, 2918, 1721, 1168 cm^{-1}. The first peak centred in the vicinity of 3680 cm^{-1} region is attributed to phenol OH group bounded by intermolecular H bonds. The $2918cm^{-1}$ band usually has absorption maximum at 2918 cm^{-1} which is due to C–H stretching of alkane group (CH_2). The next major absorption band is 1721 cm^{-1}. This band has been commonly ascribed to C=O stretching of mainly carboxyl group (COOH) with trace amount of ketones. The last peak was observed at 1168 cm^{-1} due to C–O stretching of polysaccharides and this peak appeared also in the spectra of humic acid from peat soil. The FTIR spectra of the isolated humic acid contained all major characteristic absorption peaks of humic acid. These absorption peaks indicated the presence of the major structural elements of humic acid namely H bonded OH, C=C of aromatic ring, C=O of carbonyl group (both carboxyl and ketonic), CH_2 group. This strongly supports the presence of humic acid.

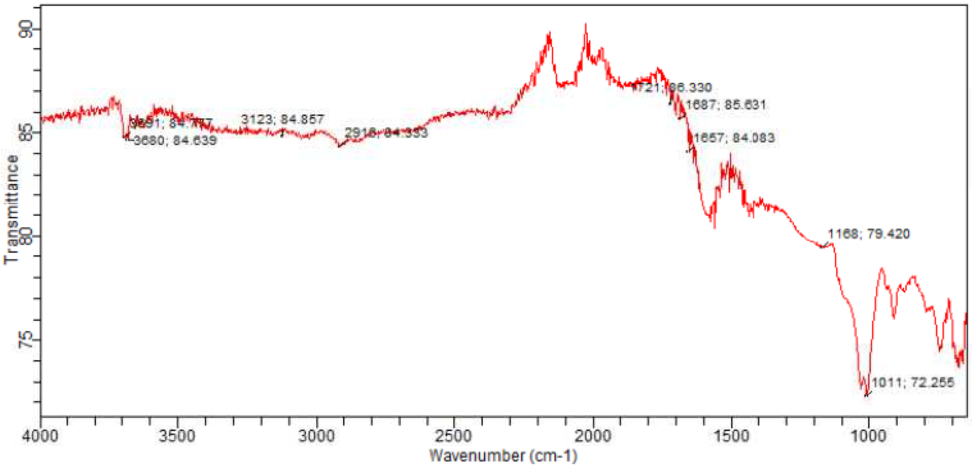


Fig. 2 : FT-IR spectraof peatsoilhumic acid (PSHA)

Evaluation of acid dissociation constant (pka) of acid hydrolysed peat soil humicacid at phenolic group

The value of the dissociation constant of the peat soil humic acid (PSHA) that underwent acidhydrolysis studied was found to be 8.9299 as shown Table 1, which is lower than the literaturevalues reported by Almeida and Szpoganics, (2015), Borges *et al*., (2005); Badr *et al*., (2012)and Fernandes *et al*,.(2009) of 9.73, 9.47 and 10.30. The difference between the obtained valuesand the reported values in this study might be probably as a result of acid hydrolysis of humicacid.

Table 1: PKa of (Hydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	$\log(\frac{nA}{1-nA})$	pKa
8.50	5.30	6.29	0.99	0.3594	-0.2510	8.2490
8.72	5.35	6.37	1.02	0.3400	-0.2880	8.4320
9.00	5.40	6.46	1.06	0.3141	-0.3391	8.6609
9.22	5.45	6.55	1.10	0.2882	-0.3927	8.8273
9.51	5.50	6.66	1.16	0.2494	-0.4786	9.0314
9.73	5.55	6.78	1.23	0.2041	-0.5910	9.1390
10.00	5.60	6.90	1.30	0.1589	-0.7238	9.2762
10.23	5.65	7.05	1.40	0.0941	-0.9835	9.2465
10.49	5.70	7.10	1.40	0.0941	-0.9835	9.5065

Average pKa = 8.9299 ± 0.4186

Table 2: PKa of (Unhydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	$\text{Log}(\frac{nA}{1-n})$	pKa
8.50	5.30	5.81	0.51	0.6619	0.2919	8.7919
8.72	5.35	5.90	0.55	0.6357	0.2418	8.9618
9.00	5.40	6.00	0.60	0.6029	0.1813	9.1813
9.22	5.45	6.10	0.65	0.5701	0.1226	9.3426
9.51	5.50	6.20	0.70	0.5376	0.0654	9.5754
9.73	5.55	6.33	0.78	0.4851	-0.0259	9.7041
10.00	5.60	6.47	0.87	0.4262	-0.1291	9.8709
10.23	5.65	6.62	0.99	0.3609	-0.2481	9.9819
10.49	5.70	6.80	1.10	0.2759	-0.4690	10.0210

Average pKa = 9.4923± 0.4410

Metal-ligand stability constant (Log K)

The stabilityconstants require the accurate values of proton-ligand stability constants (Anil and Maroti, 2008). Metal titration curves crossed over ligand titration curve indicated the formation of complex upon proton release (Santosh, *et al*., 2011). If the values of n- are within range 0.2-0.8 and 1.2-18 this indicates the formation of 1:1 and 1:2 complexes (Sayyed and Mazahar, 2012).

The metal (II)-humate stepwise stability constants (log k) at phenolic group (Tables 3-18)

Table 3: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$\log(\frac{n}{1-n})$	LogK_1
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

LogK_1 (Average value) = 2.4788± 0.2203

Table 4: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$\text{Log}(\frac{n-1}{2-n})$	LogK_2
9.51	5.50	6.66	6.73	0.07	1.3509	1.70	-0.2671	1.4329
9.73	5.55	6.78	6.85	0.07	1.6383	1.51	0.2467	1.7567
10.00	5.60	6.90	6.98	0.08	2.1783	1.31	-0.2158	1.0942
10.23	5.65	7.05	7.13	0.08	4.1904	1.27		
10.49	5.70	7.10	7.19	0.09	4.6920			

LogK_2(Average value) = 1.4280 ± 0.3312

Table 5:Point-wise method,Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	Log($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430

$LogK_1$ **(Average value)** = 2.3059± 0.6153

Table 6:Point-wise method, Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
9.73	5.55	6.33	6.42	0.09	0.9000	1.69		
10.00	5.60	6.47	6.58	0.11	1.2578	1.44	-0.4592	0.9808
10.23	5.65	6.62	6.84	0.12	1.6137	1.26	-0.2010	1.4610
10.49	5.70	6.80	6.92	0.12	2.1052	1.03		

$LogK_2$ **(Average value)** = 1.2209± 0.3398

Table 7:Point-wise method,Pb (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n}{1-n}$)	$LogK_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.60	0.05	0.8333	1.96	0.6989	2.6589

$LogK_1$ (Average value) = 2.5832 ±0.1614

Table 8:Point-wise method,Pb-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n-1}{2-n}$)	$logK_2$
9.51	5.50	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.83	0.05	1.1702	1.44		
10.00	5.60	6.90	6.90	0.05	1.4864	1.22	-0.0237	1.1963
10.23	5.65	7.05	7.10	0.05	2.0190	1.09		
10.49	5.70	7.10	7.17	0.07	3.6492	1.00		

$LogK_2$(Average value) = 1.1963

Table 9:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log ($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.5477	2.3123
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	0.0272	2.2072
9.51	5.50	6.20	6.26	0.07	0.6417	1.89	0.2530	2.1430
9.73	5.55	6.40	6.40	0.07	0.7000	1.67	0.3680	2.0380

$LogK_1$ **(Average value)** = 2.2364 ± 0.1602

Table 10:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
10.00	5.60	6.47	6.55	0.08	1.9503	1.41		
10.23	5.65	6.62	6.72	0.11	1.4792	1.26	-0.0361	1.2239

$LogK_2$ **(Average value)** = 1.2239

Table 11:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n}{n-1}$)	$LogK_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4290	2.2110
8.72	5.35	6.37	6.39	0.02	0.2858	2.42	-0.3978	2.0222
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

$LogK_1$ (Average value)=2.1382**±**0.1046

Table 12:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	log($\frac{n-1}{2-n}$)	$LogK_2$
9.51	5.55	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.84	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.93	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.10		
10.49	5.70	7.10	7.18	0.07	3.6492	0.83		

$LogK_2$(Average value) = 1.5453 **±** 0.3450

Table 13:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$V_3\text{-}V_2$	n	pL	Log($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.3477	2.3123
9.00	5.40	6.00	6.04	0.04	0.3236	2.38	-0.3202	2.0598
9.22	5.45	6.10	6.15	0.05	0.4297	2.17	-0.1230	2.0470
9.51	5.50	6.20	6.26	0.06	0.5500	1.89	0.0871	1.9771
9.73	5.55	6.33	6.40	0.07	0.7000	1.67	0.3680	2.0380

$LogK_1$ **(Average value)** = 2.1568 ± 0.2069

Table 14:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$V_3\text{-}V_2$	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
10.00	5.60	6.47	6.55	0.08	0.9148	1.41		
10.23	5.65	6.62	6.71	0.09	1.2102	1.20	-0.5749	0.6251
10.49	5.70	6.80	6.92	0.09	1.5968	1.03	0.1703	1.2003

$LogK_2$ **(Average value)** = 0.9127± 0.4070

Table15:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	Log($\frac{n}{1-n}$)	$LogK_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4210	2.2190
8.72	5.35	6.37	6.40	0.03	0.4286	2.42	-0.1249	2.2951
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.96	0.3010	2.2610
9.51	5.55	6.66	6.70	0.04	0.7720	1.67	0.5297	2.1997

$LogK_1$ (Average value) = 2.2108± 0.0825

Table 16:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
9.73	5.55	6.78	6.83	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.95	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.09		
10.49	5.70	7.10	7.16	0.06	3.1429	0.89		

$LogK_2$ **(Average value)** = 1.5453± 0.3450

Table 17:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$V_3\text{-}V_2$	n	pL	Log($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.86	0.05	0.3717	2.88	-0.2280	2.6520
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.06	0.06	0.4853	2.38	-0.0255	2.3545
9.22	5.45	6.10	6.16	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430
9.73	5.55	6.33	6.41	0.08	0.8000	1.69	0.6020	2.2920

$LogK_1$ **(Average value)** = 2.2516± 0.5380

Table 18:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$\text{Log}(\frac{n-1}{2-n})$	Log K_2
10.00	5.60	6.47	6.57	0.10	1.1434	1.43		
10.23	5.65	6.62	6.72	0.10	1.3448	1.23	-0.2788	0.9512
10.49	5.70	6.80	6.90	0.10	1.7742	1.03	0.5351	1.5651

LogK_2 **(Average value)** = 1.2581± 0.4340

Table 19: Stepwise and overall Stability constants of thehydrolysed and unhydrolysed divalent metal (II) complexes

Chelates	**LogK_1**	**LogK_2**	**Logβ**
[Cu (Hydrolysed PSHA-1)$_2$]	2.4788	1.4280	3.9068
[Pb (Hydrolysed PSHA-1)$_2$]	2.5832	1.1963	3.7795
[Cd (Hydrolysed PSHA-1)$_2$]	2.2108	1.5453	3.7561
[Mg (Hydrolysed PSHA-1)$_2$]	2.1382	1.5453	3.6835
[Cu (Unhydrolysed PSHA-1)$_2$]	2.3059	1.2209	3.5268
[Pb (Unhydrolysed PSHA-1)$_2$]	2.2364	1.2239	3.4603
[Cd (Unhydrolysed PSHA-1)$_2$]	2.2516	1.2581	3.5097
[Mg (Unydrolysed PSHA-1)$_2$]	2.1568	0.9127	3.0695

The results obtained (Table19) shows the stepwise and overall stability constants to be not high indicating low stability of the complexes, because the solubility of most metal ions in the basic pH range is minimal due to metal hydroxide precipitation (Karimi, 2017). In general, the stepwise stability constants (K_1 and K_2) follow the order $K_1 > K_2$ for the copper, lead, magnesium and cadmium complexes respectively. The steady decrease of the values with increasing number of ligands is in agreement with the prediction made by researchers (Na'aliya, 2013). The decrease could be attributed to the fact that as the number of the ligands (Humate ions) that enters the coordination zone increases the aqua molecules available for replacement by the ligands become less. Thus, the metal ions become less electron loving with progressive intake of the ligand and this results in the decrease in the values of the constants (Na'aliya, 2013). Also the stability of the complexes is influenced by the size and number of the chelate rings(Mackay and Mackay,2002).All the complexes form rings in their structure as humate, a bidentate ligand, bond the metal ions in the ratio 1:2 (Boguta and Sokolowska, 2016) forming chelate rings. The values of the overall stability constants (logβ) obtained for humate complexes are not high indicating low stability as the values are not high. LogK values for copper-humates (Table 3 to 6) obtained in this study are lower than those reported for the complexes of humic acids (Pandey *et al*., 2015; Dinu, 2013; Kaschl *et al*., 2010 and Gilbeto and Jorg, 2001). The values of LogK(Table 7 to 10) forlead-humates are lower than those reported for the lead in the literature (Dinu, 2013; Gilbeto and Jorg 2001). Log K values(Table 11 to 14) for magnesium-humates obtained in this study are close to those reported by (Pandey *et al*., 2015). Log K values of cadmium-humates (Table 15 to 18) obtained in this work near to the one reported by (Dinu, 2013 and Pandey *et al*., 2015).The difference between the reported values and the values obtained in this study might be probably as a result of acid hydrolysis of humic acid. The values of the overall stability constants (log β) of the copper humates complexes presented in Table 19 is high than that of other metal humate complexes, show relatively high stability of Cu-HA complexes, show the following order of stability: Cu >Pb> Cd > Mg; which are in close agreement to the findings of (Dinu, 2013 and Pandey *et al*., 2015).The high stability of Cu-humate chelate could be attributed to the existence of coordinate covalent bond between the complexing agents and the Cu^{2+} ions. Since, Cu^{2+} being a metal of the transitional series with $3d^9$ electronic configurations can accept the electrons from the complexing agents. Similarly,the low stabilities of Pb,Cd and Mg -complexes could be explained by that Pb^{2+} with $6s^2$, Cd^{2+} with $4d^{10}$ and Mg^{2+} with $2p^6$ their electronic configuration has a completely filled d,p and s orbitals. Moreover, the stabilities of metal ions with hydrolysed humic acid from peat soil were higher than those with unhydrolysed humic acid from peat soil; which is ascribed to the high content of acidity in hydrolysed humic acid than unhydrolysed humic acid.

CONCLUSION

The values of logK for Cu(II) hydrolysed humic acid complex was higher followed by Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes as compared with metal(II) unhydrolysed humic acid complexes . This indicates acid hydrolysis of humic acid can enhance the complexation behavior of humic acid with metal (II) ions. However, the higher values of logβ for Cu(II), Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes indicates more stable stepwise complexes formed as compared with Cu(II), Pb(II), Cd(II) and Mg(II) unhydrolysed humic acid complexes.

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STABILITY CONSTANTS OF COMPLEXES OF METAL IONS WITH PEATSOIL HUMIC ACIDS UNDER NON-ACID-CONDITIONS

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ABSTRACT

Stability constants of complexes of four divalent metal ions viz. Cu^{2+}, Pb^{2+},Mg^{2+} and Cd^{2+} with humic acids (HA) were determined by potentiometric titration of humic acids with the corresponding salt of the divalent metals in aqueous media under non-acid-condition. The log K (logarithm of the stability constant) ranged from 1.0942 to 2.7471 for metal-humic acid complexes were determined using point-wise computational method. The order of stability constants were obtained as follows: Cu >Pb> Cd > Mg for metal -HA complexes respectively, indicating a higher degree of complexation with Cu metal ion.

Keywords: stability constant, humic acid, potentiometric titration, divalent metals, acid hydrolysis.

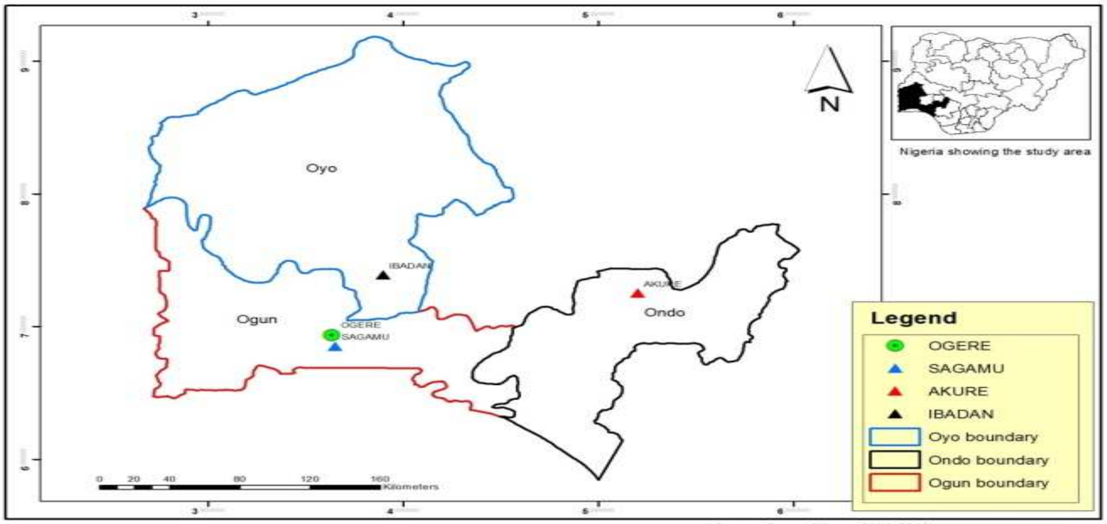
NTRODUCTION

The stability constant of a complex is the numerical expression of its stability and provides a quantitative measure of affinity of the metal ion to the complexing agent. An understanding of the relative stability of metal-complexes helps in predicting the behavior of metal ions in the soil (Ram and Raman, 1982). Extensive researches has been done to determine the stability constants of the complexes formed between humic acid (HA) with a number of metal ions. Ashok *et al*., (2000) reported that humic acid with hydroxyl, phenoxyl and carboxyl reactive groups can form coordination compound with metal ions at pH 3.5. The stability constants(Log K) for different metal-humic acid complexes indicated the following order of the stabilities of complexes formed between humic acid and metal ion, Cu >Fe >Pb> Ni > Co > Ca > Cd > Zn >Mn> Mg. Andelkovic *et al*., (2010) investigated the binding of Cd(II) to soil humic acid at pH 6.5 and in 0.1M KNO_3 ionic medium. The stability constant for binding indicating greater stability in the case when carboxyl groups are involved in complexation reaction. Kostic *et al*.,(2012) investigated the complexation of humic acid with certain heavy metal ions (Co(II), Ni(II),Cu(II), Zn(II), and Pb(II). The experiment was performed at 25°C, at pH 4.0 and ionic strength of 0.01M. Stability constant of complex between Pb(II) ions and humic acid is greater than stability constants of other investigated metal-humate complexes. Bogata and Sokolowska (2016) analyses the interaction between humic acids from different soils and Zn (II) ions at wide concentration ranges and at pH 5. Studies have showed significant impact of Zn concentration, pH and some properties of humic acids with zinc.But all of these studies were limited to acidic pH range. Therefore, the present study was carried out to determine and compare the stability constants of complexes of metal ions with hydrolysed peat soil humic acid and unhydrolysed peat soil humic under non-acid conditions.

MATERIALS AND METHODS

Analytical grade chemicals used includes hydrochloric acid (HCl), nitric acid (HNO_3), sodium hydroxide (NaOH), lead nitrate $Pb(NO_3)_2$, copper nitrate $Cu(NO_3)_2.3H_2O$, cadmium nitrate $Cd(NO_3)_2.4H_2O$, magnesium nitrate $Mg(NO_3)_2.6H_2O$, potassium nitrate (KNO_3), calcium chloride ($CaCl_2$), (sigma-Aldrich). Dowex 50WX8, (20-50 mesh) from Fluka.

Area of study



Source: Dept. of Geog. BUK (2016)

Figure 1: Map showing the sampling point at Sagamu Town, Ogun State.

Description of Sampling Area

Sagamu has geographical coordinates between 6°50′ north; 3° 38′ east is located in south western region of Nigeria. The region has tropical wet and dry climate with a lengthy wet season and relatively constant temperatures throughout the course of the year. Wet season runs from March to October, November to December forms the region dry season. The vegetation type of the region is savannah which is really grassland with small bushes and occasional big trees. Grassland soils have substantially higher organic matter content than forest soils (Novackova, 2011).

Sample Collection

The Peatsoil samples were collected from four different sampling points (0-10cm depth) in Sagamu into polyethylene bag with plastic spoons. Samples were taken to the laboratory, extraneous materials were removed; the samples were air-dried, crushed and ground to a fine powder in a mortar passed through a 0.20mm sieve. The samples were kept for analysis.

Isolation and purification of humic acid from peat soil sample

Peatsoil sample (100g) was mixed with 1000 cm^3 of 0.1M NaOH solution, shaken for 3hours and left to stand overnight. Dark-coloured supernatant was obtained and decanted from solid residue. The dark-coloured supernatant was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 6 hours. Yellowish brown supernatant and dark-brown precipitate were obtained. The yellowish brown supernatant was decanted followed by centrifuge and discarded. The dark-brown precipitate was mixed with 500$cm^3$of 0.1M NaOH solution followed by passing through dowex resin. The dark-brown solution was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 3 hours. The dark-brown precipitate was washed several times with deionized water. The supernatant was treated with $AgNO_3$ solution until no white precipitate observed. The humic acid was transferred to weighed crucible and dried at 60°C in an oven for 12 hours. The humic acid was cooled and dried in the desiccator, weighed and recorded. The obtained humic acid was dried again at 60°C for additional 6 hours cooled and dried in the desiccator, weighed and recorded constant weight was obtained (Baruah *et al*., 2015).

FT-IR analysis

FT-IR spectra of humic acid sample was analysed using Carry 630 FT-IR Agilent Technologies.

Unhydrolysed compost humic acid

The unhydrolysed humic acid was obtained after isolation and purification of compost humic acid and kept for investigation.

Acid hydrolysis of Peatsoil acid

Peatsoil humic acid sample (1g) was refluxed for 12 hours at (160°C) with 50cm^3 of 6M HCl. The mixture was allowed to cool, decanted, and centrifuged after hydrolysis. The insoluble residues were washed with distilled water via centrifugation several times, and the supernatant was treated with $AgNO_3$ solution until no white precipitate was observed. The residue was thoroughly dried over $CaCl_2$ in a desiccator at room temperature (Chefetz *et al*., 2002). Finally, the obtained hydrolysed humic acid was kept for investigation.

Potentiometric Titrations

Potentiometric measurements were carried out using a pH-meter Jenway (model 3510) with combine electrode, the sensitivity of the pH - meter is 0.01 units. The pH meter was switched on half an hour before starting the titration for initial warm up of the instrument. The instrument was calibrated with an aqueous standard buffer solution of pH 4.00 and 10.0 (borate buffer) prepared from a "Qualigens" buffer tablets.

The following sets of solutions were prepared in a 250cm^3 volumetric flask separately for pH metric titrations.

(i) 5 cm^3 0.1 M HCl + 40 cm^3 deionized water
(ii) 5 cm^3 0.1 M HCl + 39 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid
(iii) 5 cm^3 0.1 M HCl + 37 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid + 2 cm^3 0.01 M Cu(II)

The solutions were titrated against standardized 0.110MNaOH separately. The total volume of each mixture was adjusted to 50 cm^3 and the ionic strength of the solutions was maintained constant at by adding appropriate amount of stock solution of 1M KNO$_3$ (Gamal, 2015; Omar and Ali, 2015). A magnetic stirrer was used to achieve thorough mixing of the interacting solutions at 550 rpm. The same set of experimental conditions was applied for potentiometric titration of remaining samples.

Evaluation of pKa of Hydrolysed peat soil Humic Acids

The proton-ligand formation number n$_{\mathbf{A}}$ were calculated by Irving and Rossotti expression (Omar and Ali, 2015).

nA = Y- $\frac{(V2-V1)(No-Eo)}{(Vo+V1)TcL}$ 1

Where: Y is number of dissociable proton, (V$_2$-V$_1$) is the measure of displacement of the ligand curve relative to acid curve, N^o and E^o are the resultant concentration of alkali solution, free acid solution, T$_{cL}$^{o} is the total ligand concentration, V^o is the total volume of titration solution,V$_1$ is the volume of alkali added to acid solution,V$_2$ is the volume of alkali added to acid solution + ligand solution, acid dissociation constants (pKa - values) of ligand were calculated by algebraic method point wise calculation (Tables 1). The dissociation constants (pKa) were calculated according to the following relation:

pKa = pH + log($\frac{nA}{1-nA}$) 2

Where: pKa is the acid dissociation constant, n$_A$is the Proton-ligand formation number and pH is the pH-values (Omar and Ali, 2015).

Determination of metal-ligand stability constants (log K) of complexes

The potentiometric measurement for the determination of stability constant of a complex in solution is based on the fact that the redox potential of the couple $\frac{M^{+(m-n)}}{M^{+m}}$ is shifted significantly on complexation of the metal ion with the ligand. This method involves change in hydrogen ion concentration [H$^+$] due to the displacement or association of one or more protons taking place during complexation reaction. This change can be found out by titrating the solutions containing free acid, acid with ligand, and acid with ligand and metal ion, individually against a standard alkali solution at a constant ionic strength or temperature. Either ionic strength or temperature may be varied for different sets of solutions. In all the cases, the change in the pH of the solution is measured after each addition of a known amount of alkali to the reaction cell which contains the reaction mixture. The titration curves are then drawn by plotting the measured pH values against the corresponding volume of alkali added and the stability constants of the complexes are determined from the titration curves by employing pH-metric titration technique given by (Irving and Rossoti).

Metal-ligand stability constants (Log K) were determined by using the following relations:

$$\bar{n} = \frac{(V_3 - V_2)(E^0 + N^0)}{(V^0 + V_2)\bar{n}_A T_m^0} \quad \text{...3}$$

and

$$PL = \log_{10}\left\{\frac{1 + \beta_n^H \frac{1}{[anti\ \log \text{pH}]^n}}{T_L^0 - \bar{n} T_m^0} X \frac{(V^0 + V_3)}{V^0}\right\} \quad \text{...4}$$

Where $T_{L,}$ T^o, E°, and V^ohavethe same significance as in equation (1) above, T_m denotes the total concentration of metal present in solution, V_3 is the volume of metal ions present in solution and β^H is the overall proton ligand stability constant. The metal-ligand stability constants (log K) were determined by employing point wise computational Method (eq. 5 and 6).

$\text{LogK}_1 = \log\left(\frac{n}{1-n}\right) + \text{pL}$ 5

$\text{LogK}_2 = \log\left(\frac{1-n}{2-n}\right) + \text{pL}$.......................6

Where: Log K is the metal-ligand stability constant, pL is the Free ligand exponent function, **n** is the Average number of ligand attached with metal ion (Janrao*et al.*, 2014).The results obtained were analyzed by an ORIGIN 2016 program using titration data and then the proton-ligand stability constants (pKa) and Metal-ligand stability constant (LogK) calculated (Omar and Ali, 2015).

RESULTS AND DISCUSSION

Fourier transformed infrared (FT-IR) spectra of isolated humic acid from peat soils Figure 2 had distinct clear absorption bands indicating the presence of major humic acid structural elemental groups such as H bonded OH ($3680cm^{-1}$ peak), C=O of carbonyl ($1721cm^{-1}$ peak), functional groups of aliphatic components CH_2 ($2918cm^{-1}$ peak) and C-O stretching of polysaccharide ($1168cm^{-1}$ peak). The positions of the absorption bands of the spectra fell within typical major absorption bands of humic acid which is at frequencies 3680, 2918, 1721, 1168 cm^{-1}. The first peak centred in the vicinity of 3680 cm^{-1} region is attributed to phenol OH group bounded by intermolecular H bonds. The $2918cm^{-1}$ band usually has absorption maximum at 2918 cm^{-1} which is due to C–H stretching of alkane group (CH_2). The next major absorption band is 1721 cm^{-1}. This band has been commonly ascribed to C=O stretching of mainly carboxyl group (COOH) with trace amount of ketones. The last peak was observed at 1168 cm^{-1} due to C–O stretching of polysaccharides and this peak appeared also in the spectra of humic acid from peat soil. The FTIR spectra of the isolated humic acid contained all major characteristic absorption peaks of humic acid. These absorption peaks indicated the presence of the major structural elements of humic acid namely H bonded OH, C=C of aromatic ring, C=O of carbonyl group (both carboxyl and ketonic), CH_2 group. This strongly supports the presence of humic acid.

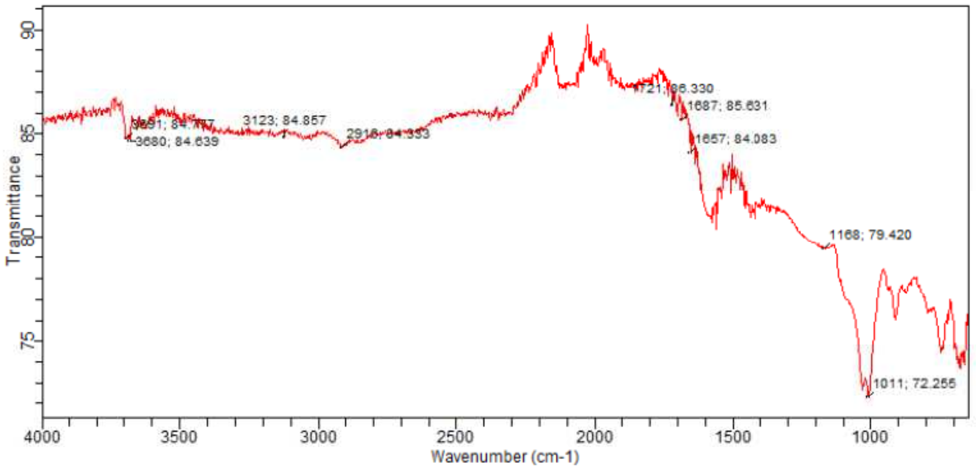


Fig. 2 : FT-IR spectraof peatsoilhumic acid (PSHA)

Evaluation of acid dissociation constant (pka) of acid hydrolysed peat soil humicacid at phenolic group

The value of the dissociation constant of the peat soil humic acid (PSHA) that underwent acidhydrolysis studied was found to be 8.9299 as shown Table 1, which is lower than the literaturevalues reported by Almeida and Szpoganics, (2015), Borges *et al.*, (2005); Badr *et al.*, (2012)and Fernandes *et al*,.(2009) of 9.73, 9.47 and 10.30. The difference between the obtained valuesand the reported values in this study might be probably as a result of acid hydrolysis of humicacid.

Table 1: PKa of (Hydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	$\log(\frac{nA}{1-nA})$	pKa
8.50	5.30	6.29	0.99	0.3594	-0.2510	8.2490
8.72	5.35	6.37	1.02	0.3400	-0.2880	8.4320
9.00	5.40	6.46	1.06	0.3141	-0.3391	8.6609
9.22	5.45	6.55	1.10	0.2882	-0.3927	8.8273
9.51	5.50	6.66	1.16	0.2494	-0.4786	9.0314
9.73	5.55	6.78	1.23	0.2041	-0.5910	9.1390
10.00	5.60	6.90	1.30	0.1589	-0.7238	9.2762
10.23	5.65	7.05	1.40	0.0941	-0.9835	9.2465
10.49	5.70	7.10	1.40	0.0941	-0.9835	9.5065

Average pKa = 8.9299 ± 0.4186

Table 2: PKa of (Unhydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	$\text{Log}(\frac{nA}{1-n})$	pKa
8.50	5.30	5.81	0.51	0.6619	0.2919	8.7919
8.72	5.35	5.90	0.55	0.6357	0.2418	8.9618
9.00	5.40	6.00	0.60	0.6029	0.1813	9.1813
9.22	5.45	6.10	0.65	0.5701	0.1226	9.3426
9.51	5.50	6.20	0.70	0.5376	0.0654	9.5754
9.73	5.55	6.33	0.78	0.4851	-0.0259	9.7041
10.00	5.60	6.47	0.87	0.4262	-0.1291	9.8709
10.23	5.65	6.62	0.99	0.3609	-0.2481	9.9819
10.49	5.70	6.80	1.10	0.2759	-0.4690	10.0210

Average pKa = 9.4923± 0.4410

Metal-ligand stability constant (Log K)

The stabilityconstants require the accurate values of proton-ligand stability constants (Anil and Maroti, 2008). Metal titration curves crossed over ligand titration curve indicated the formation of complex upon proton release (Santosh, *et al.*, 2011). If the values of n- are within range 0.2-0.8 and 1.2-18 this indicates the formation of 1:1 and 1:2 complexes (Sayyed and Mazahar, 2012).

The metal (II)-humate stepwise stability constants (log k) at phenolic group (Tables 3-18)

Table 3: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$\log(\frac{n}{1-n})$	LogK_1
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

LogK_1 (Average value) = 2.4788± 0.2203

Table 4: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$\text{Log}(\frac{n-1}{2-n})$	LogK_2
9.51	5.50	6.66	6.73	0.07	1.3509	1.70	-0.2671	1.4329
9.73	5.55	6.78	6.85	0.07	1.6383	1.51	0.2467	1.7567
10.00	5.60	6.90	6.98	0.08	2.1783	1.31	-0.2158	1.0942
10.23	5.65	7.05	7.13	0.08	4.1904	1.27		
10.49	5.70	7.10	7.19	0.09	4.6920			

LogK_2(Average value) = 1.4280 ± 0.3312

Table 5:Point-wise method,Cu (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	Log($\frac{n}{n-1}$)	Log K$_1$
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430

LogK$_1$ **(Average value)** = 2.3059± 0.6153

Table 6:Point-wise method, Cu (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	V$_3$-V$_2$	n	pL	Log($\frac{n-1}{2-n}$)	Log K$_2$
9.73	5.55	6.33	6.42	0.09	0.9000	1.69		
10.00	5.60	6.47	6.58	0.11	1.2578	1.44	-0.4592	0.9808
10.23	5.65	6.62	6.84	0.12	1.6137	1.26	-0.2010	1.4610
10.49	5.70	6.80	6.92	0.12	2.1052	1.03		

LogK$_2$ **(Average value)** = 1.2209± 0.3398

Table 7:Point-wise method,Pb (Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	log($\frac{n}{1-n}$)	LogK$_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.60	0.05	0.8333	1.96	0.6989	2.6589

LogK$_1$ (Average value) = 2.5832 ±0.1614

Table 8:Point-wise method,Pb-(Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	log($\frac{n-1}{2-n}$)	logK$_2$
9.51	5.50	6.66	6.71	0.05	0.9650	1.67	-0.0237	1.1963
9.73	5.55	6.78	6.83	0.05	1.1702	1.44		
10.00	5.60	6.90	6.90	0.05	1.4864	1.22		
10.23	5.65	7.05	7.10	0.05	2.0190	1.09		
10.49	5.70	7.10	7.17	0.07	3.6492	1.00		

LogK$_2$(Average value) = 1.1963

Table 9:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	V$_3$-V$_2$	n	pL	Log ($\frac{n}{n-1}$)	Log K$_1$
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.5477	2.3123
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	0.0272	2.2072
9.51	5.50	6.20	6.26	0.07	0.6417	1.89	0.2530	2.1430
9.73	5.55	6.40	6.40	0.07	0.7000	1.67	0.3680	2.0380

LogK$_1$ **(Average value)** = 2.2364 ± 0.1602

Table 10:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	V$_3$-V$_2$	n	pL	Log($\frac{n-1}{2-n}$)	Log K$_2$
10.00	5.60	6.47	6.55	0.08	1.9503	1.41		
10.23	5.65	6.62	6.72	0.11	1.4792	1.26	-0.0361	1.2239

LogK$_2$ **(Average value)** = 1.2239

Table 11:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	log($\frac{n}{n-1}$)	LogK$_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4290	2.2110
8.72	5.35	6.37	6.39	0.02	0.2858	2.42	-0.3978	2.0222
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

LogK$_1$ (Average value)=2.1382**±**0.1046

Table 12:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n-1}{2-n}$)	$LogK_2$
9.51	5.55	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.84	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.93	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.10		
10.49	5.70	7.10	7.18	0.07	3.6492	0.83		

$LogK_2$(Average value) = 1.5453 **±** 0.3450

Table 13:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.3477	2.3123
9.00	5.40	6.00	6.04	0.04	0.3236	2.38	-0.3202	2.0598
9.22	5.45	6.10	6.15	0.05	0.4297	2.17	-0.1230	2.0470
9.51	5.50	6.20	6.26	0.06	0.5500	1.89	0.0871	1.9771
9.73	5.55	6.33	6.40	0.07	0.7000	1.67	0.3680	2.0380

$LogK_1$ **(Average value)** = 2.1568 ± 0.2069

Table 14:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
10.00	5.60	6.47	6.55	0.08	0.9148	1.41		
10.23	5.65	6.62	6.71	0.09	1.2102	1.20	-0.5749	0.6251
10.49	5.70	6.80	6.92	0.09	1.5968	1.03	0.1703	1.2003

$LogK_2$ **(Average value)** = 0.9127± 0.4070

Table15:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	Log($\frac{n}{1-n}$)	$LogK_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4210	2.2190
8.72	5.35	6.37	6.40	0.03	0.4286	2.42	-0.1249	2.2951
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.96	0.3010	2.2610
9.51	5.55	6.66	6.70	0.04	0.7720	1.67	0.5297	2.1997

$LogK_1$ (Average value) = 2.2108± 0.0825

Table 16:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
9.73	5.55	6.78	6.83	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.95	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.09		
10.49	5.70	7.10	7.16	0.06	3.1429	0.89		

$LogK_2$ **(Average value)** = 1.5453± 0.3450

Table 17:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.86	0.05	0.3717	2.88	-0.2280	2.6520
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.06	0.06	0.4853	2.38	-0.0255	2.3545
9.22	5.45	6.10	6.16	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430
9.73	5.55	6.33	6.41	0.08	0.8000	1.69	0.6020	2.2920

$LogK_1$ **(Average value)** = 2.2516± 0.5380

Table 18:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$\text{Log}(\frac{n-1}{2-n})$	Log K_2
10.00	5.60	6.47	6.57	0.10	1.1434	1.43		
10.23	5.65	6.62	6.72	0.10	1.3448	1.23	-0.2788	0.9512
10.49	5.70	6.80	6.90	0.10	1.7742	1.03	0.5351	1.5651

LogK_2 **(Average value)** = 1.2581± 0.4340

Table 19: Stepwise and overall Stability constants of thehydrolysed and unhydrolysed divalent metal (II) complexes

Chelates	**LogK₁**	**LogK₂**	**Logβ**
[Cu (Hydrolysed PSHA-1)$_2$]	2.4788	1.4280	3.9068
[Pb (Hydrolysed PSHA-1)$_2$]	2.5832	1.1963	3.7795
[Cd (Hydrolysed PSHA-1)$_2$]	2.2108	1.5453	3.7561
[Mg (Hydrolysed PSHA-1)$_2$]	2.1382	1.5453	3.6835
[Cu (Unhydrolysed PSHA-1)$_2$]	2.3059	1.2209	3.5268
[Pb (Unhydrolysed PSHA-1)$_2$]	2.2364	1.2239	3.4603
[Cd (Unhydrolysed PSHA-1)$_2$]	2.2516	1.2581	3.5097
[Mg (Unydrolysed PSHA-1)$_2$]	2.1568	0.9127	3.0695

The results obtained (Table19) shows the stepwise and overall stability constants to be not high indicating low stability of the complexes, because the solubility of most metal ions in the basic pH range is minimal due to metal hydroxide precipitation (Karimi, 2017). In general, the stepwise stability constants (K_1 and K_2) follow the order $K_1 > K_2$ for the copper, lead, magnesium and cadmium complexes respectively. The steady decrease of the values with increasing number of ligands is in agreement with the prediction made by researchers (Na'aliya, 2013). The decrease could be attributed to the fact that as the number of the ligands (Humate ions) that enters the coordination zone increases the aqua molecules available for replacement by the ligands become less. Thus, the metal ions become less electron loving with progressive intake of the ligand and this results in the decrease in the values of the constants (Na'aliya, 2013). Also the stability of the complexes is influenced by the size and number of the chelate rings(Mackay and Mackay,2002).All the complexes form rings in their structure as humate, a bidentate ligand, bond the metal ions in the ratio 1:2 (Boguta and Sokolowska, 2016) forming chelate rings. The values of the overall stability constants (logβ) obtained for humate complexes are not high indicating low stability as the values are not high. LogK values for copper-humates (Table 3 to 6) obtained in this study are lower than those reported for the complexes of humic acids (Pandey *et al.*, 2015; Dinu, 2013; Kaschl *et al.*, 2010 and Gilbeto and Jorg, 2001). The values of LogK(Table 7 to 10) forlead-humates are lower than those reported for the lead in the literature (Dinu, 2013; Gilbeto and Jorg 2001). Log K values(Table 11 to 14) for magnesium-humates obtained in this study are close to those reported by (Pandey *et al.*, 2015). Log K values of cadmium-humates (Table 15 to 18) obtained in this work near to the one reported by (Dinu, 2013 and Pandey *et al.*, 2015).The difference between the reported values and the values obtained in this study might be probably as a result of acid hydrolysis of humic acid. The values of the overall stability constants (log β) of the copper humates complexes presented in Table 19 is high than that of other metal humate complexes, show relatively high stability of Cu-HA complexes, show the following order of stability: Cu >Pb> Cd > Mg; which are in close agreement to the findings of (Dinu, 2013 and Pandey *et al.*, 2015).The high stability of Cu-humate chelate could be attributed to the existence of coordinate covalent bond between the complexing agents and the Cu^{2+} ions. Since, Cu^{2+} being a metal of the transitional series with $3d^9$ electronic configurations can accept the electrons from the complexing agents. Similarly,the low stabilities of Pb,Cd and Mg -complexes could be explained by that Pb^{2+} with $6s^2$, Cd^{2+} with $4d^{10}$ and Mg^{2+} with $2p^6$ their electronic configuration has a completely filled d,p and s orbitals. Moreover, the stabilities of metal ions with hydrolysed humic acid from peat soil were higher than those with unhydrolysed humic acid from peat soil; which is ascribed to the high content of acidity in hydrolysed humic acid than unhydrolysed humic acid.

CONCLUSION

The values of logK for Cu(II) hydrolysed humic acid complex was higher followed by Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes as compared with metal(II) unhydrolysed humic acid complexes . This indicates acid hydrolysis of humic acid can enhance the complexation behavior of humic acid with metal (II) ions. However, the higher values of logβ for Cu(II), Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes indicates more stable stepwise complexes formed as compared with Cu(II), Pb(II), Cd(II) and Mg(II) unhydrolysed humic acid complexes.

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STABILITY CONSTANTS OF COMPLEXES OF METAL IONS WITH PEATSOIL HUMIC ACIDS UNDER NON-ACID-CONDITIONS

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ABSTRACT

Stability constants of complexes of four divalent metal ions viz. Cu^{2+}, Pb^{2+},Mg^{2+} and Cd^{2+} with humic acids (HA) were determined by potentiometric titration of humic acids with the corresponding salt of the divalent metals in aqueous media under non-acid-condition. The log K (logarithm of the stability constant) ranged from 1.0942 to 2.7471 for metal-humic acid complexes were determined using point-wise computational method. The order of stability constants were obtained as follows: Cu >Pb> Cd > Mg for metal -HA complexes respectively, indicating a higher degree of complexation with Cu metal ion.

Keywords: stability constant, humic acid, potentiometric titration, divalent metals, acid hydrolysis.

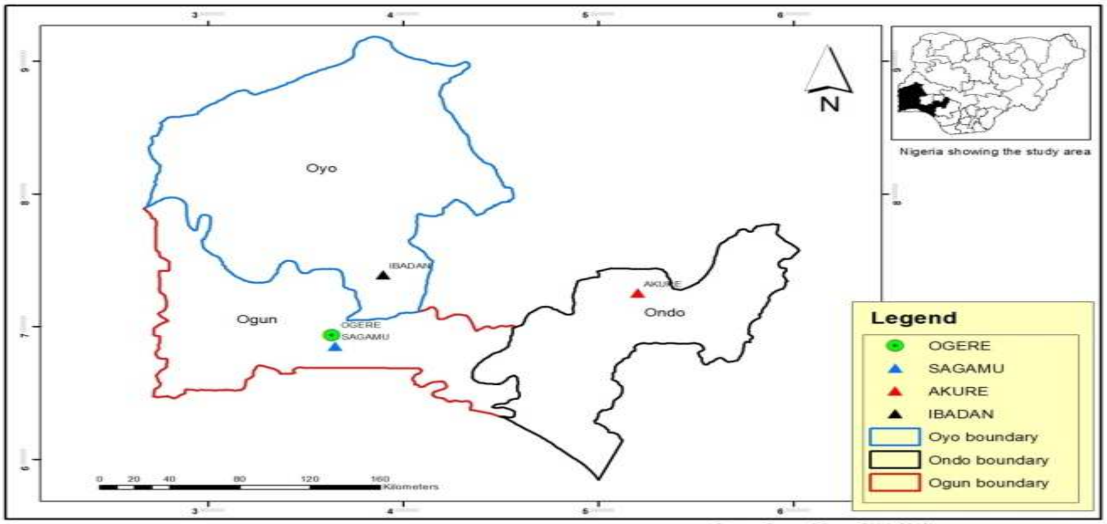
NTRODUCTION

The stability constant of a complex is the numerical expression of its stability and provides a quantitative measure of affinity of the metal ion to the complexing agent. An understanding of the relative stability of metal-complexes helps in predicting the behavior of metal ions in the soil (Ram and Raman, 1982). Extensive researches has been done to determine the stability constants of the complexes formed between humic acid (HA) with a number of metal ions. Ashok *et al*., (2000) reported that humic acid with hydroxyl, phenoxyl and carboxyl reactive groups can form coordination compound with metal ions at pH 3.5. The stability constants(Log K) for different metal-humic acid complexes indicated the following order of the stabilities of complexes formed between humic acid and metal ion, Cu >Fe >Pb> Ni > Co > Ca > Cd > Zn >Mn> Mg. Andelkovic *et al*., (2010) investigated the binding of Cd(II) to soil humic acid at pH 6.5 and in 0.1M KNO_3 ionic medium. The stability constant for binding indicating greater stability in the case when carboxyl groups are involved in complexation reaction. Kostic *et al*.,(2012) investigated the complexation of humic acid with certain heavy metal ions (Co(II), Ni(II),Cu(II), Zn(II), and Pb(II). The experiment was performed at 25°C, at pH 4.0 and ionic strength of 0.01M. Stability constant of complex between Pb(II) ions and humic acid is greater than stability constants of other investigated metal-humate complexes. Bogata and Sokolowska (2016) analyses the interaction between humic acids from different soils and Zn (II) ions at wide concentration ranges and at pH 5. Studies have showed significant impact of Zn concentration, pH and some properties of humic acids with zinc.But all of these studies were limited to acidic pH range. Therefore, the present study was carried out to determine and compare the stability constants of complexes of metal ions with hydrolysed peat soil humic acid and unhydrolysed peat soil humic under non-acid conditions.

MATERIALS AND METHODS

Analytical grade chemicals used includes hydrochloric acid (HCl), nitric acid (HNO_3), sodium hydroxide (NaOH), lead nitrate $Pb(NO_3)_2$, copper nitrate $Cu(NO_3)_2.3H_2O$, cadmium nitrate $Cd(NO_3)_2.4H_2O$, magnesium nitrate $Mg(NO_3)_2.6H_2O$, potassium nitrate (KNO_3), calcium chloride ($CaCl_2$), (sigma-Aldrich). Dowex 50WX8, (20-50 mesh) from Fluka.

Area of study



Source: Dept. of Geog. BUK (2016)

Figure 1: Map showing the sampling point at Sagamu Town, Ogun State.

Description of Sampling Area

Sagamu has geographical coordinates between 6°50′ north; 3° 38′ east is located in south western region of Nigeria. The region has tropical wet and dry climate with a lengthy wet season and relatively constant temperatures throughout the course of the year. Wet season runs from March to October, November to December forms the region dry season. The vegetation type of the region is savannah which is really grassland with small bushes and occasional big trees. Grassland soils have substantially higher organic matter content than forest soils (Novackova, 2011).

Sample Collection

The Peatsoil samples were collected from four different sampling points (0-10cm depth) in Sagamu into polyethylene bag with plastic spoons. Samples were taken to the laboratory, extraneous materials were removed; the samples were air-dried, crushed and ground to a fine powder in a mortar passed through a 0.20mm sieve. The samples were kept for analysis.

Isolation and purification of humic acid from peat soil sample

Peatsoil sample (100g) was mixed with 1000 cm^3 of 0.1M NaOH solution, shaken for 3hours and left to stand overnight. Dark-coloured supernatant was obtained and decanted from solid residue. The dark-coloured supernatant was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 6 hours. Yellowish brown supernatant and dark-brown precipitate were obtained. The yellowish brown supernatant was decanted followed by centrifuge and discarded. The dark-brown precipitate was mixed with $500cm^3$of 0.1M NaOH solution followed by passing through dowex resin. The dark-brown solution was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 3 hours. The dark-brown precipitate was washed several times with deionized water. The supernatant was treated with $AgNO_3$ solution until no white precipitate observed. The humic acid was transferred to weighed crucible and dried at 60°C in an oven for 12 hours. The humic acid was cooled and dried in the desiccator, weighed and recorded. The obtained humic acid was dried again at 60°C for additional 6 hours cooled and dried in the desiccator, weighed and recorded constant weight was obtained (Baruah *et al*., 2015).

FT-IR analysis

FT-IR spectra of humic acid sample was analysed using Carry 630 FT-IR Agilent Technologies.

Unhydrolysed compost humic acid

The unhydrolysed humic acid was obtained after isolation and purification of compost humic acid and kept for investigation.

Acid hydrolysis of Peatsoil acid

Peatsoil humic acid sample (1g) was refluxed for 12 hours at (160°C) with $50cm^3$ of 6M HCl. The mixture was allowed to cool, decanted, and centrifuged after hydrolysis. The insoluble residues were washed with distilled water via centrifugation several times, and the supernatant was treated with $AgNO_3$ solution until no white precipitate was observed. The residue was thoroughly dried over $CaCl_2$ in a desiccator at room temperature (Chefetz *et al*., 2002). Finally, the obtained hydrolysed humic acid was kept for investigation.

Potentiometric Titrations

Potentiometric measurements were carried out using a pH-meter Jenway (model 3510) with combine electrode, the sensitivity of the pH - meter is 0.01 units. The pH meter was switched on half an hour before starting the titration for initial warm up of the instrument. The instrument was calibrated with an aqueous standard buffer solution of pH 4.00 and 10.0 (borate buffer) prepared from a "Qualigens" buffer tablets.

The following sets of solutions were prepared in a 250cm^3 volumetric flask separately for pH metric titrations.

(i) 5 cm^3 0.1 M HCl + 40 cm^3 deionized water

(ii) 5 cm^3 0.1 M HCl + 39 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid

(iii) 5 cm^3 0.1 M HCl + 37 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid + 2 cm^3 0.01 M Cu(II)

The solutions were titrated against standardized 0.110MNaOH separately. The total volume of each mixture was adjusted to 50 cm^3 and the ionic strength of the solutions was maintained constant at by adding appropriate amount of stock solution of 1M KNO_3 (Gamal, 2015; Omar and Ali, 2015). A magnetic stirrer was used to achieve thorough mixing of the interacting solutions at 550 rpm. The same set of experimental conditions was applied for potentiometric titration of remaining samples.

Evaluation of pKa of Hydrolysed peat soil Humic Acids

The proton-ligand formation number n_A were calculated by Irving and Rossotti expression (Omar and Ali, 2015).

$$nA = Y - \frac{(V2-V1)(No-Eo)}{(Vo+V1)TcL} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 1$$

Where: Y is number of dissociable proton, (V_2-V_1) is the measure of displacement of the ligand curve relative to acid curve, N^o and E^o are the resultant concentration of alkali solution, free acid solution, $T_{cL}{}^o$ is the total ligand concentration, V^o is the total volume of titration solution,V_1 is the volume of alkali added to acid solution,V_2 is the volume of alkali added to acid solution + ligand solution, acid dissociation constants (pKa - values) of ligand were calculated by algebraic method point wise calculation (Tables 1). The dissociation constants (pKa) were calculated according to the following relation:

$$pKa = pH + \log\left(\frac{nA}{1-nA}\right) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 2$$

Where: pKa is the acid dissociation constant, $n_A$is the Proton-ligand formation number and pH is the pH-values (Omar and Ali, 2015).

Determination of metal-ligand stability constants (log K) of complexes

The potentiometric measurement for the determination of stability constant of a complex in solution is based on the fact that the redox potential of the couple $\frac{M^{+(m-n)}}{M^{+m}}$ is shifted significantly on complexation of the metal ion with the ligand. This method involves change in hydrogen ion concentration [H$^+$] due to the displacement or association of one or more protons taking place during complexation reaction. This change can be found out by titrating the solutions containing free acid, acid with ligand, and acid with ligand and metal ion, individually against a standard alkali solution at a constant ionic strength or temperature. Either ionic strength or temperature may be varied for different sets of solutions. In all the cases, the change in the pH of the solution is measured after each addition of a known amount of alkali to the reaction cell which contains the reaction mixture. The titration curves are then drawn by plotting the measured pH values against the corresponding volume of alkali added and the stability constants of the complexes are determined from the titration curves by employing pH-metric titration technique given by (Irving and Rossoti).

Metal-ligand stability constants (Log K) were determined by using the following relations:

$$\bar{n} = \frac{(V_3 - V_2)(E^0 + N^0)}{(V^0 + V_2)\bar{n}_A T_m^0} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 3$$

and

$$PL = \log_{10}\left\{\frac{1 + \beta_n^H \dfrac{1}{[anti\ \log pH]^n}}{T_L^0 - \bar{n}T_m^0} X \frac{(V^0 + V_3)}{V^0}\right\} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 4$$

Where $T_{L,}$ T^{o}, E°, and V^{o}havethe same significance as in equation (1) above, T_m denotes the total concentration of metal present in solution, V_3 is the volume of metal ions present in solution and β^H is the overall proton ligand stability constant. The metal-ligand stability constants (log K) were determined by employing point wise computational Method (eq. 5 and 6).

$\text{LogK}_1 = \log\left(\frac{n}{1-n}\right) + \text{pL}$ 5

$\text{LogK}_2 = \log\left(\frac{1-n}{2-n}\right) + \text{pL}$.......................6

Where: Log K is the metal-ligand stability constant, pL is the Free ligand exponent function, **n** is the Average number of ligand attached with metal ion (Janrao*et al.*, 2014).The results obtained were analyzed by an ORIGIN 2016 program using titration data and then the proton-ligand stability constants (pKa) and Metal-ligand stability constant (LogK) calculated (Omar and Ali, 2015).

RESULTS AND DISCUSSION

Fourier transformed infrared (FT-IR) spectra of isolated humic acid from peat soils Figure 2 had distinct clear absorption bands indicating the presence of major humic acid structural elemental groups such as H bonded OH (3680cm^{-1} peak), C=O of carbonyl (1721cm^{-1} peak), functional groups of aliphatic components CH_2 (2918cm^{-1} peak) and C-O stretching of polysaccharide (1168cm^{-1} peak). The positions of the absorption bands of the spectra fell within typical major absorption bands of humic acid which is at frequencies 3680, 2918, 1721, 1168 cm^{-1}. The first peak centred in the vicinity of 3680 cm^{-1} region is attributed to phenol OH group bounded by intermolecular H bonds. The 2918cm^{-1} band usually has absorption maximum at 2918 cm^{-1} which is due to C–H stretching of alkane group (CH_2). The next major absorption band is 1721 cm^{-1}. This band has been commonly ascribed to C=O stretching of mainly carboxyl group (COOH) with trace amount of ketones. The last peak was observed at 1168 cm^{-1} due to C–O stretching of polysaccharides and this peak appeared also in the spectra of humic acid from peat soil. The FTIR spectra of the isolated humic acid contained all major characteristic absorption peaks of humic acid. These absorption peaks indicated the presence of the major structural elements of humic acid namely H bonded OH, C=C of aromatic ring, C=O of carbonyl group (both carboxyl and ketonic), CH_2 group. This strongly supports the presence of humic acid.

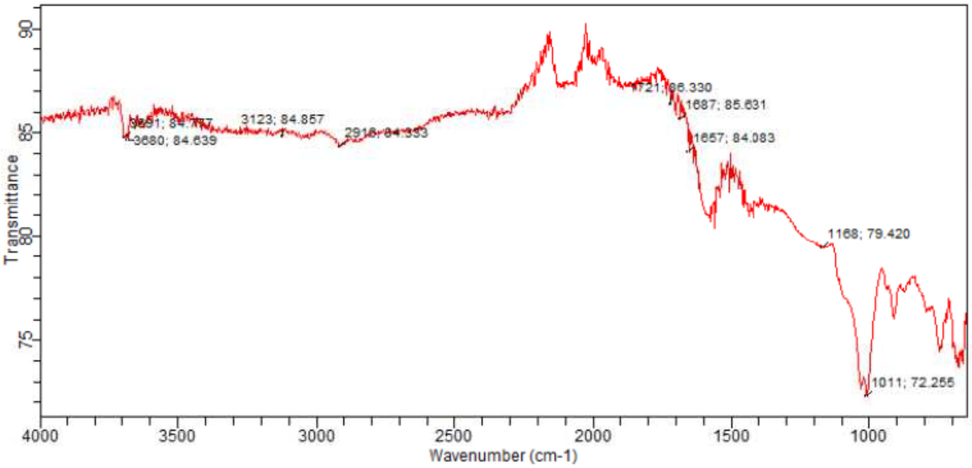


Fig. 2 : FT-IR spectraof peatsoilhumic acid (PSHA)

Evaluation of acid dissociation constant (pka) of acid hydrolysed peat soil humicacid at phenolic group

The value of the dissociation constant of the peat soil humic acid (PSHA) that underwent acidhydrolysis studied was found to be 8.9299 as shown Table 1, which is lower than the literaturevalues reported by Almeida and Szpoganics, (2015), Borges *et al.*, (2005); Badr *et al.*, (2012)and Fernandes *et al*,.(2009) of 9.73, 9.47 and 10.30. The difference between the obtained valuesand the reported values in this study might be probably as a result of acid hydrolysis of humicacid.

Table 1: PKa of (Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	V$_2$-V$_1$	nA	log$(\frac{nA}{1-nA})$	pKa
8.50	5.30	6.29	0.99	0.3594	-0.2510	8.2490
8.72	5.35	6.37	1.02	0.3400	-0.2880	8.4320
9.00	5.40	6.46	1.06	0.3141	-0.3391	8.6609
9.22	5.45	6.55	1.10	0.2882	-0.3927	8.8273
9.51	5.50	6.66	1.16	0.2494	-0.4786	9.0314
9.73	5.55	6.78	1.23	0.2041	-0.5910	9.1390
10.00	5.60	6.90	1.30	0.1589	-0.7238	9.2762
10.23	5.65	7.05	1.40	0.0941	-0.9835	9.2465
10.49	5.70	7.10	1.40	0.0941	-0.9835	9.5065

Average pKa = 8.9299 ± 0.4186

Table 2: PKa of (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	V$_2$-V$_1$	nA	Log$(\frac{nA}{1-n})$	pKa
8.50	5.30	5.81	0.51	0.6619	0.2919	8.7919
8.72	5.35	5.90	0.55	0.6357	0.2418	8.9618
9.00	5.40	6.00	0.60	0.6029	0.1813	9.1813
9.22	5.45	6.10	0.65	0.5701	0.1226	9.3426
9.51	5.50	6.20	0.70	0.5376	0.0654	9.5754
9.73	5.55	6.33	0.78	0.4851	-0.0259	9.7041
10.00	5.60	6.47	0.87	0.4262	-0.1291	9.8709
10.23	5.65	6.62	0.99	0.3609	-0.2481	9.9819
10.49	5.70	6.80	1.10	0.2759	-0.4690	10.0210

Average pKa = 9.4923± 0.4410

Metal-ligand stability constant (Log K)

The stabilityconstants require the accurate values of proton-ligand stability constants (Anil and Maroti, 2008). Metal titration curves crossed over ligand titration curve indicated the formation of complex upon proton release (Santosh, *et al.*, 2011). If the values of n- are within range 0.2-0.8 and 1.2-18 this indicates the formation of 1:1 and 1:2 complexes (Sayyed and Mazahar, 2012).

The metal (II)-humate stepwise stability constants (log k) at phenolic group (Tables 3-18)

Table 3: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	log$(\frac{n}{1-n})$	LogK$_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

LogK$_1$ (Average value) = 2.4788± 0.2203

Table 4: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	Log$(\frac{n-1}{2-n})$	LogK$_2$
9.51	5.50	6.66	6.73	0.07	1.3509	1.70	-0.2671	1.4329
9.73	5.55	6.78	6.85	0.07	1.6383	1.51	0.2467	1.7567
10.00	5.60	6.90	6.98	0.08	2.1783	1.31	-0.2158	1.0942
10.23	5.65	7.05	7.13	0.08	4.1904	1.27		
10.49	5.70	7.10	7.19	0.09	4.6920			

LogK$_2$(Average value) = 1.4280 ± 0.3312

Table 5:Point-wise method,Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	Log($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430

$LogK_1$ **(Average value)** = 2.3059± 0.6153

Table 6:Point-wise method, Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
9.73	5.55	6.33	6.42	0.09	0.9000	1.69		
10.00	5.60	6.47	6.58	0.11	1.2578	1.44	-0.4592	0.9808
10.23	5.65	6.62	6.84	0.12	1.6137	1.26	-0.2010	1.4610
10.49	5.70	6.80	6.92	0.12	2.1052	1.03		

$LogK_2$ **(Average value)** = 1.2209± 0.3398

Table 7:Point-wise method,Pb (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n}{1-n}$)	$LogK_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.60	0.05	0.8333	1.96	0.6989	2.6589

$LogK_1$ (Average value) = 2.5832 ±0.1614

Table 8:Point-wise method,Pb-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n-1}{2-n}$)	$logK_2$
9.51	5.50	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.83	0.05	1.1702	1.44		
10.00	5.60	6.90	6.90	0.05	1.4864	1.22	-0.0237	1.1963
10.23	5.65	7.05	7.10	0.05	2.0190	1.09		
10.49	5.70	7.10	7.17	0.07	3.6492	1.00		

$LogK_2$(Average value) = 1.1963

Table 9:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log ($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.5477	2.3123
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	0.0272	2.2072
9.51	5.50	6.20	6.26	0.07	0.6417	1.89	0.2530	2.1430
9.73	5.55	6.40	6.40	0.07	0.7000	1.67	0.3680	2.0380

$LogK_1$ **(Average value)** = 2.2364 ± 0.1602

Table 10:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
10.00	5.60	6.47	6.55	0.08	1.9503	1.41		
10.23	5.65	6.62	6.72	0.11	1.4792	1.26	-0.0361	1.2239

$LogK_2$ **(Average value)** = 1.2239

Table 11:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n}{n-1}$)	$LogK_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4290	2.2110
8.72	5.35	6.37	6.39	0.02	0.2858	2.42	-0.3978	2.0222
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

$LogK_1$ (Average value)=2.1382**±**0.1046

Table 12:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$\log(\frac{n-1}{2-n})$	$\text{Log}K_2$
9.51	5.55	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.84	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.93	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.10		
10.49	5.70	7.10	7.18	0.07	3.6492	0.83		

$\text{Log}K_2$(Average value) = 1.5453 **±** 0.3450

Table 13:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$\text{Log}(\frac{n}{n-1})$	$\text{Log } K_1$
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.3477	2.3123
9.00	5.40	6.00	6.04	0.04	0.3236	2.38	-0.3202	2.0598
9.22	5.45	6.10	6.15	0.05	0.4297	2.17	-0.1230	2.0470
9.51	5.50	6.20	6.26	0.06	0.5500	1.89	0.0871	1.9771
9.73	5.55	6.33	6.40	0.07	0.7000	1.67	0.3680	2.0380

$\text{Log}K_1$ **(Average value)** = 2.1568 ± 0.2069

Table 14:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$\text{Log}(\frac{n-1}{2-n})$	$\text{Log } K_2$
10.00	5.60	6.47	6.55	0.08	0.9148	1.41		
10.23	5.65	6.62	6.71	0.09	1.2102	1.20	-0.5749	0.6251
10.49	5.70	6.80	6.92	0.09	1.5968	1.03	0.1703	1.2003

$\text{Log}K_2$ **(Average value)** = 0.9127± 0.4070

Table15:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$\text{Log}(\frac{n}{1-n})$	$\text{Log}K_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4210	2.2190
8.72	5.35	6.37	6.40	0.03	0.4286	2.42	-0.1249	2.2951
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.96	0.3010	2.2610
9.51	5.55	6.66	6.70	0.04	0.7720	1.67	0.5297	2.1997

$\text{Log}K_1$ (Average value) = 2.2108± 0.0825

Table 16:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$\text{Log}(\frac{n-1}{2-n})$	$\text{Log } K_2$
9.73	5.55	6.78	6.83	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.95	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.09		
10.49	5.70	7.10	7.16	0.06	3.1429	0.89		

$\text{Log}K_2$ **(Average value)** = 1.5453± 0.3450

Table 17:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$\text{Log}(\frac{n}{n-1})$	$\text{Log } K_1$
8.50	5.30	5.81	5.86	0.05	0.3717	2.88	-0.2280	2.6520
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.06	0.06	0.4853	2.38	-0.0255	2.3545
9.22	5.45	6.10	6.16	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430
9.73	5.55	6.33	6.41	0.08	0.8000	1.69	0.6020	2.2920

$\text{Log}K_1$ **(Average value)** = 2.2516± 0.5380

Table 18:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
10.00	5.60	6.47	6.57	0.10	1.1434	1.43		
10.23	5.65	6.62	6.72	0.10	1.3448	1.23	-0.2788	0.9512
10.49	5.70	6.80	6.90	0.10	1.7742	1.03	0.5351	1.5651

LogK_2 **(Average value)** = 1.2581± 0.4340

Table 19: Stepwise and overall Stability constants of thehydrolysed and unhydrolysed divalent metal (II) complexes

Chelates	**LogK_1**	**LogK_2**	**Logβ**
[Cu (Hydrolysed PSHA-1)$_2$]	2.4788	1.4280	3.9068
[Pb (Hydrolysed PSHA-1)$_2$]	2.5832	1.1963	3.7795
[Cd (Hydrolysed PSHA-1)$_2$]	2.2108	1.5453	3.7561
[Mg (Hydrolysed PSHA-1)$_2$]	2.1382	1.5453	3.6835
[Cu (Unhydrolysed PSHA-1)$_2$]	2.3059	1.2209	3.5268
[Pb (Unhydrolysed PSHA-1)$_2$]	2.2364	1.2239	3.4603
[Cd (Unhydrolysed PSHA-1)$_2$]	2.2516	1.2581	3.5097
[Mg (Unydrolysed PSHA-1)$_2$]	2.1568	0.9127	3.0695

The results obtained (Table19) shows the stepwise and overall stability constants to be not high indicating low stability of the complexes, because the solubility of most metal ions in the basic pH range is minimal due to metal hydroxide precipitation (Karimi, 2017). In general, the stepwise stability constants (K_1 and K_2) follow the order $K_1 > K_2$ for the copper, lead, magnesium and cadmium complexes respectively. The steady decrease of the values with increasing number of ligands is in agreement with the prediction made by researchers (Na'aliya, 2013). The decrease could be attributed to the fact that as the number of the ligands (Humate ions) that enters the coordination zone increases the aqua molecules available for replacement by the ligands become less. Thus, the metal ions become less electron loving with progressive intake of the ligand and this results in the decrease in the values of the constants (Na'aliya, 2013). Also the stability of the complexes is influenced by the size and number of the chelate rings(Mackay and Mackay,2002).All the complexes form rings in their structure as humate, a bidentate ligand, bond the metal ions in the ratio 1:2 (Boguta and Sokolowska, 2016) forming chelate rings. The values of the overall stability constants (logβ) obtained for humate complexes are not high indicating low stability as the values are not high. LogK values for copper-humates (Table 3 to 6) obtained in this study are lower than those reported for the complexes of humic acids (Pandey *et al.*, 2015; Dinu, 2013; Kaschl *et al.*, 2010 and Gilbeto and Jorg, 2001). The values of LogK(Table 7 to 10) forlead-humates are lower than those reported for the lead in the literature (Dinu, 2013; Gilbeto and Jorg 2001). Log K values(Table 11 to 14) for magnesium-humates obtained in this study are close to those reported by (Pandey *et al.*, 2015). Log K values of cadmium-humates (Table 15 to 18) obtained in this work near to the one reported by (Dinu, 2013 and Pandey *et al.*, 2015).The difference between the reported values and the values obtained in this study might be probably as a result of acid hydrolysis of humic acid. The values of the overall stability constants (log β) of the copper humates complexes presented in Table 19 is high than that of other metal humate complexes, show relatively high stability of Cu-HA complexes, show the following order of stability: Cu >Pb> Cd > Mg; which are in close agreement to the findings of (Dinu, 2013 and Pandey *et al.*, 2015).The high stability of Cu-humate chelate could be attributed to the existence of coordinate covalent bond between the complexing agents and the Cu^{2+} ions. Since, Cu^{2+} being a metal of the transitional series with $3d^9$ electronic configurations can accept the electrons from the complexing agents. Similarly,the low stabilities of Pb,Cd and Mg -complexes could be explained by that Pb^{2+} with $6s^2$, Cd^{2+} with $4d^{10}$ and Mg^{2+} with $2p^6$ their electronic configuration has a completely filled d,p and s orbitals. Moreover, the stabilities of metal ions with hydrolysed humic acid from peat soil were higher than those with unhydrolysed humic acid from peat soil; which is ascribed to the high content of acidity in hydrolysed humic acid than unhydrolysed humic acid.

CONCLUSION

The values of logK for Cu(II) hydrolysed humic acid complex was higher followed by Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes as compared with metal(II) unhydrolysed humic acid complexes . This indicates acid hydrolysis of humic acid can enhance the complexation behavior of humic acid with metal (II) ions. However, the higher values of logβ for Cu(II), Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes indicates more stable stepwise complexes formed as compared with Cu(II), Pb(II), Cd(II) and Mg(II) unhydrolysed humic acid complexes.

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STABILITY CONSTANTS OF COMPLEXES OF METAL IONS WITH PEATSOIL HUMIC ACIDS UNDER NON-ACID-CONDITIONS

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ABSTRACT

Stability constants of complexes of four divalent metal ions viz. Cu^{2+}, Pb^{2+},Mg^{2+} and Cd^{2+} with humic acids (HA) were determined by potentiometric titration of humic acids with the corresponding salt of the divalent metals in aqueous media under non-acid-condition. The log K (logarithm of the stability constant) ranged from 1.0942 to 2.7471 for metal-humic acid complexes were determined using point-wise computational method. The order of stability constants were obtained as follows: Cu >Pb> Cd > Mg for metal -HA complexes respectively, indicating a higher degree of complexation with Cu metal ion.

Keywords: stability constant, humic acid, potentiometric titration, divalent metals, acid hydrolysis.

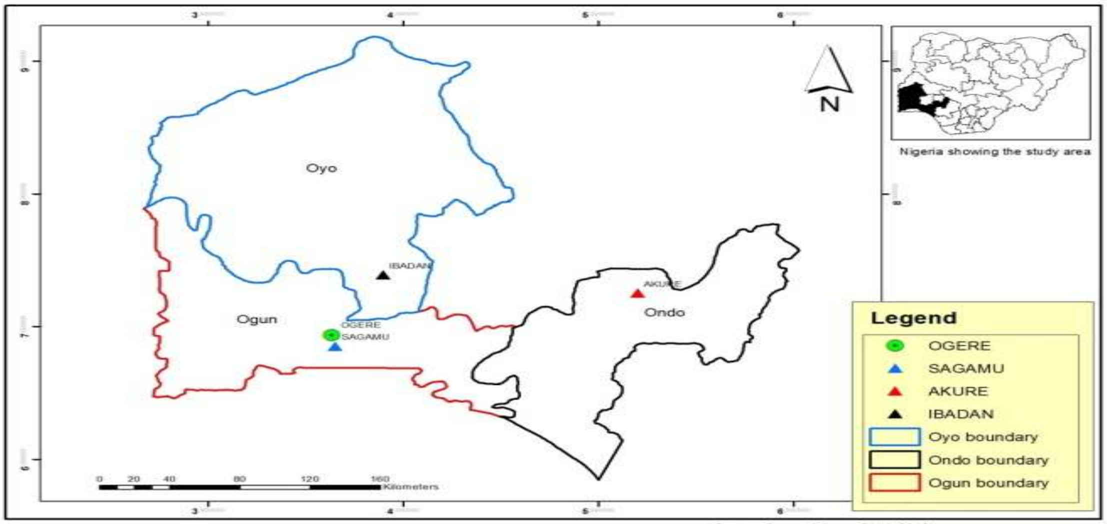
NTRODUCTION

The stability constant of a complex is the numerical expression of its stability and provides a quantitative measure of affinity of the metal ion to the complexing agent. An understanding of the relative stability of metal-complexes helps in predicting the behavior of metal ions in the soil (Ram and Raman, 1982). Extensive researches has been done to determine the stability constants of the complexes formed between humic acid (HA) with a number of metal ions. Ashok *et al*., (2000) reported that humic acid with hydroxyl, phenoxyl and carboxyl reactive groups can form coordination compound with metal ions at pH 3.5. The stability constants(Log K) for different metal-humic acid complexes indicated the following order of the stabilities of complexes formed between humic acid and metal ion, Cu >Fe >Pb> Ni > Co > Ca > Cd > Zn >Mn> Mg. Andelkovic *et al*., (2010) investigated the binding of Cd(II) to soil humic acid at pH 6.5 and in 0.1M KNO_3 ionic medium. The stability constant for binding indicating greater stability in the case when carboxyl groups are involved in complexation reaction. Kostic *et al*.,(2012) investigated the complexation of humic acid with certain heavy metal ions (Co(II), Ni(II),Cu(II), Zn(II), and Pb(II). The experiment was performed at 25°C, at pH 4.0 and ionic strength of 0.01M. Stability constant of complex between Pb(II) ions and humic acid is greater than stability constants of other investigated metal-humate complexes. Bogata and Sokolowska (2016) analyses the interaction between humic acids from different soils and Zn (II) ions at wide concentration ranges and at pH 5. Studies have showed significant impact of Zn concentration, pH and some properties of humic acids with zinc.But all of these studies were limited to acidic pH range. Therefore, the present study was carried out to determine and compare the stability constants of complexes of metal ions with hydrolysed peat soil humic acid and unhydrolysed peat soil humic under non-acid conditions.

MATERIALS AND METHODS

Analytical grade chemicals used includes hydrochloric acid (HCl), nitric acid (HNO_3), sodium hydroxide (NaOH), lead nitrate $Pb(NO_3)_2$, copper nitrate $Cu(NO_3)_2.3H_2O$, cadmium nitrate $Cd(NO_3)_2.4H_2O$, magnesium nitrate $Mg(NO_3)_2.6H_2O$, potassium nitrate (KNO_3), calcium chloride ($CaCl_2$), (sigma-Aldrich). Dowex 50WX8, (20-50 mesh) from Fluka.

Area of study



Source: Dept. of Geog. BUK (2016)

Figure 1: Map showing the sampling point at Sagamu Town, Ogun State.

Description of Sampling Area

Sagamu has geographical coordinates between 6°50′ north; 3° 38′ east is located in south western region of Nigeria. The region has tropical wet and dry climate with a lengthy wet season and relatively constant temperatures throughout the course of the year. Wet season runs from March to October, November to December forms the region dry season. The vegetation type of the region is savannah which is really grassland with small bushes and occasional big trees. Grassland soils have substantially higher organic matter content than forest soils (Novackova, 2011).

Sample Collection

The Peatsoil samples were collected from four different sampling points (0-10cm depth) in Sagamu into polyethylene bag with plastic spoons. Samples were taken to the laboratory, extraneous materials were removed; the samples were air-dried, crushed and ground to a fine powder in a mortar passed through a 0.20mm sieve. The samples were kept for analysis.

Isolation and purification of humic acid from peat soil sample

Peatsoil sample (100g) was mixed with 1000 cm^3 of 0.1M NaOH solution, shaken for 3hours and left to stand overnight. Dark-coloured supernatant was obtained and decanted from solid residue. The dark-coloured supernatant was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 6 hours. Yellowish brown supernatant and dark-brown precipitate were obtained. The yellowish brown supernatant was decanted followed by centrifuge and discarded. The dark-brown precipitate was mixed with 500$cm^3$of 0.1M NaOH solution followed by passing through dowex resin. The dark-brown solution was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 3 hours. The dark-brown precipitate was washed several times with deionized water. The supernatant was treated with $AgNO_3$ solution until no white precipitate observed. The humic acid was transferred to weighed crucible and dried at 60°C in an oven for 12 hours. The humic acid was cooled and dried in the desiccator, weighed and recorded. The obtained humic acid was dried again at 60°C for additional 6 hours cooled and dried in the desiccator, weighed and recorded constant weight was obtained (Baruah *et al.*, 2015).

FT-IR analysis

FT-IR spectra of humic acid sample was analysed using Carry 630 FT-IR Agilent Technologies.

Unhydrolysed compost humic acid

The unhydrolysed humic acid was obtained after isolation and purification of compost humic acid and kept for investigation.

Acid hydrolysis of Peatsoil acid

Peatsoil humic acid sample (1g) was refluxed for 12 hours at (160°C) with 50cm^3 of 6M HCl. The mixture was allowed to cool, decanted, and centrifuged after hydrolysis. The insoluble residues were washed with distilled water via centrifugation several times, and the supernatant was treated with $AgNO_3$ solution until no white precipitate was observed. The residue was thoroughly dried over $CaCl_2$ in a desiccator at room temperature (Chefetz *et al.*, 2002). Finally, the obtained hydrolysed humic acid was kept for investigation.

Potentiometric Titrations

Potentiometric measurements were carried out using a pH-meter Jenway (model 3510) with combine electrode, the sensitivity of the pH - meter is 0.01 units. The pH meter was switched on half an hour before starting the titration for initial warm up of the instrument. The instrument was calibrated with an aqueous standard buffer solution of pH 4.00 and 10.0 (borate buffer) prepared from a "Qualigens" buffer tablets.

The following sets of solutions were prepared in a 250cm^3 volumetric flask separately for pH metric titrations.

(i) 5 cm^3 0.1 M HCl + 40 cm^3 deionized water
(ii) 5 cm^3 0.1 M HCl + 39 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid
(iii) 5 cm^3 0.1 M HCl + 37 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid + 2 cm^3 0.01 M Cu(II)

The solutions were titrated against standardized 0.110MNaOH separately. The total volume of each mixture was adjusted to 50 cm^3 and the ionic strength of the solutions was maintained constant at by adding appropriate amount of stock solution of 1M KNO$_3$ (Gamal, 2015; Omar and Ali, 2015). A magnetic stirrer was used to achieve thorough mixing of the interacting solutions at 550 rpm. The same set of experimental conditions was applied for potentiometric titration of remaining samples.

Evaluation of pKa of Hydrolysed peat soil Humic Acids

The proton-ligand formation number n$_{\mathbf{A}}$ were calculated by Irving and Rossotti expression (Omar and Ali, 2015).

$$nA = Y- \frac{(V2-V1)(No-Eo)}{(Vo+V1)TcL} \quad \text{......................................1}$$

Where: Y is number of dissociable proton, (V$_2$-V$_1$) is the measure of displacement of the ligand curve relative to acid curve, N^o and E^o are the resultant concentration of alkali solution, free acid solution, T$_{cL}$^{o} is the total ligand concentration, V^o is the total volume of titration solution,V$_1$ is the volume of alkali added to acid solution,V$_2$ is the volume of alkali added to acid solution + ligand solution, acid dissociation constants (pKa - values) of ligand were calculated by algebraic method point wise calculation (Tables 1). The dissociation constants (pKa) were calculated according to the following relation:

$$pKa = pH + \log\left(\frac{nA}{1-nA}\right) \quad \text{..............................2}$$

Where: pKa is the acid dissociation constant, n$_A$is the Proton-ligand formation number and pH is the pH-values (Omar and Ali, 2015).

Determination of metal-ligand stability constants (log K) of complexes

The potentiometric measurement for the determination of stability constant of a complex in solution is based on the fact that the redox potential of the couple $\frac{M^{+(m-n)}}{M^{+m}}$ is shifted significantly on complexation of the metal ion with the ligand. This method involves change in hydrogen ion concentration [H$^+$] due to the displacement or association of one or more protons taking place during complexation reaction. This change can be found out by titrating the solutions containing free acid, acid with ligand, and acid with ligand and metal ion, individually against a standard alkali solution at a constant ionic strength or temperature. Either ionic strength or temperature may be varied for different sets of solutions. In all the cases, the change in the pH of the solution is measured after each addition of a known amount of alkali to the reaction cell which contains the reaction mixture. The titration curves are then drawn by plotting the measured pH values against the corresponding volume of alkali added and the stability constants of the complexes are determined from the titration curves by employing pH-metric titration technique given by (Irving and Rossoti).

Metal-ligand stability constants (Log K) were determined by using the following relations:

$$\bar{n} = \frac{(V_3 - V_2)(E^0 + N^0)}{(V^0 + V_2)\bar{n}_A T_m^0} \quad \text{...3}$$

and

$$PL = \log_{10}\{\frac{1+\beta_n^H \frac{1}{[anti\ \log pH]^n}}{T_L^0 - \bar{n}T_m^0} X \frac{(V^0 + V_3)}{V^0}\} \quad \text{...4}$$

Where $T_{L,}$ T^{o}, E°, and V^{o}havethe same significance as in equation (1) above, T_m denotes the total concentration of metal present in solution, V_3 is the volume of metal ions present in solution and β^H is the overall proton ligand stability constant. The metal-ligand stability constants (log K) were determined by employing point wise computational Method (eq. 5 and 6).

$$\mathrm{Log}K_1 = \log\left(\frac{n}{1-n}\right) + pL \qquad \ldots\ldots\ldots\ldots.5$$

$$\mathrm{Log}K_2 = \log\left(\frac{1-n}{2-n}\right) + pL\ldots\ldots\ldots\ldots\ldots\ldots\ldots.6$$

Where: Log K is the metal-ligand stability constant, pL is the Free ligand exponent function, **n** is the Average number of ligand attached with metal ion (Janrao*et al.*, 2014).The results obtained were analyzed by an ORIGIN 2016 program using titration data and then the proton-ligand stability constants (pKa) and Metal-ligand stability constant (LogK) calculated (Omar and Ali, 2015).

RESULTS AND DISCUSSION

Fourier transformed infrared (FT-IR) spectra of isolated humic acid from peat soils Figure 2 had distinct clear absorption bands indicating the presence of major humic acid structural elemental groups such as H bonded OH ($3680cm^{-1}$ peak), C=O of carbonyl ($1721cm^{-1}$ peak), functional groups of aliphatic components CH_2 ($2918cm^{-1}$ peak) and C-O stretching of polysaccharide ($1168cm^{-1}$ peak). The positions of the absorption bands of the spectra fell within typical major absorption bands of humic acid which is at frequencies 3680, 2918, 1721, 1168 cm^{-1}. The first peak centred in the vicinity of 3680 cm^{-1} region is attributed to phenol OH group bounded by intermolecular H bonds. The $2918cm^{-1}$ band usually has absorption maximum at 2918 cm^{-1} which is due to C–H stretching of alkane group (CH_2). The next major absorption band is 1721 cm^{-1}. This band has been commonly ascribed to C=O stretching of mainly carboxyl group (COOH) with trace amount of ketones. The last peak was observed at 1168 cm^{-1} due to C–O stretching of polysaccharides and this peak appeared also in the spectra of humic acid from peat soil. The FTIR spectra of the isolated humic acid contained all major characteristic absorption peaks of humic acid. These absorption peaks indicated the presence of the major structural elements of humic acid namely H bonded OH, C=C of aromatic ring, C=O of carbonyl group (both carboxyl and ketonic), CH_2 group. This strongly supports the presence of humic acid.

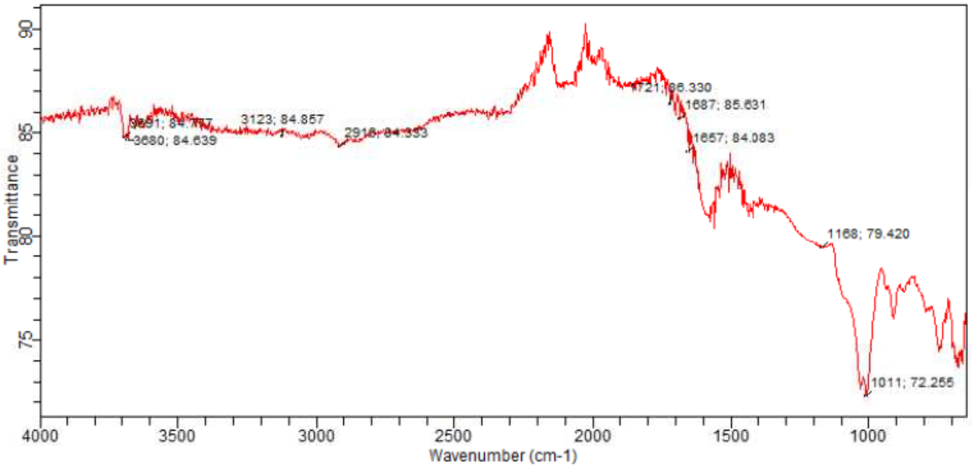


Fig. 2 : FT-IR spectraof peatsoilhumic acid (PSHA)

Evaluation of acid dissociation constant (pka) of acid hydrolysed peat soil humicacid at phenolic group

The value of the dissociation constant of the peat soil humic acid (PSHA) that underwent acidhydrolysis studied was found to be 8.9299 as shown Table 1, which is lower than the literaturevalues reported by Almeida and Szpoganics, (2015), Borges *et al.*, (2005); Badr *et al.*, (2012)and Fernandes *et al*,.(2009) of 9.73, 9.47 and 10.30. The difference between the obtained valuesand the reported values in this study might be probably as a result of acid hydrolysis of humicacid.

Table 1: PKa of (Hydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	log($\frac{nA}{1-nA}$)	pKa
8.50	5.30	6.29	0.99	0.3594	-0.2510	8.2490
8.72	5.35	6.37	1.02	0.3400	-0.2880	8.4320
9.00	5.40	6.46	1.06	0.3141	-0.3391	8.6609
9.22	5.45	6.55	1.10	0.2882	-0.3927	8.8273
9.51	5.50	6.66	1.16	0.2494	-0.4786	9.0314
9.73	5.55	6.78	1.23	0.2041	-0.5910	9.1390
10.00	5.60	6.90	1.30	0.1589	-0.7238	9.2762
10.23	5.65	7.05	1.40	0.0941	-0.9835	9.2465
10.49	5.70	7.10	1.40	0.0941	-0.9835	9.5065

Average pKa = 8.9299 ± 0.4186

Table 2: PKa of (Unhydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	Log($\frac{nA}{1-n}$)	pKa
8.50	5.30	5.81	0.51	0.6619	0.2919	8.7919
8.72	5.35	5.90	0.55	0.6357	0.2418	8.9618
9.00	5.40	6.00	0.60	0.6029	0.1813	9.1813
9.22	5.45	6.10	0.65	0.5701	0.1226	9.3426
9.51	5.50	6.20	0.70	0.5376	0.0654	9.5754
9.73	5.55	6.33	0.78	0.4851	-0.0259	9.7041
10.00	5.60	6.47	0.87	0.4262	-0.1291	9.8709
10.23	5.65	6.62	0.99	0.3609	-0.2481	9.9819
10.49	5.70	6.80	1.10	0.2759	-0.4690	10.0210

Average pKa = 9.4923± 0.4410

Metal-ligand stability constant (Log K)

The stabilityconstants require the accurate values of proton-ligand stability constants (Anil and Maroti, 2008). Metal titration curves crossed over ligand titration curve indicated the formation of complex upon proton release (Santosh, *et al.*, 2011). If the values of n- are within range 0.2-0.8 and 1.2-18 this indicates the formation of 1:1 and 1:2 complexes (Sayyed and Mazahar, 2012).

The metal (II)-humate stepwise stability constants (log k) at phenolic group (Tables 3-18)

Table 3: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n}{1-n}$)	$LogK_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

$LogK_1$ (Average value) = 2.4788± 0.2203

Table 4: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	Log($\frac{n-1}{2-n}$)	$LogK_2$
9.51	5.50	6.66	6.73	0.07	1.3509	1.70	-0.2671	1.4329
9.73	5.55	6.78	6.85	0.07	1.6383	1.51	0.2467	1.7567
10.00	5.60	6.90	6.98	0.08	2.1783	1.31	-0.2158	1.0942
10.23	5.65	7.05	7.13	0.08	4.1904	1.27		
10.49	5.70	7.10	7.19	0.09	4.6920			

$LogK_2$(Average value) = 1.4280 ± 0.3312

Table 5:Point-wise method,Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	Log($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430

$LogK_1$ **(Average value)** = 2.3059± 0.6153

Table 6:Point-wise method, Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
9.73	5.55	6.33	6.42	0.09	0.9000	1.69		
10.00	5.60	6.47	6.58	0.11	1.2578	1.44	-0.4592	0.9808
10.23	5.65	6.62	6.84	0.12	1.6137	1.26	-0.2010	1.4610
10.49	5.70	6.80	6.92	0.12	2.1052	1.03		

$LogK_2$ **(Average value)** = 1.2209± 0.3398

Table 7:Point-wise method,Pb (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n}{1-n}$)	$LogK_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.60	0.05	0.8333	1.96	0.6989	2.6589

$LogK_1$ (Average value) = 2.5832 ±0.1614

Table 8:Point-wise method,Pb-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n-1}{2-n}$)	$logK_2$
9.51	5.50	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.83	0.05	1.1702	1.44		
10.00	5.60	6.90	6.90	0.05	1.4864	1.22	-0.0237	1.1963
10.23	5.65	7.05	7.10	0.05	2.0190	1.09		
10.49	5.70	7.10	7.17	0.07	3.6492	1.00		

$LogK_2$(Average value) = 1.1963

Table 9:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log ($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.5477	2.3123
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	0.0272	2.2072
9.51	5.50	6.20	6.26	0.07	0.6417	1.89	0.2530	2.1430
9.73	5.55	6.40	6.40	0.07	0.7000	1.67	0.3680	2.0380

$LogK_1$ **(Average value)** = 2.2364 ± 0.1602

Table 10:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
10.00	5.60	6.47	6.55	0.08	1.9503	1.41		
10.23	5.65	6.62	6.72	0.11	1.4792	1.26	-0.0361	1.2239

$LogK_2$ **(Average value)** = 1.2239

Table 11:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n}{n-1}$)	$LogK_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4290	2.2110
8.72	5.35	6.37	6.39	0.02	0.2858	2.42	-0.3978	2.0222
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

$LogK_1$ (Average value)=2.1382**±**0.1046

Table 12:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	log($\frac{n-1}{2-n}$)	LogK$_2$
9.51	5.55	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.84	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.93	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.10		
10.49	5.70	7.10	7.18	0.07	3.6492	0.83		

LogK$_2$(Average value) = 1.5453 **±** 0.3450

Table 13:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	V$_3$-V$_2$	n	pL	Log($\frac{n}{n-1}$)	Log K$_1$
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.3477	2.3123
9.00	5.40	6.00	6.04	0.04	0.3236	2.38	-0.3202	2.0598
9.22	5.45	6.10	6.15	0.05	0.4297	2.17	-0.1230	2.0470
9.51	5.50	6.20	6.26	0.06	0.5500	1.89	0.0871	1.9771
9.73	5.55	6.33	6.40	0.07	0.7000	1.67	0.3680	2.0380

LogK$_1$ **(Average value)** = 2.1568 ± 0.2069

Table 14:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	V$_3$-V$_2$	n	pL	Log($\frac{n-1}{2-n}$)	Log K$_2$
10.00	5.60	6.47	6.55	0.08	0.9148	1.41		
10.23	5.65	6.62	6.71	0.09	1.2102	1.20	-0.5749	0.6251
10.49	5.70	6.80	6.92	0.09	1.5968	1.03	0.1703	1.2003

LogK$_2$ **(Average value)** = 0.9127± 0.4070

Table15:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	Log($\frac{n}{1-n}$)	LogK$_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4210	2.2190
8.72	5.35	6.37	6.40	0.03	0.4286	2.42	-0.1249	2.2951
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.96	0.3010	2.2610
9.51	5.55	6.66	6.70	0.04	0.7720	1.67	0.5297	2.1997

LogK$_1$ (Average value) = 2.2108± 0.0825

Table 16:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	Log($\frac{n-1}{2-n}$)	Log K$_2$
9.73	5.55	6.78	6.83	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.95	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.09		
10.49	5.70	7.10	7.16	0.06	3.1429	0.89		

LogK$_2$ **(Average value)** = 1.5453± 0.3450

Table 17:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	V$_3$-V$_2$	n	pL	Log($\frac{n}{n-1}$)	Log K$_1$
8.50	5.30	5.81	5.86	0.05	0.3717	2.88	-0.2280	2.6520
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.06	0.06	0.4853	2.38	-0.0255	2.3545
9.22	5.45	6.10	6.16	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430
9.73	5.55	6.33	6.41	0.08	0.8000	1.69	0.6020	2.2920

LogK$_1$ **(Average value)** = 2.2516± 0.5380

Table 18:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$\text{Log}(\frac{n-1}{2-n})$	Log K_2
10.00	5.60	6.47	6.57	0.10	1.1434	1.43		
10.23	5.65	6.62	6.72	0.10	1.3448	1.23	-0.2788	0.9512
10.49	5.70	6.80	6.90	0.10	1.7742	1.03	0.5351	1.5651

LogK_2 **(Average value)** = 1.2581± 0.4340

Table 19: Stepwise and overall Stability constants of thehydrolysed and unhydrolysed divalent metal (II) complexes

Chelates	**LogK_1**	**LogK_2**	**Logβ**
[Cu (Hydrolysed PSHA-1)$_2$]	2.4788	1.4280	3.9068
[Pb (Hydrolysed PSHA-1)$_2$]	2.5832	1.1963	3.7795
[Cd (Hydrolysed PSHA-1)$_2$]	2.2108	1.5453	3.7561
[Mg (Hydrolysed PSHA-1)$_2$]	2.1382	1.5453	3.6835
[Cu (Unhydrolysed PSHA-1)$_2$]	2.3059	1.2209	3.5268
[Pb (Unhydrolysed PSHA-1)$_2$]	2.2364	1.2239	3.4603
[Cd (Unhydrolysed PSHA-1)$_2$]	2.2516	1.2581	3.5097
[Mg (Unydrolysed PSHA-1)$_2$]	2.1568	0.9127	3.0695

The results obtained (Table19) shows the stepwise and overall stability constants to be not high indicating low stability of the complexes, because the solubility of most metal ions in the basic pH range is minimal due to metal hydroxide precipitation (Karimi, 2017). In general, the stepwise stability constants (K_1 and K_2) follow the order $K_1 > K_2$ for the copper, lead, magnesium and cadmium complexes respectively. The steady decrease of the values with increasing number of ligands is in agreement with the prediction made by researchers (Na'aliya, 2013). The decrease could be attributed to the fact that as the number of the ligands (Humate ions) that enters the coordination zone increases the aqua molecules available for replacement by the ligands become less. Thus, the metal ions become less electron loving with progressive intake of the ligand and this results in the decrease in the values of the constants (Na'aliya, 2013). Also the stability of the complexes is influenced by the size and number of the chelate rings(Mackay and Mackay,2002).All the complexes form rings in their structure as humate, a bidentate ligand, bond the metal ions in the ratio 1:2 (Boguta and Sokolowska, 2016) forming chelate rings. The values of the overall stability constants (logβ) obtained for humate complexes are not high indicating low stability as the values are not high. LogK values for copper-humates (Table 3 to 6) obtained in this study are lower than those reported for the complexes of humic acids (Pandey *et al*., 2015; Dinu, 2013; Kaschl *et al*., 2010 and Gilbeto and Jorg, 2001). The values of LogK(Table 7 to 10) forlead-humates are lower than those reported for the lead in the literature (Dinu, 2013; Gilbeto and Jorg 2001). Log K values(Table 11 to 14) for magnesium-humates obtained in this study are close to those reported by (Pandey *et al*., 2015). Log K values of cadmium-humates (Table 15 to 18) obtained in this work near to the one reported by (Dinu, 2013 and Pandey *et al*., 2015).The difference between the reported values and the values obtained in this study might be probably as a result of acid hydrolysis of humic acid. The values of the overall stability constants (log β) of the copper humates complexes presented in Table 19 is high than that of other metal humate complexes, show relatively high stability of Cu-HA complexes, show the following order of stability: Cu >Pb> Cd > Mg; which are in close agreement to the findings of (Dinu, 2013 and Pandey *et al*., 2015).The high stability of Cu-humate chelate could be attributed to the existence of coordinate covalent bond between the complexing agents and the Cu^{2+} ions. Since, Cu^{2+} being a metal of the transitional series with $3d^9$ electronic configurations can accept the electrons from the complexing agents. Similarly,the low stabilities of Pb,Cd and Mg -complexes could be explained by that Pb^{2+} with $6s^2$, Cd^{2+} with $4d^{10}$ and Mg^{2+} with $2p^6$ their electronic configuration has a completely filled d,p and s orbitals. Moreover, the stabilities of metal ions with hydrolysed humic acid from peat soil were higher than those with unhydrolysed humic acid from peat soil; which is ascribed to the high content of acidity in hydrolysed humic acid than unhydrolysed humic acid.

CONCLUSION

The values of logK for Cu(II) hydrolysed humic acid complex was higher followed by Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes as compared with metal(II) unhydrolysed humic acid complexes . This indicates acid hydrolysis of humic acid can enhance the complexation behavior of humic acid with metal (II) ions. However, the higher values of logβ for Cu(II), Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes indicates more stable stepwise complexes formed as compared with Cu(II), Pb(II), Cd(II) and Mg(II) unhydrolysed humic acid complexes.

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STABILITY CONSTANTS OF COMPLEXES OF METAL IONS WITH PEATSOIL HUMIC ACIDS UNDER NON-ACID-CONDITIONS

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ABSTRACT

Stability constants of complexes of four divalent metal ions viz. Cu^{2+}, Pb^{2+},Mg^{2+} and Cd^{2+} with humic acids (HA) were determined by potentiometric titration of humic acids with the corresponding salt of the divalent metals in aqueous media under non-acid-condition. The log K (logarithm of the stability constant) ranged from 1.0942 to 2.7471 for metal-humic acid complexes were determined using point-wise computational method. The order of stability constants were obtained as follows: Cu >Pb> Cd > Mg for metal -HA complexes respectively, indicating a higher degree of complexation with Cu metal ion.

Keywords: stability constant, humic acid, potentiometric titration, divalent metals, acid hydrolysis.

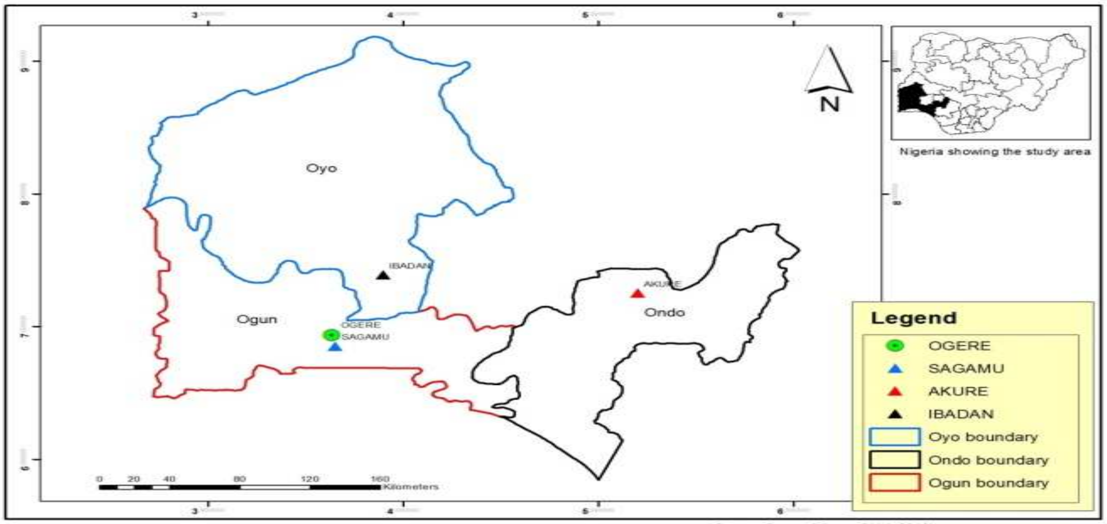
NTRODUCTION

The stability constant of a complex is the numerical expression of its stability and provides a quantitative measure of affinity of the metal ion to the complexing agent. An understanding of the relative stability of metal-complexes helps in predicting the behavior of metal ions in the soil (Ram and Raman, 1982). Extensive researches has been done to determine the stability constants of the complexes formed between humic acid (HA) with a number of metal ions. Ashok *et al.*, (2000) reported that humic acid with hydroxyl, phenoxyl and carboxyl reactive groups can form coordination compound with metal ions at pH 3.5. The stability constants(Log K) for different metal-humic acid complexes indicated the following order of the stabilities of complexes formed between humic acid and metal ion, Cu >Fe >Pb> Ni > Co > Ca > Cd > Zn >Mn> Mg. Andelkovic *et al.*, (2010) investigated the binding of Cd(II) to soil humic acid at pH 6.5 and in 0.1M KNO$_3$ ionic medium. The stability constant for binding indicating greater stability in the case when carboxyl groups are involved in complexation reaction. Kostic *et al.*,(2012) investigated the complexation of humic acid with certain heavy metal ions (Co(II), Ni(II),Cu(II), Zn(II), and Pb(II). The experiment was performed at 25°C, at pH 4.0 and ionic strength of 0.01M. Stability constant of complex between Pb(II) ions and humic acid is greater than stability constants of other investigated metal-humate complexes. Bogata and Sokolowska (2016) analyses the interaction between humic acids from different soils and Zn (II) ions at wide concentration ranges and at pH 5. Studies have showed significant impact of Zn concentration, pH and some properties of humic acids with zinc.But all of these studies were limited to acidic pH range. Therefore, the present study was carried out to determine and compare the stability constants of complexes of metal ions with hydrolysed peat soil humic acid and unhydrolysed peat soil humic under non-acid conditions.

MATERIALS AND METHODS

Analytical grade chemicals used includes hydrochloric acid (HCl), nitric acid (HNO$_3$), sodium hydroxide (NaOH), lead nitrate Pb(NO$_3$)$_2$, copper nitrate Cu(NO$_3$)$_2$.3H$_2$O, cadmium nitrate Cd(NO$_3$)$_2$.4H$_2$O, magnesium nitrate Mg(NO$_3$)$_2$.6H$_2$O, potassium nitrate (KNO$_3$), calcium chloride (CaCl$_2$), (sigma-Aldrich). Dowex 50WX8, (20-50 mesh) from Fluka.

Area of study



Source: Dept. of Geog. BUK (2016)

Figure 1: Map showing the sampling point at Sagamu Town, Ogun State.

Description of Sampling Area

Sagamu has geographical coordinates between 6°50′ north; 3° 38′ east is located in south western region of Nigeria. The region has tropical wet and dry climate with a lengthy wet season and relatively constant temperatures throughout the course of the year. Wet season runs from March to October, November to December forms the region dry season. The vegetation type of the region is savannah which is really grassland with small bushes and occasional big trees. Grassland soils have substantially higher organic matter content than forest soils (Novackova, 2011).

Sample Collection

The Peatsoil samples were collected from four different sampling points (0-10cm depth) in Sagamu into polyethylene bag with plastic spoons. Samples were taken to the laboratory, extraneous materials were removed; the samples were air-dried, crushed and ground to a fine powder in a mortar passed through a 0.20mm sieve. The samples were kept for analysis.

Isolation and purification of humic acid from peat soil sample

Peatsoil sample (100g) was mixed with 1000 cm^3 of 0.1M NaOH solution, shaken for 3hours and left to stand overnight. Dark-coloured supernatant was obtained and decanted from solid residue. The dark-coloured supernatant was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 6 hours. Yellowish brown supernatant and dark-brown precipitate were obtained. The yellowish brown supernatant was decanted followed by centrifuge and discarded. The dark-brown precipitate was mixed with $500cm^3$of 0.1M NaOH solution followed by passing through dowex resin. The dark-brown solution was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 3 hours. The dark-brown precipitate was washed several times with deionized water. The supernatant was treated with $AgNO_3$ solution until no white precipitate observed. The humic acid was transferred to weighed crucible and dried at 60°C in an oven for 12 hours. The humic acid was cooled and dried in the desiccator, weighed and recorded. The obtained humic acid was dried again at 60°C for additional 6 hours cooled and dried in the desiccator, weighed and recorded constant weight was obtained (Baruah *et al.*, 2015).

FT-IR analysis

FT-IR spectra of humic acid sample was analysed using Carry 630 FT-IR Agilent Technologies.

Unhydrolysed compost humic acid

The unhydrolysed humic acid was obtained after isolation and purification of compost humic acid and kept for investigation.

Acid hydrolysis of Peatsoil acid

Peatsoil humic acid sample (1g) was refluxed for 12 hours at (160°C) with $50cm^3$ of 6M HCl. The mixture was allowed to cool, decanted, and centrifuged after hydrolysis. The insoluble residues were washed with distilled water via centrifugation several times, and the supernatant was treated with $AgNO_3$ solution until no white precipitate was observed. The residue was thoroughly dried over $CaCl_2$ in a desiccator at room temperature (Chefetz *et al.*, 2002). Finally, the obtained hydrolysed humic acid was kept for investigation.

Potentiometric Titrations

Potentiometric measurements were carried out using a pH-meter Jenway (model 3510) with combine electrode, the sensitivity of the pH - meter is 0.01 units. The pH meter was switched on half an hour before starting the titration for initial warm up of the instrument. The instrument was calibrated with an aqueous standard buffer solution of pH 4.00 and 10.0 (borate buffer) prepared from a "Qualigens" buffer tablets.

The following sets of solutions were prepared in a 250cm^3 volumetric flask separately for pH metric titrations.

(i) 5 cm^3 0.1 M HCl + 40 cm^3 deionized water
(ii) 5 cm^3 0.1 M HCl + 39 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid
(iii) 5 cm^3 0.1 M HCl + 37 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid + 2 cm^3 0.01 M Cu(II)

The solutions were titrated against standardized 0.110MNaOH separately. The total volume of each mixture was adjusted to 50 cm^3 and the ionic strength of the solutions was maintained constant at by adding appropriate amount of stock solution of 1M KNO$_3$ (Gamal, 2015; Omar and Ali, 2015). A magnetic stirrer was used to achieve thorough mixing of the interacting solutions at 550 rpm. The same set of experimental conditions was applied for potentiometric titration of remaining samples.

Evaluation of pKa of Hydrolysed peat soil Humic Acids

The proton-ligand formation number n$_{\mathbf{A}}$ were calculated by Irving and Rossotti expression (Omar and Ali, 2015).

$$nA = Y - \frac{(V2-V1)(No-Eo)}{(Vo+V1)TcL} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 1$$

Where: Y is number of dissociable proton, (V$_2$-V$_1$) is the measure of displacement of the ligand curve relative to acid curve, N^o and E^o are the resultant concentration of alkali solution, free acid solution, T$_{cL}$^{o} is the total ligand concentration, V^o is the total volume of titration solution,V$_1$ is the volume of alkali added to acid solution,V$_2$ is the volume of alkali added to acid solution + ligand solution, acid dissociation constants (pKa - values) of ligand were calculated by algebraic method point wise calculation (Tables 1). The dissociation constants (pKa) were calculated according to the following relation:

$$pKa = pH + \log(\frac{nA}{1-nA}) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 2$$

Where: pKa is the acid dissociation constant, n$_A$is the Proton-ligand formation number and pH is the pH-values (Omar and Ali, 2015).

Determination of metal-ligand stability constants (log K) of complexes

The potentiometric measurement for the determination of stability constant of a complex in solution is based on the fact that the redox potential of the couple $\frac{M^{+(m-n)}}{M^{+m}}$ is shifted significantly on complexation of the metal ion with the ligand. This method involves change in hydrogen ion concentration [H$^+$] due to the displacement or association of one or more protons taking place during complexation reaction. This change can be found out by titrating the solutions containing free acid, acid with ligand, and acid with ligand and metal ion, individually against a standard alkali solution at a constant ionic strength or temperature. Either ionic strength or temperature may be varied for different sets of solutions. In all the cases, the change in the pH of the solution is measured after each addition of a known amount of alkali to the reaction cell which contains the reaction mixture. The titration curves are then drawn by plotting the measured pH values against the corresponding volume of alkali added and the stability constants of the complexes are determined from the titration curves by employing pH-metric titration technique given by (Irving and Rossoti).

Metal-ligand stability constants (Log K) were determined by using the following relations:

$$\bar{n} = \frac{(V_3 - V_2)(E^0 + N^0)}{(V^0 + V_2)\bar{n}_A T_m^0} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 3$$

and

$$PL = \log_{10}\{\frac{1+\beta_n^H \frac{1}{[anti\ \log pH]^n}}{T_L^0 - \bar{n}T_m^0} X \frac{(V^0 + V_3)}{V^0}\} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 4$$

Where $T_{L,}$ T^o, E°, and V^ohavethe same significance as in equation (1) above, T_m denotes the total concentration of metal present in solution, V_3 is the volume of metal ions present in solution and β^H is the overall proton ligand stability constant. The metal-ligand stability constants (log K) were determined by employing point wise computational Method (eq. 5 and 6).

$$\mathrm{LogK}_1 = \log\left(\frac{n}{1-n}\right) + \mathrm{pL} \quad \ldots\ldots\ldots\ldots.5$$

$$\mathrm{LogK}_2 = \log\left(\frac{1-n}{2-n}\right) + \mathrm{pL}\ldots\ldots\ldots\ldots\ldots\ldots\ldots.6$$

Where: Log K is the metal-ligand stability constant, pL is the Free ligand exponent function, **n** is the Average number of ligand attached with metal ion (Janrao*et al.*, 2014).The results obtained were analyzed by an ORIGIN 2016 program using titration data and then the proton-ligand stability constants (pKa) and Metal-ligand stability constant (LogK) calculated (Omar and Ali, 2015).

RESULTS AND DISCUSSION

Fourier transformed infrared (FT-IR) spectra of isolated humic acid from peat soils Figure 2 had distinct clear absorption bands indicating the presence of major humic acid structural elemental groups such as H bonded OH (3680cm^{-1} peak), C=O of carbonyl (1721cm^{-1} peak), functional groups of aliphatic components CH_2 (2918cm^{-1} peak) and C-O stretching of polysaccharide (1168cm^{-1} peak). The positions of the absorption bands of the spectra fell within typical major absorption bands of humic acid which is at frequencies 3680, 2918, 1721, 1168 cm^{-1}. The first peak centred in the vicinity of 3680 cm^{-1} region is attributed to phenol OH group bounded by intermolecular H bonds. The 2918cm^{-1} band usually has absorption maximum at 2918 cm^{-1} which is due to C–H stretching of alkane group (CH_2). The next major absorption band is 1721 cm^{-1}. This band has been commonly ascribed to C=O stretching of mainly carboxyl group (COOH) with trace amount of ketones. The last peak was observed at 1168 cm^{-1} due to C–O stretching of polysaccharides and this peak appeared also in the spectra of humic acid from peat soil. The FTIR spectra of the isolated humic acid contained all major characteristic absorption peaks of humic acid. These absorption peaks indicated the presence of the major structural elements of humic acid namely H bonded OH, C=C of aromatic ring, C=O of carbonyl group (both carboxyl and ketonic), CH_2 group. This strongly supports the presence of humic acid.

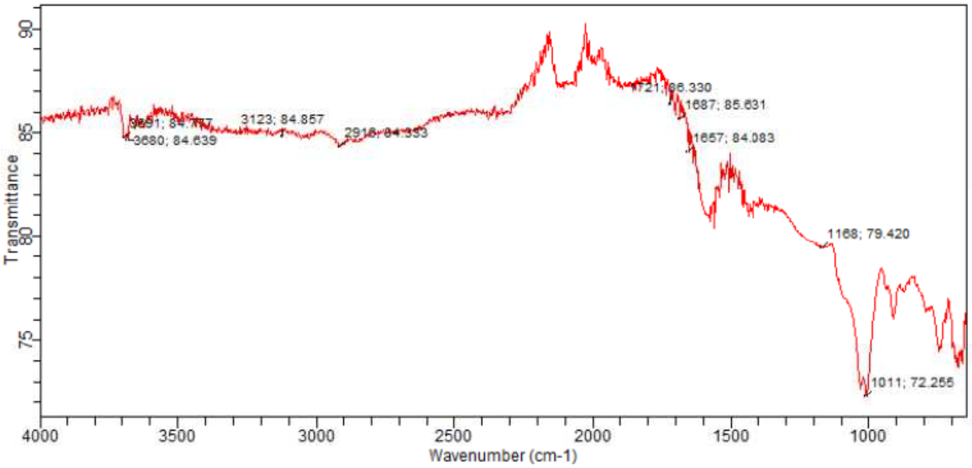


Fig. 2 : FT-IR spectraof peatsoilhumic acid (PSHA)

Evaluation of acid dissociation constant (pka) of acid hydrolysed peat soil humicacid at phenolic group

The value of the dissociation constant of the peat soil humic acid (PSHA) that underwent acidhydrolysis studied was found to be 8.9299 as shown Table 1, which is lower than the literaturevalues reported by Almeida and Szpoganics, (2015), Borges *et al.*, (2005); Badr *et al.*, (2012)and Fernandes *et al*,.(2009) of 9.73, 9.47 and 10.30. The difference between the obtained valuesand the reported values in this study might be probably as a result of acid hydrolysis of humicacid.

Table 1: PKa of (Hydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	log($\frac{nA}{1-nA}$)	pKa
8.50	5.30	6.29	0.99	0.3594	-0.2510	8.2490
8.72	5.35	6.37	1.02	0.3400	-0.2880	8.4320
9.00	5.40	6.46	1.06	0.3141	-0.3391	8.6609
9.22	5.45	6.55	1.10	0.2882	-0.3927	8.8273
9.51	5.50	6.66	1.16	0.2494	-0.4786	9.0314
9.73	5.55	6.78	1.23	0.2041	-0.5910	9.1390
10.00	5.60	6.90	1.30	0.1589	-0.7238	9.2762
10.23	5.65	7.05	1.40	0.0941	-0.9835	9.2465
10.49	5.70	7.10	1.40	0.0941	-0.9835	9.5065

Average pKa = 8.9299 ± 0.4186

Table 2: PKa of (Unhydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	Log($\frac{nA}{1-n}$)	pKa
8.50	5.30	5.81	0.51	0.6619	0.2919	8.7919
8.72	5.35	5.90	0.55	0.6357	0.2418	8.9618
9.00	5.40	6.00	0.60	0.6029	0.1813	9.1813
9.22	5.45	6.10	0.65	0.5701	0.1226	9.3426
9.51	5.50	6.20	0.70	0.5376	0.0654	9.5754
9.73	5.55	6.33	0.78	0.4851	-0.0259	9.7041
10.00	5.60	6.47	0.87	0.4262	-0.1291	9.8709
10.23	5.65	6.62	0.99	0.3609	-0.2481	9.9819
10.49	5.70	6.80	1.10	0.2759	-0.4690	10.0210

Average pKa = 9.4923± 0.4410

Metal-ligand stability constant (Log K)

The stabilityconstants require the accurate values of proton-ligand stability constants (Anil and Maroti, 2008). Metal titration curves crossed over ligand titration curve indicated the formation of complex upon proton release (Santosh, *et al.*, 2011). If the values of n- are within range 0.2-0.8 and 1.2-18 this indicates the formation of 1:1 and 1:2 complexes (Sayyed and Mazahar, 2012).

The metal (II)-humate stepwise stability constants (log k) at phenolic group (Tables 3-18)

Table 3: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n}{1-n}$)	$LogK_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

$LogK_1$ (Average value) = 2.4788± 0.2203

Table 4: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	Log($\frac{n-1}{2-n}$)	$LogK_2$
9.51	5.50	6.66	6.73	0.07	1.3509	1.70	-0.2671	1.4329
9.73	5.55	6.78	6.85	0.07	1.6383	1.51	0.2467	1.7567
10.00	5.60	6.90	6.98	0.08	2.1783	1.31	-0.2158	1.0942
10.23	5.65	7.05	7.13	0.08	4.1904	1.27		
10.49	5.70	7.10	7.19	0.09	4.6920			

$LogK_2$(Average value) = 1.4280 ± 0.3312

Table 5:Point-wise method,Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$Log(\frac{n}{n-1})$	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430

$LogK_1$ **(Average value)** = 2.3059± 0.6153

Table 6:Point-wise method, Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$Log(\frac{n-1}{2-n})$	Log K_2
9.73	5.55	6.33	6.42	0.09	0.9000	1.69		
10.00	5.60	6.47	6.58	0.11	1.2578	1.44	-0.4592	0.9808
10.23	5.65	6.62	6.84	0.12	1.6137	1.26	-0.2010	1.4610
10.49	5.70	6.80	6.92	0.12	2.1052	1.03		

$LogK_2$ **(Average value)** = 1.2209± 0.3398

Table 7:Point-wise method,Pb (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$log(\frac{n}{1-n})$	$LogK_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.60	0.05	0.8333	1.96	0.6989	2.6589

$LogK_1$ (Average value) = 2.5832 ±0.1614

Table 8:Point-wise method,Pb-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$log(\frac{n-1}{2-n})$	$logK_2$
9.51	5.50	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.83	0.05	1.1702	1.44		
10.00	5.60	6.90	6.90	0.05	1.4864	1.22	-0.0237	1.1963
10.23	5.65	7.05	7.10	0.05	2.0190	1.09		
10.49	5.70	7.10	7.17	0.07	3.6492	1.00		

$LogK_2$(Average value) = 1.1963

Table 9:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log $(\frac{n}{n-1})$	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.5477	2.3123
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	0.0272	2.2072
9.51	5.50	6.20	6.26	0.07	0.6417	1.89	0.2530	2.1430
9.73	5.55	6.40	6.40	0.07	0.7000	1.67	0.3680	2.0380

$LogK_1$ **(Average value)** = 2.2364 ± 0.1602

Table 10:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$Log(\frac{n-1}{2-n})$	Log K_2
10.00	5.60	6.47	6.55	0.08	1.9503	1.41		
10.23	5.65	6.62	6.72	0.11	1.4792	1.26	-0.0361	1.2239

$LogK_2$ **(Average value)** = 1.2239

Table 11:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$log(\frac{n}{n-1})$	$LogK_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4290	2.2110
8.72	5.35	6.37	6.39	0.02	0.2858	2.42	-0.3978	2.0222
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

$LogK_1$ (Average value)=2.1382**±**0.1046

Table 12:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	$\log(\frac{n-1}{2-n})$	$LogK_2$
9.51	5.55	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.84	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.93	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.10		
10.49	5.70	7.10	7.18	0.07	3.6492	0.83		

$LogK_2$(Average value) = 1.5453 **±** 0.3450

Table 13:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$V_3\text{-}V_2$	n	pL	$Log(\frac{n}{n-1})$	$Log\ K_1$
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.3477	2.3123
9.00	5.40	6.00	6.04	0.04	0.3236	2.38	-0.3202	2.0598
9.22	5.45	6.10	6.15	0.05	0.4297	2.17	-0.1230	2.0470
9.51	5.50	6.20	6.26	0.06	0.5500	1.89	0.0871	1.9771
9.73	5.55	6.33	6.40	0.07	0.7000	1.67	0.3680	2.0380

$LogK_1$ **(Average value)** = 2.1568 ± 0.2069

Table 14:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$V_3\text{-}V_2$	n	pL	$Log(\frac{n-1}{2-n})$	$Log\ K_2$
10.00	5.60	6.47	6.55	0.08	0.9148	1.41		
10.23	5.65	6.62	6.71	0.09	1.2102	1.20	-0.5749	0.6251
10.49	5.70	6.80	6.92	0.09	1.5968	1.03	0.1703	1.2003

$LogK_2$ **(Average value)** = 0.9127± 0.4070

Table15:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	$Log(\frac{n}{1-n})$	$LogK_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4210	2.2190
8.72	5.35	6.37	6.40	0.03	0.4286	2.42	-0.1249	2.2951
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.96	0.3010	2.2610
9.51	5.55	6.66	6.70	0.04	0.7720	1.67	0.5297	2.1997

$LogK_1$ (Average value) = 2.2108± 0.0825

Table 16:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	$Log(\frac{n-1}{2-n})$	$Log\ K_2$
9.73	5.55	6.78	6.83	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.95	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.09		
10.49	5.70	7.10	7.16	0.06	3.1429	0.89		

$LogK_2$ **(Average value)** = 1.5453± 0.3450

Table 17:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$V_3\text{-}V_2$	n	pL	$Log(\frac{n}{n-1})$	$Log\ K_1$
8.50	5.30	5.81	5.86	0.05	0.3717	2.88	-0.2280	2.6520
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.06	0.06	0.4853	2.38	-0.0255	2.3545
9.22	5.45	6.10	6.16	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430
9.73	5.55	6.33	6.41	0.08	0.8000	1.69	0.6020	2.2920

$LogK_1$ **(Average value)** = 2.2516± 0.5380

Table 18:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$\text{Log}(\frac{n-1}{2-n})$	Log K_2
10.00	5.60	6.47	6.57	0.10	1.1434	1.43		
10.23	5.65	6.62	6.72	0.10	1.3448	1.23	-0.2788	0.9512
10.49	5.70	6.80	6.90	0.10	1.7742	1.03	0.5351	1.5651

LogK_2 **(Average value)** = 1.2581± 0.4340

Table 19: Stepwise and overall Stability constants of thehydrolysed and unhydrolysed divalent metal (II) complexes

Chelates	**LogK_1**	**LogK_2**	**Logβ**
[Cu (Hydrolysed PSHA-1)$_2$]	2.4788	1.4280	3.9068
[Pb (Hydrolysed PSHA-1)$_2$]	2.5832	1.1963	3.7795
[Cd (Hydrolysed PSHA-1)$_2$]	2.2108	1.5453	3.7561
[Mg (Hydrolysed PSHA-1)$_2$]	2.1382	1.5453	3.6835
[Cu (Unhydrolysed PSHA-1)$_2$]	2.3059	1.2209	3.5268
[Pb (Unhydrolysed PSHA-1)$_2$]	2.2364	1.2239	3.4603
[Cd (Unhydrolysed PSHA-1)$_2$]	2.2516	1.2581	3.5097
[Mg (Unydrolysed PSHA-1)$_2$]	2.1568	0.9127	3.0695

The results obtained (Table19) shows the stepwise and overall stability constants to be not high indicating low stability of the complexes, because the solubility of most metal ions in the basic pH range is minimal due to metal hydroxide precipitation (Karimi, 2017). In general, the stepwise stability constants (K_1 and K_2) follow the order $K_1 > K_2$ for the copper, lead, magnesium and cadmium complexes respectively. The steady decrease of the values with increasing number of ligands is in agreement with the prediction made by researchers (Na'aliya, 2013). The decrease could be attributed to the fact that as the number of the ligands (Humate ions) that enters the coordination zone increases the aqua molecules available for replacement by the ligands become less. Thus, the metal ions become less electron loving with progressive intake of the ligand and this results in the decrease in the values of the constants (Na'aliya, 2013). Also the stability of the complexes is influenced by the size and number of the chelate rings(Mackay and Mackay,2002).All the complexes form rings in their structure as humate, a bidentate ligand, bond the metal ions in the ratio 1:2 (Boguta and Sokolowska, 2016) forming chelate rings. The values of the overall stability constants (logβ) obtained for humate complexes are not high indicating low stability as the values are not high. LogK values for copper-humates (Table 3 to 6) obtained in this study are lower than those reported for the complexes of humic acids (Pandey *et al.*, 2015; Dinu, 2013; Kaschl *et al.*, 2010 and Gilbeto and Jorg, 2001). The values of LogK(Table 7 to 10) forlead-humates are lower than those reported for the lead in the literature (Dinu, 2013; Gilbeto and Jorg 2001). Log K values(Table 11 to 14) for magnesium-humates obtained in this study are close to those reported by (Pandey *et al.*, 2015). Log K values of cadmium-humates (Table 15 to 18) obtained in this work near to the one reported by (Dinu, 2013 and Pandey *et al.*, 2015).The difference between the reported values and the values obtained in this study might be probably as a result of acid hydrolysis of humic acid. The values of the overall stability constants (log β) of the copper humates complexes presented in Table 19 is high than that of other metal humate complexes, show relatively high stability of Cu-HA complexes, show the following order of stability: Cu >Pb> Cd > Mg; which are in close agreement to the findings of (Dinu, 2013 and Pandey *et al.*, 2015).The high stability of Cu-humate chelate could be attributed to the existence of coordinate covalent bond between the complexing agents and the Cu^{2+} ions. Since, Cu^{2+} being a metal of the transitional series with $3d^9$ electronic configurations can accept the electrons from the complexing agents. Similarly,the low stabilities of Pb,Cd and Mg -complexes could be explained by that Pb^{2+} with $6s^2$, Cd^{2+} with $4d^{10}$ and Mg^{2+} with $2p^6$ their electronic configuration has a completely filled d,p and s orbitals. Moreover, the stabilities of metal ions with hydrolysed humic acid from peat soil were higher than those with unhydrolysed humic acid from peat soil; which is ascribed to the high content of acidity in hydrolysed humic acid than unhydrolysed humic acid.

CONCLUSION

The values of logK for Cu(II) hydrolysed humic acid complex was higher followed by Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes as compared with metal(II) unhydrolysed humic acid complexes . This indicates acid hydrolysis of humic acid can enhance the complexation behavior of humic acid with metal (II) ions. However, the higher values of logβ for Cu(II), Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes indicates more stable stepwise complexes formed as compared with Cu(II), Pb(II), Cd(II) and Mg(II) unhydrolysed humic acid complexes.

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STABILITY CONSTANTS OF COMPLEXES OF METAL IONS WITH PEATSOIL HUMIC ACIDS UNDER NON-ACID-CONDITIONS

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ABSTRACT

Stability constants of complexes of four divalent metal ions viz. Cu^{2+}, Pb^{2+},Mg^{2+} and Cd^{2+} with humic acids (HA) were determined by potentiometric titration of humic acids with the corresponding salt of the divalent metals in aqueous media under non-acid-condition. The log K (logarithm of the stability constant) ranged from 1.0942 to 2.7471 for metal-humic acid complexes were determined using point-wise computational method. The order of stability constants were obtained as follows: Cu >Pb> Cd > Mg for metal -HA complexes respectively, indicating a higher degree of complexation with Cu metal ion.

Keywords: stability constant, humic acid, potentiometric titration, divalent metals, acid hydrolysis.

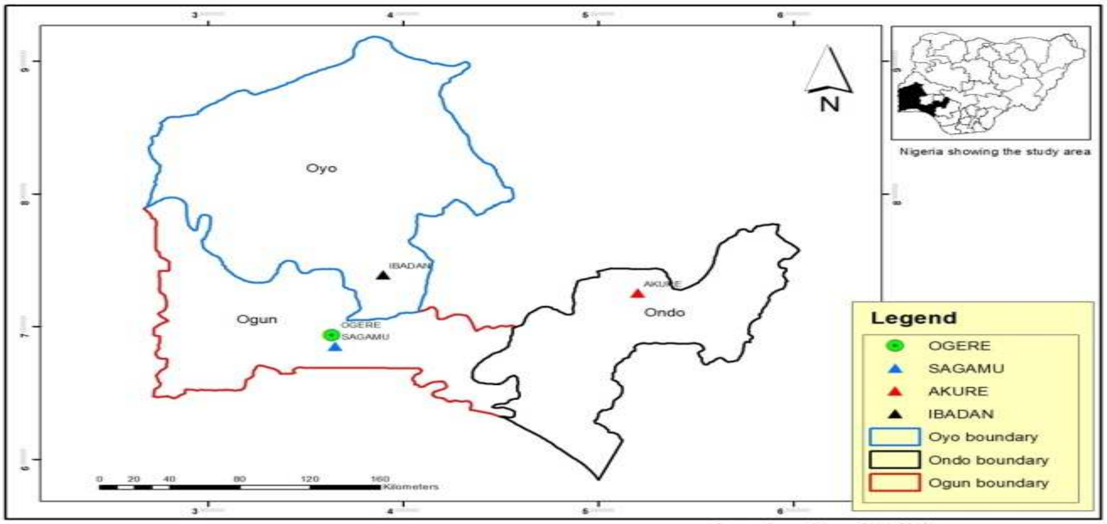
NTRODUCTION

The stability constant of a complex is the numerical expression of its stability and provides a quantitative measure of affinity of the metal ion to the complexing agent. An understanding of the relative stability of metal-complexes helps in predicting the behavior of metal ions in the soil (Ram and Raman, 1982). Extensive researches has been done to determine the stability constants of the complexes formed between humic acid (HA) with a number of metal ions. Ashok *et al*., (2000) reported that humic acid with hydroxyl, phenoxyl and carboxyl reactive groups can form coordination compound with metal ions at pH 3.5. The stability constants(Log K) for different metal-humic acid complexes indicated the following order of the stabilities of complexes formed between humic acid and metal ion, Cu >Fe >Pb> Ni > Co > Ca > Cd > Zn >Mn> Mg. Andelkovic *et al*., (2010) investigated the binding of Cd(II) to soil humic acid at pH 6.5 and in 0.1M KNO_3 ionic medium. The stability constant for binding indicating greater stability in the case when carboxyl groups are involved in complexation reaction. Kostic *et al*.,(2012) investigated the complexation of humic acid with certain heavy metal ions (Co(II), Ni(II),Cu(II), Zn(II), and Pb(II). The experiment was performed at 25°C, at pH 4.0 and ionic strength of 0.01M. Stability constant of complex between Pb(II) ions and humic acid is greater than stability constants of other investigated metal-humate complexes. Bogata and Sokolowska (2016) analyses the interaction between humic acids from different soils and Zn (II) ions at wide concentration ranges and at pH 5. Studies have showed significant impact of Zn concentration, pH and some properties of humic acids with zinc.But all of these studies were limited to acidic pH range. Therefore, the present study was carried out to determine and compare the stability constants of complexes of metal ions with hydrolysed peat soil humic acid and unhydrolysed peat soil humic under non-acid conditions.

MATERIALS AND METHODS

Analytical grade chemicals used includes hydrochloric acid (HCl), nitric acid (HNO_3), sodium hydroxide (NaOH), lead nitrate $Pb(NO_3)_2$, copper nitrate $Cu(NO_3)_2.3H_2O$, cadmium nitrate $Cd(NO_3)_2.4H_2O$, magnesium nitrate $Mg(NO_3)_2.6H_2O$, potassium nitrate (KNO_3), calcium chloride ($CaCl_2$), (sigma-Aldrich). Dowex 50WX8, (20-50 mesh) from Fluka.

Area of study



Source: Dept. of Geog. BUK (2016)

Figure 1: Map showing the sampling point at Sagamu Town, Ogun State.

Description of Sampling Area

Sagamu has geographical coordinates between 6°50′ north; 3° 38′ east is located in south western region of Nigeria. The region has tropical wet and dry climate with a lengthy wet season and relatively constant temperatures throughout the course of the year. Wet season runs from March to October, November to December forms the region dry season. The vegetation type of the region is savannah which is really grassland with small bushes and occasional big trees. Grassland soils have substantially higher organic matter content than forest soils (Novackova, 2011).

Sample Collection

The Peatsoil samples were collected from four different sampling points (0-10cm depth) in Sagamu into polyethylene bag with plastic spoons. Samples were taken to the laboratory, extraneous materials were removed; the samples were air-dried, crushed and ground to a fine powder in a mortar passed through a 0.20mm sieve. The samples were kept for analysis.

Isolation and purification of humic acid from peat soil sample

Peatsoil sample (100g) was mixed with 1000 cm^3 of 0.1M NaOH solution, shaken for 3hours and left to stand overnight. Dark-coloured supernatant was obtained and decanted from solid residue. The dark-coloured supernatant was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 6 hours. Yellowish brown supernatant and dark-brown precipitate were obtained. The yellowish brown supernatant was decanted followed by centrifuge and discarded. The dark-brown precipitate was mixed with 500$cm^3$of 0.1M NaOH solution followed by passing through dowex resin. The dark-brown solution was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 3 hours. The dark-brown precipitate was washed several times with deionized water. The supernatant was treated with $AgNO_3$ solution until no white precipitate observed. The humic acid was transferred to weighed crucible and dried at 60°C in an oven for 12 hours. The humic acid was cooled and dried in the desiccator, weighed and recorded. The obtained humic acid was dried again at 60°C for additional 6 hours cooled and dried in the desiccator, weighed and recorded constant weight was obtained (Baruah *et al*., 2015).

FT-IR analysis

FT-IR spectra of humic acid sample was analysed using Carry 630 FT-IR Agilent Technologies.

Unhydrolysed compost humic acid

The unhydrolysed humic acid was obtained after isolation and purification of compost humic acid and kept for investigation.

Acid hydrolysis of Peatsoil acid

Peatsoil humic acid sample (1g) was refluxed for 12 hours at (160°C) with 50cm^3 of 6M HCl. The mixture was allowed to cool, decanted, and centrifuged after hydrolysis. The insoluble residues were washed with distilled water via centrifugation several times, and the supernatant was treated with $AgNO_3$ solution until no white precipitate was observed. The residue was thoroughly dried over $CaCl_2$ in a desiccator at room temperature (Chefetz *et al*., 2002). Finally, the obtained hydrolysed humic acid was kept for investigation.

Potentiometric Titrations

Potentiometric measurements were carried out using a pH-meter Jenway (model 3510) with combine electrode, the sensitivity of the pH - meter is 0.01 units. The pH meter was switched on half an hour before starting the titration for initial warm up of the instrument. The instrument was calibrated with an aqueous standard buffer solution of pH 4.00 and 10.0 (borate buffer) prepared from a "Qualigens" buffer tablets.

The following sets of solutions were prepared in a 250cm^3 volumetric flask separately for pH metric titrations.

(i) 5 cm^3 0.1 M HCl + 40 cm^3 deionized water
(ii) 5 cm^3 0.1 M HCl + 39 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid
(iii) 5 cm^3 0.1 M HCl + 37 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid + 2 cm^3 0.01 M Cu(II)

The solutions were titrated against standardized 0.110MNaOH separately. The total volume of each mixture was adjusted to 50 cm^3 and the ionic strength of the solutions was maintained constant at by adding appropriate amount of stock solution of 1M KNO$_3$ (Gamal, 2015; Omar and Ali, 2015). A magnetic stirrer was used to achieve thorough mixing of the interacting solutions at 550 rpm. The same set of experimental conditions was applied for potentiometric titration of remaining samples.

Evaluation of pKa of Hydrolysed peat soil Humic Acids

The proton-ligand formation number n_A were calculated by Irving and Rossotti expression (Omar and Ali, 2015).

nA = Y- $\frac{(V2-V1)(No-Eo)}{(Vo+V1)TcL}$ ………………………………1

Where: Y is number of dissociable proton, (V_2-V_1) is the measure of displacement of the ligand curve relative to acid curve, N^o and E^o are the resultant concentration of alkali solution, free acid solution, $T_{cL}{}^o$ is the total ligand concentration, V^o is the total volume of titration solution,V_1 is the volume of alkali added to acid solution,V_2 is the volume of alkali added to acid solution + ligand solution, acid dissociation constants (pKa - values) of ligand were calculated by algebraic method point wise calculation (Tables 1). The dissociation constants (pKa) were calculated according to the following relation:

pKa = pH + log($\frac{nA}{1-nA}$) …………………………2

Where: pKa is the acid dissociation constant, $n_A$is the Proton-ligand formation number and pH is the pH-values (Omar and Ali, 2015).

Determination of metal-ligand stability constants (log K) of complexes

The potentiometric measurement for the determination of stability constant of a complex in solution is based on the fact that the redox potential of the couple $\frac{M^{+(m-n)}}{M^{+m}}$ is shifted significantly on complexation of the metal ion with the ligand. This method involves change in hydrogen ion concentration [H$^+$] due to the displacement or association of one or more protons taking place during complexation reaction. This change can be found out by titrating the solutions containing free acid, acid with ligand, and acid with ligand and metal ion, individually against a standard alkali solution at a constant ionic strength or temperature. Either ionic strength or temperature may be varied for different sets of solutions. In all the cases, the change in the pH of the solution is measured after each addition of a known amount of alkali to the reaction cell which contains the reaction mixture. The titration curves are then drawn by plotting the measured pH values against the corresponding volume of alkali added and the stability constants of the complexes are determined from the titration curves by employing pH-metric titration technique given by (Irving and Rossoti).

Metal-ligand stability constants (Log K) were determined by using the following relations:

$$\bar{n} = \frac{(V_3 - V_2)(E^0 + N^0)}{(V^0 + V_2)\bar{n}_A T_m^0} \quad \text{……………………………………………………………………3}$$

and

$$PL = \log_{10}\{\frac{1 + \beta_n^H \frac{1}{[anti\ \log \mathrm{pH}]^n}}{\mathrm{T}_\mathrm{L}^0 - \bar{n}T_m^0} \mathrm{X} \frac{(V^0 + V_3)}{V^0}\} \quad \text{…………………………………………………………4}$$

Where $T_{L,}$ T^{o}, E°, and V^{o}havethe same significance as in equation (1) above, T_m denotes the total concentration of metal present in solution, V_3 is the volume of metal ions present in solution and β^H is the overall proton ligand stability constant. The metal-ligand stability constants (log K) were determined by employing point wise computational Method (eq. 5 and 6).

$LogK_1 = \log\left(\frac{n}{1-n}\right) + pL$ 5

$LogK_2 = \log\left(\frac{1-n}{2-n}\right) + pL$.......................6

Where: Log K is the metal-ligand stability constant, pL is the Free ligand exponent function, **n** is the Average number of ligand attached with metal ion (Janrao*et al.*, 2014).The results obtained were analyzed by an ORIGIN 2016 program using titration data and then the proton-ligand stability constants (pKa) and Metal-ligand stability constant (LogK) calculated (Omar and Ali, 2015).

RESULTS AND DISCUSSION

Fourier transformed infrared (FT-IR) spectra of isolated humic acid from peat soils Figure 2 had distinct clear absorption bands indicating the presence of major humic acid structural elemental groups such as H bonded OH ($3680cm^{-1}$ peak), C=O of carbonyl ($1721cm^{-1}$ peak), functional groups of aliphatic components CH_2 ($2918cm^{-1}$ peak) and C-O stretching of polysaccharide ($1168cm^{-1}$ peak). The positions of the absorption bands of the spectra fell within typical major absorption bands of humic acid which is at frequencies 3680, 2918, 1721, 1168 cm^{-1}. The first peak centred in the vicinity of 3680 cm^{-1} region is attributed to phenol OH group bounded by intermolecular H bonds. The $2918cm^{-1}$ band usually has absorption maximum at 2918 cm^{-1} which is due to C–H stretching of alkane group (CH_2). The next major absorption band is 1721 cm^{-1}. This band has been commonly ascribed to C=O stretching of mainly carboxyl group (COOH) with trace amount of ketones. The last peak was observed at 1168 cm^{-1} due to C–O stretching of polysaccharides and this peak appeared also in the spectra of humic acid from peat soil. The FTIR spectra of the isolated humic acid contained all major characteristic absorption peaks of humic acid. These absorption peaks indicated the presence of the major structural elements of humic acid namely H bonded OH, C=C of aromatic ring, C=O of carbonyl group (both carboxyl and ketonic), CH_2 group. This strongly supports the presence of humic acid.

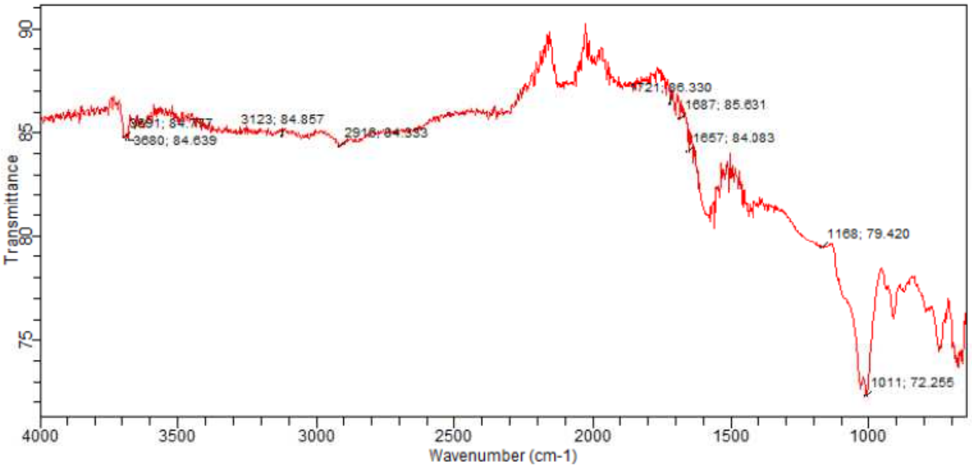


Fig. 2 : FT-IR spectraof peatsoilhumic acid (PSHA)

Evaluation of acid dissociation constant (pka) of acid hydrolysed peat soil humicacid at phenolic group

The value of the dissociation constant of the peat soil humic acid (PSHA) that underwent acidhydrolysis studied was found to be 8.9299 as shown Table 1, which is lower than the literaturevalues reported by Almeida and Szpoganics, (2015), Borges *et al.*, (2005); Badr *et al.*, (2012)and Fernandes *et al*,.(2009) of 9.73, 9.47 and 10.30. The difference between the obtained valuesand the reported values in this study might be probably as a result of acid hydrolysis of humicacid.

Table 1: PKa of (Hydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	$\log(\frac{nA}{1-nA})$	pKa
8.50	5.30	6.29	0.99	0.3594	-0.2510	8.2490
8.72	5.35	6.37	1.02	0.3400	-0.2880	8.4320
9.00	5.40	6.46	1.06	0.3141	-0.3391	8.6609
9.22	5.45	6.55	1.10	0.2882	-0.3927	8.8273
9.51	5.50	6.66	1.16	0.2494	-0.4786	9.0314
9.73	5.55	6.78	1.23	0.2041	-0.5910	9.1390
10.00	5.60	6.90	1.30	0.1589	-0.7238	9.2762
10.23	5.65	7.05	1.40	0.0941	-0.9835	9.2465
10.49	5.70	7.10	1.40	0.0941	-0.9835	9.5065

Average pKa = 8.9299 ± 0.4186

Table 2: PKa of (Unhydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	$\mathrm{Log}(\frac{nA}{1-n})$	pKa
8.50	5.30	5.81	0.51	0.6619	0.2919	8.7919
8.72	5.35	5.90	0.55	0.6357	0.2418	8.9618
9.00	5.40	6.00	0.60	0.6029	0.1813	9.1813
9.22	5.45	6.10	0.65	0.5701	0.1226	9.3426
9.51	5.50	6.20	0.70	0.5376	0.0654	9.5754
9.73	5.55	6.33	0.78	0.4851	-0.0259	9.7041
10.00	5.60	6.47	0.87	0.4262	-0.1291	9.8709
10.23	5.65	6.62	0.99	0.3609	-0.2481	9.9819
10.49	5.70	6.80	1.10	0.2759	-0.4690	10.0210

Average pKa = 9.4923± 0.4410

Metal-ligand stability constant (Log K)

The stabilityconstants require the accurate values of proton-ligand stability constants (Anil and Maroti, 2008). Metal titration curves crossed over ligand titration curve indicated the formation of complex upon proton release (Santosh, *et al.*, 2011). If the values of n- are within range 0.2-0.8 and 1.2-18 this indicates the formation of 1:1 and 1:2 complexes (Sayyed and Mazahar, 2012).

The metal (II)-humate stepwise stability constants (log k) at phenolic group (Tables 3-18)

Table 3: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$\log(\frac{n}{1-n})$	$\mathrm{Log}K_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

$\mathrm{LogK_1}$ (Average value) = 2.4788± 0.2203

Table 4: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$\mathrm{Log}(\frac{n-1}{2-n})$	$\mathrm{Log}K_2$
9.51	5.50	6.66	6.73	0.07	1.3509	1.70	-0.2671	1.4329
9.73	5.55	6.78	6.85	0.07	1.6383	1.51	0.2467	1.7567
10.00	5.60	6.90	6.98	0.08	2.1783	1.31	-0.2158	1.0942
10.23	5.65	7.05	7.13	0.08	4.1904	1.27		
10.49	5.70	7.10	7.19	0.09	4.6920			

$\mathrm{LogK_2}$(Average value) = 1.4280 ± 0.3312

Table 5:Point-wise method,Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	Log$(\frac{n}{n-1})$	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430

$LogK_1$ **(Average value)** = 2.3059± 0.6153

Table 6:Point-wise method, Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log$(\frac{n-1}{2-n})$	Log K_2
9.73	5.55	6.33	6.42	0.09	0.9000	1.69		
10.00	5.60	6.47	6.58	0.11	1.2578	1.44	-0.4592	0.9808
10.23	5.65	6.62	6.84	0.12	1.6137	1.26	-0.2010	1.4610
10.49	5.70	6.80	6.92	0.12	2.1052	1.03		

$LogK_2$ **(Average value)** = 1.2209± 0.3398

Table 7:Point-wise method,Pb (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log$(\frac{n}{1-n})$	$LogK_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.60	0.05	0.8333	1.96	0.6989	2.6589

$LogK_1$ (Average value) = 2.5832 ±0.1614

Table 8:Point-wise method,Pb-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log$(\frac{n-1}{2-n})$	$logK_2$
9.51	5.50	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.83	0.05	1.1702	1.44		
10.00	5.60	6.90	6.90	0.05	1.4864	1.22	-0.0237	1.1963
10.23	5.65	7.05	7.10	0.05	2.0190	1.09		
10.49	5.70	7.10	7.17	0.07	3.6492	1.00		

$LogK_2$(Average value) = 1.1963

Table 9:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log $(\frac{n}{n-1})$	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.5477	2.3123
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	0.0272	2.2072
9.51	5.50	6.20	6.26	0.07	0.6417	1.89	0.2530	2.1430
9.73	5.55	6.40	6.40	0.07	0.7000	1.67	0.3680	2.0380

$LogK_1$ **(Average value)** = 2.2364 ± 0.1602

Table 10:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log$(\frac{n-1}{2-n})$	Log K_2
10.00	5.60	6.47	6.55	0.08	1.9503	1.41		
10.23	5.65	6.62	6.72	0.11	1.4792	1.26	-0.0361	1.2239

$LogK_2$ **(Average value)** = 1.2239

Table 11:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log$(\frac{n}{n-1})$	$LogK_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4290	2.2110
8.72	5.35	6.37	6.39	0.02	0.2858	2.42	-0.3978	2.0222
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

$LogK_1$ (Average value)=2.1382±0.1046

Table 12:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$\log(\frac{n-1}{2-n})$	$LogK_2$
9.51	5.55	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.84	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.93	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.10		
10.49	5.70	7.10	7.18	0.07	3.6492	0.83		

$LogK_2$(Average value) = 1.5453 **±** 0.3450

Table 13:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$Log(\frac{n}{n-1})$	$Log K_1$
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.3477	2.3123
9.00	5.40	6.00	6.04	0.04	0.3236	2.38	-0.3202	2.0598
9.22	5.45	6.10	6.15	0.05	0.4297	2.17	-0.1230	2.0470
9.51	5.50	6.20	6.26	0.06	0.5500	1.89	0.0871	1.9771
9.73	5.55	6.33	6.40	0.07	0.7000	1.67	0.3680	2.0380

$LogK_1$ **(Average value)** = 2.1568 ± 0.2069

Table 14:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$Log(\frac{n-1}{2-n})$	$Log K_2$
10.00	5.60	6.47	6.55	0.08	0.9148	1.41		
10.23	5.65	6.62	6.71	0.09	1.2102	1.20	-0.5749	0.6251
10.49	5.70	6.80	6.92	0.09	1.5968	1.03	0.1703	1.2003

$LogK_2$ **(Average value)** = 0.9127± 0.4070

Table15:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$Log(\frac{n}{1-n})$	$LogK_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4210	2.2190
8.72	5.35	6.37	6.40	0.03	0.4286	2.42	-0.1249	2.2951
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.96	0.3010	2.2610
9.51	5.55	6.66	6.70	0.04	0.7720	1.67	0.5297	2.1997

$LogK_1$ (Average value) = 2.2108± 0.0825

Table 16:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$Log(\frac{n-1}{2-n})$	$Log K_2$
9.73	5.55	6.78	6.83	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.95	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.09		
10.49	5.70	7.10	7.16	0.06	3.1429	0.89		

$LogK_2$ **(Average value)** = 1.5453± 0.3450

Table 17:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$Log(\frac{n}{n-1})$	$Log K_1$
8.50	5.30	5.81	5.86	0.05	0.3717	2.88	-0.2280	2.6520
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.06	0.06	0.4853	2.38	-0.0255	2.3545
9.22	5.45	6.10	6.16	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430
9.73	5.55	6.33	6.41	0.08	0.8000	1.69	0.6020	2.2920

$LogK_1$ **(Average value)** = 2.2516± 0.5380

Table 18:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$\text{Log}(\frac{n-1}{2-n})$	Log K_2
10.00	5.60	6.47	6.57	0.10	1.1434	1.43		
10.23	5.65	6.62	6.72	0.10	1.3448	1.23	-0.2788	0.9512
10.49	5.70	6.80	6.90	0.10	1.7742	1.03	0.5351	1.5651

LogK_2 **(Average value)** = 1.2581± 0.4340

Table 19: Stepwise and overall Stability constants of thehydrolysed and unhydrolysed divalent metal (II) complexes

Chelates	**LogK_1**	**LogK_2**	**Logβ**
[Cu (Hydrolysed PSHA-1)$_2$]	2.4788	1.4280	3.9068
[Pb (Hydrolysed PSHA-1)$_2$]	2.5832	1.1963	3.7795
[Cd (Hydrolysed PSHA-1)$_2$]	2.2108	1.5453	3.7561
[Mg (Hydrolysed PSHA-1)$_2$]	2.1382	1.5453	3.6835
[Cu (Unhydrolysed PSHA-1)$_2$]	2.3059	1.2209	3.5268
[Pb (Unhydrolysed PSHA-1)$_2$]	2.2364	1.2239	3.4603
[Cd (Unhydrolysed PSHA-1)$_2$]	2.2516	1.2581	3.5097
[Mg (Unydrolysed PSHA-1)$_2$]	2.1568	0.9127	3.0695

The results obtained (Table19) shows the stepwise and overall stability constants to be not high indicating low stability of the complexes, because the solubility of most metal ions in the basic pH range is minimal due to metal hydroxide precipitation (Karimi, 2017). In general, the stepwise stability constants (K_1 and K_2) follow the order $K_1 > K_2$ for the copper, lead, magnesium and cadmium complexes respectively. The steady decrease of the values with increasing number of ligands is in agreement with the prediction made by researchers (Na'aliya, 2013). The decrease could be attributed to the fact that as the number of the ligands (Humate ions) that enters the coordination zone increases the aqua molecules available for replacement by the ligands become less. Thus, the metal ions become less electron loving with progressive intake of the ligand and this results in the decrease in the values of the constants (Na'aliya, 2013). Also the stability of the complexes is influenced by the size and number of the chelate rings(Mackay and Mackay,2002).All the complexes form rings in their structure as humate, a bidentate ligand, bond the metal ions in the ratio 1:2 (Boguta and Sokolowska, 2016) forming chelate rings. The values of the overall stability constants (logβ) obtained for humate complexes are not high indicating low stability as the values are not high. LogK values for copper-humates (Table 3 to 6) obtained in this study are lower than those reported for the complexes of humic acids (Pandey *et al*., 2015; Dinu, 2013; Kaschl *et al*., 2010 and Gilbeto and Jorg, 2001). The values of LogK(Table 7 to 10) forlead-humates are lower than those reported for the lead in the literature (Dinu, 2013; Gilbeto and Jorg 2001). Log K values(Table 11 to 14) for magnesium-humates obtained in this study are close to those reported by (Pandey *et al*., 2015). Log K values of cadmium-humates (Table 15 to 18) obtained in this work near to the one reported by (Dinu, 2013 and Pandey *et al*., 2015).The difference between the reported values and the values obtained in this study might be probably as a result of acid hydrolysis of humic acid. The values of the overall stability constants (log β) of the copper humates complexes presented in Table 19 is high than that of other metal humate complexes, show relatively high stability of Cu-HA complexes, show the following order of stability: Cu >Pb> Cd > Mg; which are in close agreement to the findings of (Dinu, 2013 and Pandey *et al*., 2015).The high stability of Cu-humate chelate could be attributed to the existence of coordinate covalent bond between the complexing agents and the Cu^{2+} ions. Since, Cu^{2+} being a metal of the transitional series with $3d^9$ electronic configurations can accept the electrons from the complexing agents. Similarly,the low stabilities of Pb,Cd and Mg -complexes could be explained by that Pb^{2+} with $6s^2$, Cd^{2+} with $4d^{10}$ and Mg^{2+} with $2p^6$ their electronic configuration has a completely filled d,p and s orbitals. Moreover, the stabilities of metal ions with hydrolysed humic acid from peat soil were higher than those with unhydrolysed humic acid from peat soil; which is ascribed to the high content of acidity in hydrolysed humic acid than unhydrolysed humic acid.

CONCLUSION

The values of logK for Cu(II) hydrolysed humic acid complex was higher followed by Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes as compared with metal(II) unhydrolysed humic acid complexes . This indicates acid hydrolysis of humic acid can enhance the complexation behavior of humic acid with metal (II) ions. However, the higher values of logβ for Cu(II), Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes indicates more stable stepwise complexes formed as compared with Cu(II), Pb(II), Cd(II) and Mg(II) unhydrolysed humic acid complexes.

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STABILITY CONSTANTS OF COMPLEXES OF METAL IONS WITH PEATSOIL HUMIC ACIDS UNDER NON-ACID-CONDITIONS

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ABSTRACT

Stability constants of complexes of four divalent metal ions viz. Cu^{2+}, Pb^{2+},Mg^{2+} and Cd^{2+} with humic acids (HA) were determined by potentiometric titration of humic acids with the corresponding salt of the divalent metals in aqueous media under non-acid-condition. The log K (logarithm of the stability constant) ranged from 1.0942 to 2.7471 for metal-humic acid complexes were determined using point-wise computational method. The order of stability constants were obtained as follows: Cu >Pb> Cd > Mg for metal -HA complexes respectively, indicating a higher degree of complexation with Cu metal ion.

Keywords: stability constant, humic acid, potentiometric titration, divalent metals, acid hydrolysis.

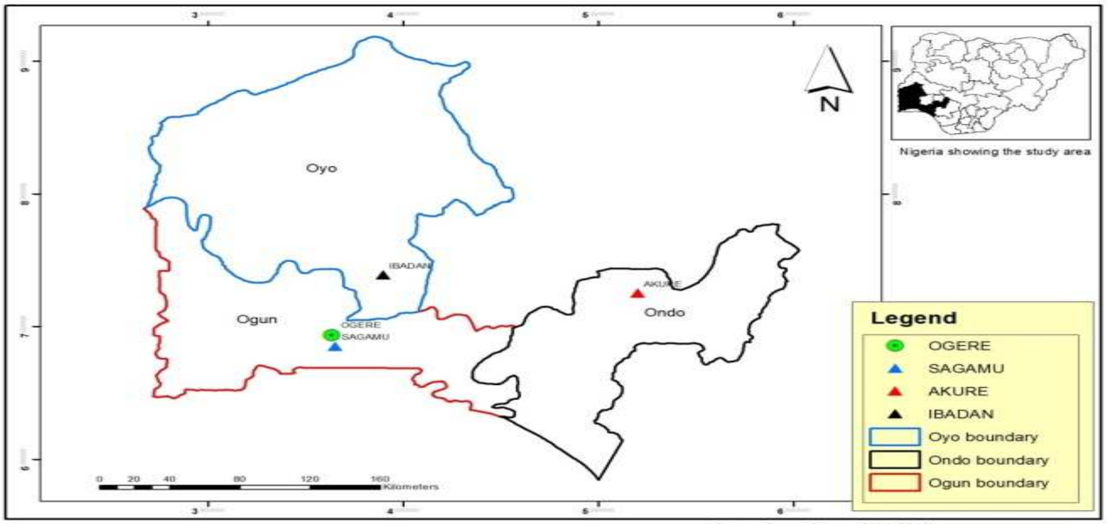
NTRODUCTION

The stability constant of a complex is the numerical expression of its stability and provides a quantitative measure of affinity of the metal ion to the complexing agent. An understanding of the relative stability of metal-complexes helps in predicting the behavior of metal ions in the soil (Ram and Raman, 1982). Extensive researches has been done to determine the stability constants of the complexes formed between humic acid (HA) with a number of metal ions. Ashok *et al*., (2000) reported that humic acid with hydroxyl, phenoxyl and carboxyl reactive groups can form coordination compound with metal ions at pH 3.5. The stability constants(Log K) for different metal-humic acid complexes indicated the following order of the stabilities of complexes formed between humic acid and metal ion, Cu >Fe >Pb> Ni > Co > Ca > Cd > Zn >Mn> Mg. Andelkovic *et al*., (2010) investigated the binding of Cd(II) to soil humic acid at pH 6.5 and in 0.1M KNO_3 ionic medium. The stability constant for binding indicating greater stability in the case when carboxyl groups are involved in complexation reaction. Kostic *et al*.,(2012) investigated the complexation of humic acid with certain heavy metal ions (Co(II), Ni(II),Cu(II), Zn(II), and Pb(II). The experiment was performed at 25^oC, at pH 4.0 and ionic strength of 0.01M. Stability constant of complex between Pb(II) ions and humic acid is greater than stability constants of other investigated metal-humate complexes. Bogata and Sokolowska (2016) analyses the interaction between humic acids from different soils and Zn (II) ions at wide concentration ranges and at pH 5. Studies have showed significant impact of Zn concentration, pH and some properties of humic acids with zinc.But all of these studies were limited to acidic pH range. Therefore, the present study was carried out to determine and compare the stability constants of complexes of metal ions with hydrolysed peat soil humic acid and unhydrolysed peat soil humic under non-acid conditions.

MATERIALS AND METHODS

Analytical grade chemicals used includes hydrochloric acid (HCl), nitric acid (HNO_3), sodium hydroxide (NaOH), lead nitrate $Pb(NO_3)_2$, copper nitrate $Cu(NO_3)_2.3H_2O$, cadmium nitrate $Cd(NO_3)_2.4H_2O$, magnesium nitrate $Mg(NO_3)_2.6H_2O$, potassium nitrate (KNO_3), calcium chloride ($CaCl_2$), (sigma-Aldrich). Dowex 50WX8, (20-50 mesh) from Fluka.

Area of study



Source: Dept. of Geog. BUK (2016)

Figure 1: Map showing the sampling point at Sagamu Town, Ogun State.

Description of Sampling Area

Sagamu has geographical coordinates between 6°50′ north; 3° 38′ east is located in south western region of Nigeria. The region has tropical wet and dry climate with a lengthy wet season and relatively constant temperatures throughout the course of the year. Wet season runs from March to October, November to December forms the region dry season. The vegetation type of the region is savannah which is really grassland with small bushes and occasional big trees. Grassland soils have substantially higher organic matter content than forest soils (Novackova, 2011).

Sample Collection

The Peatsoil samples were collected from four different sampling points (0-10cm depth) in Sagamu into polyethylene bag with plastic spoons. Samples were taken to the laboratory, extraneous materials were removed; the samples were air-dried, crushed and ground to a fine powder in a mortar passed through a 0.20mm sieve. The samples were kept for analysis.

Isolation and purification of humic acid from peat soil sample

Peatsoil sample (100g) was mixed with 1000 cm^3 of 0.1M NaOH solution, shaken for 3hours and left to stand overnight. Dark-coloured supernatant was obtained and decanted from solid residue. The dark-coloured supernatant was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 6 hours. Yellowish brown supernatant and dark-brown precipitate were obtained. The yellowish brown supernatant was decanted followed by centrifuge and discarded. The dark-brown precipitate was mixed with $500cm^3$of 0.1M NaOH solution followed by passing through dowex resin. The dark-brown solution was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 3 hours. The dark-brown precipitate was washed several times with deionized water. The supernatant was treated with $AgNO_3$ solution until no white precipitate observed. The humic acid was transferred to weighed crucible and dried at 60°C in an oven for 12 hours. The humic acid was cooled and dried in the desiccator, weighed and recorded. The obtained humic acid was dried again at 60°C for additional 6 hours cooled and dried in the desiccator, weighed and recorded constant weight was obtained (Baruah *et al*., 2015).

FT-IR analysis

FT-IR spectra of humic acid sample was analysed using Carry 630 FT-IR Agilent Technologies.

Unhydrolysed compost humic acid

The unhydrolysed humic acid was obtained after isolation and purification of compost humic acid and kept for investigation.

Acid hydrolysis of Peatsoil acid

Peatsoil humic acid sample (1g) was refluxed for 12 hours at (160°C) with $50cm^3$ of 6M HCl. The mixture was allowed to cool, decanted, and centrifuged after hydrolysis. The insoluble residues were washed with distilled water via centrifugation several times, and the supernatant was treated with $AgNO_3$ solution until no white precipitate was observed. The residue was thoroughly dried over $CaCl_2$ in a desiccator at room temperature (Chefetz *et al*., 2002). Finally, the obtained hydrolysed humic acid was kept for investigation.

Potentiometric Titrations

Potentiometric measurements were carried out using a pH-meter Jenway (model 3510) with combine electrode, the sensitivity of the pH - meter is 0.01 units. The pH meter was switched on half an hour before starting the titration for initial warm up of the instrument. The instrument was calibrated with an aqueous standard buffer solution of pH 4.00 and 10.0 (borate buffer) prepared from a "Qualigens" buffer tablets.

The following sets of solutions were prepared in a 250cm^3 volumetric flask separately for pH metric titrations.

(i) 5 cm^3 0.1 M HCl + 40 cm^3 deionized water

(ii) 5 cm^3 0.1 M HCl + 39 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid

(iii) 5 cm^3 0.1 M HCl + 37 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid + 2 cm^3 0.01 M Cu(II)

The solutions were titrated against standardized 0.110MNaOH separately. The total volume of each mixture was adjusted to 50 cm^3 and the ionic strength of the solutions was maintained constant at by adding appropriate amount of stock solution of 1M KNO_3 (Gamal, 2015; Omar and Ali, 2015). A magnetic stirrer was used to achieve thorough mixing of the interacting solutions at 550 rpm. The same set of experimental conditions was applied for potentiometric titration of remaining samples.

Evaluation of pKa of Hydrolysed peat soil Humic Acids

The proton-ligand formation number n_A were calculated by Irving and Rossotti expression (Omar and Ali, 2015).

$$nA = Y- \frac{(V2-V1)(No-Eo)}{(Vo+V1)TcL} \qquad \text{...................................1}$$

Where: Y is number of dissociable proton, (V_2-V_1) is the measure of displacement of the ligand curve relative to acid curve, N^o and E^o are the resultant concentration of alkali solution, free acid solution, $T_{cL}{}^o$ is the total ligand concentration, V^o is the total volume of titration solution,V_1 is the volume of alkali added to acid solution,V_2 is the volume of alkali added to acid solution + ligand solution, acid dissociation constants (pKa - values) of ligand were calculated by algebraic method point wise calculation (Tables 1). The dissociation constants (pKa) were calculated according to the following relation:

$$pKa = pH + \log(\frac{nA}{1-nA}) \qquad \text{.............................2}$$

Where: pKa is the acid dissociation constant, $n_A$is the Proton-ligand formation number and pH is the pH-values (Omar and Ali, 2015).

Determination of metal-ligand stability constants (log K) of complexes

The potentiometric measurement for the determination of stability constant of a complex in solution is based on the fact that the redox potential of the couple $\frac{M^{+(m-n)}}{M^{+m}}$ is shifted significantly on complexation of the metal ion with the ligand. This method involves change in hydrogen ion concentration [H$^+$] due to the displacement or association of one or more protons taking place during complexation reaction. This change can be found out by titrating the solutions containing free acid, acid with ligand, and acid with ligand and metal ion, individually against a standard alkali solution at a constant ionic strength or temperature. Either ionic strength or temperature may be varied for different sets of solutions. In all the cases, the change in the pH of the solution is measured after each addition of a known amount of alkali to the reaction cell which contains the reaction mixture. The titration curves are then drawn by plotting the measured pH values against the corresponding volume of alkali added and the stability constants of the complexes are determined from the titration curves by employing pH-metric titration technique given by (Irving and Rossoti).

Metal-ligand stability constants (Log K) were determined by using the following relations:

$$\bar{n} = \frac{(V_3 - V_2)(E^0 + N^0)}{(V^0 + V_2)\bar{n}_A T_m^0} \qquad \text{..3}$$

and

$$PL = \log_{10}\{\frac{1 + \beta_n^H \frac{1}{[anti\ \log pH]^n}}{T_L^0 - \bar{n}T_m^0} X \frac{(V^0 + V_3)}{V^0}\} \qquad \text{..4}$$

Where $T_{L,}$ T^{o}, E°, and V^{o}havethe same significance as in equation (1) above, T_m denotes the total concentration of metal present in solution, V_3 is the volume of metal ions present in solution and β^H is the overall proton ligand stability constant. The metal-ligand stability constants (log K) were determined by employing point wise computational Method (eq. 5 and 6).

$$\text{LogK}_1 = \log\left(\frac{n}{1-n}\right) + \text{pL} \quad \ldots\ldots\ldots\ldots.5$$

$$\text{LogK}_2 = \log\left(\frac{1-n}{2-n}\right) + \text{pL}\ldots\ldots\ldots\ldots\ldots\ldots\ldots.6$$

Where: Log K is the metal-ligand stability constant, pL is the Free ligand exponent function, **n** is the Average number of ligand attached with metal ion (Janrao*et al*., 2014).The results obtained were analyzed by an ORIGIN 2016 program using titration data and then the proton-ligand stability constants (pKa) and Metal-ligand stability constant (LogK) calculated (Omar and Ali, 2015).

RESULTS AND DISCUSSION

Fourier transformed infrared (FT-IR) spectra of isolated humic acid from peat soils Figure 2 had distinct clear absorption bands indicating the presence of major humic acid structural elemental groups such as H bonded OH ($3680cm^{-1}$ peak), C=O of carbonyl ($1721cm^{-1}$ peak), functional groups of aliphatic components CH_2 ($2918cm^{-1}$ peak) and C-O stretching of polysaccharide ($1168cm^{-1}$ peak). The positions of the absorption bands of the spectra fell within typical major absorption bands of humic acid which is at frequencies 3680, 2918, 1721, 1168 cm^{-1}. The first peak centred in the vicinity of 3680 cm^{-1} region is attributed to phenol OH group bounded by intermolecular H bonds. The $2918cm^{-1}$ band usually has absorption maximum at 2918 cm^{-1} which is due to C–H stretching of alkane group (CH_2). The next major absorption band is 1721 cm^{-1}. This band has been commonly ascribed to C=O stretching of mainly carboxyl group (COOH) with trace amount of ketones. The last peak was observed at 1168 cm^{-1} due to C–O stretching of polysaccharides and this peak appeared also in the spectra of humic acid from peat soil. The FTIR spectra of the isolated humic acid contained all major characteristic absorption peaks of humic acid. These absorption peaks indicated the presence of the major structural elements of humic acid namely H bonded OH, C=C of aromatic ring, C=O of carbonyl group (both carboxyl and ketonic), CH_2 group. This strongly supports the presence of humic acid.

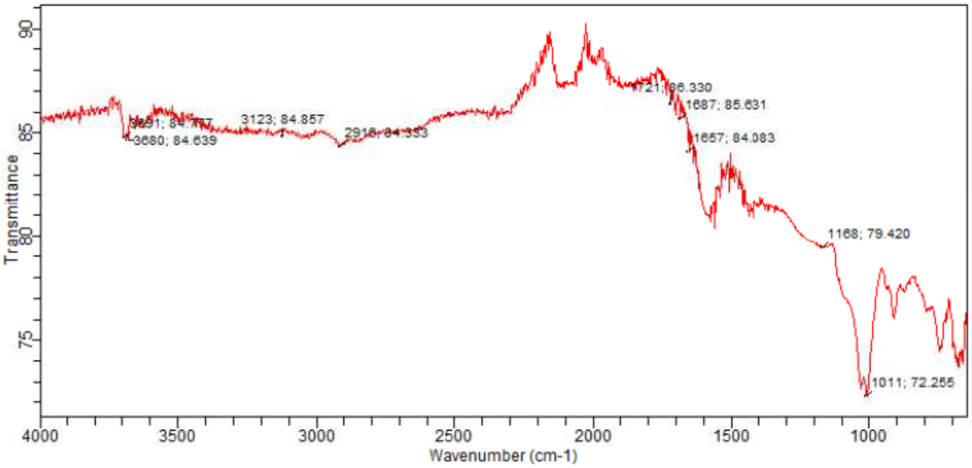


Fig. 2 : FT-IR spectraof peatsoilhumic acid (PSHA)

Evaluation of acid dissociation constant (pka) of acid hydrolysed peat soil humicacid at phenolic group

The value of the dissociation constant of the peat soil humic acid (PSHA) that underwent acidhydrolysis studied was found to be 8.9299 as shown Table 1, which is lower than the literaturevalues reported by Almeida and Szpoganics, (2015), Borges *et al*., (2005); Badr *et al*., (2012)and Fernandes *et al*,.(2009) of 9.73, 9.47 and 10.30. The difference between the obtained valuesand the reported values in this study might be probably as a result of acid hydrolysis of humicacid.

Table 1: PKa of (Hydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	$\log(\frac{nA}{1-nA})$	pKa
8.50	5.30	6.29	0.99	0.3594	-0.2510	8.2490
8.72	5.35	6.37	1.02	0.3400	-0.2880	8.4320
9.00	5.40	6.46	1.06	0.3141	-0.3391	8.6609
9.22	5.45	6.55	1.10	0.2882	-0.3927	8.8273
9.51	5.50	6.66	1.16	0.2494	-0.4786	9.0314
9.73	5.55	6.78	1.23	0.2041	-0.5910	9.1390
10.00	5.60	6.90	1.30	0.1589	-0.7238	9.2762
10.23	5.65	7.05	1.40	0.0941	-0.9835	9.2465
10.49	5.70	7.10	1.40	0.0941	-0.9835	9.5065

Average pKa = 8.9299 ± 0.4186

Table 2: PKa of (Unhydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	$\text{Log}(\frac{nA}{1-n})$	pKa
8.50	5.30	5.81	0.51	0.6619	0.2919	8.7919
8.72	5.35	5.90	0.55	0.6357	0.2418	8.9618
9.00	5.40	6.00	0.60	0.6029	0.1813	9.1813
9.22	5.45	6.10	0.65	0.5701	0.1226	9.3426
9.51	5.50	6.20	0.70	0.5376	0.0654	9.5754
9.73	5.55	6.33	0.78	0.4851	-0.0259	9.7041
10.00	5.60	6.47	0.87	0.4262	-0.1291	9.8709
10.23	5.65	6.62	0.99	0.3609	-0.2481	9.9819
10.49	5.70	6.80	1.10	0.2759	-0.4690	10.0210

Average pKa = 9.4923± 0.4410

Metal-ligand stability constant (Log K)

The stabilityconstants require the accurate values of proton-ligand stability constants (Anil and Maroti, 2008). Metal titration curves crossed over ligand titration curve indicated the formation of complex upon proton release (Santosh, *et al.*, 2011). If the values of n- are within range 0.2-0.8 and 1.2-18 this indicates the formation of 1:1 and 1:2 complexes (Sayyed and Mazahar, 2012).

The metal (II)-humate stepwise stability constants (log k) at phenolic group (Tables 3-18)

Table 3: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$\log(\frac{n}{1-n})$	LogK_1
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

LogK_1 (Average value) = 2.4788± 0.2203

Table 4: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$\text{Log}(\frac{n-1}{2-n})$	LogK_2
9.51	5.50	6.66	6.73	0.07	1.3509	1.70	-0.2671	1.4329
9.73	5.55	6.78	6.85	0.07	1.6383	1.51	0.2467	1.7567
10.00	5.60	6.90	6.98	0.08	2.1783	1.31	-0.2158	1.0942
10.23	5.65	7.05	7.13	0.08	4.1904	1.27		
10.49	5.70	7.10	7.19	0.09	4.6920			

LogK_2(Average value) = 1.4280 ± 0.3312

Table 5:Point-wise method,Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	$\text{Log}(\frac{n}{n-1})$	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430

LogK_1 **(Average value)** = 2.3059± 0.6153

Table 6:Point-wise method, Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$V_3\text{-}V_2$	n	pL	$\text{Log}(\frac{n-1}{2-n})$	Log K_2
9.73	5.55	6.33	6.42	0.09	0.9000	1.69		
10.00	5.60	6.47	6.58	0.11	1.2578	1.44	-0.4592	0.9808
10.23	5.65	6.62	6.84	0.12	1.6137	1.26	-0.2010	1.4610
10.49	5.70	6.80	6.92	0.12	2.1052	1.03		

LogK_2 **(Average value)** = 1.2209± 0.3398

Table 7:Point-wise method,Pb (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	$\log(\frac{n}{1-n})$	LogK_1
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.60	0.05	0.8333	1.96	0.6989	2.6589

$\textbf{LogK}_1$ **(Average value)** = 2.5832 ±0.1614

Table 8:Point-wise method,Pb-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	$\log(\frac{n-1}{2-n})$	logK_2
9.51	5.50	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.83	0.05	1.1702	1.44		
10.00	5.60	6.90	6.90	0.05	1.4864	1.22	-0.0237	1.1963
10.23	5.65	7.05	7.10	0.05	2.0190	1.09		
10.49	5.70	7.10	7.17	0.07	3.6492	1.00		

$\textbf{LogK}_2$**(Average value)** = 1.1963

Table 9:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$V_3\text{-}V_2$	n	pL	Log $(\frac{n}{n-1})$	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.5477	2.3123
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	0.0272	2.2072
9.51	5.50	6.20	6.26	0.07	0.6417	1.89	0.2530	2.1430
9.73	5.55	6.40	6.40	0.07	0.7000	1.67	0.3680	2.0380

LogK_1 **(Average value)** = 2.2364 ± 0.1602

Table 10:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$V_3\text{-}V_2$	n	pL	$\text{Log}(\frac{n-1}{2-n})$	Log K_2
10.00	5.60	6.47	6.55	0.08	1.9503	1.41		
10.23	5.65	6.62	6.72	0.11	1.4792	1.26	-0.0361	1.2239

LogK_2 **(Average value)** = 1.2239

Table 11:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	$\log(\frac{n}{n-1})$	LogK_1
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4290	2.2110
8.72	5.35	6.37	6.39	0.02	0.2858	2.42	-0.3978	2.0222
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

$\textbf{LogK}_1$ **(Average value)=**2.1382**±**0.1046

Table 12:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	$\log(\frac{n-1}{2-n})$	$\log K_2$
9.51	5.55	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.84	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.93	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.10		
10.49	5.70	7.10	7.18	0.07	3.6492	0.83		

$\log K_2$(Average value) = 1.5453 **±** 0.3450

Table 13:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$V_3\text{-}V_2$	n	pL	$\log(\frac{n}{n-1})$	$\log K_1$
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.3477	2.3123
9.00	5.40	6.00	6.04	0.04	0.3236	2.38	-0.3202	2.0598
9.22	5.45	6.10	6.15	0.05	0.4297	2.17	-0.1230	2.0470
9.51	5.50	6.20	6.26	0.06	0.5500	1.89	0.0871	1.9771
9.73	5.55	6.33	6.40	0.07	0.7000	1.67	0.3680	2.0380

$\log K_1$ **(Average value)** = 2.1568 ± 0.2069

Table 14:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$V_3\text{-}V_2$	n	pL	$\log(\frac{n-1}{2-n})$	$\log K_2$
10.00	5.60	6.47	6.55	0.08	0.9148	1.41		
10.23	5.65	6.62	6.71	0.09	1.2102	1.20	-0.5749	0.6251
10.49	5.70	6.80	6.92	0.09	1.5968	1.03	0.1703	1.2003

$\log K_2$ **(Average value)** = 0.9127± 0.4070

Table15:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	$\log(\frac{n}{1-n})$	$\log K_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4210	2.2190
8.72	5.35	6.37	6.40	0.03	0.4286	2.42	-0.1249	2.2951
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.96	0.3010	2.2610
9.51	5.55	6.66	6.70	0.04	0.7720	1.67	0.5297	2.1997

$\log K_1$ (Average value) = 2.2108± 0.0825

Table 16:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	$\log(\frac{n-1}{2-n})$	$\log K_2$
9.73	5.55	6.78	6.83	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.95	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.09		
10.49	5.70	7.10	7.16	0.06	3.1429	0.89		

$\log K_2$ **(Average value)** = 1.5453± 0.3450

Table 17:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$V_3\text{-}V_2$	n	pL	$\log(\frac{n}{n-1})$	$\log K_1$
8.50	5.30	5.81	5.86	0.05	0.3717	2.88	-0.2280	2.6520
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.06	0.06	0.4853	2.38	-0.0255	2.3545
9.22	5.45	6.10	6.16	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430
9.73	5.55	6.33	6.41	0.08	0.8000	1.69	0.6020	2.2920

$\log K_1$ **(Average value)** = 2.2516± 0.5380

Table 18:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$Log(\frac{n-1}{2-n})$	Log K_2
10.00	5.60	6.47	6.57	0.10	1.1434	1.43		
10.23	5.65	6.62	6.72	0.10	1.3448	1.23	-0.2788	0.9512
10.49	5.70	6.80	6.90	0.10	1.7742	1.03	0.5351	1.5651

$LogK_2$ **(Average value)** = 1.2581± 0.4340

Table 19: Stepwise and overall Stability constants of thehydrolysed and unhydrolysed divalent metal (II) complexes

Chelates	**$LogK_1$**	**$LogK_2$**	**Logβ**
[Cu (Hydrolysed PSHA-1)$_2$]	2.4788	1.4280	3.9068
[Pb (Hydrolysed PSHA-1)$_2$]	2.5832	1.1963	3.7795
[Cd (Hydrolysed PSHA-1)$_2$]	2.2108	1.5453	3.7561
[Mg (Hydrolysed PSHA-1)$_2$]	2.1382	1.5453	3.6835
[Cu (Unhydrolysed PSHA-1)$_2$]	2.3059	1.2209	3.5268
[Pb (Unhydrolysed PSHA-1)$_2$]	2.2364	1.2239	3.4603
[Cd (Unhydrolysed PSHA-1)$_2$]	2.2516	1.2581	3.5097
[Mg (Unydrolysed PSHA-1)$_2$]	2.1568	0.9127	3.0695

The results obtained (Table19) shows the stepwise and overall stability constants to be not high indicating low stability of the complexes, because the solubility of most metal ions in the basic pH range is minimal due to metal hydroxide precipitation (Karimi, 2017). In general, the stepwise stability constants (K_1 and K_2) follow the order $K_1 > K_2$ for the copper, lead, magnesium and cadmium complexes respectively. The steady decrease of the values with increasing number of ligands is in agreement with the prediction made by researchers (Na'aliya, 2013). The decrease could be attributed to the fact that as the number of the ligands (Humate ions) that enters the coordination zone increases the aqua molecules available for replacement by the ligands become less. Thus, the metal ions become less electron loving with progressive intake of the ligand and this results in the decrease in the values of the constants (Na'aliya, 2013). Also the stability of the complexes is influenced by the size and number of the chelate rings(Mackay and Mackay,2002).All the complexes form rings in their structure as humate, a bidentate ligand, bond the metal ions in the ratio 1:2 (Boguta and Sokolowska, 2016) forming chelate rings. The values of the overall stability constants (logβ) obtained for humate complexes are not high indicating low stability as the values are not high. LogK values for copper-humates (Table 3 to 6) obtained in this study are lower than those reported for the complexes of humic acids (Pandey *et al.*, 2015; Dinu, 2013; Kaschl *et al.*, 2010 and Gilbeto and Jorg, 2001). The values of LogK(Table 7 to 10) forlead-humates are lower than those reported for the lead in the literature (Dinu, 2013; Gilbeto and Jorg 2001). Log K values(Table 11 to 14) for magnesium-humates obtained in this study are close to those reported by (Pandey *et al.*, 2015). Log K values of cadmium-humates (Table 15 to 18) obtained in this work near to the one reported by (Dinu, 2013 and Pandey *et al.*, 2015).The difference between the reported values and the values obtained in this study might be probably as a result of acid hydrolysis of humic acid. The values of the overall stability constants (log β) of the copper humates complexes presented in Table 19 is high than that of other metal humate complexes, show relatively high stability of Cu-HA complexes, show the following order of stability: Cu >Pb> Cd > Mg; which are in close agreement to the findings of (Dinu, 2013 and Pandey *et al.*, 2015).The high stability of Cu-humate chelate could be attributed to the existence of coordinate covalent bond between the complexing agents and the Cu^{2+} ions. Since, Cu^{2+} being a metal of the transitional series with $3d^9$ electronic configurations can accept the electrons from the complexing agents. Similarly,the low stabilities of Pb,Cd and Mg -complexes could be explained by that Pb^{2+} with $6s^2$, Cd^{2+} with $4d^{10}$ and Mg^{2+} with $2p^6$ their electronic configuration has a completely filled d,p and s orbitals. Moreover, the stabilities of metal ions with hydrolysed humic acid from peat soil were higher than those with unhydrolysed humic acid from peat soil; which is ascribed to the high content of acidity in hydrolysed humic acid than unhydrolysed humic acid.

CONCLUSION

The values of logK for Cu(II) hydrolysed humic acid complex was higher followed by Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes as compared with metal(II) unhydrolysed humic acid complexes . This indicates acid hydrolysis of humic acid can enhance the complexation behavior of humic acid with metal (II) ions. However, the higher values of logβ for Cu(II), Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes indicates more stable stepwise complexes formed as compared with Cu(II), Pb(II), Cd(II) and Mg(II) unhydrolysed humic acid complexes.

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STABILITY CONSTANTS OF COMPLEXES OF METAL IONS WITH PEATSOIL HUMIC ACIDS UNDER NON-ACID-CONDITIONS

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ABSTRACT

Stability constants of complexes of four divalent metal ions viz. Cu^{2+}, Pb^{2+},Mg^{2+} and Cd^{2+} with humic acids (HA) were determined by potentiometric titration of humic acids with the corresponding salt of the divalent metals in aqueous media under non-acid-condition. The log K (logarithm of the stability constant) ranged from 1.0942 to 2.7471 for metal-humic acid complexes were determined using point-wise computational method. The order of stability constants were obtained as follows: Cu >Pb> Cd > Mg for metal -HA complexes respectively, indicating a higher degree of complexation with Cu metal ion.

Keywords: stability constant, humic acid, potentiometric titration, divalent metals, acid hydrolysis.

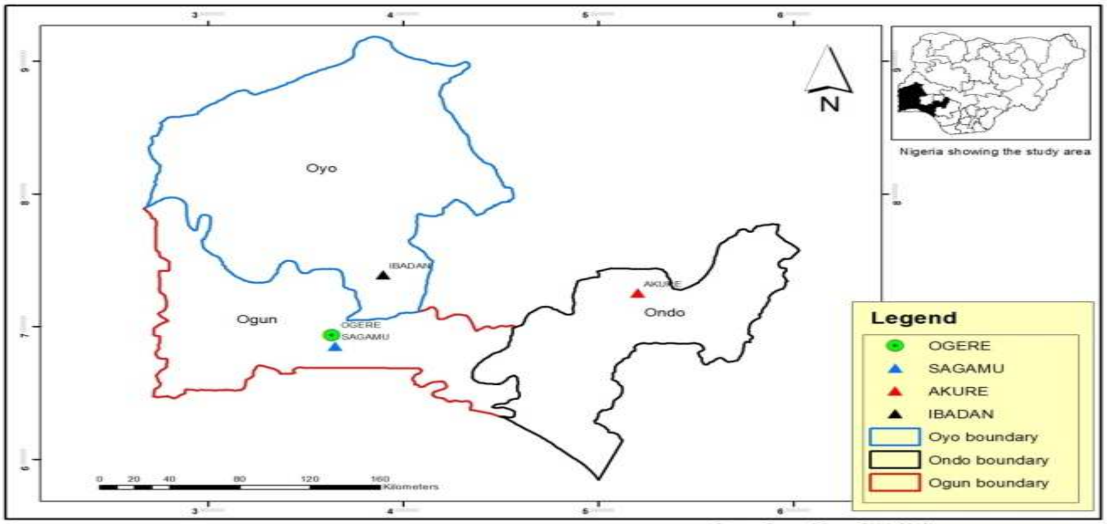
NTRODUCTION

The stability constant of a complex is the numerical expression of its stability and provides a quantitative measure of affinity of the metal ion to the complexing agent. An understanding of the relative stability of metal-complexes helps in predicting the behavior of metal ions in the soil (Ram and Raman, 1982). Extensive researches has been done to determine the stability constants of the complexes formed between humic acid (HA) with a number of metal ions. Ashok *et al*., (2000) reported that humic acid with hydroxyl, phenoxyl and carboxyl reactive groups can form coordination compound with metal ions at pH 3.5. The stability constants(Log K) for different metal-humic acid complexes indicated the following order of the stabilities of complexes formed between humic acid and metal ion, Cu >Fe >Pb> Ni > Co > Ca > Cd > Zn >Mn> Mg. Andelkovic *et al*., (2010) investigated the binding of Cd(II) to soil humic acid at pH 6.5 and in 0.1M KNO_3 ionic medium. The stability constant for binding indicating greater stability in the case when carboxyl groups are involved in complexation reaction. Kostic *et al*.,(2012) investigated the complexation of humic acid with certain heavy metal ions (Co(II), Ni(II),Cu(II), Zn(II), and Pb(II). The experiment was performed at 25°C, at pH 4.0 and ionic strength of 0.01M. Stability constant of complex between Pb(II) ions and humic acid is greater than stability constants of other investigated metal-humate complexes. Bogata and Sokolowska (2016) analyses the interaction between humic acids from different soils and Zn (II) ions at wide concentration ranges and at pH 5. Studies have showed significant impact of Zn concentration, pH and some properties of humic acids with zinc.But all of these studies were limited to acidic pH range. Therefore, the present study was carried out to determine and compare the stability constants of complexes of metal ions with hydrolysed peat soil humic acid and unhydrolysed peat soil humic under non-acid conditions.

MATERIALS AND METHODS

Analytical grade chemicals used includes hydrochloric acid (HCl), nitric acid (HNO_3), sodium hydroxide (NaOH), lead nitrate $Pb(NO_3)_2$, copper nitrate $Cu(NO_3)_2.3H_2O$, cadmium nitrate $Cd(NO_3)_2.4H_2O$, magnesium nitrate $Mg(NO_3)_2.6H_2O$, potassium nitrate (KNO_3), calcium chloride ($CaCl_2$), (sigma-Aldrich). Dowex 50WX8, (20-50 mesh) from Fluka.

Area of study



Source: Dept. of Geog. BUK (2016)

Figure 1: Map showing the sampling point at Sagamu Town, Ogun State.

Description of Sampling Area

Sagamu has geographical coordinates between 6°50′ north; 3° 38′ east is located in south western region of Nigeria. The region has tropical wet and dry climate with a lengthy wet season and relatively constant temperatures throughout the course of the year. Wet season runs from March to October, November to December forms the region dry season. The vegetation type of the region is savannah which is really grassland with small bushes and occasional big trees. Grassland soils have substantially higher organic matter content than forest soils (Novackova, 2011).

Sample Collection

The Peatsoil samples were collected from four different sampling points (0-10cm depth) in Sagamu into polyethylene bag with plastic spoons. Samples were taken to the laboratory, extraneous materials were removed; the samples were air-dried, crushed and ground to a fine powder in a mortar passed through a 0.20mm sieve. The samples were kept for analysis.

Isolation and purification of humic acid from peat soil sample

Peatsoil sample (100g) was mixed with 1000 cm^3 of 0.1M NaOH solution, shaken for 3hours and left to stand overnight. Dark-coloured supernatant was obtained and decanted from solid residue. The dark-coloured supernatant was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 6 hours. Yellowish brown supernatant and dark-brown precipitate were obtained. The yellowish brown supernatant was decanted followed by centrifuge and discarded. The dark-brown precipitate was mixed with $500cm^3$of 0.1M NaOH solution followed by passing through dowex resin. The dark-brown solution was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 3 hours. The dark-brown precipitate was washed several times with deionized water. The supernatant was treated with $AgNO_3$ solution until no white precipitate observed. The humic acid was transferred to weighed crucible and dried at 60°C in an oven for 12 hours. The humic acid was cooled and dried in the desiccator, weighed and recorded. The obtained humic acid was dried again at 60°C for additional 6 hours cooled and dried in the desiccator, weighed and recorded constant weight was obtained (Baruah *et al*., 2015).

FT-IR analysis

FT-IR spectra of humic acid sample was analysed using Carry 630 FT-IR Agilent Technologies.

Unhydrolysed compost humic acid

The unhydrolysed humic acid was obtained after isolation and purification of compost humic acid and kept for investigation.

Acid hydrolysis of Peatsoil acid

Peatsoil humic acid sample (1g) was refluxed for 12 hours at (160°C) with $50cm^3$ of 6M HCl. The mixture was allowed to cool, decanted, and centrifuged after hydrolysis. The insoluble residues were washed with distilled water via centrifugation several times, and the supernatant was treated with $AgNO_3$ solution until no white precipitate was observed. The residue was thoroughly dried over $CaCl_2$ in a desiccator at room temperature (Chefetz *et al*., 2002). Finally, the obtained hydrolysed humic acid was kept for investigation.

Potentiometric Titrations

Potentiometric measurements were carried out using a pH-meter Jenway (model 3510) with combine electrode, the sensitivity of the pH -meter is 0.01 units. The pH meter was switched on half an hour before starting the titration for initial warm up of the instrument. The instrument was calibrated with an aqueous standard buffer solution of pH 4.00 and 10.0 (borate buffer) prepared from a "Qualigens" buffer tablets.

The following sets of solutions were prepared in a 250cm^3 volumetric flask separately for pH metric titrations.

(i) 5 cm^3 0.1 M HCl + 40 cm^3 deionized water

(ii) 5 cm^3 0.1 M HCl + 39 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid

(iii) 5 cm^3 0.1 M HCl + 37 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid + 2 cm^3 0.01 M Cu(II)

The solutions were titrated against standardized 0.110MNaOH separately. The total volume of each mixture was adjusted to 50 cm^3 and the ionic strength of the solutions was maintained constant at by adding appropriate amount of stock solution of 1M KNO$_3$ (Gamal, 2015; Omar and Ali, 2015). A magnetic stirrer was used to achieve thorough mixing of the interacting solutions at 550 rpm. The same set of experimental conditions was applied for potentiometric titration of remaining samples.

Evaluation of pKa of Hydrolysed peat soil Humic Acids

The proton-ligand formation number n$_\mathbf{A}$ were calculated by Irving and Rossotti expression (Omar and Ali, 2015).

$$nA = Y - \frac{(V2-V1)(No-Eo)}{(Vo+V1)TcL} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots 1$$

Where: Y is number of dissociable proton, (V$_2$-V$_1$) is the measure of displacement of the ligand curve relative to acid curve, N^o and E^o are the resultant concentration of alkali solution, free acid solution, T_{cL}^o is the total ligand concentration, V^o is the total volume of titration solution,V$_1$ is the volume of alkali added to acid solution,V$_2$ is the volume of alkali added to acid solution + ligand solution, acid dissociation constants (pKa - values) of ligand were calculated by algebraic method point wise calculation (Tables 1). The dissociation constants (pKa) were calculated according to the following relation:

$$pKa = pH + \log\left(\frac{nA}{1-nA}\right) \quad \ldots\ldots\ldots\ldots\ldots\ldots 2$$

Where: pKa is the acid dissociation constant, n$_A$is the Proton-ligand formation number and pH is the pH-values (Omar and Ali, 2015).

Determination of metal-ligand stability constants (log K) of complexes

The potentiometric measurement for the determination of stability constant of a complex in solution is based on the fact that the redox potential of the couple $\frac{M^{+(m-n)}}{M^{+m}}$ is shifted significantly on complexation of the metal ion with the ligand. This method involves change in hydrogen ion concentration [H$^+$] due to the displacement or association of one or more protons taking place during complexation reaction. This change can be found out by titrating the solutions containing free acid, acid with ligand, and acid with ligand and metal ion, individually against a standard alkali solution at a constant ionic strength or temperature. Either ionic strength or temperature may be varied for different sets of solutions. In all the cases, the change in the pH of the solution is measured after each addition of a known amount of alkali to the reaction cell which contains the reaction mixture. The titration curves are then drawn by plotting the measured pH values against the corresponding volume of alkali added and the stability constants of the complexes are determined from the titration curves by employing pH-metric titration technique given by (Irving and Rossoti).

Metal-ligand stability constants (Log K) were determined by using the following relations:

$$\bar{n} = \frac{(V_3 - V_2)(E^0 + N^0)}{(V^0 + V_2)\bar{n}_A T_m^0} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 3$$

and

$$PL = \log_{10}\left\{\frac{1 + \beta_n^H \dfrac{1}{[anti\ \log pH]^n}}{T_L^0 - \bar{n}T_m^0} X \frac{(V^0 + V_3)}{V^0}\right\} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots 4$$

Where $T_{L,}$ T^{o}, E°, and V^{o}havethe same significance as in equation (1) above, T_m denotes the total concentration of metal present in solution, V_3 is the volume of metal ions present in solution and β^H is the overall proton ligand stability constant. The metal-ligand stability constants (log K) were determined by employing point wise computational Method (eq. 5 and 6).

$$LogK_1 = \log\left(\frac{n}{1-n}\right) + pL \qquad ....5$$

$$LogK_2 = \log\left(\frac{1-n}{2-n}\right) + pL.......................6$$

Where: Log K is the metal-ligand stability constant, pL is the Free ligand exponent function, **n** is the Average number of ligand attached with metal ion (Janrao*et al.*, 2014).The results obtained were analyzed by an ORIGIN 2016 program using titration data and then the proton-ligand stability constants (pKa) and Metal-ligand stability constant (LogK) calculated (Omar and Ali, 2015).

RESULTS AND DISCUSSION

Fourier transformed infrared (FT-IR) spectra of isolated humic acid from peat soils Figure 2 had distinct clear absorption bands indicating the presence of major humic acid structural elemental groups such as H bonded OH ($3680cm^{-1}$ peak), C=O of carbonyl ($1721cm^{-1}$ peak), functional groups of aliphatic components CH_2 ($2918cm^{-1}$ peak) and C-O stretching of polysaccharide ($1168cm^{-1}$ peak). The positions of the absorption bands of the spectra fell within typical major absorption bands of humic acid which is at frequencies 3680, 2918, 1721, 1168 cm^{-1}. The first peak centred in the vicinity of 3680 cm^{-1} region is attributed to phenol OH group bounded by intermolecular H bonds. The $2918cm^{-1}$ band usually has absorption maximum at 2918 cm^{-1} which is due to C–H stretching of alkane group (CH_2). The next major absorption band is 1721 cm^{-1}. This band has been commonly ascribed to C=O stretching of mainly carboxyl group (COOH) with trace amount of ketones. The last peak was observed at 1168 cm^{-1} due to C–O stretching of polysaccharides and this peak appeared also in the spectra of humic acid from peat soil. The FTIR spectra of the isolated humic acid contained all major characteristic absorption peaks of humic acid. These absorption peaks indicated the presence of the major structural elements of humic acid namely H bonded OH, C=C of aromatic ring, C=O of carbonyl group (both carboxyl and ketonic), CH_2 group. This strongly supports the presence of humic acid.

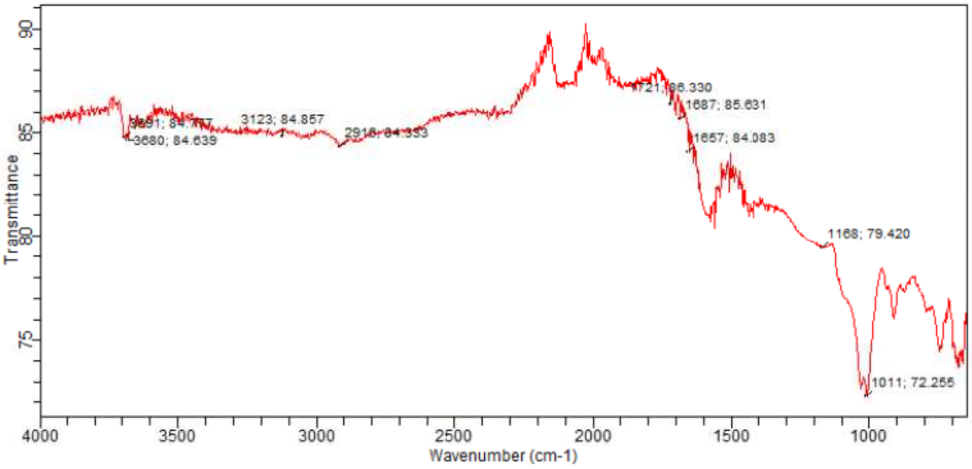


Fig. 2 : FT-IR spectraof peatsoilhumic acid (PSHA)

Evaluation of acid dissociation constant (pka) of acid hydrolysed peat soil humicacid at phenolic group

The value of the dissociation constant of the peat soil humic acid (PSHA) that underwent acidhydrolysis studied was found to be 8.9299 as shown Table 1, which is lower than the literaturevalues reported by Almeida and Szpoganics, (2015), Borges *et al.*, (2005); Badr *et al.*, (2012)and Fernandes *et al*,.(2009) of 9.73, 9.47 and 10.30. The difference between the obtained valuesand the reported values in this study might be probably as a result of acid hydrolysis of humicacid.

Table 1: PKa of (Hydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	$\log(\frac{nA}{1-nA})$	pKa
8.50	5.30	6.29	0.99	0.3594	-0.2510	8.2490
8.72	5.35	6.37	1.02	0.3400	-0.2880	8.4320
9.00	5.40	6.46	1.06	0.3141	-0.3391	8.6609
9.22	5.45	6.55	1.10	0.2882	-0.3927	8.8273
9.51	5.50	6.66	1.16	0.2494	-0.4786	9.0314
9.73	5.55	6.78	1.23	0.2041	-0.5910	9.1390
10.00	5.60	6.90	1.30	0.1589	-0.7238	9.2762
10.23	5.65	7.05	1.40	0.0941	-0.9835	9.2465
10.49	5.70	7.10	1.40	0.0941	-0.9835	9.5065

Average pKa = 8.9299 ± 0.4186

Table 2: PKa of (Unhydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	$\text{Log}(\frac{nA}{1-n})$	pKa
8.50	5.30	5.81	0.51	0.6619	0.2919	8.7919
8.72	5.35	5.90	0.55	0.6357	0.2418	8.9618
9.00	5.40	6.00	0.60	0.6029	0.1813	9.1813
9.22	5.45	6.10	0.65	0.5701	0.1226	9.3426
9.51	5.50	6.20	0.70	0.5376	0.0654	9.5754
9.73	5.55	6.33	0.78	0.4851	-0.0259	9.7041
10.00	5.60	6.47	0.87	0.4262	-0.1291	9.8709
10.23	5.65	6.62	0.99	0.3609	-0.2481	9.9819
10.49	5.70	6.80	1.10	0.2759	-0.4690	10.0210

Average pKa = 9.4923± 0.4410

Metal-ligand stability constant (Log K)

The stabilityconstants require the accurate values of proton-ligand stability constants (Anil and Maroti, 2008). Metal titration curves crossed over ligand titration curve indicated the formation of complex upon proton release (Santosh, *et al.*, 2011). If the values of n- are within range 0.2-0.8 and 1.2-18 this indicates the formation of 1:1 and 1:2 complexes (Sayyed and Mazahar, 2012).

The metal (II)-humate stepwise stability constants (log k) at phenolic group (Tables 3-18)

Table 3: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$\log(\frac{n}{1-n})$	$\text{Log}K_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

$\text{Log}K_1$ (Average value) = 2.4788± 0.2203

Table 4: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$\text{Log}(\frac{n-1}{2-n})$	$\text{Log}K_2$
9.51	5.50	6.66	6.73	0.07	1.3509	1.70	-0.2671	1.4329
9.73	5.55	6.78	6.85	0.07	1.6383	1.51	0.2467	1.7567
10.00	5.60	6.90	6.98	0.08	2.1783	1.31	-0.2158	1.0942
10.23	5.65	7.05	7.13	0.08	4.1904	1.27		
10.49	5.70	7.10	7.19	0.09	4.6920			

$\text{Log}K_2$(Average value) = 1.4280 ± 0.3312

Table 5:Point-wise method,Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	Log($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430

$LogK_1$ **(Average value)** = 2.3059± 0.6153

Table 6:Point-wise method, Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
9.73	5.55	6.33	6.42	0.09	0.9000	1.69		
10.00	5.60	6.47	6.58	0.11	1.2578	1.44	-0.4592	0.9808
10.23	5.65	6.62	6.84	0.12	1.6137	1.26	-0.2010	1.4610
10.49	5.70	6.80	6.92	0.12	2.1052	1.03		

$LogK_2$ **(Average value)** = 1.2209± 0.3398

Table 7:Point-wise method,Pb (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n}{1-n}$)	$LogK_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.60	0.05	0.8333	1.96	0.6989	2.6589

$LogK_1$ (Average value) = 2.5832 ±0.1614

Table 8:Point-wise method,Pb-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n-1}{2-n}$)	$logK_2$
9.51	5.50	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.83	0.05	1.1702	1.44		
10.00	5.60	6.90	6.90	0.05	1.4864	1.22	-0.0237	1.1963
10.23	5.65	7.05	7.10	0.05	2.0190	1.09		
10.49	5.70	7.10	7.17	0.07	3.6492	1.00		

$LogK_2$(Average value) = 1.1963

Table 9:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log ($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.5477	2.3123
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	0.0272	2.2072
9.51	5.50	6.20	6.26	0.07	0.6417	1.89	0.2530	2.1430
9.73	5.55	6.40	6.40	0.07	0.7000	1.67	0.3680	2.0380

$LogK_1$ **(Average value)** = 2.2364 ± 0.1602

Table 10:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
10.00	5.60	6.47	6.55	0.08	1.9503	1.41		
10.23	5.65	6.62	6.72	0.11	1.4792	1.26	-0.0361	1.2239

$LogK_2$ **(Average value)** = 1.2239

Table 11:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n}{n-1}$)	$LogK_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4290	2.2110
8.72	5.35	6.37	6.39	0.02	0.2858	2.42	-0.3978	2.0222
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

$LogK_1$ (Average value)=2.1382**±**0.1046

Table 12:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	log($\frac{n-1}{2-n}$)	LogK$_2$
9.51	5.55	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.84	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.93	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.10		
10.49	5.70	7.10	7.18	0.07	3.6492	0.83		

LogK$_2$(Average value) = 1.5453 **±** 0.3450

Table 13:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	V$_3$-V$_2$	n	pL	Log($\frac{n}{n-1}$)	Log K$_1$
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.3477	2.3123
9.00	5.40	6.00	6.04	0.04	0.3236	2.38	-0.3202	2.0598
9.22	5.45	6.10	6.15	0.05	0.4297	2.17	-0.1230	2.0470
9.51	5.50	6.20	6.26	0.06	0.5500	1.89	0.0871	1.9771
9.73	5.55	6.33	6.40	0.07	0.7000	1.67	0.3680	2.0380

LogK$_1$ **(Average value)** = 2.1568 ± 0.2069

Table 14:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	V$_3$-V$_2$	n	pL	Log($\frac{n-1}{2-n}$)	Log K$_2$
10.00	5.60	6.47	6.55	0.08	0.9148	1.41		
10.23	5.65	6.62	6.71	0.09	1.2102	1.20	-0.5749	0.6251
10.49	5.70	6.80	6.92	0.09	1.5968	1.03	0.1703	1.2003

LogK$_2$ **(Average value)** = 0.9127± 0.4070

Table15:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	Log($\frac{n}{1-n}$)	LogK$_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4210	2.2190
8.72	5.35	6.37	6.40	0.03	0.4286	2.42	-0.1249	2.2951
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.96	0.3010	2.2610
9.51	5.55	6.66	6.70	0.04	0.7720	1.67	0.5297	2.1997

LogK$_1$ (Average value) = 2.2108± 0.0825

Table 16:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	Log($\frac{n-1}{2-n}$)	Log K$_2$
9.73	5.55	6.78	6.83	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.95	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.09		
10.49	5.70	7.10	7.16	0.06	3.1429	0.89		

LogK$_2$ **(Average value)** = 1.5453± 0.3450

Table 17:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	V$_3$-V$_2$	n	pL	Log($\frac{n}{n-1}$)	Log K$_1$
8.50	5.30	5.81	5.86	0.05	0.3717	2.88	-0.2280	2.6520
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.06	0.06	0.4853	2.38	-0.0255	2.3545
9.22	5.45	6.10	6.16	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430
9.73	5.55	6.33	6.41	0.08	0.8000	1.69	0.6020	2.2920

LogK$_1$ **(Average value)** = 2.2516± 0.5380

Table 18:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$\text{Log}(\frac{n-1}{2-n})$	Log K_2
10.00	5.60	6.47	6.57	0.10	1.1434	1.43		
10.23	5.65	6.62	6.72	0.10	1.3448	1.23	-0.2788	0.9512
10.49	5.70	6.80	6.90	0.10	1.7742	1.03	0.5351	1.5651

LogK_2 **(Average value)** = 1.2581± 0.4340

Table 19: Stepwise and overall Stability constants of thehydrolysed and unhydrolysed divalent metal (II) complexes

Chelates	**LogK_1**	**LogK_2**	**Logβ**
[Cu (Hydrolysed PSHA-1)$_2$]	2.4788	1.4280	3.9068
[Pb (Hydrolysed PSHA-1)$_2$]	2.5832	1.1963	3.7795
[Cd (Hydrolysed PSHA-1)$_2$]	2.2108	1.5453	3.7561
[Mg (Hydrolysed PSHA-1)$_2$]	2.1382	1.5453	3.6835
[Cu (Unhydrolysed PSHA-1)$_2$]	2.3059	1.2209	3.5268
[Pb (Unhydrolysed PSHA-1)$_2$]	2.2364	1.2239	3.4603
[Cd (Unhydrolysed PSHA-1)$_2$]	2.2516	1.2581	3.5097
[Mg (Unydrolysed PSHA-1)$_2$]	2.1568	0.9127	3.0695

The results obtained (Table19) shows the stepwise and overall stability constants to be not high indicating low stability of the complexes, because the solubility of most metal ions in the basic pH range is minimal due to metal hydroxide precipitation (Karimi, 2017). In general, the stepwise stability constants (K_1 and K_2) follow the order $K_1 > K_2$ for the copper, lead, magnesium and cadmium complexes respectively. The steady decrease of the values with increasing number of ligands is in agreement with the prediction made by researchers (Na'aliya, 2013). The decrease could be attributed to the fact that as the number of the ligands (Humate ions) that enters the coordination zone increases the aqua molecules available for replacement by the ligands become less. Thus, the metal ions become less electron loving with progressive intake of the ligand and this results in the decrease in the values of the constants (Na'aliya, 2013). Also the stability of the complexes is influenced by the size and number of the chelate rings(Mackay and Mackay,2002).All the complexes form rings in their structure as humate, a bidentate ligand, bond the metal ions in the ratio 1:2 (Boguta and Sokolowska, 2016) forming chelate rings. The values of the overall stability constants (logβ) obtained for humate complexes are not high indicating low stability as the values are not high. LogK values for copper-humates (Table 3 to 6) obtained in this study are lower than those reported for the complexes of humic acids (Pandey *et al*., 2015; Dinu, 2013; Kaschl *et al*., 2010 and Gilbeto and Jorg, 2001). The values of LogK(Table 7 to 10) forlead-humates are lower than those reported for the lead in the literature (Dinu, 2013; Gilbeto and Jorg 2001). Log K values(Table 11 to 14) for magnesium-humates obtained in this study are close to those reported by (Pandey *et al*., 2015). Log K values of cadmium-humates (Table 15 to 18) obtained in this work near to the one reported by (Dinu, 2013 and Pandey *et al*., 2015).The difference between the reported values and the values obtained in this study might be probably as a result of acid hydrolysis of humic acid. The values of the overall stability constants (log β) of the copper humates complexes presented in Table 19 is high than that of other metal humate complexes, show relatively high stability of Cu-HA complexes, show the following order of stability: Cu >Pb> Cd > Mg; which are in close agreement to the findings of (Dinu, 2013 and Pandey *et al*., 2015).The high stability of Cu-humate chelate could be attributed to the existence of coordinate covalent bond between the complexing agents and the Cu^{2+} ions. Since, Cu^{2+} being a metal of the transitional series with $3d^9$ electronic configurations can accept the electrons from the complexing agents. Similarly,the low stabilities of Pb,Cd and Mg - complexes could be explained by that Pb^{2+} with $6s^2$, Cd^{2+} with $4d^{10}$ and Mg^{2+} with $2p^6$ their electronic configuration has a completely filled d,p and s orbitals. Moreover, the stabilities of metal ions with hydrolysed humic acid from peat soil were higher than those with unhydrolysed humic acid from peat soil; which is ascribed to the high content of acidity in hydrolysed humic acid than unhydrolysed humic acid.

CONCLUSION

The values of logK for Cu(II) hydrolysed humic acid complex was higher followed by Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes as compared with metal(II) unhydrolysed humic acid complexes . This indicates acid hydrolysis of humic acid can enhance the complexation behavior of humic acid with metal (II) ions. However, the higher values of logβ for Cu(II), Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes indicates more stable stepwise complexes formed as compared with Cu(II), Pb(II), Cd(II) and Mg(II) unhydrolysed humic acid complexes.

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STABILITY CONSTANTS OF COMPLEXES OF METAL IONS WITH PEATSOIL HUMIC ACIDS UNDER NON-ACID-CONDITIONS

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ABSTRACT

Stability constants of complexes of four divalent metal ions viz. Cu^{2+}, Pb^{2+},Mg^{2+} and Cd^{2+} with humic acids (HA) were determined by potentiometric titration of humic acids with the corresponding salt of the divalent metals in aqueous media under non-acid-condition. The log K (logarithm of the stability constant) ranged from 1.0942 to 2.7471 for metal-humic acid complexes were determined using point-wise computational method. The order of stability constants were obtained as follows: Cu >Pb> Cd > Mg for metal -HA complexes respectively, indicating a higher degree of complexation with Cu metal ion.

Keywords: stability constant, humic acid, potentiometric titration, divalent metals, acid hydrolysis.

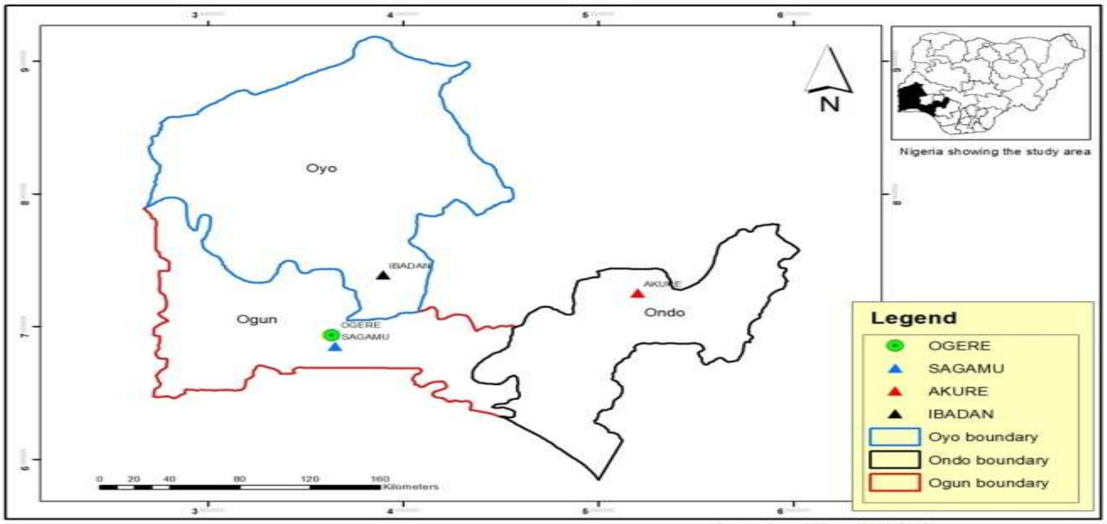
NTRODUCTION

The stability constant of a complex is the numerical expression of its stability and provides a quantitative measure of affinity of the metal ion to the complexing agent. An understanding of the relative stability of metal-complexes helps in predicting the behavior of metal ions in the soil (Ram and Raman, 1982). Extensive researches has been done to determine the stability constants of the complexes formed between humic acid (HA) with a number of metal ions. Ashok *et al.*, (2000) reported that humic acid with hydroxyl, phenoxyl and carboxyl reactive groups can form coordination compound with metal ions at pH 3.5. The stability constants(Log K) for different metal-humic acid complexes indicated the following order of the stabilities of complexes formed between humic acid and metal ion, Cu >Fe >Pb> Ni > Co > Ca > Cd > Zn >Mn> Mg. Andelkovic *et al.*, (2010) investigated the binding of Cd(II) to soil humic acid at pH 6.5 and in 0.1M KNO_3 ionic medium. The stability constant for binding indicating greater stability in the case when carboxyl groups are involved in complexation reaction. Kostic *et al.*,(2012) investigated the complexation of humic acid with certain heavy metal ions (Co(II), Ni(II),Cu(II), Zn(II), and Pb(II). The experiment was performed at 25°C, at pH 4.0 and ionic strength of 0.01M. Stability constant of complex between Pb(II) ions and humic acid is greater than stability constants of other investigated metal-humate complexes. Bogata and Sokolowska (2016) analyses the interaction between humic acids from different soils and Zn (II) ions at wide concentration ranges and at pH 5. Studies have showed significant impact of Zn concentration, pH and some properties of humic acids with zinc.But all of these studies were limited to acidic pH range. Therefore, the present study was carried out to determine and compare the stability constants of complexes of metal ions with hydrolysed peat soil humic acid and unhydrolysed peat soil humic under non-acid conditions.

MATERIALS AND METHODS

Analytical grade chemicals used includes hydrochloric acid (HCl), nitric acid (HNO_3), sodium hydroxide (NaOH), lead nitrate $Pb(NO_3)_2$, copper nitrate $Cu(NO_3)_2.3H_2O$, cadmium nitrate $Cd(NO_3)_2.4H_2O$, magnesium nitrate $Mg(NO_3)_2.6H_2O$, potassium nitrate (KNO_3), calcium chloride ($CaCl_2$), (sigma-Aldrich). Dowex 50WX8, (20-50 mesh) from Fluka.

Area of study



Source: Dept. of Geog. BUK (2016)

Figure 1: Map showing the sampling point at Sagamu Town, Ogun State.

Description of Sampling Area

Sagamu has geographical coordinates between 6°50′ north; 3° 38′ east is located in south western region of Nigeria. The region has tropical wet and dry climate with a lengthy wet season and relatively constant temperatures throughout the course of the year. Wet season runs from March to October, November to December forms the region dry season. The vegetation type of the region is savannah which is really grassland with small bushes and occasional big trees. Grassland soils have substantially higher organic matter content than forest soils (Novackova, 2011).

Sample Collection

The Peatsoil samples were collected from four different sampling points (0-10cm depth) in Sagamu into polyethylene bag with plastic spoons. Samples were taken to the laboratory, extraneous materials were removed; the samples were air-dried, crushed and ground to a fine powder in a mortar passed through a 0.20mm sieve. The samples were kept for analysis.

Isolation and purification of humic acid from peat soil sample

Peatsoil sample (100g) was mixed with 1000 cm^3 of 0.1M NaOH solution, shaken for 3hours and left to stand overnight. Dark-coloured supernatant was obtained and decanted from solid residue. The dark-coloured supernatant was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 6 hours. Yellowish brown supernatant and dark-brown precipitate were obtained. The yellowish brown supernatant was decanted followed by centrifuge and discarded. The dark-brown precipitate was mixed with 500cm^{3}of 0.1M NaOH solution followed by passing through dowex resin. The dark-brown solution was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 3 hours. The dark-brown precipitate was washed several times with deionized water. The supernatant was treated with AgNO$_3$ solution until no white precipitate observed. The humic acid was transferred to weighed crucible and dried at 60^{o}C in an oven for 12 hours. The humic acid was cooled and dried in the desiccator, weighed and recorded. The obtained humic acid was dried again at 60^{o}C for additional 6 hours cooled and dried in the desiccator, weighed and recorded constant weight was obtained (Baruah *et al*., 2015).

FT-IR analysis

FT-IR spectra of humic acid sample was analysed using Carry 630 FT-IR Agilent Technologies.

Unhydrolysed compost humic acid

The unhydrolysed humic acid was obtained after isolation and purification of compost humic acid and kept for investigation.

Acid hydrolysis of Peatsoil acid

Peatsoil humic acid sample (1g) was refluxed for 12 hours at (160^{o}C) with 50cm^3 of 6M HCl. The mixture was allowed to cool, decanted, and centrifuged after hydrolysis. The insoluble residues were washed with distilled water via centrifugation several times, and the supernatant was treated with AgNO$_3$ solution until no white precipitate was observed. The residue was thoroughly dried over CaCl$_2$ in a desiccator at room temperature (Chefetz *et al*., 2002). Finally, the obtained hydrolysed humic acid was kept for investigation.

Potentiometric Titrations

Potentiometric measurements were carried out using a pH-meter Jenway (model 3510) with combine electrode, the sensitivity of the pH - meter is 0.01 units. The pH meter was switched on half an hour before starting the titration for initial warm up of the instrument. The instrument was calibrated with an aqueous standard buffer solution of pH 4.00 and 10.0 (borate buffer) prepared from a "Qualigens" buffer tablets.

The following sets of solutions were prepared in a 250cm^3 volumetric flask separately for pH metric titrations.

(i) 5 cm^3 0.1 M HCl + 40 cm^3 deionized water

(ii) 5 cm^3 0.1 M HCl + 39 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid

(iii) 5 cm^3 0.1 M HCl + 37 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid + 2 cm^3 0.01 M Cu(II)

The solutions were titrated against standardized 0.110MNaOH separately. The total volume of each mixture was adjusted to 50 cm^3 and the ionic strength of the solutions was maintained constant at by adding appropriate amount of stock solution of 1M KNO$_3$ (Gamal, 2015; Omar and Ali, 2015). A magnetic stirrer was used to achieve thorough mixing of the interacting solutions at 550 rpm. The same set of experimental conditions was applied for potentiometric titration of remaining samples.

Evaluation of pKa of Hydrolysed peat soil Humic Acids

The proton-ligand formation number n$_{\mathbf{A}}$ were calculated by Irving and Rossotti expression (Omar and Ali, 2015).

$$nA = Y - \frac{(V2-V1)(No-Eo)}{(Vo+V1)TcL} \quad \text{..................................1}$$

Where: Y is number of dissociable proton, (V$_2$-V$_1$) is the measure of displacement of the ligand curve relative to acid curve, N^o and E^o are the resultant concentration of alkali solution, free acid solution, T$_{cL}{}^o$ is the total ligand concentration, V^o is the total volume of titration solution,V$_1$ is the volume of alkali added to acid solution,V$_2$ is the volume of alkali added to acid solution + ligand solution, acid dissociation constants (pKa - values) of ligand were calculated by algebraic method point wise calculation (Tables 1). The dissociation constants (pKa) were calculated according to the following relation:

$$pKa = pH + \log\left(\frac{nA}{1-nA}\right) \quad \text{.............................2}$$

Where: pKa is the acid dissociation constant, n$_A$is the Proton-ligand formation number and pH is the pH-values (Omar and Ali, 2015).

Determination of metal-ligand stability constants (log K) of complexes

The potentiometric measurement for the determination of stability constant of a complex in solution is based on the fact that the redox potential of the couple $\frac{M^{+(m-n)}}{M^{+m}}$ is shifted significantly on complexation of the metal ion with the ligand. This method involves change in hydrogen ion concentration [H$^+$] due to the displacement or association of one or more protons taking place during complexation reaction. This change can be found out by titrating the solutions containing free acid, acid with ligand, and acid with ligand and metal ion, individually against a standard alkali solution at a constant ionic strength or temperature. Either ionic strength or temperature may be varied for different sets of solutions. In all the cases, the change in the pH of the solution is measured after each addition of a known amount of alkali to the reaction cell which contains the reaction mixture. The titration curves are then drawn by plotting the measured pH values against the corresponding volume of alkali added and the stability constants of the complexes are determined from the titration curves by employing pH-metric titration technique given by (Irving and Rossoti).

Metal-ligand stability constants (Log K) were determined by using the following relations:

$$\bar{n} = \frac{(V_3 - V_2)(E^0 + N^0)}{(V^0 + V_2)\bar{n}_A T_m^0} \quad \text{...3}$$

and

$$PL = \log_{10}\left\{\frac{1 + \beta_n^H \frac{1}{[anti \ \log pH]^n}}{T_L^0 - \bar{n}T_m^0} X \frac{(V^0 + V_3)}{V^0}\right\} \quad \text{...4}$$

Where $T_{L,}$ T^o, E°, and V^ohavethe same significance as in equation (1) above, T_m denotes the total concentration of metal present in solution, V_3 is the volume of metal ions present in solution and β^H is the overall proton ligand stability constant. The metal-ligand stability constants (log K) were determined by employing point wise computational Method (eq. 5 and 6).

$$\mathrm{Log}K_1 = \log\left(\frac{n}{1-n}\right) + pL \qquad ....5$$

$$\mathrm{Log}K_2 = \log\left(\frac{1-n}{2-n}\right) + pL.......................6$$

Where: Log K is the metal-ligand stability constant, pL is the Free ligand exponent function, **n** is the Average number of ligand attached with metal ion (Janrao*et al.*, 2014).The results obtained were analyzed by an ORIGIN 2016 program using titration data and then the proton-ligand stability constants (pKa) and Metal-ligand stability constant (LogK) calculated (Omar and Ali, 2015).

RESULTS AND DISCUSSION

Fourier transformed infrared (FT-IR) spectra of isolated humic acid from peat soils Figure 2 had distinct clear absorption bands indicating the presence of major humic acid structural elemental groups such as H bonded OH ($3680cm^{-1}$ peak), C=O of carbonyl ($1721cm^{-1}$ peak), functional groups of aliphatic components CH_2 ($2918cm^{-1}$ peak) and C-O stretching of polysaccharide ($1168cm^{-1}$ peak). The positions of the absorption bands of the spectra fell within typical major absorption bands of humic acid which is at frequencies 3680, 2918, 1721, 1168 cm^{-1}. The first peak centred in the vicinity of 3680 cm^{-1} region is attributed to phenol OH group bounded by intermolecular H bonds. The $2918cm^{-1}$ band usually has absorption maximum at 2918 cm^{-1} which is due to C–H stretching of alkane group (CH_2). The next major absorption band is 1721 cm^{-1}. This band has been commonly ascribed to C=O stretching of mainly carboxyl group (COOH) with trace amount of ketones. The last peak was observed at 1168 cm^{-1} due to C–O stretching of polysaccharides and this peak appeared also in the spectra of humic acid from peat soil. The FTIR spectra of the isolated humic acid contained all major characteristic absorption peaks of humic acid. These absorption peaks indicated the presence of the major structural elements of humic acid namely H bonded OH, C=C of aromatic ring, C=O of carbonyl group (both carboxyl and ketonic), CH_2 group. This strongly supports the presence of humic acid.

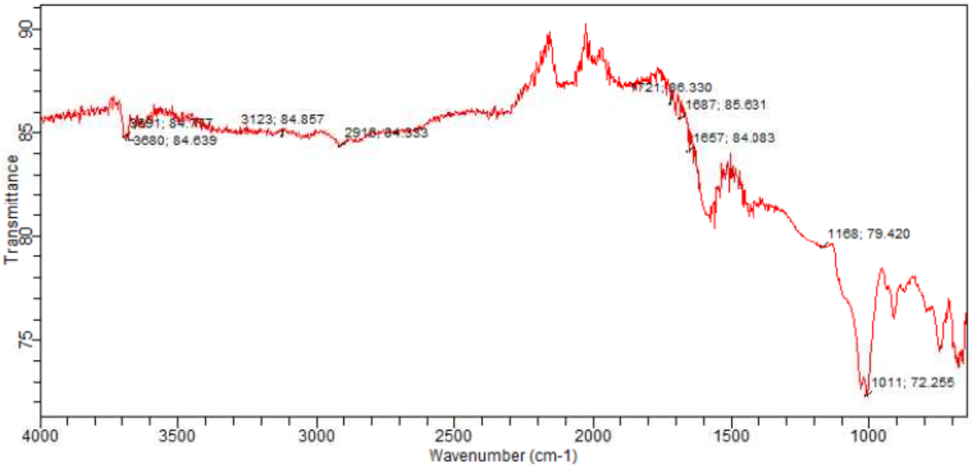


Fig. 2 : FT-IR spectraof peatsoilhumic acid (PSHA)

Evaluation of acid dissociation constant (pka) of acid hydrolysed peat soil humicacid at phenolic group

The value of the dissociation constant of the peat soil humic acid (PSHA) that underwent acidhydrolysis studied was found to be 8.9299 as shown Table 1, which is lower than the literaturevalues reported by Almeida and Szpoganics, (2015), Borges *et al.*, (2005); Badr *et al.*, (2012)and Fernandes *et al*,.(2009) of 9.73, 9.47 and 10.30. The difference between the obtained valuesand the reported values in this study might be probably as a result of acid hydrolysis of humicacid.

Table 1: PKa of (Hydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	log($\frac{nA}{1-nA}$)	pKa
8.50	5.30	6.29	0.99	0.3594	-0.2510	8.2490
8.72	5.35	6.37	1.02	0.3400	-0.2880	8.4320
9.00	5.40	6.46	1.06	0.3141	-0.3391	8.6609
9.22	5.45	6.55	1.10	0.2882	-0.3927	8.8273
9.51	5.50	6.66	1.16	0.2494	-0.4786	9.0314
9.73	5.55	6.78	1.23	0.2041	-0.5910	9.1390
10.00	5.60	6.90	1.30	0.1589	-0.7238	9.2762
10.23	5.65	7.05	1.40	0.0941	-0.9835	9.2465
10.49	5.70	7.10	1.40	0.0941	-0.9835	9.5065

Average pKa = 8.9299 ± 0.4186

Table 2: PKa of (Unhydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	Log($\frac{nA}{1-n}$)	pKa
8.50	5.30	5.81	0.51	0.6619	0.2919	8.7919
8.72	5.35	5.90	0.55	0.6357	0.2418	8.9618
9.00	5.40	6.00	0.60	0.6029	0.1813	9.1813
9.22	5.45	6.10	0.65	0.5701	0.1226	9.3426
9.51	5.50	6.20	0.70	0.5376	0.0654	9.5754
9.73	5.55	6.33	0.78	0.4851	-0.0259	9.7041
10.00	5.60	6.47	0.87	0.4262	-0.1291	9.8709
10.23	5.65	6.62	0.99	0.3609	-0.2481	9.9819
10.49	5.70	6.80	1.10	0.2759	-0.4690	10.0210

Average pKa = 9.4923± 0.4410

Metal-ligand stability constant (Log K)

The stabilityconstants require the accurate values of proton-ligand stability constants (Anil and Maroti, 2008). Metal titration curves crossed over ligand titration curve indicated the formation of complex upon proton release (Santosh, *et al.*, 2011). If the values of n- are within range 0.2-0.8 and 1.2-18 this indicates the formation of 1:1 and 1:2 complexes (Sayyed and Mazahar, 2012).

The metal (II)-humate stepwise stability constants (log k) at phenolic group (Tables 3-18)

Table 3: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n}{1-n}$)	$LogK_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

$LogK_1$ (Average value) = 2.4788± 0.2203

Table 4: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	Log($\frac{n-1}{2-n}$)	$LogK_2$
9.51	5.50	6.66	6.73	0.07	1.3509	1.70	-0.2671	1.4329
9.73	5.55	6.78	6.85	0.07	1.6383	1.51	0.2467	1.7567
10.00	5.60	6.90	6.98	0.08	2.1783	1.31	-0.2158	1.0942
10.23	5.65	7.05	7.13	0.08	4.1904	1.27		
10.49	5.70	7.10	7.19	0.09	4.6920			

$LogK_2$(Average value) = 1.4280 ± 0.3312

Table 5:Point-wise method,Cu (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	Log($\frac{n}{n-1}$)	Log K$_1$
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430

LogK$_1$ **(Average value)** = 2.3059± 0.6153

Table 6:Point-wise method, Cu (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	V$_3$-V$_2$	n	pL	Log($\frac{n-1}{2-n}$)	Log K$_2$
9.73	5.55	6.33	6.42	0.09	0.9000	1.69		
10.00	5.60	6.47	6.58	0.11	1.2578	1.44	-0.4592	0.9808
10.23	5.65	6.62	6.84	0.12	1.6137	1.26	-0.2010	1.4610
10.49	5.70	6.80	6.92	0.12	2.1052	1.03		

LogK$_2$ **(Average value)** = 1.2209± 0.3398

Table 7:Point-wise method,Pb (Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	log($\frac{n}{1-n}$)	LogK$_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.60	0.05	0.8333	1.96	0.6989	2.6589

LogK$_1$ (Average value) = 2.5832 ±0.1614

Table 8:Point-wise method,Pb-(Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	log($\frac{n-1}{2-n}$)	logK$_2$
9.51	5.50	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.83	0.05	1.1702	1.44		
10.00	5.60	6.90	6.90	0.05	1.4864	1.22	-0.0237	1.1963
10.23	5.65	7.05	7.10	0.05	2.0190	1.09		
10.49	5.70	7.10	7.17	0.07	3.6492	1.00		

LogK$_2$(Average value) = 1.1963

Table 9:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	V$_3$-V$_2$	n	pL	Log ($\frac{n}{n-1}$)	Log K$_1$
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.5477	2.3123
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	0.0272	2.2072
9.51	5.50	6.20	6.26	0.07	0.6417	1.89	0.2530	2.1430
9.73	5.55	6.40	6.40	0.07	0.7000	1.67	0.3680	2.0380

LogK$_1$ **(Average value)** = 2.2364 ± 0.1602

Table 10:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	V$_3$-V$_2$	n	pL	Log($\frac{n-1}{2-n}$)	Log K$_2$
10.00	5.60	6.47	6.55	0.08	1.9503	1.41		
10.23	5.65	6.62	6.72	0.11	1.4792	1.26	-0.0361	1.2239

LogK$_2$ **(Average value)** = 1.2239

Table 11:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	log($\frac{n}{n-1}$)	LogK$_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4290	2.2110
8.72	5.35	6.37	6.39	0.02	0.2858	2.42	-0.3978	2.0222
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

LogK$_1$ (Average value)=2.1382**±**0.1046

Table 12:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$\log(\frac{n-1}{2-n})$	$LogK_2$
9.51	5.55	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.84	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.93	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.10		
10.49	5.70	7.10	7.18	0.07	3.6492	0.83		

$LogK_2$(Average value) = 1.5453 **±** 0.3450

Table 13:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$Log(\frac{n}{n-1})$	$Log\ K_1$
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.3477	2.3123
9.00	5.40	6.00	6.04	0.04	0.3236	2.38	-0.3202	2.0598
9.22	5.45	6.10	6.15	0.05	0.4297	2.17	-0.1230	2.0470
9.51	5.50	6.20	6.26	0.06	0.5500	1.89	0.0871	1.9771
9.73	5.55	6.33	6.40	0.07	0.7000	1.67	0.3680	2.0380

$LogK_1$ **(Average value)** = 2.1568 ± 0.2069

Table 14:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$Log(\frac{n-1}{2-n})$	$Log\ K_2$
10.00	5.60	6.47	6.55	0.08	0.9148	1.41		
10.23	5.65	6.62	6.71	0.09	1.2102	1.20	-0.5749	0.6251
10.49	5.70	6.80	6.92	0.09	1.5968	1.03	0.1703	1.2003

$LogK_2$ **(Average value)** = 0.9127± 0.4070

Table15:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$Log(\frac{n}{1-n})$	$LogK_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4210	2.2190
8.72	5.35	6.37	6.40	0.03	0.4286	2.42	-0.1249	2.2951
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.96	0.3010	2.2610
9.51	5.55	6.66	6.70	0.04	0.7720	1.67	0.5297	2.1997

$LogK_1$ (Average value) = 2.2108± 0.0825

Table 16:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$Log(\frac{n-1}{2-n})$	$Log\ K_2$
9.73	5.55	6.78	6.83	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.95	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.09		
10.49	5.70	7.10	7.16	0.06	3.1429	0.89		

$LogK_2$ **(Average value)** = 1.5453± 0.3450

Table 17:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$Log(\frac{n}{n-1})$	$Log\ K_1$
8.50	5.30	5.81	5.86	0.05	0.3717	2.88	-0.2280	2.6520
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.06	0.06	0.4853	2.38	-0.0255	2.3545
9.22	5.45	6.10	6.16	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430
9.73	5.55	6.33	6.41	0.08	0.8000	1.69	0.6020	2.2920

$LogK_1$ **(Average value)** = 2.2516± 0.5380

Table 18:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$\text{Log}(\frac{n-1}{2-n})$	Log K_2
10.00	5.60	6.47	6.57	0.10	1.1434	1.43		
10.23	5.65	6.62	6.72	0.10	1.3448	1.23	-0.2788	0.9512
10.49	5.70	6.80	6.90	0.10	1.7742	1.03	0.5351	1.5651

LogK_2 **(Average value)** = 1.2581± 0.4340

Table 19: Stepwise and overall Stability constants of thehydrolysed and unhydrolysed divalent metal (II) complexes

Chelates	**LogK_1**	**LogK_2**	**Logβ**
[Cu (Hydrolysed PSHA-1)$_2$]	2.4788	1.4280	3.9068
[Pb (Hydrolysed PSHA-1)$_2$]	2.5832	1.1963	3.7795
[Cd (Hydrolysed PSHA-1)$_2$]	2.2108	1.5453	3.7561
[Mg (Hydrolysed PSHA-1)$_2$]	2.1382	1.5453	3.6835
[Cu (Unhydrolysed PSHA-1)$_2$]	2.3059	1.2209	3.5268
[Pb (Unhydrolysed PSHA-1)$_2$]	2.2364	1.2239	3.4603
[Cd (Unhydrolysed PSHA-1)$_2$]	2.2516	1.2581	3.5097
[Mg (Unydrolysed PSHA-1)$_2$]	2.1568	0.9127	3.0695

The results obtained (Table19) shows the stepwise and overall stability constants to be not high indicating low stability of the complexes, because the solubility of most metal ions in the basic pH range is minimal due to metal hydroxide precipitation (Karimi, 2017). In general, the stepwise stability constants (K_1 and K_2) follow the order $K_1 > K_2$ for the copper, lead, magnesium and cadmium complexes respectively. The steady decrease of the values with increasing number of ligands is in agreement with the prediction made by researchers (Na'aliya, 2013). The decrease could be attributed to the fact that as the number of the ligands (Humate ions) that enters the coordination zone increases the aqua molecules available for replacement by the ligands become less. Thus, the metal ions become less electron loving with progressive intake of the ligand and this results in the decrease in the values of the constants (Na'aliya, 2013). Also the stability of the complexes is influenced by the size and number of the chelate rings(Mackay and Mackay,2002).All the complexes form rings in their structure as humate, a bidentate ligand, bond the metal ions in the ratio 1:2 (Boguta and Sokolowska, 2016) forming chelate rings. The values of the overall stability constants (logβ) obtained for humate complexes are not high indicating low stability as the values are not high. LogK values for copper-humates (Table 3 to 6) obtained in this study are lower than those reported for the complexes of humic acids (Pandey *et al.*, 2015; Dinu, 2013; Kaschl *et al.*, 2010 and Gilbeto and Jorg, 2001). The values of LogK(Table 7 to 10) forlead-humates are lower than those reported for the lead in the literature (Dinu, 2013; Gilbeto and Jorg 2001). Log K values(Table 11 to 14) for magnesium-humates obtained in this study are close to those reported by (Pandey *et al.*, 2015). Log K values of cadmium-humates (Table 15 to 18) obtained in this work near to the one reported by (Dinu, 2013 and Pandey *et al.*, 2015).The difference between the reported values and the values obtained in this study might be probably as a result of acid hydrolysis of humic acid. The values of the overall stability constants (log β) of the copper humates complexes presented in Table 19 is high than that of other metal humate complexes, show relatively high stability of Cu-HA complexes, show the following order of stability: Cu >Pb> Cd > Mg; which are in close agreement to the findings of (Dinu, 2013 and Pandey *et al.*, 2015).The high stability of Cu-humate chelate could be attributed to the existence of coordinate covalent bond between the complexing agents and the Cu^{2+} ions. Since, Cu^{2+} being a metal of the transitional series with $3d^9$ electronic configurations can accept the electrons from the complexing agents. Similarly,the low stabilities of Pb,Cd and Mg - complexes could be explained by that Pb^{2+} with $6s^2$, Cd^{2+} with $4d^{10}$ and Mg^{2+} with $2p^6$ their electronic configuration has a completely filled d,p and s orbitals. Moreover, the stabilities of metal ions with hydrolysed humic acid from peat soil were higher than those with unhydrolysed humic acid from peat soil; which is ascribed to the high content of acidity in hydrolysed humic acid than unhydrolysed humic acid.

CONCLUSION

The values of logK for Cu(II) hydrolysed humic acid complex was higher followed by Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes as compared with metal(II) unhydrolysed humic acid complexes . This indicates acid hydrolysis of humic acid can enhance the complexation behavior of humic acid with metal (II) ions. However, the higher values of logβ for Cu(II), Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes indicates more stable stepwise complexes formed as compared with Cu(II), Pb(II), Cd(II) and Mg(II) unhydrolysed humic acid complexes.

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STABILITY CONSTANTS OF COMPLEXES OF METAL IONS WITH PEATSOIL HUMIC ACIDS UNDER NON-ACID-CONDITIONS

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ABSTRACT

Stability constants of complexes of four divalent metal ions viz. Cu^{2+}, Pb^{2+},Mg^{2+} and Cd^{2+} with humic acids (HA) were determined by potentiometric titration of humic acids with the corresponding salt of the divalent metals in aqueous media under non-acid-condition. The log K (logarithm of the stability constant) ranged from 1.0942 to 2.7471 for metal-humic acid complexes were determined using point-wise computational method. The order of stability constants were obtained as follows: Cu >Pb> Cd > Mg for metal -HA complexes respectively, indicating a higher degree of complexation with Cu metal ion.

Keywords: stability constant, humic acid, potentiometric titration, divalent metals, acid hydrolysis.

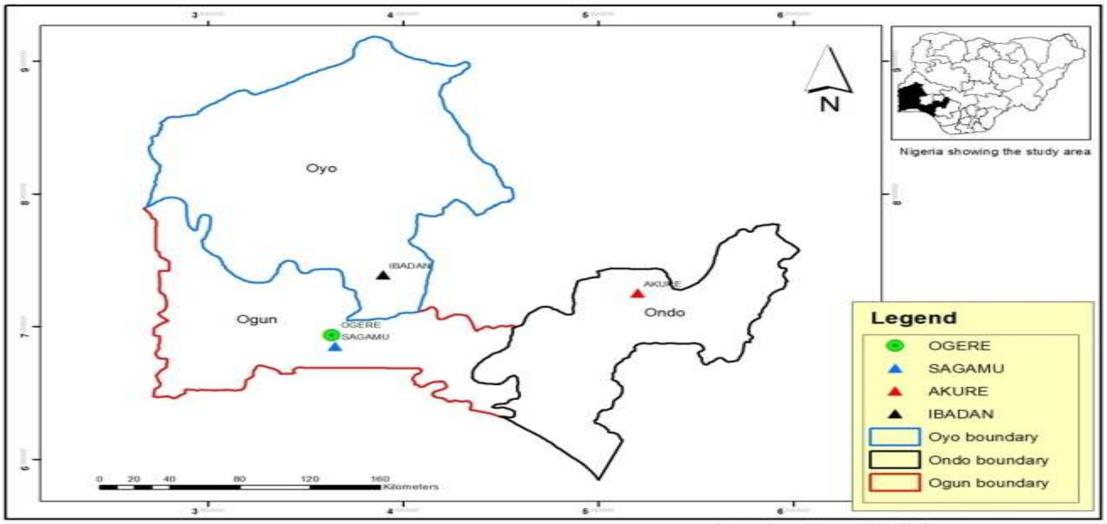
NTRODUCTION

The stability constant of a complex is the numerical expression of its stability and provides a quantitative measure of affinity of the metal ion to the complexing agent. An understanding of the relative stability of metal-complexes helps in predicting the behavior of metal ions in the soil (Ram and Raman, 1982). Extensive researches has been done to determine the stability constants of the complexes formed between humic acid (HA) with a number of metal ions. Ashok *et al*., (2000) reported that humic acid with hydroxyl, phenoxyl and carboxyl reactive groups can form coordination compound with metal ions at pH 3.5. The stability constants(Log K) for different metal-humic acid complexes indicated the following order of the stabilities of complexes formed between humic acid and metal ion, Cu >Fe >Pb> Ni > Co > Ca > Cd > Zn >Mn> Mg. Andelkovic *et al*., (2010) investigated the binding of Cd(II) to soil humic acid at pH 6.5 and in 0.1M KNO_3 ionic medium. The stability constant for binding indicating greater stability in the case when carboxyl groups are involved in complexation reaction. Kostic *et al*.,(2012) investigated the complexation of humic acid with certain heavy metal ions (Co(II), Ni(II),Cu(II), Zn(II), and Pb(II). The experiment was performed at 25°C, at pH 4.0 and ionic strength of 0.01M. Stability constant of complex between Pb(II) ions and humic acid is greater than stability constants of other investigated metal-humate complexes. Bogata and Sokolowska (2016) analyses the interaction between humic acids from different soils and Zn (II) ions at wide concentration ranges and at pH 5. Studies have showed significant impact of Zn concentration, pH and some properties of humic acids with zinc.But all of these studies were limited to acidic pH range. Therefore, the present study was carried out to determine and compare the stability constants of complexes of metal ions with hydrolysed peat soil humic acid and unhydrolysed peat soil humic under non-acid conditions.

MATERIALS AND METHODS

Analytical grade chemicals used includes hydrochloric acid (HCl), nitric acid (HNO_3), sodium hydroxide (NaOH), lead nitrate $Pb(NO_3)_2$, copper nitrate $Cu(NO_3)_2.3H_2O$, cadmium nitrate $Cd(NO_3)_2.4H_2O$, magnesium nitrate $Mg(NO_3)_2.6H_2O$, potassium nitrate (KNO_3), calcium chloride ($CaCl_2$), (sigma-Aldrich). Dowex 50WX8, (20-50 mesh) from Fluka.

Area of study



Source: Dept. of Geog. BUK (2016)

Figure 1: Map showing the sampling point at Sagamu Town, Ogun State.

Description of Sampling Area

Sagamu has geographical coordinates between 6°50′ north; 3° 38′ east is located in south western region of Nigeria. The region has tropical wet and dry climate with a lengthy wet season and relatively constant temperatures throughout the course of the year. Wet season runs from March to October, November to December forms the region dry season. The vegetation type of the region is savannah which is really grassland with small bushes and occasional big trees. Grassland soils have substantially higher organic matter content than forest soils (Novackova, 2011).

Sample Collection

The Peatsoil samples were collected from four different sampling points (0-10cm depth) in Sagamu into polyethylene bag with plastic spoons. Samples were taken to the laboratory, extraneous materials were removed; the samples were air-dried, crushed and ground to a fine powder in a mortar passed through a 0.20mm sieve. The samples were kept for analysis.

Isolation and purification of humic acid from peat soil sample

Peatsoil sample (100g) was mixed with 1000 cm^3 of 0.1M NaOH solution, shaken for 3hours and left to stand overnight. Dark-coloured supernatant was obtained and decanted from solid residue. The dark-coloured supernatant was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 6 hours. Yellowish brown supernatant and dark-brown precipitate were obtained. The yellowish brown supernatant was decanted followed by centrifuge and discarded. The dark-brown precipitate was mixed with $500cm^3$of 0.1M NaOH solution followed by passing through dowex resin. The dark-brown solution was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 3 hours. The dark-brown precipitate was washed several times with deionized water. The supernatant was treated with $AgNO_3$ solution until no white precipitate observed. The humic acid was transferred to weighed crucible and dried at 60°C in an oven for 12 hours. The humic acid was cooled and dried in the desiccator, weighed and recorded. The obtained humic acid was dried again at 60°C for additional 6 hours cooled and dried in the desiccator, weighed and recorded constant weight was obtained (Baruah *et al.*, 2015).

FT-IR analysis

FT-IR spectra of humic acid sample was analysed using Carry 630 FT-IR Agilent Technologies.

Unhydrolysed compost humic acid

The unhydrolysed humic acid was obtained after isolation and purification of compost humic acid and kept for investigation.

Acid hydrolysis of Peatsoil acid

Peatsoil humic acid sample (1g) was refluxed for 12 hours at (160°C) with $50cm^3$ of 6M HCl. The mixture was allowed to cool, decanted, and centrifuged after hydrolysis. The insoluble residues were washed with distilled water via centrifugation several times, and the supernatant was treated with $AgNO_3$ solution until no white precipitate was observed. The residue was thoroughly dried over $CaCl_2$ in a desiccator at room temperature (Chefetz *et al.*, 2002). Finally, the obtained hydrolysed humic acid was kept for investigation.

Potentiometric Titrations

Potentiometric measurements were carried out using a pH-meter Jenway (model 3510) with combine electrode, the sensitivity of the pH - meter is 0.01 units. The pH meter was switched on half an hour before starting the titration for initial warm up of the instrument. The instrument was calibrated with an aqueous standard buffer solution of pH 4.00 and 10.0 (borate buffer) prepared from a "Qualigens" buffer tablets.

The following sets of solutions were prepared in a 250cm^3 volumetric flask separately for pH metric titrations.

(i) 5 cm^3 0.1 M HCl + 40 cm^3 deionized water
(ii) 5 cm^3 0.1 M HCl + 39 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid
(iii) 5 cm^3 0.1 M HCl + 37 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid + 2 cm^3 0.01 M Cu(II)

The solutions were titrated against standardized 0.110MNaOH separately. The total volume of each mixture was adjusted to 50 cm^3 and the ionic strength of the solutions was maintained constant at by adding appropriate amount of stock solution of 1M KNO$_3$ (Gamal, 2015; Omar and Ali, 2015). A magnetic stirrer was used to achieve thorough mixing of the interacting solutions at 550 rpm. The same set of experimental conditions was applied for potentiometric titration of remaining samples.

Evaluation of pKa of Hydrolysed peat soil Humic Acids

The proton-ligand formation number n$_{\mathbf{A}}$ were calculated by Irving and Rossotti expression (Omar and Ali, 2015).

$$nA = Y - \frac{(V2-V1)(No-Eo)}{(Vo+V1)TcL} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 1$$

Where: Y is number of dissociable proton, (V_2-V_1) is the measure of displacement of the ligand curve relative to acid curve, N^o and E^o are the resultant concentration of alkali solution, free acid solution, T_{cL}^o is the total ligand concentration, V^o is the total volume of titration solution,V_1 is the volume of alkali added to acid solution,V_2 is the volume of alkali added to acid solution + ligand solution, acid dissociation constants (pKa - values) of ligand were calculated by algebraic method point wise calculation (Tables 1). The dissociation constants (pKa) were calculated according to the following relation:

$$pKa = pH + \log\left(\frac{nA}{1-nA}\right) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots 2$$

Where: pKa is the acid dissociation constant, $n_A$is the Proton-ligand formation number and pH is the pH-values (Omar and Ali, 2015).

Determination of metal-ligand stability constants (log K) of complexes

The potentiometric measurement for the determination of stability constant of a complex in solution is based on the fact that the redox potential of the couple $\frac{M^{+(m-n)}}{M^{+m}}$ is shifted significantly on complexation of the metal ion with the ligand. This method involves change in hydrogen ion concentration [H$^+$] due to the displacement or association of one or more protons taking place during complexation reaction. This change can be found out by titrating the solutions containing free acid, acid with ligand, and acid with ligand and metal ion, individually against a standard alkali solution at a constant ionic strength or temperature. Either ionic strength or temperature may be varied for different sets of solutions. In all the cases, the change in the pH of the solution is measured after each addition of a known amount of alkali to the reaction cell which contains the reaction mixture. The titration curves are then drawn by plotting the measured pH values against the corresponding volume of alkali added and the stability constants of the complexes are determined from the titration curves by employing pH-metric titration technique given by (Irving and Rossoti).

Metal-ligand stability constants (Log K) were determined by using the following relations:

$$\bar{n} = \frac{(V_3 - V_2)(E^0 + N^0)}{(V^0 + V_2)\bar{n}_A T_m^0} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 3$$

and

$$PL = \log_{10}\left\{\frac{1 + \beta_n^H \frac{1}{[anti\ \log pH]^n}}{T_L^0 - \bar{n}T_m^0} \mathrm{X} \frac{(V^0 + V_3)}{V^0}\right\} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 4$$

Where $T_{L,}$ T^{o}, E°, and V^{o}havethe same significance as in equation (1) above, T_m denotes the total concentration of metal present in solution, V_3 is the volume of metal ions present in solution and β^H is the overall proton ligand stability constant. The metal-ligand stability constants (log K) were determined by employing point wise computational Method (eq. 5 and 6).

$$\mathrm{Log}K_1 = \log\left(\frac{n}{1-n}\right) + pL \qquad \ldots\ldots\ldots\ldots.5$$

$$\mathrm{Log}K_2 = \log\left(\frac{1-n}{2-n}\right) + pL\ldots\ldots\ldots\ldots\ldots\ldots\ldots.6$$

Where: Log K is the metal-ligand stability constant, pL is the Free ligand exponent function, **n** is the Average number of ligand attached with metal ion (Janrao*et al.*, 2014).The results obtained were analyzed by an ORIGIN 2016 program using titration data and then the proton-ligand stability constants (pKa) and Metal-ligand stability constant (LogK) calculated (Omar and Ali, 2015).

RESULTS AND DISCUSSION

Fourier transformed infrared (FT-IR) spectra of isolated humic acid from peat soils Figure 2 had distinct clear absorption bands indicating the presence of major humic acid structural elemental groups such as H bonded OH ($3680cm^{-1}$ peak), C=O of carbonyl ($1721cm^{-1}$ peak), functional groups of aliphatic components CH_2 ($2918cm^{-1}$ peak) and C-O stretching of polysaccharide ($1168cm^{-1}$ peak). The positions of the absorption bands of the spectra fell within typical major absorption bands of humic acid which is at frequencies 3680, 2918, 1721, 1168 cm^{-1}. The first peak centred in the vicinity of 3680 cm^{-1} region is attributed to phenol OH group bounded by intermolecular H bonds. The $2918cm^{-1}$ band usually has absorption maximum at 2918 cm^{-1} which is due to C–H stretching of alkane group (CH_2). The next major absorption band is 1721 cm^{-1}. This band has been commonly ascribed to C=O stretching of mainly carboxyl group (COOH) with trace amount of ketones. The last peak was observed at 1168 cm^{-1} due to C–O stretching of polysaccharides and this peak appeared also in the spectra of humic acid from peat soil. The FTIR spectra of the isolated humic acid contained all major characteristic absorption peaks of humic acid. These absorption peaks indicated the presence of the major structural elements of humic acid namely H bonded OH, C=C of aromatic ring, C=O of carbonyl group (both carboxyl and ketonic), CH_2 group. This strongly supports the presence of humic acid.

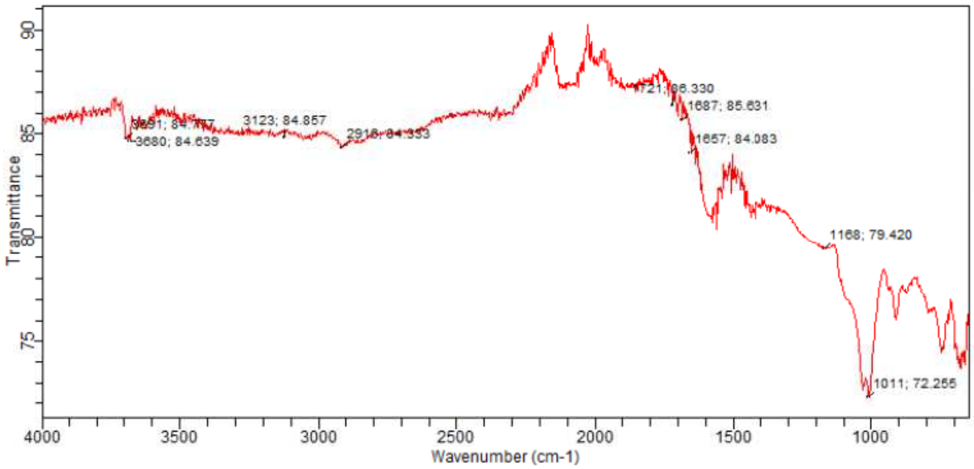


Fig. 2 : FT-IR spectraof peatsoilhumic acid (PSHA)

Evaluation of acid dissociation constant (pka) of acid hydrolysed peat soil humicacid at phenolic group

The value of the dissociation constant of the peat soil humic acid (PSHA) that underwent acidhydrolysis studied was found to be 8.9299 as shown Table 1, which is lower than the literaturevalues reported by Almeida and Szpoganics, (2015), Borges *et al.*, (2005); Badr *et al.*, (2012)and Fernandes *et al*,.(2009) of 9.73, 9.47 and 10.30. The difference between the obtained valuesand the reported values in this study might be probably as a result of acid hydrolysis of humicacid.

Table 1: PKa of (Hydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	log($\frac{nA}{1-nA}$)	pKa
8.50	5.30	6.29	0.99	0.3594	-0.2510	8.2490
8.72	5.35	6.37	1.02	0.3400	-0.2880	8.4320
9.00	5.40	6.46	1.06	0.3141	-0.3391	8.6609
9.22	5.45	6.55	1.10	0.2882	-0.3927	8.8273
9.51	5.50	6.66	1.16	0.2494	-0.4786	9.0314
9.73	5.55	6.78	1.23	0.2041	-0.5910	9.1390
10.00	5.60	6.90	1.30	0.1589	-0.7238	9.2762
10.23	5.65	7.05	1.40	0.0941	-0.9835	9.2465
10.49	5.70	7.10	1.40	0.0941	-0.9835	9.5065

Average pKa = 8.9299 ± 0.4186

Table 2: PKa of (Unhydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	Log($\frac{nA}{1-n}$)	pKa
8.50	5.30	5.81	0.51	0.6619	0.2919	8.7919
8.72	5.35	5.90	0.55	0.6357	0.2418	8.9618
9.00	5.40	6.00	0.60	0.6029	0.1813	9.1813
9.22	5.45	6.10	0.65	0.5701	0.1226	9.3426
9.51	5.50	6.20	0.70	0.5376	0.0654	9.5754
9.73	5.55	6.33	0.78	0.4851	-0.0259	9.7041
10.00	5.60	6.47	0.87	0.4262	-0.1291	9.8709
10.23	5.65	6.62	0.99	0.3609	-0.2481	9.9819
10.49	5.70	6.80	1.10	0.2759	-0.4690	10.0210

Average pKa = 9.4923± 0.4410

Metal-ligand stability constant (Log K)

The stabilityconstants require the accurate values of proton-ligand stability constants (Anil and Maroti, 2008). Metal titration curves crossed over ligand titration curve indicated the formation of complex upon proton release (Santosh, *et al.*, 2011). If the values of n- are within range 0.2-0.8 and 1.2-18 this indicates the formation of 1:1 and 1:2 complexes (Sayyed and Mazahar, 2012).

The metal (II)-humate stepwise stability constants (log k) at phenolic group (Tables 3-18)

Table 3: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n}{1-n}$)	$LogK_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

$LogK_1$ (Average value) = 2.4788± 0.2203

Table 4: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	Log($\frac{n-1}{2-n}$)	$LogK_2$
9.51	5.50	6.66	6.73	0.07	1.3509	1.70	-0.2671	1.4329
9.73	5.55	6.78	6.85	0.07	1.6383	1.51	0.2467	1.7567
10.00	5.60	6.90	6.98	0.08	2.1783	1.31	-0.2158	1.0942
10.23	5.65	7.05	7.13	0.08	4.1904	1.27		
10.49	5.70	7.10	7.19	0.09	4.6920			

$LogK_2$(Average value) = 1.4280 ± 0.3312

Table 5:Point-wise method,Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	Log($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430

$LogK_1$ **(Average value)** = 2.3059± 0.6153

Table 6:Point-wise method, Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$V_3\text{-}V_2$	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
9.73	5.55	6.33	6.42	0.09	0.9000	1.69		
10.00	5.60	6.47	6.58	0.11	1.2578	1.44	-0.4592	0.9808
10.23	5.65	6.62	6.84	0.12	1.6137	1.26	-0.2010	1.4610
10.49	5.70	6.80	6.92	0.12	2.1052	1.03		

$LogK_2$ **(Average value)** = 1.2209± 0.3398

Table 7:Point-wise method,Pb (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	log($\frac{n}{1-n}$)	$LogK_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.60	0.05	0.8333	1.96	0.6989	2.6589

$LogK_1$ (Average value) = 2.5832 ±0.1614

Table 8:Point-wise method,Pb-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	log($\frac{n-1}{2-n}$)	$logK_2$
9.51	5.50	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.83	0.05	1.1702	1.44		
10.00	5.60	6.90	6.90	0.05	1.4864	1.22	-0.0237	1.1963
10.23	5.65	7.05	7.10	0.05	2.0190	1.09		
10.49	5.70	7.10	7.17	0.07	3.6492	1.00		

$LogK_2$(Average value) = 1.1963

Table 9:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$V_3\text{-}V_2$	n	pL	Log ($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.5477	2.3123
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	0.0272	2.2072
9.51	5.50	6.20	6.26	0.07	0.6417	1.89	0.2530	2.1430
9.73	5.55	6.40	6.40	0.07	0.7000	1.67	0.3680	2.0380

$LogK_1$ **(Average value)** = 2.2364 ± 0.1602

Table 10:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$V_3\text{-}V_2$	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
10.00	5.60	6.47	6.55	0.08	1.9503	1.41		
10.23	5.65	6.62	6.72	0.11	1.4792	1.26	-0.0361	1.2239

$LogK_2$ **(Average value)** = 1.2239

Table 11:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	log($\frac{n}{n-1}$)	$LogK_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4290	2.2110
8.72	5.35	6.37	6.39	0.02	0.2858	2.42	-0.3978	2.0222
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

$LogK_1$ (Average value)=2.1382**±**0.1046

Table 12:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n-1}{2-n}$)	$LogK_2$
9.51	5.55	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.84	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.93	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.10		
10.49	5.70	7.10	7.18	0.07	3.6492	0.83		

$LogK_2$(Average value) = 1.5453 **±** 0.3450

Table 13:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.3477	2.3123
9.00	5.40	6.00	6.04	0.04	0.3236	2.38	-0.3202	2.0598
9.22	5.45	6.10	6.15	0.05	0.4297	2.17	-0.1230	2.0470
9.51	5.50	6.20	6.26	0.06	0.5500	1.89	0.0871	1.9771
9.73	5.55	6.33	6.40	0.07	0.7000	1.67	0.3680	2.0380

$LogK_1$ **(Average value)** = 2.1568 ± 0.2069

Table 14:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
10.00	5.60	6.47	6.55	0.08	0.9148	1.41		
10.23	5.65	6.62	6.71	0.09	1.2102	1.20	-0.5749	0.6251
10.49	5.70	6.80	6.92	0.09	1.5968	1.03	0.1703	1.2003

$LogK_2$ **(Average value)** = 0.9127± 0.4070

Table15:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	Log($\frac{n}{1-n}$)	$LogK_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4210	2.2190
8.72	5.35	6.37	6.40	0.03	0.4286	2.42	-0.1249	2.2951
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.96	0.3010	2.2610
9.51	5.55	6.66	6.70	0.04	0.7720	1.67	0.5297	2.1997

$LogK_1$ (Average value) = 2.2108± 0.0825

Table 16:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
9.73	5.55	6.78	6.83	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.95	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.09		
10.49	5.70	7.10	7.16	0.06	3.1429	0.89		

$LogK_2$ **(Average value)** = 1.5453± 0.3450

Table 17:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.86	0.05	0.3717	2.88	-0.2280	2.6520
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.06	0.06	0.4853	2.38	-0.0255	2.3545
9.22	5.45	6.10	6.16	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430
9.73	5.55	6.33	6.41	0.08	0.8000	1.69	0.6020	2.2920

$LogK_1$ **(Average value)** = 2.2516± 0.5380

Table 18:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$\text{Log}(\frac{n-1}{2-n})$	Log K_2
10.00	5.60	6.47	6.57	0.10	1.1434	1.43		
10.23	5.65	6.62	6.72	0.10	1.3448	1.23	-0.2788	0.9512
10.49	5.70	6.80	6.90	0.10	1.7742	1.03	0.5351	1.5651

LogK_2 **(Average value)** = 1.2581± 0.4340

Table 19: Stepwise and overall Stability constants of thehydrolysed and unhydrolysed divalent metal (II) complexes

Chelates	**LogK_1**	**LogK_2**	**Logβ**
[Cu (Hydrolysed PSHA-1)$_2$]	2.4788	1.4280	3.9068
[Pb (Hydrolysed PSHA-1)$_2$]	2.5832	1.1963	3.7795
[Cd (Hydrolysed PSHA-1)$_2$]	2.2108	1.5453	3.7561
[Mg (Hydrolysed PSHA-1)$_2$]	2.1382	1.5453	3.6835
[Cu (Unhydrolysed PSHA-1)$_2$]	2.3059	1.2209	3.5268
[Pb (Unhydrolysed PSHA-1)$_2$]	2.2364	1.2239	3.4603
[Cd (Unhydrolysed PSHA-1)$_2$]	2.2516	1.2581	3.5097
[Mg (Unydrolysed PSHA-1)$_2$]	2.1568	0.9127	3.0695

The results obtained (Table19) shows the stepwise and overall stability constants to be not high indicating low stability of the complexes, because the solubility of most metal ions in the basic pH range is minimal due to metal hydroxide precipitation (Karimi, 2017). In general, the stepwise stability constants (K_1 and K_2) follow the order $K_1 > K_2$ for the copper, lead, magnesium and cadmium complexes respectively. The steady decrease of the values with increasing number of ligands is in agreement with the prediction made by researchers (Na'aliya, 2013). The decrease could be attributed to the fact that as the number of the ligands (Humate ions) that enters the coordination zone increases the aqua molecules available for replacement by the ligands become less. Thus, the metal ions become less electron loving with progressive intake of the ligand and this results in the decrease in the values of the constants (Na'aliya, 2013). Also the stability of the complexes is influenced by the size and number of the chelate rings(Mackay and Mackay,2002).All the complexes form rings in their structure as humate, a bidentate ligand, bond the metal ions in the ratio 1:2 (Boguta and Sokolowska, 2016) forming chelate rings. The values of the overall stability constants (logβ) obtained for humate complexes are not high indicating low stability as the values are not high. LogK values for copper-humates (Table 3 to 6) obtained in this study are lower than those reported for the complexes of humic acids (Pandey *et al*., 2015; Dinu, 2013; Kaschl *et al*., 2010 and Gilbeto and Jorg, 2001). The values of LogK(Table 7 to 10) forlead-humates are lower than those reported for the lead in the literature (Dinu, 2013; Gilbeto and Jorg 2001). Log K values(Table 11 to 14) for magnesium-humates obtained in this study are close to those reported by (Pandey *et al*., 2015). Log K values of cadmium-humates (Table 15 to 18) obtained in this work near to the one reported by (Dinu, 2013 and Pandey *et al*., 2015).The difference between the reported values and the values obtained in this study might be probably as a result of acid hydrolysis of humic acid. The values of the overall stability constants (log β) of the copper humates complexes presented in Table 19 is high than that of other metal humate complexes, show relatively high stability of Cu-HA complexes, show the following order of stability: Cu >Pb> Cd > Mg; which are in close agreement to the findings of (Dinu, 2013 and Pandey *et al*., 2015).The high stability of Cu-humate chelate could be attributed to the existence of coordinate covalent bond between the complexing agents and the Cu^{2+} ions. Since, Cu^{2+} being a metal of the transitional series with $3d^9$ electronic configurations can accept the electrons from the complexing agents. Similarly,the low stabilities of Pb,Cd and Mg - complexes could be explained by that Pb^{2+} with $6s^2$, Cd^{2+} with $4d^{10}$ and Mg^{2+} with $2p^6$ their electronic configuration has a completely filled d,p and s orbitals. Moreover, the stabilities of metal ions with hydrolysed humic acid from peat soil were higher than those with unhydrolysed humic acid from peat soil; which is ascribed to the high content of acidity in hydrolysed humic acid than unhydrolysed humic acid.

CONCLUSION

The values of logK for Cu(II) hydrolysed humic acid complex was higher followed by Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes as compared with metal(II) unhydrolysed humic acid complexes . This indicates acid hydrolysis of humic acid can enhance the complexation behavior of humic acid with metal (II) ions. However, the higher values of logβ for Cu(II), Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes indicates more stable stepwise complexes formed as compared with Cu(II), Pb(II), Cd(II) and Mg(II) unhydrolysed humic acid complexes.

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STABILITY CONSTANTS OF COMPLEXES OF METAL IONS WITH PEATSOIL HUMIC ACIDS UNDER NON-ACID-CONDITIONS

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ABSTRACT

Stability constants of complexes of four divalent metal ions viz. Cu^{2+}, Pb^{2+},Mg^{2+} and Cd^{2+} with humic acids (HA) were determined by potentiometric titration of humic acids with the corresponding salt of the divalent metals in aqueous media under non-acid-condition. The log K (logarithm of the stability constant) ranged from 1.0942 to 2.7471 for metal-humic acid complexes were determined using point-wise computational method. The order of stability constants were obtained as follows: Cu >Pb> Cd > Mg for metal -HA complexes respectively, indicating a higher degree of complexation with Cu metal ion.

Keywords: stability constant, humic acid, potentiometric titration, divalent metals, acid hydrolysis.

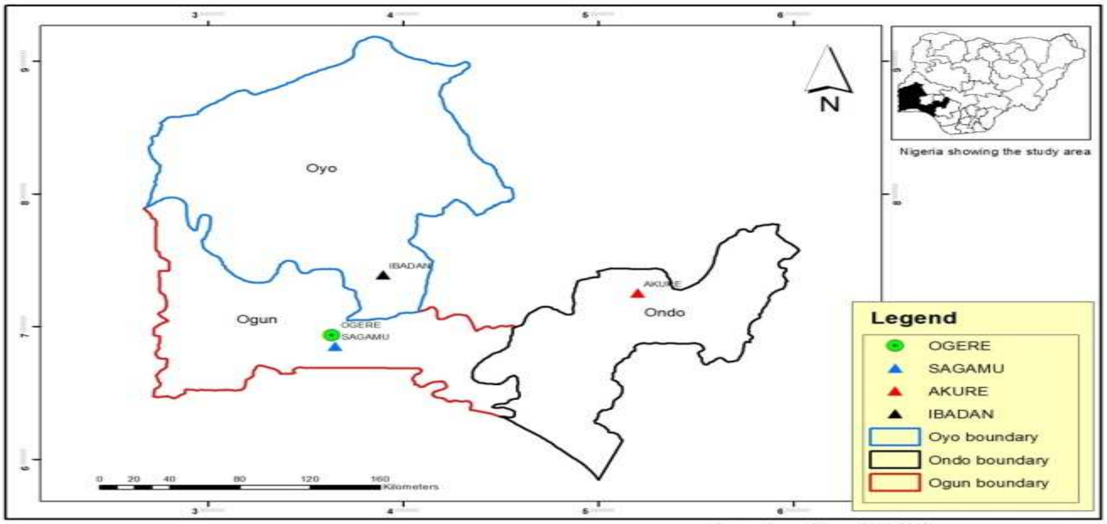
NTRODUCTION

The stability constant of a complex is the numerical expression of its stability and provides a quantitative measure of affinity of the metal ion to the complexing agent. An understanding of the relative stability of metal-complexes helps in predicting the behavior of metal ions in the soil (Ram and Raman, 1982). Extensive researches has been done to determine the stability constants of the complexes formed between humic acid (HA) with a number of metal ions. Ashok *et al.*, (2000) reported that humic acid with hydroxyl, phenoxyl and carboxyl reactive groups can form coordination compound with metal ions at pH 3.5. The stability constants(Log K) for different metal-humic acid complexes indicated the following order of the stabilities of complexes formed between humic acid and metal ion, Cu >Fe >Pb> Ni > Co > Ca > Cd > Zn >Mn> Mg. Andelkovic *et al.*, (2010) investigated the binding of Cd(II) to soil humic acid at pH 6.5 and in 0.1M KNO_3 ionic medium. The stability constant for binding indicating greater stability in the case when carboxyl groups are involved in complexation reaction. Kostic *et al.*,(2012) investigated the complexation of humic acid with certain heavy metal ions (Co(II), Ni(II),Cu(II), Zn(II), and Pb(II). The experiment was performed at 25°C, at pH 4.0 and ionic strength of 0.01M. Stability constant of complex between Pb(II) ions and humic acid is greater than stability constants of other investigated metal-humate complexes. Bogata and Sokolowska (2016) analyses the interaction between humic acids from different soils and Zn (II) ions at wide concentration ranges and at pH 5. Studies have showed significant impact of Zn concentration, pH and some properties of humic acids with zinc.But all of these studies were limited to acidic pH range. Therefore, the present study was carried out to determine and compare the stability constants of complexes of metal ions with hydrolysed peat soil humic acid and unhydrolysed peat soil humic under non-acid conditions.

MATERIALS AND METHODS

Analytical grade chemicals used includes hydrochloric acid (HCl), nitric acid (HNO_3), sodium hydroxide (NaOH), lead nitrate $Pb(NO_3)_2$, copper nitrate $Cu(NO_3)_2.3H_2O$, cadmium nitrate $Cd(NO_3)_2.4H_2O$, magnesium nitrate $Mg(NO_3)_2.6H_2O$, potassium nitrate (KNO_3), calcium chloride ($CaCl_2$), (sigma-Aldrich). Dowex 50WX8, (20-50 mesh) from Fluka.

Area of study



Source: Dept. of Geog. BUK (2016)

Figure 1: Map showing the sampling point at Sagamu Town, Ogun State.

Description of Sampling Area

Sagamu has geographical coordinates between 6°50′ north; 3° 38′ east is located in south western region of Nigeria. The region has tropical wet and dry climate with a lengthy wet season and relatively constant temperatures throughout the course of the year. Wet season runs from March to October, November to December forms the region dry season. The vegetation type of the region is savannah which is really grassland with small bushes and occasional big trees. Grassland soils have substantially higher organic matter content than forest soils (Novackova, 2011).

Sample Collection

The Peatsoil samples were collected from four different sampling points (0-10cm depth) in Sagamu into polyethylene bag with plastic spoons. Samples were taken to the laboratory, extraneous materials were removed; the samples were air-dried, crushed and ground to a fine powder in a mortar passed through a 0.20mm sieve. The samples were kept for analysis.

Isolation and purification of humic acid from peat soil sample

Peatsoil sample (100g) was mixed with 1000 cm^3 of 0.1M NaOH solution, shaken for 3hours and left to stand overnight. Dark-coloured supernatant was obtained and decanted from solid residue. The dark-coloured supernatant was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 6 hours. Yellowish brown supernatant and dark-brown precipitate were obtained. The yellowish brown supernatant was decanted followed by centrifuge and discarded. The dark-brown precipitate was mixed with 500$cm^3$of 0.1M NaOH solution followed by passing through dowex resin. The dark-brown solution was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 3 hours. The dark-brown precipitate was washed several times with deionized water. The supernatant was treated with $AgNO_3$ solution until no white precipitate observed. The humic acid was transferred to weighed crucible and dried at 60°C in an oven for 12 hours. The humic acid was cooled and dried in the desiccator, weighed and recorded. The obtained humic acid was dried again at 60°C for additional 6 hours cooled and dried in the desiccator, weighed and recorded constant weight was obtained (Baruah *et al*., 2015).

FT-IR analysis

FT-IR spectra of humic acid sample was analysed using Carry 630 FT-IR Agilent Technologies.

Unhydrolysed compost humic acid

The unhydrolysed humic acid was obtained after isolation and purification of compost humic acid and kept for investigation.

Acid hydrolysis of Peatsoil acid

Peatsoil humic acid sample (1g) was refluxed for 12 hours at (160°C) with 50cm^3 of 6M HCl. The mixture was allowed to cool, decanted, and centrifuged after hydrolysis. The insoluble residues were washed with distilled water via centrifugation several times, and the supernatant was treated with $AgNO_3$ solution until no white precipitate was observed. The residue was thoroughly dried over $CaCl_2$ in a desiccator at room temperature (Chefetz *et al*., 2002). Finally, the obtained hydrolysed humic acid was kept for investigation.

Potentiometric Titrations

Potentiometric measurements were carried out using a pH-meter Jenway (model 3510) with combine electrode, the sensitivity of the pH - meter is 0.01 units. The pH meter was switched on half an hour before starting the titration for initial warm up of the instrument. The instrument was calibrated with an aqueous standard buffer solution of pH 4.00 and 10.0 (borate buffer) prepared from a "Qualigens" buffer tablets.

The following sets of solutions were prepared in a 250cm^3 volumetric flask separately for pH metric titrations.

(i) 5 cm^3 0.1 M HCl + 40 cm^3 deionized water
(ii) 5 cm^3 0.1 M HCl + 39 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid
(iii) 5 cm^3 0.1 M HCl + 37 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid + 2 cm^3 0.01 M Cu(II)

The solutions were titrated against standardized 0.110MNaOH separately. The total volume of each mixture was adjusted to 50 cm^3 and the ionic strength of the solutions was maintained constant at by adding appropriate amount of stock solution of 1M KNO$_3$ (Gamal, 2015; Omar and Ali, 2015). A magnetic stirrer was used to achieve thorough mixing of the interacting solutions at 550 rpm. The same set of experimental conditions was applied for potentiometric titration of remaining samples.

Evaluation of pKa of Hydrolysed peat soil Humic Acids

The proton-ligand formation number n$_{\mathbf{A}}$ were calculated by Irving and Rossotti expression (Omar and Ali, 2015).

$$nA = Y - \frac{(V2-V1)(No-Eo)}{(Vo+V1)TcL} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 1$$

Where: Y is number of dissociable proton, (V$_2$-V$_1$) is the measure of displacement of the ligand curve relative to acid curve, N^o and E^o are the resultant concentration of alkali solution, free acid solution, T$_{cL}$^{o} is the total ligand concentration, V^o is the total volume of titration solution,V$_1$ is the volume of alkali added to acid solution,V$_2$ is the volume of alkali added to acid solution + ligand solution, acid dissociation constants (pKa - values) of ligand were calculated by algebraic method point wise calculation (Tables 1). The dissociation constants (pKa) were calculated according to the following relation:

$$pKa = pH + \log\left(\frac{nA}{1-nA}\right) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 2$$

Where: pKa is the acid dissociation constant, n$_A$is the Proton-ligand formation number and pH is the pH-values (Omar and Ali, 2015).

Determination of metal-ligand stability constants (log K) of complexes

The potentiometric measurement for the determination of stability constant of a complex in solution is based on the fact that the redox potential of the couple $\frac{M^{+(m-n)}}{M^{+m}}$ is shifted significantly on complexation of the metal ion with the ligand. This method involves change in hydrogen ion concentration [H$^+$] due to the displacement or association of one or more protons taking place during complexation reaction. This change can be found out by titrating the solutions containing free acid, acid with ligand, and acid with ligand and metal ion, individually against a standard alkali solution at a constant ionic strength or temperature. Either ionic strength or temperature may be varied for different sets of solutions. In all the cases, the change in the pH of the solution is measured after each addition of a known amount of alkali to the reaction cell which contains the reaction mixture. The titration curves are then drawn by plotting the measured pH values against the corresponding volume of alkali added and the stability constants of the complexes are determined from the titration curves by employing pH-metric titration technique given by (Irving and Rossoti).

Metal-ligand stability constants (Log K) were determined by using the following relations:

$$\bar{n} = \frac{(V_3 - V_2)(E^0 + N^0)}{(V^0 + V_2)\bar{n}_A T_m^0} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 3$$

and

$$PL = \log_{10}\{\frac{1+\beta_n^H \frac{1}{[anti\ \log \mathrm{pH}]^n}}{\mathrm{T}_\mathrm{L}^0 - \bar{n}T_m^0} \mathrm{X} \frac{(V^0+V_3)}{V^0}\} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 4$$

Where $T_{L,}$ T^o, $E°$, and V^ohavethe same significance as in equation (1) above, T_m denotes the total concentration of metal present in solution, V_3 is the volume of metal ions present in solution and β^H is the overall proton ligand stability constant. The metal-ligand stability constants (log K) were determined by employing point wise computational Method (eq. 5 and 6).

$$\text{LogK}_1 = \log\left(\frac{n}{1-n}\right) + \text{pL} \qquad \ldots\ldots\ldots\ldots.5$$

$$\text{LogK}_2 = \log\left(\frac{1-n}{2-n}\right) + \text{pL}\ldots\ldots\ldots\ldots\ldots\ldots\ldots.6$$

Where: Log K is the metal-ligand stability constant, pL is the Free ligand exponent function, **n** is the Average number of ligand attached with metal ion (Janrao*et al*., 2014).The results obtained were analyzed by an ORIGIN 2016 program using titration data and then the proton-ligand stability constants (pKa) and Metal-ligand stability constant (LogK) calculated (Omar and Ali, 2015).

RESULTS AND DISCUSSION

Fourier transformed infrared (FT-IR) spectra of isolated humic acid from peat soils Figure 2 had distinct clear absorption bands indicating the presence of major humic acid structural elemental groups such as H bonded OH (3680cm^{-1} peak), C=O of carbonyl (1721cm^{-1} peak), functional groups of aliphatic components CH_2 (2918cm^{-1} peak) and C-O stretching of polysaccharide (1168cm^{-1} peak). The positions of the absorption bands of the spectra fell within typical major absorption bands of humic acid which is at frequencies 3680, 2918, 1721, 1168 cm^{-1}. The first peak centred in the vicinity of 3680 cm^{-1} region is attributed to phenol OH group bounded by intermolecular H bonds. The 2918cm^{-1} band usually has absorption maximum at 2918 cm^{-1} which is due to C–H stretching of alkane group (CH_2). The next major absorption band is 1721 cm^{-1}. This band has been commonly ascribed to C=O stretching of mainly carboxyl group (COOH) with trace amount of ketones. The last peak was observed at 1168 cm^{-1} due to C–O stretching of polysaccharides and this peak appeared also in the spectra of humic acid from peat soil. The FTIR spectra of the isolated humic acid contained all major characteristic absorption peaks of humic acid. These absorption peaks indicated the presence of the major structural elements of humic acid namely H bonded OH, C=C of aromatic ring, C=O of carbonyl group (both carboxyl and ketonic), CH_2 group. This strongly supports the presence of humic acid.

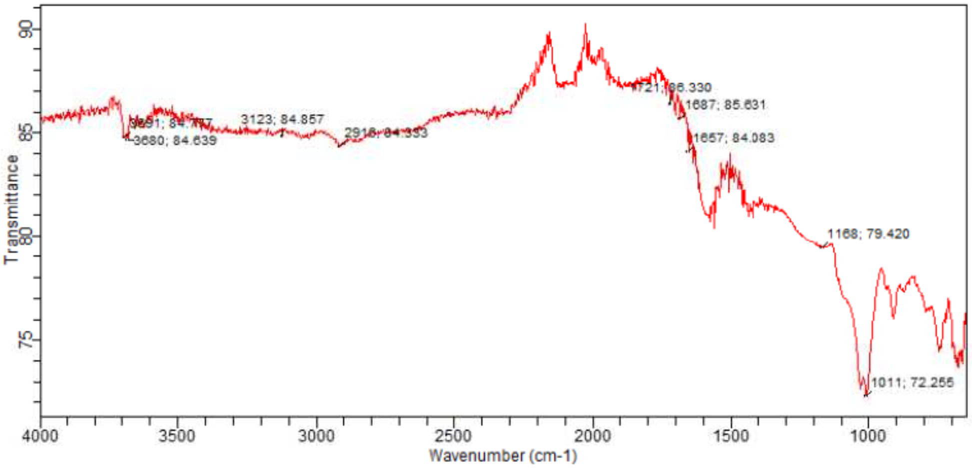


Fig. 2 : FT-IR spectraof peatsoilhumic acid (PSHA)

Evaluation of acid dissociation constant (pka) of acid hydrolysed peat soil humicacid at phenolic group

The value of the dissociation constant of the peat soil humic acid (PSHA) that underwent acidhydrolysis studied was found to be 8.9299 as shown Table 1, which is lower than the literaturevalues reported by Almeida and Szpoganics, (2015), Borges *et al*., (2005); Badr *et al*., (2012)and Fernandes *et al*,.(2009) of 9.73, 9.47 and 10.30. The difference between the obtained valuesand the reported values in this study might be probably as a result of acid hydrolysis of humicacid.

Table 1: PKa of (Hydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	log($\frac{nA}{1-nA}$)	pKa
8.50	5.30	6.29	0.99	0.3594	-0.2510	8.2490
8.72	5.35	6.37	1.02	0.3400	-0.2880	8.4320
9.00	5.40	6.46	1.06	0.3141	-0.3391	8.6609
9.22	5.45	6.55	1.10	0.2882	-0.3927	8.8273
9.51	5.50	6.66	1.16	0.2494	-0.4786	9.0314
9.73	5.55	6.78	1.23	0.2041	-0.5910	9.1390
10.00	5.60	6.90	1.30	0.1589	-0.7238	9.2762
10.23	5.65	7.05	1.40	0.0941	-0.9835	9.2465
10.49	5.70	7.10	1.40	0.0941	-0.9835	9.5065

Average pKa = 8.9299 ± 0.4186

Table 2: PKa of (Unhydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	Log($\frac{nA}{1-n}$)	pKa
8.50	5.30	5.81	0.51	0.6619	0.2919	8.7919
8.72	5.35	5.90	0.55	0.6357	0.2418	8.9618
9.00	5.40	6.00	0.60	0.6029	0.1813	9.1813
9.22	5.45	6.10	0.65	0.5701	0.1226	9.3426
9.51	5.50	6.20	0.70	0.5376	0.0654	9.5754
9.73	5.55	6.33	0.78	0.4851	-0.0259	9.7041
10.00	5.60	6.47	0.87	0.4262	-0.1291	9.8709
10.23	5.65	6.62	0.99	0.3609	-0.2481	9.9819
10.49	5.70	6.80	1.10	0.2759	-0.4690	10.0210

Average pKa = 9.4923± 0.4410

Metal-ligand stability constant (Log K)

The stabilityconstants require the accurate values of proton-ligand stability constants (Anil and Maroti, 2008). Metal titration curves crossed over ligand titration curve indicated the formation of complex upon proton release (Santosh, *et al.*, 2011). If the values of n- are within range 0.2-0.8 and 1.2-18 this indicates the formation of 1:1 and 1:2 complexes (Sayyed and Mazahar, 2012).

The metal (II)-humate stepwise stability constants (log k) at phenolic group (Tables 3-18)

Table 3: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n}{1-n}$)	$LogK_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

$LogK_1$ (Average value) = 2.4788± 0.2203

Table 4: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	Log($\frac{n-1}{2-n}$)	$LogK_2$
9.51	5.50	6.66	6.73	0.07	1.3509	1.70	-0.2671	1.4329
9.73	5.55	6.78	6.85	0.07	1.6383	1.51	0.2467	1.7567
10.00	5.60	6.90	6.98	0.08	2.1783	1.31	-0.2158	1.0942
10.23	5.65	7.05	7.13	0.08	4.1904	1.27		
10.49	5.70	7.10	7.19	0.09	4.6920			

$LogK_2$(Average value) = 1.4280 ± 0.3312

Table 5:Point-wise method,Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	Log$(\frac{n}{n-1})$	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430

LogK_1 **(Average value)** = 2.3059± 0.6153

Table 6:Point-wise method, Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$V_3\text{-}V_2$	n	pL	Log$(\frac{n-1}{2-n})$	Log K_2
9.73	5.55	6.33	6.42	0.09	0.9000	1.69		
10.00	5.60	6.47	6.58	0.11	1.2578	1.44	-0.4592	0.9808
10.23	5.65	6.62	6.84	0.12	1.6137	1.26	-0.2010	1.4610
10.49	5.70	6.80	6.92	0.12	2.1052	1.03		

LogK_2 **(Average value)** = 1.2209± 0.3398

Table 7:Point-wise method,Pb (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	log$(\frac{n}{1-n})$	LogK_1
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.60	0.05	0.8333	1.96	0.6989	2.6589

LogK_1 (Average value) = 2.5832 ±0.1614

Table 8:Point-wise method,Pb-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	log$(\frac{n-1}{2-n})$	logK_2
9.51	5.50	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.83	0.05	1.1702	1.44		
10.00	5.60	6.90	6.90	0.05	1.4864	1.22	-0.0237	1.1963
10.23	5.65	7.05	7.10	0.05	2.0190	1.09		
10.49	5.70	7.10	7.17	0.07	3.6492	1.00		

LogK_2(Average value) = 1.1963

Table 9:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$V_3\text{-}V_2$	n	pL	Log $(\frac{n}{n-1})$	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.5477	2.3123
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	0.0272	2.2072
9.51	5.50	6.20	6.26	0.07	0.6417	1.89	0.2530	2.1430
9.73	5.55	6.40	6.40	0.07	0.7000	1.67	0.3680	2.0380

LogK_1 **(Average value)** = 2.2364 ± 0.1602

Table 10:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$V_3\text{-}V_2$	n	pL	Log$(\frac{n-1}{2-n})$	Log K_2
10.00	5.60	6.47	6.55	0.08	1.9503	1.41		
10.23	5.65	6.62	6.72	0.11	1.4792	1.26	-0.0361	1.2239

LogK_2 **(Average value)** = 1.2239

Table 11:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	log$(\frac{n}{n-1})$	LogK_1
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4290	2.2110
8.72	5.35	6.37	6.39	0.02	0.2858	2.42	-0.3978	2.0222
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

LogK_1 (Average value)=2.1382**±**0.1046

Table 12:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n-1}{2-n}$)	LogK_2
9.51	5.55	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.84	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.93	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.10		
10.49	5.70	7.10	7.18	0.07	3.6492	0.83		

LogK_2(Average value) = 1.5453 **±** 0.3450

Table 13:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.3477	2.3123
9.00	5.40	6.00	6.04	0.04	0.3236	2.38	-0.3202	2.0598
9.22	5.45	6.10	6.15	0.05	0.4297	2.17	-0.1230	2.0470
9.51	5.50	6.20	6.26	0.06	0.5500	1.89	0.0871	1.9771
9.73	5.55	6.33	6.40	0.07	0.7000	1.67	0.3680	2.0380

LogK_1 **(Average value)** = 2.1568 ± 0.2069

Table 14:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
10.00	5.60	6.47	6.55	0.08	0.9148	1.41		
10.23	5.65	6.62	6.71	0.09	1.2102	1.20	-0.5749	0.6251
10.49	5.70	6.80	6.92	0.09	1.5968	1.03	0.1703	1.2003

LogK_2 **(Average value)** = 0.9127± 0.4070

Table15:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	Log($\frac{n}{1-n}$)	LogK_1
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4210	2.2190
8.72	5.35	6.37	6.40	0.03	0.4286	2.42	-0.1249	2.2951
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.96	0.3010	2.2610
9.51	5.55	6.66	6.70	0.04	0.7720	1.67	0.5297	2.1997

LogK_1 (Average value) = 2.2108± 0.0825

Table 16:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
9.73	5.55	6.78	6.83	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.95	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.09		
10.49	5.70	7.10	7.16	0.06	3.1429	0.89		

LogK_2 **(Average value)** = 1.5453± 0.3450

Table 17:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.86	0.05	0.3717	2.88	-0.2280	2.6520
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.06	0.06	0.4853	2.38	-0.0255	2.3545
9.22	5.45	6.10	6.16	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430
9.73	5.55	6.33	6.41	0.08	0.8000	1.69	0.6020	2.2920

LogK_1 **(Average value)** = 2.2516± 0.5380

Table 18:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log$(\frac{n-1}{2-n})$	Log K_2
10.00	5.60	6.47	6.57	0.10	1.1434	1.43		
10.23	5.65	6.62	6.72	0.10	1.3448	1.23	-0.2788	0.9512
10.49	5.70	6.80	6.90	0.10	1.7742	1.03	0.5351	1.5651

LogK_2 **(Average value)** = 1.2581± 0.4340

Table 19: Stepwise and overall Stability constants of thehydrolysed and unhydrolysed divalent metal (II) complexes

Chelates	**LogK_1**	**LogK_2**	**Logβ**
[Cu (Hydrolysed PSHA-1)$_2$]	2.4788	1.4280	3.9068
[Pb (Hydrolysed PSHA-1)$_2$]	2.5832	1.1963	3.7795
[Cd (Hydrolysed PSHA-1)$_2$]	2.2108	1.5453	3.7561
[Mg (Hydrolysed PSHA-1)$_2$]	2.1382	1.5453	3.6835
[Cu (Unhydrolysed PSHA-1)$_2$]	2.3059	1.2209	3.5268
[Pb (Unhydrolysed PSHA-1)$_2$]	2.2364	1.2239	3.4603
[Cd (Unhydrolysed PSHA-1)$_2$]	2.2516	1.2581	3.5097
[Mg (Unydrolysed PSHA-1)$_2$]	2.1568	0.9127	3.0695

The results obtained (Table19) shows the stepwise and overall stability constants to be not high indicating low stability of the complexes, because the solubility of most metal ions in the basic pH range is minimal due to metal hydroxide precipitation (Karimi, 2017). In general, the stepwise stability constants (K_1 and K_2) follow the order $K_1 > K_2$ for the copper, lead, magnesium and cadmium complexes respectively. The steady decrease of the values with increasing number of ligands is in agreement with the prediction made by researchers (Na'aliya, 2013). The decrease could be attributed to the fact that as the number of the ligands (Humate ions) that enters the coordination zone increases the aqua molecules available for replacement by the ligands become less. Thus, the metal ions become less electron loving with progressive intake of the ligand and this results in the decrease in the values of the constants (Na'aliya, 2013). Also the stability of the complexes is influenced by the size and number of the chelate rings(Mackay and Mackay,2002).All the complexes form rings in their structure as humate, a bidentate ligand, bond the metal ions in the ratio 1:2 (Boguta and Sokolowska, 2016) forming chelate rings. The values of the overall stability constants (logβ) obtained for humate complexes are not high indicating low stability as the values are not high. LogK values for copper-humates (Table 3 to 6) obtained in this study are lower than those reported for the complexes of humic acids (Pandey *et al.*, 2015; Dinu, 2013; Kaschl *et al.*, 2010 and Gilbeto and Jorg, 2001). The values of LogK(Table 7 to 10) forlead-humates are lower than those reported for the lead in the literature (Dinu, 2013; Gilbeto and Jorg 2001). Log K values(Table 11 to 14) for magnesium-humates obtained in this study are close to those reported by (Pandey *et al.*, 2015). Log K values of cadmium-humates (Table 15 to 18) obtained in this work near to the one reported by (Dinu, 2013 and Pandey *et al.*, 2015).The difference between the reported values and the values obtained in this study might be probably as a result of acid hydrolysis of humic acid. The values of the overall stability constants (log β) of the copper humates complexes presented in Table 19 is high than that of other metal humate complexes, show relatively high stability of Cu-HA complexes, show the following order of stability: Cu >Pb> Cd > Mg; which are in close agreement to the findings of (Dinu, 2013 and Pandey *et al.*, 2015).The high stability of Cu-humate chelate could be attributed to the existence of coordinate covalent bond between the complexing agents and the Cu^{2+} ions. Since, Cu^{2+} being a metal of the transitional series with $3d^9$ electronic configurations can accept the electrons from the complexing agents. Similarly,the low stabilities of Pb,Cd and Mg - complexes could be explained by that Pb^{2+} with $6s^2$, Cd^{2+} with $4d^{10}$ and Mg^{2+} with $2p^6$ their electronic configuration has a completely filled d,p and s orbitals. Moreover, the stabilities of metal ions with hydrolysed humic acid from peat soil were higher than those with unhydrolysed humic acid from peat soil; which is ascribed to the high content of acidity in hydrolysed humic acid than unhydrolysed humic acid.

CONCLUSION

The values of logK for Cu(II) hydrolysed humic acid complex was higher followed by Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes as compared with metal(II) unhydrolysed humic acid complexes . This indicates acid hydrolysis of humic acid can enhance the complexation behavior of humic acid with metal (II) ions. However, the higher values of logβ for Cu(II), Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes indicates more stable stepwise complexes formed as compared with Cu(II), Pb(II), Cd(II) and Mg(II) unhydrolysed humic acid complexes.

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STABILITY CONSTANTS OF COMPLEXES OF METAL IONS WITH PEATSOIL HUMIC ACIDS UNDER NON-ACID-CONDITIONS

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ABSTRACT

Stability constants of complexes of four divalent metal ions viz. Cu^{2+}, Pb^{2+},Mg^{2+} and Cd^{2+} with humic acids (HA) were determined by potentiometric titration of humic acids with the corresponding salt of the divalent metals in aqueous media under non-acid-condition. The log K (logarithm of the stability constant) ranged from 1.0942 to 2.7471 for metal-humic acid complexes were determined using point-wise computational method. The order of stability constants were obtained as follows: Cu >Pb> Cd > Mg for metal -HA complexes respectively, indicating a higher degree of complexation with Cu metal ion.

Keywords: stability constant, humic acid, potentiometric titration, divalent metals, acid hydrolysis.

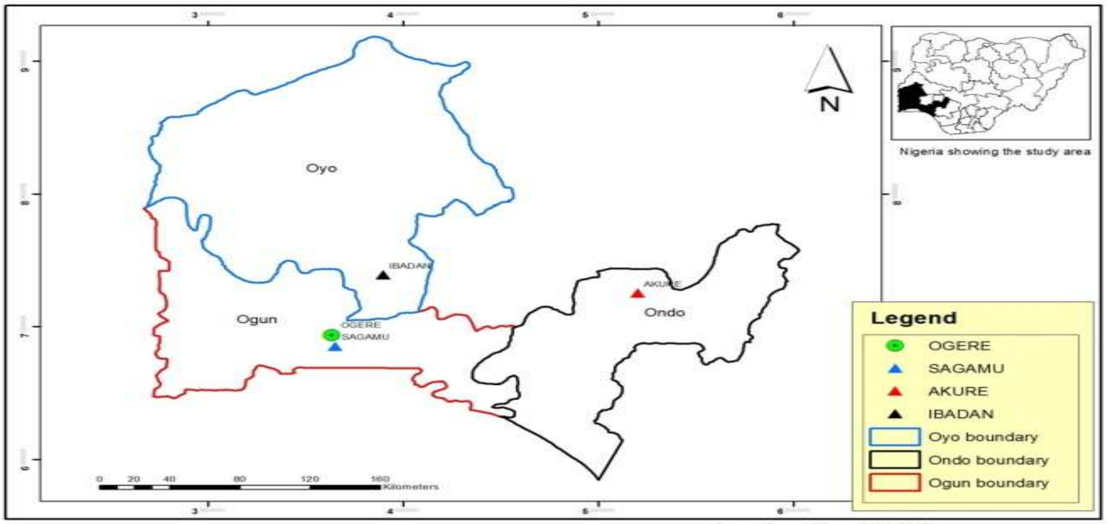
NTRODUCTION

The stability constant of a complex is the numerical expression of its stability and provides a quantitative measure of affinity of the metal ion to the complexing agent. An understanding of the relative stability of metal-complexes helps in predicting the behavior of metal ions in the soil (Ram and Raman, 1982). Extensive researches has been done to determine the stability constants of the complexes formed between humic acid (HA) with a number of metal ions. Ashok *et al*., (2000) reported that humic acid with hydroxyl, phenoxyl and carboxyl reactive groups can form coordination compound with metal ions at pH 3.5. The stability constants(Log K) for different metal-humic acid complexes indicated the following order of the stabilities of complexes formed between humic acid and metal ion, Cu >Fe >Pb> Ni > Co > Ca > Cd > Zn >Mn> Mg. Andelkovic *et al*., (2010) investigated the binding of Cd(II) to soil humic acid at pH 6.5 and in 0.1M KNO_3 ionic medium. The stability constant for binding indicating greater stability in the case when carboxyl groups are involved in complexation reaction. Kostic *et al*.,(2012) investigated the complexation of humic acid with certain heavy metal ions (Co(II), Ni(II),Cu(II), Zn(II), and Pb(II). The experiment was performed at 25°C, at pH 4.0 and ionic strength of 0.01M. Stability constant of complex between Pb(II) ions and humic acid is greater than stability constants of other investigated metal-humate complexes. Bogata and Sokolowska (2016) analyses the interaction between humic acids from different soils and Zn (II) ions at wide concentration ranges and at pH 5. Studies have showed significant impact of Zn concentration, pH and some properties of humic acids with zinc.But all of these studies were limited to acidic pH range. Therefore, the present study was carried out to determine and compare the stability constants of complexes of metal ions with hydrolysed peat soil humic acid and unhydrolysed peat soil humic under non-acid conditions.

MATERIALS AND METHODS

Analytical grade chemicals used includes hydrochloric acid (HCl), nitric acid (HNO_3), sodium hydroxide (NaOH), lead nitrate $Pb(NO_3)_2$, copper nitrate $Cu(NO_3)_2.3H_2O$, cadmium nitrate $Cd(NO_3)_2.4H_2O$, magnesium nitrate $Mg(NO_3)_2.6H_2O$, potassium nitrate (KNO_3), calcium chloride ($CaCl_2$), (sigma-Aldrich). Dowex 50WX8, (20-50 mesh) from Fluka.

Area of study



Source: Dept. of Geog. BUK (2016)

Figure 1: Map showing the sampling point at Sagamu Town, Ogun State.

Description of Sampling Area

Sagamu has geographical coordinates between 6°50′ north; 3° 38′ east is located in south western region of Nigeria. The region has tropical wet and dry climate with a lengthy wet season and relatively constant temperatures throughout the course of the year. Wet season runs from March to October, November to December forms the region dry season. The vegetation type of the region is savannah which is really grassland with small bushes and occasional big trees. Grassland soils have substantially higher organic matter content than forest soils (Novackova, 2011).

Sample Collection

The Peatsoil samples were collected from four different sampling points (0-10cm depth) in Sagamu into polyethylene bag with plastic spoons. Samples were taken to the laboratory, extraneous materials were removed; the samples were air-dried, crushed and ground to a fine powder in a mortar passed through a 0.20mm sieve. The samples were kept for analysis.

Isolation and purification of humic acid from peat soil sample

Peatsoil sample (100g) was mixed with 1000 cm^3 of 0.1M NaOH solution, shaken for 3hours and left to stand overnight. Dark-coloured supernatant was obtained and decanted from solid residue. The dark-coloured supernatant was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 6 hours. Yellowish brown supernatant and dark-brown precipitate were obtained. The yellowish brown supernatant was decanted followed by centrifuge and discarded. The dark-brown precipitate was mixed with $500cm^3$of 0.1M NaOH solution followed by passing through dowex resin. The dark-brown solution was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 3 hours. The dark-brown precipitate was washed several times with deionized water. The supernatant was treated with $AgNO_3$ solution until no white precipitate observed. The humic acid was transferred to weighed crucible and dried at 60°C in an oven for 12 hours. The humic acid was cooled and dried in the desiccator, weighed and recorded. The obtained humic acid was dried again at 60°C for additional 6 hours cooled and dried in the desiccator, weighed and recorded constant weight was obtained (Baruah *et al.*, 2015).

FT-IR analysis

FT-IR spectra of humic acid sample was analysed using Carry 630 FT-IR Agilent Technologies.

Unhydrolysed compost humic acid

The unhydrolysed humic acid was obtained after isolation and purification of compost humic acid and kept for investigation.

Acid hydrolysis of Peatsoil acid

Peatsoil humic acid sample (1g) was refluxed for 12 hours at (160°C) with $50cm^3$ of 6M HCl. The mixture was allowed to cool, decanted, and centrifuged after hydrolysis. The insoluble residues were washed with distilled water via centrifugation several times, and the supernatant was treated with $AgNO_3$ solution until no white precipitate was observed. The residue was thoroughly dried over $CaCl_2$ in a desiccator at room temperature (Chefetz *et al.*, 2002). Finally, the obtained hydrolysed humic acid was kept for investigation.

Potentiometric Titrations

Potentiometric measurements were carried out using a pH-meter Jenway (model 3510) with combine electrode, the sensitivity of the pH -meter is 0.01 units. The pH meter was switched on half an hour before starting the titration for initial warm up of the instrument. The instrument was calibrated with an aqueous standard buffer solution of pH 4.00 and 10.0 (borate buffer) prepared from a "Qualigens" buffer tablets.

The following sets of solutions were prepared in a 250cm^3 volumetric flask separately for pH metric titrations.

(i) 5 cm^3 0.1 M HCl + 40 cm^3 deionized water
(ii) 5 cm^3 0.1 M HCl + 39 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid
(iii) 5 cm^3 0.1 M HCl + 37 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid + 2 cm^3 0.01 M Cu(II)

The solutions were titrated against standardized 0.110MNaOH separately. The total volume of each mixture was adjusted to 50 cm^3 and the ionic strength of the solutions was maintained constant at by adding appropriate amount of stock solution of 1M KNO$_3$ (Gamal, 2015; Omar and Ali, 2015). A magnetic stirrer was used to achieve thorough mixing of the interacting solutions at 550 rpm. The same set of experimental conditions was applied for potentiometric titration of remaining samples.

Evaluation of pKa of Hydrolysed peat soil Humic Acids

The proton-ligand formation number n$_{\mathbf{A}}$ were calculated by Irving and Rossotti expression (Omar and Ali, 2015).

$$nA = Y- \frac{(V2-V1)(No-Eo)}{(Vo+V1)TcL} \quad ....1$$

Where: Y is number of dissociable proton, (V$_2$-V$_1$) is the measure of displacement of the ligand curve relative to acid curve, N^o and E^o are the resultant concentration of alkali solution, free acid solution, T$_{cL}$^{o} is the total ligand concentration, V^o is the total volume of titration solution,V$_1$ is the volume of alkali added to acid solution,V$_2$ is the volume of alkali added to acid solution + ligand solution, acid dissociation constants (pKa - values) of ligand were calculated by algebraic method point wise calculation (Tables 1). The dissociation constants (pKa) were calculated according to the following relation:

$$pKa = pH + \log(\frac{nA}{1-nA}) \quad ....2$$

Where: pKa is the acid dissociation constant, n$_A$is the Proton-ligand formation number and pH is the pH-values (Omar and Ali, 2015).

Determination of metal-ligand stability constants (log K) of complexes

The potentiometric measurement for the determination of stability constant of a complex in solution is based on the fact that the redox potential of the couple $\frac{M^{+(m-n)}}{M^{+m}}$ is shifted significantly on complexation of the metal ion with the ligand. This method involves change in hydrogen ion concentration [H$^+$] due to the displacement or association of one or more protons taking place during complexation reaction. This change can be found out by titrating the solutions containing free acid, acid with ligand, and acid with ligand and metal ion, individually against a standard alkali solution at a constant ionic strength or temperature. Either ionic strength or temperature may be varied for different sets of solutions. In all the cases, the change in the pH of the solution is measured after each addition of a known amount of alkali to the reaction cell which contains the reaction mixture. The titration curves are then drawn by plotting the measured pH values against the corresponding volume of alkali added and the stability constants of the complexes are determined from the titration curves by employing pH-metric titration technique given by (Irving and Rossoti).

Metal-ligand stability constants (Log K) were determined by using the following relations:

$$\bar{n} = \frac{(V_3 - V_2)(E^0 + N^0)}{(V^0 + V_2)\bar{n}_A T_m^0} \quad ....3$$

and

$$PL = \log_{10}\{\frac{1+\beta_n^H \frac{1}{[anti\ \log \mathrm{pH}]^n}}{\mathrm{T}_\mathrm{L}^0 - \bar{n}T_m^0} \mathrm{X} \frac{(V^0 + V_3)}{V^0}\} \quad ....4$$

Where $T_{L,}$ T^{o}, E°, and V^{o}havethe same significance as in equation (1) above, T_{m} denotes the total concentration of metal present in solution, V_{3} is the volume of metal ions present in solution and β^{H} is the overall proton ligand stability constant. The metal-ligand stability constants (log K) were determined by employing point wise computational Method (eq. 5 and 6).

$$\mathrm{LogK}_1 = \log\left(\frac{n}{1-n}\right) + \mathrm{pL} \qquad \ldots\ldots\ldots\ldots.5$$

$$\mathrm{LogK}_2 = \log\left(\frac{1-n}{2-n}\right) + \mathrm{pL}\ldots\ldots\ldots\ldots\ldots\ldots\ldots.6$$

Where: Log K is the metal-ligand stability constant, pL is the Free ligand exponent function, **n** is the Average number of ligand attached with metal ion (Janrao*et al*., 2014).The results obtained were analyzed by an ORIGIN 2016 program using titration data and then the proton-ligand stability constants (pKa) and Metal-ligand stability constant (LogK) calculated (Omar and Ali, 2015).

RESULTS AND DISCUSSION

Fourier transformed infrared (FT-IR) spectra of isolated humic acid from peat soils Figure 2 had distinct clear absorption bands indicating the presence of major humic acid structural elemental groups such as H bonded OH ($3680cm^{-1}$ peak), C=O of carbonyl ($1721cm^{-1}$ peak), functional groups of aliphatic components CH_2 ($2918cm^{-1}$ peak) and C-O stretching of polysaccharide ($1168cm^{-1}$ peak). The positions of the absorption bands of the spectra fell within typical major absorption bands of humic acid which is at frequencies 3680, 2918, 1721, 1168 cm^{-1}. The first peak centred in the vicinity of 3680 cm^{-1} region is attributed to phenol OH group bounded by intermolecular H bonds. The $2918cm^{-1}$ band usually has absorption maximum at 2918 cm^{-1} which is due to C–H stretching of alkane group (CH_2). The next major absorption band is 1721 cm^{-1}. This band has been commonly ascribed to C=O stretching of mainly carboxyl group (COOH) with trace amount of ketones. The last peak was observed at 1168 cm^{-1} due to C–O stretching of polysaccharides and this peak appeared also in the spectra of humic acid from peat soil. The FTIR spectra of the isolated humic acid contained all major characteristic absorption peaks of humic acid. These absorption peaks indicated the presence of the major structural elements of humic acid namely H bonded OH, C=C of aromatic ring, C=O of carbonyl group (both carboxyl and ketonic), CH_2 group. This strongly supports the presence of humic acid.

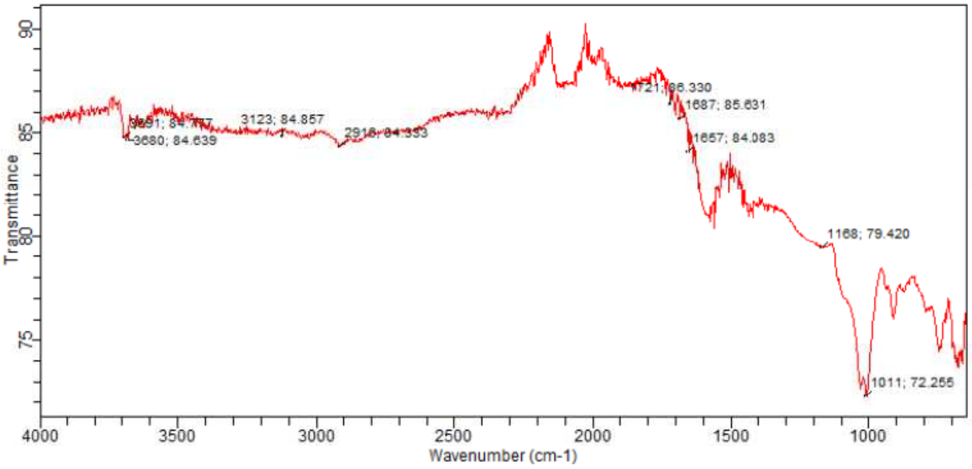


Fig. 2 : FT-IR spectraof peatsoilhumic acid (PSHA)

Evaluation of acid dissociation constant (pka) of acid hydrolysed peat soil humicacid at phenolic group

The value of the dissociation constant of the peat soil humic acid (PSHA) that underwent acidhydrolysis studied was found to be 8.9299 as shown Table 1, which is lower than the literaturevalues reported by Almeida and Szpoganics, (2015), Borges *et al*., (2005); Badr *et al*., (2012)and Fernandes *et al*,.(2009) of 9.73, 9.47 and 10.30. The difference between the obtained valuesand the reported values in this study might be probably as a result of acid hydrolysis of humicacid.

Table 1: PKa of (Hydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	$\log(\frac{nA}{1-nA})$	pKa
8.50	5.30	6.29	0.99	0.3594	-0.2510	8.2490
8.72	5.35	6.37	1.02	0.3400	-0.2880	8.4320
9.00	5.40	6.46	1.06	0.3141	-0.3391	8.6609
9.22	5.45	6.55	1.10	0.2882	-0.3927	8.8273
9.51	5.50	6.66	1.16	0.2494	-0.4786	9.0314
9.73	5.55	6.78	1.23	0.2041	-0.5910	9.1390
10.00	5.60	6.90	1.30	0.1589	-0.7238	9.2762
10.23	5.65	7.05	1.40	0.0941	-0.9835	9.2465
10.49	5.70	7.10	1.40	0.0941	-0.9835	9.5065

Average pKa = 8.9299 ± 0.4186

Table 2: PKa of (Unhydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	$\mathrm{Log}(\frac{nA}{1-n})$	pKa
8.50	5.30	5.81	0.51	0.6619	0.2919	8.7919
8.72	5.35	5.90	0.55	0.6357	0.2418	8.9618
9.00	5.40	6.00	0.60	0.6029	0.1813	9.1813
9.22	5.45	6.10	0.65	0.5701	0.1226	9.3426
9.51	5.50	6.20	0.70	0.5376	0.0654	9.5754
9.73	5.55	6.33	0.78	0.4851	-0.0259	9.7041
10.00	5.60	6.47	0.87	0.4262	-0.1291	9.8709
10.23	5.65	6.62	0.99	0.3609	-0.2481	9.9819
10.49	5.70	6.80	1.10	0.2759	-0.4690	10.0210

Average pKa = 9.4923± 0.4410

Metal-ligand stability constant (Log K)

The stabilityconstants require the accurate values of proton-ligand stability constants (Anil and Maroti, 2008). Metal titration curves crossed over ligand titration curve indicated the formation of complex upon proton release (Santosh, *et al.*, 2011). If the values of n- are within range 0.2-0.8 and 1.2-18 this indicates the formation of 1:1 and 1:2 complexes (Sayyed and Mazahar, 2012).

The metal (II)-humate stepwise stability constants (log k) at phenolic group (Tables 3-18)

Table 3: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$\log(\frac{n}{1-n})$	$\mathrm{Log}K_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

LogK_1 (Average value) = 2.4788± 0.2203

Table 4: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$\mathrm{Log}(\frac{n-1}{2-n})$	$\mathrm{Log}K_2$
9.51	5.50	6.66	6.73	0.07	1.3509	1.70	-0.2671	1.4329
9.73	5.55	6.78	6.85	0.07	1.6383	1.51	0.2467	1.7567
10.00	5.60	6.90	6.98	0.08	2.1783	1.31	-0.2158	1.0942
10.23	5.65	7.05	7.13	0.08	4.1904	1.27		
10.49	5.70	7.10	7.19	0.09	4.6920			

LogK_2(Average value) = 1.4280 ± 0.3312

Table 5:Point-wise method,Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$\mathrm{Log}(\frac{n}{n-1})$	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430

LogK_1 **(Average value)** = 2.3059± 0.6153

Table 6:Point-wise method, Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$\mathrm{Log}(\frac{n-1}{2-n})$	Log K_2
9.73	5.55	6.33	6.42	0.09	0.9000	1.69		
10.00	5.60	6.47	6.58	0.11	1.2578	1.44	-0.4592	0.9808
10.23	5.65	6.62	6.84	0.12	1.6137	1.26	-0.2010	1.4610
10.49	5.70	6.80	6.92	0.12	2.1052	1.03		

LogK_2 **(Average value)** = 1.2209± 0.3398

Table 7:Point-wise method,Pb (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$\log(\frac{n}{1-n})$	LogK_1
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.60	0.05	0.8333	1.96	0.6989	2.6589

LogK_1 (Average value) = 2.5832 ±0.1614

Table 8:Point-wise method,Pb-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$\log(\frac{n-1}{2-n})$	logK_2
9.51	5.50	6.66	6.71	0.05	0.9650	1.67	-0.0237	1.1963
9.73	5.55	6.78	6.83	0.05	1.1702	1.44		
10.00	5.60	6.90	6.90	0.05	1.4864	1.22		
10.23	5.65	7.05	7.10	0.05	2.0190	1.09		
10.49	5.70	7.10	7.17	0.07	3.6492	1.00		

LogK_2(Average value) = 1.1963

Table 9:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log $(\frac{n}{n-1})$	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.5477	2.3123
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	0.0272	2.2072
9.51	5.50	6.20	6.26	0.07	0.6417	1.89	0.2530	2.1430
9.73	5.55	6.40	6.40	0.07	0.7000	1.67	0.3680	2.0380

LogK_1 **(Average value)** = 2.2364 ± 0.1602

Table 10:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$\mathrm{Log}(\frac{n-1}{2-n})$	Log K_2
10.00	5.60	6.47	6.55	0.08	1.9503	1.41		
10.23	5.65	6.62	6.72	0.11	1.4792	1.26	-0.0361	1.2239

LogK_2 **(Average value)** = 1.2239

Table 11:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$\log(\frac{n}{n-1})$	LogK_1
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4290	2.2110
8.72	5.35	6.37	6.39	0.02	0.2858	2.42	-0.3978	2.0222
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

LogK_1 (Average value)=2.1382**±**0.1046

Table 12:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	$\log(\frac{n-1}{2-n})$	$LogK_2$
9.51	5.55	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.84	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.93	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.10		
10.49	5.70	7.10	7.18	0.07	3.6492	0.83		

$LogK_2$(Average value) = 1.5453 **±** 0.3450

Table 13:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$V_3\text{-}V_2$	n	pL	$Log(\frac{n}{n-1})$	$Log\ K_1$
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.3477	2.3123
9.00	5.40	6.00	6.04	0.04	0.3236	2.38	-0.3202	2.0598
9.22	5.45	6.10	6.15	0.05	0.4297	2.17	-0.1230	2.0470
9.51	5.50	6.20	6.26	0.06	0.5500	1.89	0.0871	1.9771
9.73	5.55	6.33	6.40	0.07	0.7000	1.67	0.3680	2.0380

$LogK_1$ **(Average value)** = 2.1568 ± 0.2069

Table 14:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$V_3\text{-}V_2$	n	pL	$Log(\frac{n-1}{2-n})$	$Log\ K_2$
10.00	5.60	6.47	6.55	0.08	0.9148	1.41		
10.23	5.65	6.62	6.71	0.09	1.2102	1.20	-0.5749	0.6251
10.49	5.70	6.80	6.92	0.09	1.5968	1.03	0.1703	1.2003

$LogK_2$ **(Average value)** = 0.9127± 0.4070

Table15:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	$Log(\frac{n}{1-n})$	$LogK_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4210	2.2190
8.72	5.35	6.37	6.40	0.03	0.4286	2.42	-0.1249	2.2951
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.96	0.3010	2.2610
9.51	5.55	6.66	6.70	0.04	0.7720	1.67	0.5297	2.1997

$LogK_1$ (Average value) = 2.2108± 0.0825

Table 16:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	$Log(\frac{n-1}{2-n})$	$Log\ K_2$
9.73	5.55	6.78	6.83	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.95	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.09		
10.49	5.70	7.10	7.16	0.06	3.1429	0.89		

$LogK_2$ **(Average value)** = 1.5453± 0.3450

Table 17:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$V_3\text{-}V_2$	n	pL	$Log(\frac{n}{n-1})$	$Log\ K_1$
8.50	5.30	5.81	5.86	0.05	0.3717	2.88	-0.2280	2.6520
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.06	0.06	0.4853	2.38	-0.0255	2.3545
9.22	5.45	6.10	6.16	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430
9.73	5.55	6.33	6.41	0.08	0.8000	1.69	0.6020	2.2920

$LogK_1$ **(Average value)** = 2.2516± 0.5380

Table 18:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$\text{Log}(\frac{n-1}{2-n})$	Log K_2
10.00	5.60	6.47	6.57	0.10	1.1434	1.43		
10.23	5.65	6.62	6.72	0.10	1.3448	1.23	-0.2788	0.9512
10.49	5.70	6.80	6.90	0.10	1.7742	1.03	0.5351	1.5651

LogK_2 **(Average value)** = 1.2581± 0.4340

Table 19: Stepwise and overall Stability constants of thehydrolysed and unhydrolysed divalent metal (II) complexes

Chelates	**LogK_1**	**LogK_2**	**Logβ**
[Cu (Hydrolysed PSHA-1)$_2$]	2.4788	1.4280	3.9068
[Pb (Hydrolysed PSHA-1)$_2$]	2.5832	1.1963	3.7795
[Cd (Hydrolysed PSHA-1)$_2$]	2.2108	1.5453	3.7561
[Mg (Hydrolysed PSHA-1)$_2$]	2.1382	1.5453	3.6835
[Cu (Unhydrolysed PSHA-1)$_2$]	2.3059	1.2209	3.5268
[Pb (Unhydrolysed PSHA-1)$_2$]	2.2364	1.2239	3.4603
[Cd (Unhydrolysed PSHA-1)$_2$]	2.2516	1.2581	3.5097
[Mg (Unydrolysed PSHA-1)$_2$]	2.1568	0.9127	3.0695

The results obtained (Table19) shows the stepwise and overall stability constants to be not high indicating low stability of the complexes, because the solubility of most metal ions in the basic pH range is minimal due to metal hydroxide precipitation (Karimi, 2017). In general, the stepwise stability constants (K_1 and K_2) follow the order $K_1 > K_2$ for the copper, lead, magnesium and cadmium complexes respectively. The steady decrease of the values with increasing number of ligands is in agreement with the prediction made by researchers (Na'aliya, 2013). The decrease could be attributed to the fact that as the number of the ligands (Humate ions) that enters the coordination zone increases the aqua molecules available for replacement by the ligands become less. Thus, the metal ions become less electron loving with progressive intake of the ligand and this results in the decrease in the values of the constants (Na'aliya, 2013). Also the stability of the complexes is influenced by the size and number of the chelate rings(Mackay and Mackay,2002).All the complexes form rings in their structure as humate, a bidentate ligand, bond the metal ions in the ratio 1:2 (Boguta and Sokolowska, 2016) forming chelate rings. The values of the overall stability constants (logβ) obtained for humate complexes are not high indicating low stability as the values are not high. LogK values for copper-humates (Table 3 to 6) obtained in this study are lower than those reported for the complexes of humic acids (Pandey *et al*., 2015; Dinu, 2013; Kaschl *et al*., 2010 and Gilbeto and Jorg, 2001). The values of LogK(Table 7 to 10) forlead-humates are lower than those reported for the lead in the literature (Dinu, 2013; Gilbeto and Jorg 2001). Log K values(Table 11 to 14) for magnesium-humates obtained in this study are close to those reported by (Pandey *et al*., 2015). Log K values of cadmium-humates (Table 15 to 18) obtained in this work near to the one reported by (Dinu, 2013 and Pandey *et al*., 2015).The difference between the reported values and the values obtained in this study might be probably as a result of acid hydrolysis of humic acid. The values of the overall stability constants (log β) of the copper humates complexes presented in Table 19 is high than that of other metal humate complexes, show relatively high stability of Cu-HA complexes, show the following order of stability: Cu >Pb> Cd > Mg; which are in close agreement to the findings of (Dinu, 2013 and Pandey *et al*., 2015).The high stability of Cu-humate chelate could be attributed to the existence of coordinate covalent bond between the complexing agents and the Cu^{2+} ions. Since, Cu^{2+} being a metal of the transitional series with $3d^9$ electronic configurations can accept the electrons from the complexing agents. Similarly,the low stabilities of Pb,Cd and Mg -complexes could be explained by that Pb^{2+} with $6s^2$, Cd^{2+} with $4d^{10}$ and Mg^{2+} with $2p^6$ their electronic configuration has a completely filled d,p and s orbitals. Moreover, the stabilities of metal ions with hydrolysed humic acid from peat soil were higher than those with unhydrolysed humic acid from peat soil; which is ascribed to the high content of acidity in hydrolysed humic acid than unhydrolysed humic acid.

CONCLUSION

The values of logK for Cu(II) hydrolysed humic acid complex was higher followed by Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes as compared with metal(II) unhydrolysed humic acid complexes . This indicates acid hydrolysis of humic acid can enhance the complexation behavior of humic acid with metal (II) ions. However, the higher values of logβ for Cu(II), Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes indicates more stable stepwise complexes formed as compared with Cu(II), Pb(II), Cd(II) and Mg(II) unhydrolysed humic acid complexes.

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STABILITY CONSTANTS OF COMPLEXES OF METAL IONS WITH PEATSOIL HUMIC ACIDS UNDER NON-ACID-CONDITIONS

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ABSTRACT

Stability constants of complexes of four divalent metal ions viz. Cu^{2+}, Pb^{2+},Mg^{2+} and Cd^{2+} with humic acids (HA) were determined by potentiometric titration of humic acids with the corresponding salt of the divalent metals in aqueous media under non-acid-condition. The log K (logarithm of the stability constant) ranged from 1.0942 to 2.7471 for metal-humic acid complexes were determined using point-wise computational method. The order of stability constants were obtained as follows: Cu >Pb> Cd > Mg for metal -HA complexes respectively, indicating a higher degree of complexation with Cu metal ion.

Keywords: stability constant, humic acid, potentiometric titration, divalent metals, acid hydrolysis.

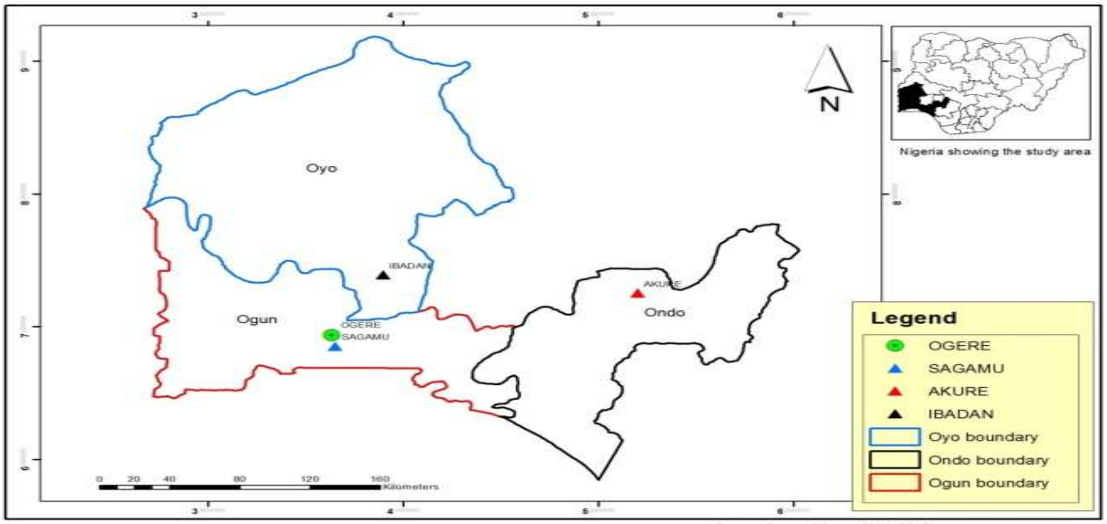
NTRODUCTION

The stability constant of a complex is the numerical expression of its stability and provides a quantitative measure of affinity of the metal ion to the complexing agent. An understanding of the relative stability of metal-complexes helps in predicting the behavior of metal ions in the soil (Ram and Raman, 1982). Extensive researches has been done to determine the stability constants of the complexes formed between humic acid (HA) with a number of metal ions. Ashok *et al*., (2000) reported that humic acid with hydroxyl, phenoxyl and carboxyl reactive groups can form coordination compound with metal ions at pH 3.5. The stability constants(Log K) for different metal-humic acid complexes indicated the following order of the stabilities of complexes formed between humic acid and metal ion, Cu >Fe >Pb> Ni > Co > Ca > Cd > Zn >Mn> Mg. Andelkovic *et al*., (2010) investigated the binding of Cd(II) to soil humic acid at pH 6.5 and in 0.1M KNO_3 ionic medium. The stability constant for binding indicating greater stability in the case when carboxyl groups are involved in complexation reaction. Kostic *et al*.,(2012) investigated the complexation of humic acid with certain heavy metal ions (Co(II), Ni(II),Cu(II), Zn(II), and Pb(II). The experiment was performed at 25°C, at pH 4.0 and ionic strength of 0.01M. Stability constant of complex between Pb(II) ions and humic acid is greater than stability constants of other investigated metal-humate complexes. Bogata and Sokolowska (2016) analyses the interaction between humic acids from different soils and Zn (II) ions at wide concentration ranges and at pH 5. Studies have showed significant impact of Zn concentration, pH and some properties of humic acids with zinc.But all of these studies were limited to acidic pH range. Therefore, the present study was carried out to determine and compare the stability constants of complexes of metal ions with hydrolysed peat soil humic acid and unhydrolysed peat soil humic under non-acid conditions.

MATERIALS AND METHODS

Analytical grade chemicals used includes hydrochloric acid (HCl), nitric acid (HNO_3), sodium hydroxide (NaOH), lead nitrate $Pb(NO_3)_2$, copper nitrate $Cu(NO_3)_2.3H_2O$, cadmium nitrate $Cd(NO_3)_2.4H_2O$, magnesium nitrate $Mg(NO_3)_2.6H_2O$, potassium nitrate (KNO_3), calcium chloride ($CaCl_2$), (sigma-Aldrich). Dowex 50WX8, (20-50 mesh) from Fluka.

Area of study



Source: Dept. of Geog. BUK (2016)

Figure 1: Map showing the sampling point at Sagamu Town, Ogun State.

Description of Sampling Area

Sagamu has geographical coordinates between 6°50′ north; 3° 38′ east is located in south western region of Nigeria. The region has tropical wet and dry climate with a lengthy wet season and relatively constant temperatures throughout the course of the year. Wet season runs from March to October, November to December forms the region dry season. The vegetation type of the region is savannah which is really grassland with small bushes and occasional big trees. Grassland soils have substantially higher organic matter content than forest soils (Novackova, 2011).

Sample Collection

The Peatsoil samples were collected from four different sampling points (0-10cm depth) in Sagamu into polyethylene bag with plastic spoons. Samples were taken to the laboratory, extraneous materials were removed; the samples were air-dried, crushed and ground to a fine powder in a mortar passed through a 0.20mm sieve. The samples were kept for analysis.

Isolation and purification of humic acid from peat soil sample

Peatsoil sample (100g) was mixed with 1000 cm^3 of 0.1M NaOH solution, shaken for 3hours and left to stand overnight. Dark-coloured supernatant was obtained and decanted from solid residue. The dark-coloured supernatant was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 6 hours. Yellowish brown supernatant and dark-brown precipitate were obtained. The yellowish brown supernatant was decanted followed by centrifuge and discarded. The dark-brown precipitate was mixed with 500$cm^3$of 0.1M NaOH solution followed by passing through dowex resin. The dark-brown solution was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 3 hours. The dark-brown precipitate was washed several times with deionized water. The supernatant was treated with $AgNO_3$ solution until no white precipitate observed. The humic acid was transferred to weighed crucible and dried at 60°C in an oven for 12 hours. The humic acid was cooled and dried in the desiccator, weighed and recorded. The obtained humic acid was dried again at 60°C for additional 6 hours cooled and dried in the desiccator, weighed and recorded constant weight was obtained (Baruah *et al*., 2015).

FT-IR analysis

FT-IR spectra of humic acid sample was analysed using Carry 630 FT-IR Agilent Technologies.

Unhydrolysed compost humic acid

The unhydrolysed humic acid was obtained after isolation and purification of compost humic acid and kept for investigation.

Acid hydrolysis of Peatsoil acid

Peatsoil humic acid sample (1g) was refluxed for 12 hours at (160°C) with 50cm^3 of 6M HCl. The mixture was allowed to cool, decanted, and centrifuged after hydrolysis. The insoluble residues were washed with distilled water via centrifugation several times, and the supernatant was treated with $AgNO_3$ solution until no white precipitate was observed. The residue was thoroughly dried over $CaCl_2$ in a desiccator at room temperature (Chefetz *et al.*, 2002). Finally, the obtained hydrolysed humic acid was kept for investigation.

Potentiometric Titrations

Potentiometric measurements were carried out using a pH-meter Jenway (model 3510) with combine electrode, the sensitivity of the pH - meter is 0.01 units. The pH meter was switched on half an hour before starting the titration for initial warm up of the instrument. The instrument was calibrated with an aqueous standard buffer solution of pH 4.00 and 10.0 (borate buffer) prepared from a "Qualigens" buffer tablets.

The following sets of solutions were prepared in a 250cm^3 volumetric flask separately for pH metric titrations.

(i) 5 cm^3 0.1 M HCl + 40 cm^3 deionized water

(ii) 5 cm^3 0.1 M HCl + 39 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid

(iii) 5 cm^3 0.1 M HCl + 37 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid + 2 cm^3 0.01 M Cu(II)

The solutions were titrated against standardized 0.110MNaOH separately. The total volume of each mixture was adjusted to 50 cm^3 and the ionic strength of the solutions was maintained constant at by adding appropriate amount of stock solution of 1M KNO$_3$ (Gamal, 2015; Omar and Ali, 2015). A magnetic stirrer was used to achieve thorough mixing of the interacting solutions at 550 rpm. The same set of experimental conditions was applied for potentiometric titration of remaining samples.

Evaluation of pKa of Hydrolysed peat soil Humic Acids

The proton-ligand formation number n$_{\mathbf{A}}$ were calculated by Irving and Rossotti expression (Omar and Ali, 2015).

$$nA = Y- \frac{(V2-V1)(No-Eo)}{(Vo+V1)TcL} \quad ....1$$

Where: Y is number of dissociable proton, (V$_2$-V$_1$) is the measure of displacement of the ligand curve relative to acid curve, N^o and E^o are the resultant concentration of alkali solution, free acid solution, T$_{cL}{}^o$ is the total ligand concentration, V^o is the total volume of titration solution,V$_1$ is the volume of alkali added to acid solution,V$_2$ is the volume of alkali added to acid solution + ligand solution, acid dissociation constants (pKa - values) of ligand were calculated by algebraic method point wise calculation (Tables 1). The dissociation constants (pKa) were calculated according to the following relation:

$$\text{pKa} = \text{pH} + \log(\frac{nA}{1-nA}) \quad ....2$$

Where: pKa is the acid dissociation constant, n$_A$is the Proton-ligand formation number and pH is the pH-values (Omar and Ali, 2015).

Determination of metal-ligand stability constants (log K) of complexes

The potentiometric measurement for the determination of stability constant of a complex in solution is based on the fact that the redox potential of the couple $\frac{M^{+(m-n)}}{M^{+m}}$ is shifted significantly on complexation of the metal ion with the ligand. This method involves change in hydrogen ion concentration [H$^+$] due to the displacement or association of one or more protons taking place during complexation reaction. This change can be found out by titrating the solutions containing free acid, acid with ligand, and acid with ligand and metal ion, individually against a standard alkali solution at a constant ionic strength or temperature. Either ionic strength or temperature may be varied for different sets of solutions. In all the cases, the change in the pH of the solution is measured after each addition of a known amount of alkali to the reaction cell which contains the reaction mixture. The titration curves are then drawn by plotting the measured pH values against the corresponding volume of alkali added and the stability constants of the complexes are determined from the titration curves by employing pH-metric titration technique given by (Irving and Rossoti).

Metal-ligand stability constants (Log K) were determined by using the following relations:

$$\bar{n} = \frac{(V_3 - V_2)(E^0 + N^0)}{(V^0 + V_2)\bar{n}_A T_m^0} \quad ....3$$

and

$$PL = \log_{10}\{\frac{1+\beta_n^H \frac{1}{[anti\ \log pH]^n}}{T_L^0 - \bar{n}T_m^0} X \frac{(V^0+V_3)}{V^0}\} \quad ....4$$

Where $T_{L,}$ T^{o}, E°, and V^{o}havethe same significance as in equation (1) above, T_m denotes the total concentration of metal present in solution, V_3 is the volume of metal ions present in solution and β^H is the overall proton ligand stability constant. The metal-ligand stability constants (log K) were determined by employing point wise computational Method (eq. 5 and 6).

$$\mathrm{LogK}_1 = \log\left(\frac{n}{1-n}\right) + \mathrm{pL} \qquad \ldots\ldots\ldots\ldots.5$$

$$\mathrm{LogK}_2 = \log\left(\frac{1-n}{2-n}\right) + \mathrm{pL}\ldots\ldots\ldots\ldots\ldots\ldots\ldots.6$$

Where: Log K is the metal-ligand stability constant, pL is the Free ligand exponent function, **n** is the Average number of ligand attached with metal ion (Janrao*et al*., 2014).The results obtained were analyzed by an ORIGIN 2016 program using titration data and then the proton-ligand stability constants (pKa) and Metal-ligand stability constant (LogK) calculated (Omar and Ali, 2015).

RESULTS AND DISCUSSION

Fourier transformed infrared (FT-IR) spectra of isolated humic acid from peat soils Figure 2 had distinct clear absorption bands indicating the presence of major humic acid structural elemental groups such as H bonded OH ($3680cm^{-1}$ peak), C=O of carbonyl ($1721cm^{-1}$ peak), functional groups of aliphatic components CH_2 ($2918cm^{-1}$ peak) and C-O stretching of polysaccharide ($1168cm^{-1}$ peak). The positions of the absorption bands of the spectra fell within typical major absorption bands of humic acid which is at frequencies 3680, 2918, 1721, 1168 cm^{-1}. The first peak centred in the vicinity of 3680 cm^{-1} region is attributed to phenol OH group bounded by intermolecular H bonds. The $2918cm^{-1}$ band usually has absorption maximum at 2918 cm^{-1} which is due to C–H stretching of alkane group (CH_2). The next major absorption band is 1721 cm^{-1}. This band has been commonly ascribed to C=O stretching of mainly carboxyl group (COOH) with trace amount of ketones. The last peak was observed at 1168 cm^{-1} due to C–O stretching of polysaccharides and this peak appeared also in the spectra of humic acid from peat soil. The FTIR spectra of the isolated humic acid contained all major characteristic absorption peaks of humic acid. These absorption peaks indicated the presence of the major structural elements of humic acid namely H bonded OH, C=C of aromatic ring, C=O of carbonyl group (both carboxyl and ketonic), CH_2 group. This strongly supports the presence of humic acid.

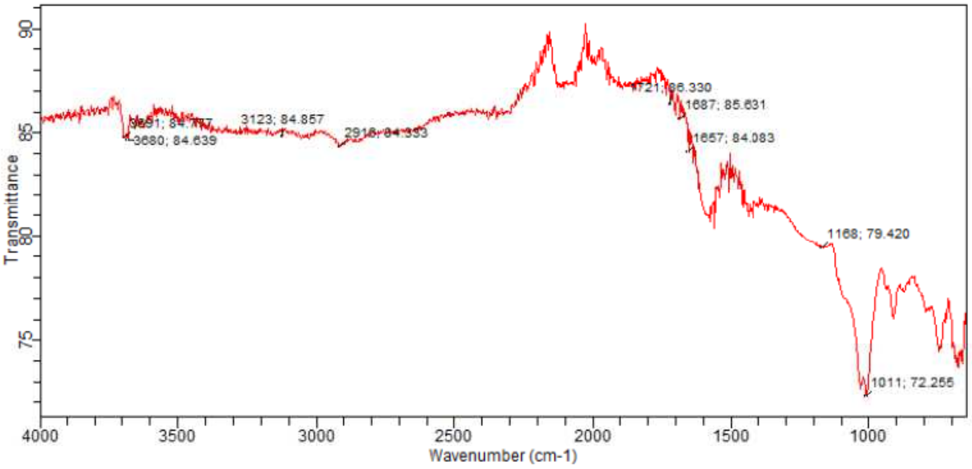


Fig. 2 : FT-IR spectraof peatsoilhumic acid (PSHA)

Evaluation of acid dissociation constant (pka) of acid hydrolysed peat soil humicacid at phenolic group

The value of the dissociation constant of the peat soil humic acid (PSHA) that underwent acidhydrolysis studied was found to be 8.9299 as shown Table 1, which is lower than the literaturevalues reported by Almeida and Szpoganics, (2015), Borges *et al*., (2005); Badr *et al*., (2012)and Fernandes *et al*,.(2009) of 9.73, 9.47 and 10.30. The difference between the obtained valuesand the reported values in this study might be probably as a result of acid hydrolysis of humicacid.

Table 1: PKa of (Hydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	log($\frac{nA}{1-nA}$)	pKa
8.50	5.30	6.29	0.99	0.3594	-0.2510	8.2490
8.72	5.35	6.37	1.02	0.3400	-0.2880	8.4320
9.00	5.40	6.46	1.06	0.3141	-0.3391	8.6609
9.22	5.45	6.55	1.10	0.2882	-0.3927	8.8273
9.51	5.50	6.66	1.16	0.2494	-0.4786	9.0314
9.73	5.55	6.78	1.23	0.2041	-0.5910	9.1390
10.00	5.60	6.90	1.30	0.1589	-0.7238	9.2762
10.23	5.65	7.05	1.40	0.0941	-0.9835	9.2465
10.49	5.70	7.10	1.40	0.0941	-0.9835	9.5065

Average pKa = 8.9299 ± 0.4186

Table 2: PKa of (Unhydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	Log($\frac{nA}{1-n}$)	pKa
8.50	5.30	5.81	0.51	0.6619	0.2919	8.7919
8.72	5.35	5.90	0.55	0.6357	0.2418	8.9618
9.00	5.40	6.00	0.60	0.6029	0.1813	9.1813
9.22	5.45	6.10	0.65	0.5701	0.1226	9.3426
9.51	5.50	6.20	0.70	0.5376	0.0654	9.5754
9.73	5.55	6.33	0.78	0.4851	-0.0259	9.7041
10.00	5.60	6.47	0.87	0.4262	-0.1291	9.8709
10.23	5.65	6.62	0.99	0.3609	-0.2481	9.9819
10.49	5.70	6.80	1.10	0.2759	-0.4690	10.0210

Average pKa = 9.4923± 0.4410

Metal-ligand stability constant (Log K)

The stabilityconstants require the accurate values of proton-ligand stability constants (Anil and Maroti, 2008). Metal titration curves crossed over ligand titration curve indicated the formation of complex upon proton release (Santosh, *et al.*, 2011). If the values of n- are within range 0.2-0.8 and 1.2-18 this indicates the formation of 1:1 and 1:2 complexes (Sayyed and Mazahar, 2012).

The metal (II)-humate stepwise stability constants (log k) at phenolic group (Tables 3-18)

Table 3: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n}{1-n}$)	$LogK_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

$LogK_1$ (Average value) = 2.4788± 0.2203

Table 4: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	Log($\frac{n-1}{2-n}$)	$LogK_2$
9.51	5.50	6.66	6.73	0.07	1.3509	1.70	-0.2671	1.4329
9.73	5.55	6.78	6.85	0.07	1.6383	1.51	0.2467	1.7567
10.00	5.60	6.90	6.98	0.08	2.1783	1.31	-0.2158	1.0942
10.23	5.65	7.05	7.13	0.08	4.1904	1.27		
10.49	5.70	7.10	7.19	0.09	4.6920			

$LogK_2$(Average value) = 1.4280 ± 0.3312

Table 5:Point-wise method,Cu (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	Log$(\frac{n}{n-1})$	Log K$_1$
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430

LogK$_1$ **(Average value)** = 2.3059± 0.6153

Table 6:Point-wise method, Cu (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	V$_3$-V$_2$	n	pL	Log$(\frac{n-1}{2-n})$	Log K$_2$
9.73	5.55	6.33	6.42	0.09	0.9000	1.69		
10.00	5.60	6.47	6.58	0.11	1.2578	1.44	-0.4592	0.9808
10.23	5.65	6.62	6.84	0.12	1.6137	1.26	-0.2010	1.4610
10.49	5.70	6.80	6.92	0.12	2.1052	1.03		

LogK$_2$ **(Average value)** = 1.2209± 0.3398

Table 7:Point-wise method,Pb (Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	log$(\frac{n}{1-n})$	LogK$_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.60	0.05	0.8333	1.96	0.6989	2.6589

LogK$_1$ (Average value) = 2.5832 ±0.1614

Table 8:Point-wise method,Pb-(Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	log$(\frac{n-1}{2-n})$	logK$_2$
9.51	5.50	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.83	0.05	1.1702	1.44		
10.00	5.60	6.90	6.90	0.05	1.4864	1.22	-0.0237	1.1963
10.23	5.65	7.05	7.10	0.05	2.0190	1.09		
10.49	5.70	7.10	7.17	0.07	3.6492	1.00		

LogK$_2$(Average value) = 1.1963

Table 9:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	V$_3$-V$_2$	n	pL	Log $(\frac{n}{n-1})$	Log K$_1$
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.5477	2.3123
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	0.0272	2.2072
9.51	5.50	6.20	6.26	0.07	0.6417	1.89	0.2530	2.1430
9.73	5.55	6.40	6.40	0.07	0.7000	1.67	0.3680	2.0380

LogK$_1$ **(Average value)** = 2.2364 ± 0.1602

Table 10:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	V$_3$-V$_2$	n	pL	Log$(\frac{n-1}{2-n})$	Log K$_2$
10.00	5.60	6.47	6.55	0.08	1.9503	1.41		
10.23	5.65	6.62	6.72	0.11	1.4792	1.26	-0.0361	1.2239

LogK$_2$ **(Average value)** = 1.2239

Table 11:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	log$(\frac{n}{n-1})$	LogK$_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4290	2.2110
8.72	5.35	6.37	6.39	0.02	0.2858	2.42	-0.3978	2.0222
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

LogK$_1$ (Average value)=2.1382**±**0.1046

Table 12:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	log($\frac{n-1}{2-n}$)	LogK$_2$
9.51	5.55	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.84	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.93	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.10		
10.49	5.70	7.10	7.18	0.07	3.6492	0.83		

LogK$_2$(Average value) = 1.5453 **±** 0.3450

Table 13:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	V$_3$-V$_2$	n	pL	Log($\frac{n}{n-1}$)	Log K$_1$
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.3477	2.3123
9.00	5.40	6.00	6.04	0.04	0.3236	2.38	-0.3202	2.0598
9.22	5.45	6.10	6.15	0.05	0.4297	2.17	-0.1230	2.0470
9.51	5.50	6.20	6.26	0.06	0.5500	1.89	0.0871	1.9771
9.73	5.55	6.33	6.40	0.07	0.7000	1.67	0.3680	2.0380

LogK$_1$ **(Average value)** = 2.1568 ± 0.2069

Table 14:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	V$_3$-V$_2$	n	pL	Log($\frac{n-1}{2-n}$)	Log K$_2$
10.00	5.60	6.47	6.55	0.08	0.9148	1.41		
10.23	5.65	6.62	6.71	0.09	1.2102	1.20	-0.5749	0.6251
10.49	5.70	6.80	6.92	0.09	1.5968	1.03	0.1703	1.2003

LogK$_2$ **(Average value)** = 0.9127± 0.4070

Table15:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	Log($\frac{n}{1-n}$)	LogK$_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4210	2.2190
8.72	5.35	6.37	6.40	0.03	0.4286	2.42	-0.1249	2.2951
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.96	0.3010	2.2610
9.51	5.55	6.66	6.70	0.04	0.7720	1.67	0.5297	2.1997

LogK$_1$ (Average value) = 2.2108± 0.0825

Table 16:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	Log($\frac{n-1}{2-n}$)	Log K$_2$
9.73	5.55	6.78	6.83	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.95	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.09		
10.49	5.70	7.10	7.16	0.06	3.1429	0.89		

LogK$_2$ **(Average value)** = 1.5453± 0.3450

Table 17:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	V$_3$-V$_2$	n	pL	Log($\frac{n}{n-1}$)	Log K$_1$
8.50	5.30	5.81	5.86	0.05	0.3717	2.88	-0.2280	2.6520
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.06	0.06	0.4853	2.38	-0.0255	2.3545
9.22	5.45	6.10	6.16	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430
9.73	5.55	6.33	6.41	0.08	0.8000	1.69	0.6020	2.2920

LogK$_1$ **(Average value)** = 2.2516± 0.5380

Table 18:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$\text{Log}(\frac{n-1}{2-n})$	Log K_2
10.00	5.60	6.47	6.57	0.10	1.1434	1.43		
10.23	5.65	6.62	6.72	0.10	1.3448	1.23	-0.2788	0.9512
10.49	5.70	6.80	6.90	0.10	1.7742	1.03	0.5351	1.5651

LogK_2 **(Average value)** = 1.2581± 0.4340

Table 19: Stepwise and overall Stability constants of thehydrolysed and unhydrolysed divalent metal (II) complexes

Chelates	**LogK_1**	**LogK_2**	**Logβ**
[Cu (Hydrolysed PSHA-1)$_2$]	2.4788	1.4280	3.9068
[Pb (Hydrolysed PSHA-1)$_2$]	2.5832	1.1963	3.7795
[Cd (Hydrolysed PSHA-1)$_2$]	2.2108	1.5453	3.7561
[Mg (Hydrolysed PSHA-1)$_2$]	2.1382	1.5453	3.6835
[Cu (Unhydrolysed PSHA-1)$_2$]	2.3059	1.2209	3.5268
[Pb (Unhydrolysed PSHA-1)$_2$]	2.2364	1.2239	3.4603
[Cd (Unhydrolysed PSHA-1)$_2$]	2.2516	1.2581	3.5097
[Mg (Unydrolysed PSHA-1)$_2$]	2.1568	0.9127	3.0695

The results obtained (Table19) shows the stepwise and overall stability constants to be not high indicating low stability of the complexes, because the solubility of most metal ions in the basic pH range is minimal due to metal hydroxide precipitation (Karimi, 2017). In general, the stepwise stability constants (K_1 and K_2) follow the order $K_1 > K_2$ for the copper, lead, magnesium and cadmium complexes respectively. The steady decrease of the values with increasing number of ligands is in agreement with the prediction made by researchers (Na'aliya, 2013). The decrease could be attributed to the fact that as the number of the ligands (Humate ions) that enters the coordination zone increases the aqua molecules available for replacement by the ligands become less. Thus, the metal ions become less electron loving with progressive intake of the ligand and this results in the decrease in the values of the constants (Na'aliya, 2013). Also the stability of the complexes is influenced by the size and number of the chelate rings(Mackay and Mackay,2002).All the complexes form rings in their structure as humate, a bidentate ligand, bond the metal ions in the ratio 1:2 (Boguta and Sokolowska, 2016) forming chelate rings. The values of the overall stability constants (logβ) obtained for humate complexes are not high indicating low stability as the values are not high. LogK values for copper-humates (Table 3 to 6) obtained in this study are lower than those reported for the complexes of humic acids (Pandey *et al*., 2015; Dinu, 2013; Kaschl *et al*., 2010 and Gilbeto and Jorg, 2001). The values of LogK(Table 7 to 10) forlead-humates are lower than those reported for the lead in the literature (Dinu, 2013; Gilbeto and Jorg 2001). Log K values(Table 11 to 14) for magnesium-humates obtained in this study are close to those reported by (Pandey *et al*., 2015). Log K values of cadmium-humates (Table 15 to 18) obtained in this work near to the one reported by (Dinu, 2013 and Pandey *et al*., 2015).The difference between the reported values and the values obtained in this study might be probably as a result of acid hydrolysis of humic acid. The values of the overall stability constants (log β) of the copper humates complexes presented in Table 19 is high than that of other metal humate complexes, show relatively high stability of Cu-HA complexes, show the following order of stability: Cu >Pb> Cd > Mg; which are in close agreement to the findings of (Dinu, 2013 and Pandey *et al*., 2015).The high stability of Cu-humate chelate could be attributed to the existence of coordinate covalent bond between the complexing agents and the Cu^{2+} ions. Since, Cu^{2+} being a metal of the transitional series with $3d^9$ electronic configurations can accept the electrons from the complexing agents. Similarly,the low stabilities of Pb,Cd and Mg -complexes could be explained by that Pb^{2+} with $6s^2$, Cd^{2+} with $4d^{10}$ and Mg^{2+} with $2p^6$ their electronic configuration has a completely filled d,p and s orbitals. Moreover, the stabilities of metal ions with hydrolysed humic acid from peat soil were higher than those with unhydrolysed humic acid from peat soil; which is ascribed to the high content of acidity in hydrolysed humic acid than unhydrolysed humic acid.

CONCLUSION

The values of logK for Cu(II) hydrolysed humic acid complex was higher followed by Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes as compared with metal(II) unhydrolysed humic acid complexes . This indicates acid hydrolysis of humic acid can enhance the complexation behavior of humic acid with metal (II) ions. However, the higher values of logβ for Cu(II), Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes indicates more stable stepwise complexes formed as compared with Cu(II), Pb(II), Cd(II) and Mg(II) unhydrolysed humic acid complexes.

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STABILITY CONSTANTS OF COMPLEXES OF METAL IONS WITH PEATSOIL HUMIC ACIDS UNDER NON-ACID-CONDITIONS

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ABSTRACT

Stability constants of complexes of four divalent metal ions viz. Cu^{2+}, Pb^{2+},Mg^{2+} and Cd^{2+} with humic acids (HA) were determined by potentiometric titration of humic acids with the corresponding salt of the divalent metals in aqueous media under non-acid-condition. The log K (logarithm of the stability constant) ranged from 1.0942 to 2.7471 for metal-humic acid complexes were determined using point-wise computational method. The order of stability constants were obtained as follows: Cu >Pb> Cd > Mg for metal -HA complexes respectively, indicating a higher degree of complexation with Cu metal ion.

Keywords: stability constant, humic acid, potentiometric titration, divalent metals, acid hydrolysis.

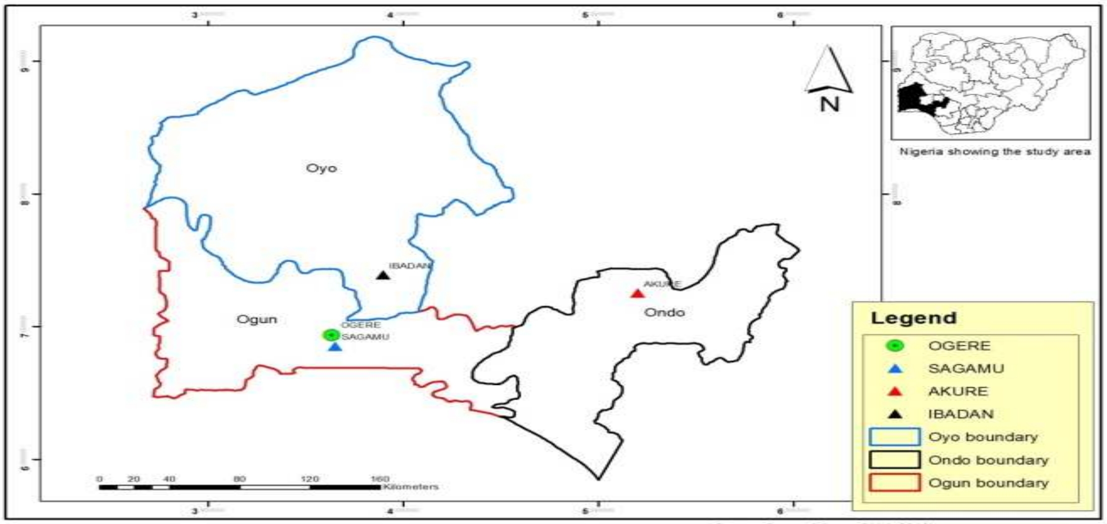
NTRODUCTION

The stability constant of a complex is the numerical expression of its stability and provides a quantitative measure of affinity of the metal ion to the complexing agent. An understanding of the relative stability of metal-complexes helps in predicting the behavior of metal ions in the soil (Ram and Raman, 1982). Extensive researches has been done to determine the stability constants of the complexes formed between humic acid (HA) with a number of metal ions. Ashok *et al*., (2000) reported that humic acid with hydroxyl, phenoxyl and carboxyl reactive groups can form coordination compound with metal ions at pH 3.5. The stability constants(Log K) for different metal-humic acid complexes indicated the following order of the stabilities of complexes formed between humic acid and metal ion, Cu >Fe >Pb> Ni > Co > Ca > Cd > Zn >Mn> Mg. Andelkovic *et al*., (2010) investigated the binding of Cd(II) to soil humic acid at pH 6.5 and in 0.1M KNO_3 ionic medium. The stability constant for binding indicating greater stability in the case when carboxyl groups are involved in complexation reaction. Kostic *et al*.,(2012) investigated the complexation of humic acid with certain heavy metal ions (Co(II), Ni(II),Cu(II), Zn(II), and Pb(II). The experiment was performed at 25°C, at pH 4.0 and ionic strength of 0.01M. Stability constant of complex between Pb(II) ions and humic acid is greater than stability constants of other investigated metal-humate complexes. Bogata and Sokolowska (2016) analyses the interaction between humic acids from different soils and Zn (II) ions at wide concentration ranges and at pH 5. Studies have showed significant impact of Zn concentration, pH and some properties of humic acids with zinc.But all of these studies were limited to acidic pH range. Therefore, the present study was carried out to determine and compare the stability constants of complexes of metal ions with hydrolysed peat soil humic acid and unhydrolysed peat soil humic under non-acid conditions.

MATERIALS AND METHODS

Analytical grade chemicals used includes hydrochloric acid (HCl), nitric acid (HNO_3), sodium hydroxide (NaOH), lead nitrate $Pb(NO_3)_2$, copper nitrate $Cu(NO_3)_2.3H_2O$, cadmium nitrate $Cd(NO_3)_2.4H_2O$, magnesium nitrate $Mg(NO_3)_2.6H_2O$, potassium nitrate (KNO_3), calcium chloride ($CaCl_2$), (sigma-Aldrich). Dowex 50WX8, (20-50 mesh) from Fluka.

Area of study



Source: Dept. of Geog. BUK (2016)

Figure 1: Map showing the sampling point at Sagamu Town, Ogun State.

Description of Sampling Area

Sagamu has geographical coordinates between 6°50′ north; 3° 38′ east is located in south western region of Nigeria. The region has tropical wet and dry climate with a lengthy wet season and relatively constant temperatures throughout the course of the year. Wet season runs from March to October, November to December forms the region dry season. The vegetation type of the region is savannah which is really grassland with small bushes and occasional big trees. Grassland soils have substantially higher organic matter content than forest soils (Novackova, 2011).

Sample Collection

The Peatsoil samples were collected from four different sampling points (0-10cm depth) in Sagamu into polyethylene bag with plastic spoons. Samples were taken to the laboratory, extraneous materials were removed; the samples were air-dried, crushed and ground to a fine powder in a mortar passed through a 0.20mm sieve. The samples were kept for analysis.

Isolation and purification of humic acid from peat soil sample

Peatsoil sample (100g) was mixed with 1000 cm^3 of 0.1M NaOH solution, shaken for 3hours and left to stand overnight. Dark-coloured supernatant was obtained and decanted from solid residue. The dark-coloured supernatant was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 6 hours. Yellowish brown supernatant and dark-brown precipitate were obtained. The yellowish brown supernatant was decanted followed by centrifuge and discarded. The dark-brown precipitate was mixed with $500cm^3$of 0.1M NaOH solution followed by passing through dowex resin. The dark-brown solution was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 3 hours. The dark-brown precipitate was washed several times with deionized water. The supernatant was treated with $AgNO_3$ solution until no white precipitate observed. The humic acid was transferred to weighed crucible and dried at 60°C in an oven for 12 hours. The humic acid was cooled and dried in the desiccator, weighed and recorded. The obtained humic acid was dried again at 60°C for additional 6 hours cooled and dried in the desiccator, weighed and recorded constant weight was obtained (Baruah *et al*., 2015).

FT-IR analysis

FT-IR spectra of humic acid sample was analysed using Carry 630 FT-IR Agilent Technologies.

Unhydrolysed compost humic acid

The unhydrolysed humic acid was obtained after isolation and purification of compost humic acid and kept for investigation.

Acid hydrolysis of Peatsoil acid

Peatsoil humic acid sample (1g) was refluxed for 12 hours at (160°C) with $50cm^3$ of 6M HCl. The mixture was allowed to cool, decanted, and centrifuged after hydrolysis. The insoluble residues were washed with distilled water via centrifugation several times, and the supernatant was treated with $AgNO_3$ solution until no white precipitate was observed. The residue was thoroughly dried over $CaCl_2$ in a desiccator at room temperature (Chefetz *et al*., 2002). Finally, the obtained hydrolysed humic acid was kept for investigation.

Potentiometric Titrations

Potentiometric measurements were carried out using a pH-meter Jenway (model 3510) with combine electrode, the sensitivity of the pH - meter is 0.01 units. The pH meter was switched on half an hour before starting the titration for initial warm up of the instrument. The instrument was calibrated with an aqueous standard buffer solution of pH 4.00 and 10.0 (borate buffer) prepared from a "Qualigens" buffer tablets.

The following sets of solutions were prepared in a 250cm^3 volumetric flask separately for pH metric titrations.

(i) 5 cm^3 0.1 M HCl + 40 cm^3 deionized water

(ii) 5 cm^3 0.1 M HCl + 39 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid

(iii) 5 cm^3 0.1 M HCl + 37 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid + 2 cm^3 0.01 M Cu(II)

The solutions were titrated against standardized 0.110MNaOH separately. The total volume of each mixture was adjusted to 50 cm^3 and the ionic strength of the solutions was maintained constant at by adding appropriate amount of stock solution of 1M KNO_3 (Gamal, 2015; Omar and Ali, 2015). A magnetic stirrer was used to achieve thorough mixing of the interacting solutions at 550 rpm. The same set of experimental conditions was applied for potentiometric titration of remaining samples.

Evaluation of pKa of Hydrolysed peat soil Humic Acids

The proton-ligand formation number $n_{\mathbf{A}}$ were calculated by Irving and Rossotti expression (Omar and Ali, 2015).

$$nA = Y - \frac{(V2-V1)(No-Eo)}{(Vo+V1)TcL} \quad \text{....................................1}$$

Where: Y is number of dissociable proton, (V_2-V_1) is the measure of displacement of the ligand curve relative to acid curve, N^o and E^o are the resultant concentration of alkali solution, free acid solution, $T_{cL}{}^o$ is the total ligand concentration, V^o is the total volume of titration solution,V_1 is the volume of alkali added to acid solution,V_2 is the volume of alkali added to acid solution + ligand solution, acid dissociation constants (pKa - values) of ligand were calculated by algebraic method point wise calculation (Tables 1). The dissociation constants (pKa) were calculated according to the following relation:

$$pKa = pH + \log(\frac{nA}{1-nA}) \quad \text{..............................2}$$

Where: pKa is the acid dissociation constant, $n_A$is the Proton-ligand formation number and pH is the pH-values (Omar and Ali, 2015).

Determination of metal-ligand stability constants (log K) of complexes

The potentiometric measurement for the determination of stability constant of a complex in solution is based on the fact that the redox potential of the couple $\frac{M^{+(m-n)}}{M^{+m}}$ is shifted significantly on complexation of the metal ion with the ligand. This method involves change in hydrogen ion concentration [H$^+$] due to the displacement or association of one or more protons taking place during complexation reaction. This change can be found out by titrating the solutions containing free acid, acid with ligand, and acid with ligand and metal ion, individually against a standard alkali solution at a constant ionic strength or temperature. Either ionic strength or temperature may be varied for different sets of solutions. In all the cases, the change in the pH of the solution is measured after each addition of a known amount of alkali to the reaction cell which contains the reaction mixture. The titration curves are then drawn by plotting the measured pH values against the corresponding volume of alkali added and the stability constants of the complexes are determined from the titration curves by employing pH-metric titration technique given by (Irving and Rossoti).

Metal-ligand stability constants (Log K) were determined by using the following relations:

$$\bar{n} = \frac{(V_3 - V_2)(E^0 + N^0)}{(V^0 + V_2)\bar{n}_A T_m^0} \quad \text{..3}$$

and

$$PL = \log_{10}\{\frac{1+\beta_n^H \frac{1}{[anti\ \log pH]^n}}{T_L^0 - \bar{n}T_m^0} X \frac{(V^0+V_3)}{V^0}\} \quad \text{..4}$$

Where $T_{L,}$ T^o, E°, and V^ohavethe same significance as in equation (1) above, T_m denotes the total concentration of metal present in solution, V_3 is the volume of metal ions present in solution and β^H is the overall proton ligand stability constant. The metal-ligand stability constants (log K) were determined by employing point wise computational Method (eq. 5 and 6).

$\mathrm{Log}K_1 = \log\left(\frac{n}{1-n}\right) + pL$ 5

$\mathrm{Log}K_2 = \log\left(\frac{1-n}{2-n}\right) + pL$.......................6

Where: Log K is the metal-ligand stability constant, pL is the Free ligand exponent function, **n** is the Average number of ligand attached with metal ion (Janrao*et al.*, 2014).The results obtained were analyzed by an ORIGIN 2016 program using titration data and then the proton-ligand stability constants (pKa) and Metal-ligand stability constant (LogK) calculated (Omar and Ali, 2015).

RESULTS AND DISCUSSION

Fourier transformed infrared (FT-IR) spectra of isolated humic acid from peat soils Figure 2 had distinct clear absorption bands indicating the presence of major humic acid structural elemental groups such as H bonded OH (3680cm^{-1} peak), C=O of carbonyl (1721cm^{-1} peak), functional groups of aliphatic components CH_2 (2918cm^{-1} peak) and C-O stretching of polysaccharide (1168cm^{-1} peak). The positions of the absorption bands of the spectra fell within typical major absorption bands of humic acid which is at frequencies 3680, 2918, 1721, 1168 cm^{-1}. The first peak centred in the vicinity of 3680 cm^{-1} region is attributed to phenol OH group bounded by intermolecular H bonds. The 2918cm^{-1} band usually has absorption maximum at 2918 cm^{-1} which is due to C–H stretching of alkane group (CH_2). The next major absorption band is 1721 cm^{-1}. This band has been commonly ascribed to C=O stretching of mainly carboxyl group (COOH) with trace amount of ketones. The last peak was observed at 1168 cm^{-1} due to C–O stretching of polysaccharides and this peak appeared also in the spectra of humic acid from peat soil. The FTIR spectra of the isolated humic acid contained all major characteristic absorption peaks of humic acid. These absorption peaks indicated the presence of the major structural elements of humic acid namely H bonded OH, C=C of aromatic ring, C=O of carbonyl group (both carboxyl and ketonic), CH_2 group. This strongly supports the presence of humic acid.

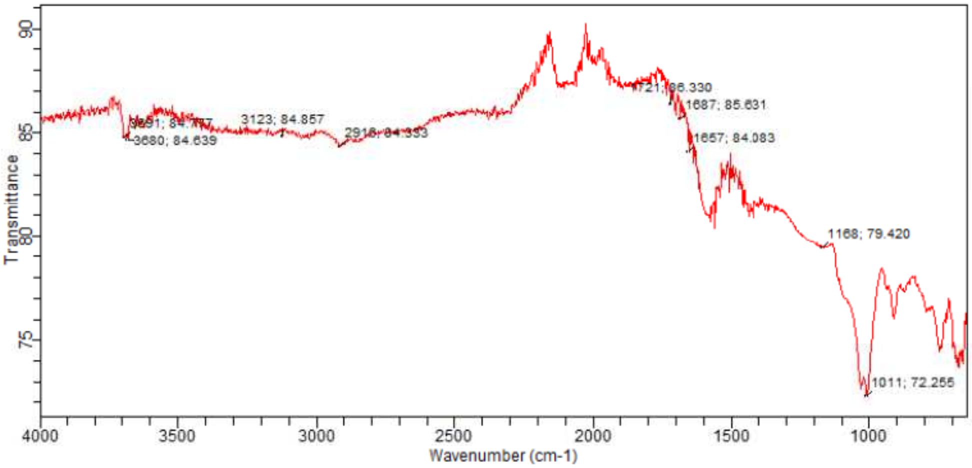


Fig. 2 : FT-IR spectraof peatsoilhumic acid (PSHA)

Evaluation of acid dissociation constant (pka) of acid hydrolysed peat soil humicacid at phenolic group

The value of the dissociation constant of the peat soil humic acid (PSHA) that underwent acidhydrolysis studied was found to be 8.9299 as shown Table 1, which is lower than the literaturevalues reported by Almeida and Szpoganics, (2015), Borges *et al.*, (2005); Badr *et al.*, (2012)and Fernandes *et al*,.(2009) of 9.73, 9.47 and 10.30. The difference between the obtained valuesand the reported values in this study might be probably as a result of acid hydrolysis of humicacid.

Table 1: PKa of (Hydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	log($\frac{nA}{1-nA}$)	pKa
8.50	5.30	6.29	0.99	0.3594	-0.2510	8.2490
8.72	5.35	6.37	1.02	0.3400	-0.2880	8.4320
9.00	5.40	6.46	1.06	0.3141	-0.3391	8.6609
9.22	5.45	6.55	1.10	0.2882	-0.3927	8.8273
9.51	5.50	6.66	1.16	0.2494	-0.4786	9.0314
9.73	5.55	6.78	1.23	0.2041	-0.5910	9.1390
10.00	5.60	6.90	1.30	0.1589	-0.7238	9.2762
10.23	5.65	7.05	1.40	0.0941	-0.9835	9.2465
10.49	5.70	7.10	1.40	0.0941	-0.9835	9.5065

Average pKa = 8.9299 ± 0.4186

Table 2: PKa of (Unhydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	Log($\frac{nA}{1-n}$)	pKa
8.50	5.30	5.81	0.51	0.6619	0.2919	8.7919
8.72	5.35	5.90	0.55	0.6357	0.2418	8.9618
9.00	5.40	6.00	0.60	0.6029	0.1813	9.1813
9.22	5.45	6.10	0.65	0.5701	0.1226	9.3426
9.51	5.50	6.20	0.70	0.5376	0.0654	9.5754
9.73	5.55	6.33	0.78	0.4851	-0.0259	9.7041
10.00	5.60	6.47	0.87	0.4262	-0.1291	9.8709
10.23	5.65	6.62	0.99	0.3609	-0.2481	9.9819
10.49	5.70	6.80	1.10	0.2759	-0.4690	10.0210

Average pKa = 9.4923± 0.4410

Metal-ligand stability constant (Log K)

The stabilityconstants require the accurate values of proton-ligand stability constants (Anil and Maroti, 2008). Metal titration curves crossed over ligand titration curve indicated the formation of complex upon proton release (Santosh, *et al.*, 2011). If the values of n- are within range 0.2-0.8 and 1.2-18 this indicates the formation of 1:1 and 1:2 complexes (Sayyed and Mazahar, 2012).

The metal (II)-humate stepwise stability constants (log k) at phenolic group (Tables 3-18)

Table 3: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n}{1-n}$)	$LogK_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

$LogK_1$ (Average value) = 2.4788± 0.2203

Table 4: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	Log($\frac{n-1}{2-n}$)	$LogK_2$
9.51	5.50	6.66	6.73	0.07	1.3509	1.70	-0.2671	1.4329
9.73	5.55	6.78	6.85	0.07	1.6383	1.51	0.2467	1.7567
10.00	5.60	6.90	6.98	0.08	2.1783	1.31	-0.2158	1.0942
10.23	5.65	7.05	7.13	0.08	4.1904	1.27		
10.49	5.70	7.10	7.19	0.09	4.6920			

$LogK_2$(Average value) = 1.4280 ± 0.3312

Table 5:Point-wise method,Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	Log($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430

$LogK_1$ **(Average value)** = 2.3059± 0.6153

Table 6:Point-wise method, Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
9.73	5.55	6.33	6.42	0.09	0.9000	1.69		
10.00	5.60	6.47	6.58	0.11	1.2578	1.44	-0.4592	0.9808
10.23	5.65	6.62	6.84	0.12	1.6137	1.26	-0.2010	1.4610
10.49	5.70	6.80	6.92	0.12	2.1052	1.03		

$LogK_2$ **(Average value)** = 1.2209± 0.3398

Table 7:Point-wise method,Pb (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n}{1-n}$)	$LogK_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.60	0.05	0.8333	1.96	0.6989	2.6589

$LogK_1$ (Average value) = 2.5832 ±0.1614

Table 8:Point-wise method,Pb-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n-1}{2-n}$)	$logK_2$
9.51	5.50	6.66	6.71	0.05	0.9650	1.67	-0.0237	1.1963
9.73	5.55	6.78	6.83	0.05	1.1702	1.44		
10.00	5.60	6.90	6.90	0.05	1.4864	1.22		
10.23	5.65	7.05	7.10	0.05	2.0190	1.09		
10.49	5.70	7.10	7.17	0.07	3.6492	1.00		

$LogK_2$(Average value) = 1.1963

Table 9:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log ($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.5477	2.3123
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	0.0272	2.2072
9.51	5.50	6.20	6.26	0.07	0.6417	1.89	0.2530	2.1430
9.73	5.55	6.40	6.40	0.07	0.7000	1.67	0.3680	2.0380

$LogK_1$ **(Average value)** = 2.2364 ± 0.1602

Table 10:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
10.00	5.60	6.47	6.55	0.08	1.9503	1.41		
10.23	5.65	6.62	6.72	0.11	1.4792	1.26	-0.0361	1.2239

$LogK_2$ **(Average value)** = 1.2239

Table 11:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n}{n-1}$)	$LogK_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4290	2.2110
8.72	5.35	6.37	6.39	0.02	0.2858	2.42	-0.3978	2.0222
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

$LogK_1$ (Average value)=2.1382**±**0.1046

Table 12:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n-1}{2-n}$)	$LogK_2$
9.51	5.55	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.84	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.93	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.10		
10.49	5.70	7.10	7.18	0.07	3.6492	0.83		

$LogK_2$(Average value) = 1.5453 **±** 0.3450

Table 13:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.3477	2.3123
9.00	5.40	6.00	6.04	0.04	0.3236	2.38	-0.3202	2.0598
9.22	5.45	6.10	6.15	0.05	0.4297	2.17	-0.1230	2.0470
9.51	5.50	6.20	6.26	0.06	0.5500	1.89	0.0871	1.9771
9.73	5.55	6.33	6.40	0.07	0.7000	1.67	0.3680	2.0380

$LogK_1$ **(Average value)** = 2.1568 ± 0.2069

Table 14:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
10.00	5.60	6.47	6.55	0.08	0.9148	1.41		
10.23	5.65	6.62	6.71	0.09	1.2102	1.20	-0.5749	0.6251
10.49	5.70	6.80	6.92	0.09	1.5968	1.03	0.1703	1.2003

$LogK_2$ **(Average value)** = 0.9127± 0.4070

Table15:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	Log($\frac{n}{1-n}$)	$LogK_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4210	2.2190
8.72	5.35	6.37	6.40	0.03	0.4286	2.42	-0.1249	2.2951
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.96	0.3010	2.2610
9.51	5.55	6.66	6.70	0.04	0.7720	1.67	0.5297	2.1997

$LogK_1$ (Average value) = 2.2108± 0.0825

Table 16:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
9.73	5.55	6.78	6.83	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.95	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.09		
10.49	5.70	7.10	7.16	0.06	3.1429	0.89		

$LogK_2$ **(Average value)** = 1.5453± 0.3450

Table 17:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.86	0.05	0.3717	2.88	-0.2280	2.6520
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.06	0.06	0.4853	2.38	-0.0255	2.3545
9.22	5.45	6.10	6.16	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430
9.73	5.55	6.33	6.41	0.08	0.8000	1.69	0.6020	2.2920

$LogK_1$ **(Average value)** = 2.2516± 0.5380

Table 18:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$\text{Log}(\frac{n-1}{2-n})$	Log K_2
10.00	5.60	6.47	6.57	0.10	1.1434	1.43		
10.23	5.65	6.62	6.72	0.10	1.3448	1.23	-0.2788	0.9512
10.49	5.70	6.80	6.90	0.10	1.7742	1.03	0.5351	1.5651

LogK_2 **(Average value)** = 1.2581± 0.4340

Table 19: Stepwise and overall Stability constants of thehydrolysed and unhydrolysed divalent metal (II) complexes

Chelates	LogK_1	LogK_2	Logβ
[Cu (Hydrolysed PSHA-1)$_2$]	2.4788	1.4280	3.9068
[Pb (Hydrolysed PSHA-1)$_2$]	2.5832	1.1963	3.7795
[Cd (Hydrolysed PSHA-1)$_2$]	2.2108	1.5453	3.7561
[Mg (Hydrolysed PSHA-1)$_2$]	2.1382	1.5453	3.6835
[Cu (Unhydrolysed PSHA-1)$_2$]	2.3059	1.2209	3.5268
[Pb (Unhydrolysed PSHA-1)$_2$]	2.2364	1.2239	3.4603
[Cd (Unhydrolysed PSHA-1)$_2$]	2.2516	1.2581	3.5097
[Mg (Unydrolysed PSHA-1)$_2$]	2.1568	0.9127	3.0695

The results obtained (Table19) shows the stepwise and overall stability constants to be not high indicating low stability of the complexes, because the solubility of most metal ions in the basic pH range is minimal due to metal hydroxide precipitation (Karimi, 2017). In general, the stepwise stability constants (K_1 and K_2) follow the order $K_1 > K_2$ for the copper, lead, magnesium and cadmium complexes respectively. The steady decrease of the values with increasing number of ligands is in agreement with the prediction made by researchers (Na'aliya, 2013). The decrease could be attributed to the fact that as the number of the ligands (Humate ions) that enters the coordination zone increases the aqua molecules available for replacement by the ligands become less. Thus, the metal ions become less electron loving with progressive intake of the ligand and this results in the decrease in the values of the constants (Na'aliya, 2013). Also the stability of the complexes is influenced by the size and number of the chelate rings(Mackay and Mackay,2002).All the complexes form rings in their structure as humate, a bidentate ligand, bond the metal ions in the ratio 1:2 (Boguta and Sokolowska, 2016) forming chelate rings. The values of the overall stability constants (logβ) obtained for humate complexes are not high indicating low stability as the values are not high. LogK values for copper-humates (Table 3 to 6) obtained in this study are lower than those reported for the complexes of humic acids (Pandey *et al.*, 2015; Dinu, 2013; Kaschl *et al.*, 2010 and Gilbeto and Jorg, 2001). The values of LogK(Table 7 to 10) forlead-humates are lower than those reported for the lead in the literature (Dinu, 2013; Gilbeto and Jorg 2001). Log K values(Table 11 to 14) for magnesium-humates obtained in this study are close to those reported by (Pandey *et al.*, 2015). Log K values of cadmium-humates (Table 15 to 18) obtained in this work near to the one reported by (Dinu, 2013 and Pandey *et al.*, 2015).The difference between the reported values and the values obtained in this study might be probably as a result of acid hydrolysis of humic acid. The values of the overall stability constants (log β) of the copper humates complexes presented in Table 19 is high than that of other metal humate complexes, show relatively high stability of Cu-HA complexes, show the following order of stability: Cu >Pb> Cd > Mg; which are in close agreement to the findings of (Dinu, 2013 and Pandey *et al.*, 2015).The high stability of Cu-humate chelate could be attributed to the existence of coordinate covalent bond between the complexing agents and the Cu^{2+} ions. Since, Cu^{2+} being a metal of the transitional series with $3d^9$ electronic configurations can accept the electrons from the complexing agents. Similarly,the low stabilities of Pb,Cd and Mg -complexes could be explained by that Pb^{2+} with $6s^2$, Cd^{2+} with $4d^{10}$ and Mg^{2+} with $2p^6$ their electronic configuration has a completely filled d,p and s orbitals. Moreover, the stabilities of metal ions with hydrolysed humic acid from peat soil were higher than those with unhydrolysed humic acid from peat soil; which is ascribed to the high content of acidity in hydrolysed humic acid than unhydrolysed humic acid.

CONCLUSION

The values of logK for Cu(II) hydrolysed humic acid complex was higher followed by Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes as compared with metal(II) unhydrolysed humic acid complexes . This indicates acid hydrolysis of humic acid can enhance the complexation behavior of humic acid with metal (II) ions. However, the higher values of logβ for Cu(II), Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes indicates more stable stepwise complexes formed as compared with Cu(II), Pb(II), Cd(II) and Mg(II) unhydrolysed humic acid complexes.

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STABILITY CONSTANTS OF COMPLEXES OF METAL IONS WITH PEATSOIL HUMIC ACIDS UNDER NON-ACID-CONDITIONS

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ABSTRACT

Stability constants of complexes of four divalent metal ions viz. Cu^{2+}, Pb^{2+},Mg^{2+} and Cd^{2+} with humic acids (HA) were determined by potentiometric titration of humic acids with the corresponding salt of the divalent metals in aqueous media under non-acid-condition. The log K (logarithm of the stability constant) ranged from 1.0942 to 2.7471 for metal-humic acid complexes were determined using point-wise computational method. The order of stability constants were obtained as follows: Cu >Pb> Cd > Mg for metal -HA complexes respectively, indicating a higher degree of complexation with Cu metal ion.

Keywords: stability constant, humic acid, potentiometric titration, divalent metals, acid hydrolysis.

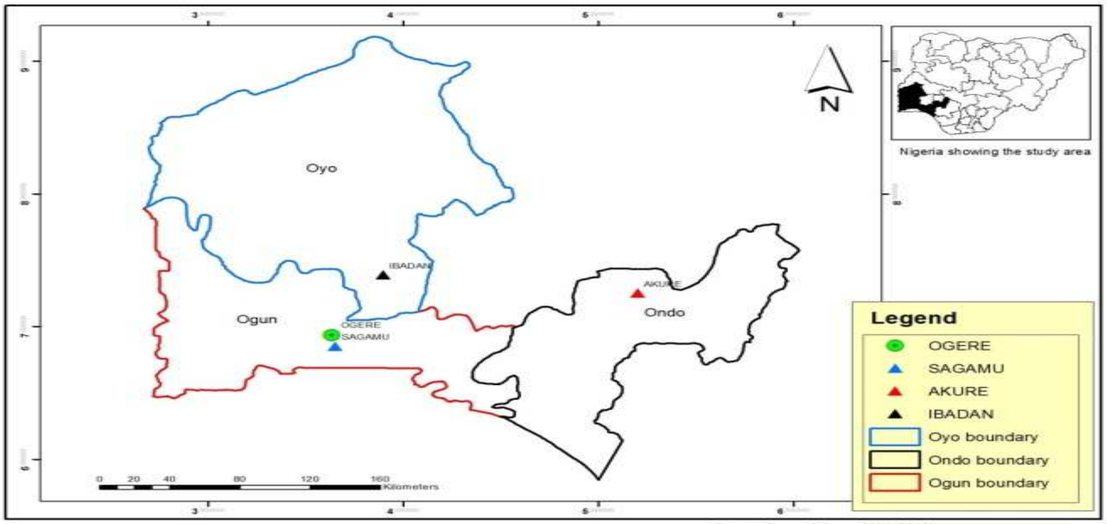
NTRODUCTION

The stability constant of a complex is the numerical expression of its stability and provides a quantitative measure of affinity of the metal ion to the complexing agent. An understanding of the relative stability of metal-complexes helps in predicting the behavior of metal ions in the soil (Ram and Raman, 1982). Extensive researches has been done to determine the stability constants of the complexes formed between humic acid (HA) with a number of metal ions. Ashok *et al*., (2000) reported that humic acid with hydroxyl, phenoxyl and carboxyl reactive groups can form coordination compound with metal ions at pH 3.5. The stability constants(Log K) for different metal-humic acid complexes indicated the following order of the stabilities of complexes formed between humic acid and metal ion, Cu >Fe >Pb> Ni > Co > Ca > Cd > Zn >Mn> Mg. Andelkovic *et al*., (2010) investigated the binding of Cd(II) to soil humic acid at pH 6.5 and in 0.1M KNO_3 ionic medium. The stability constant for binding indicating greater stability in the case when carboxyl groups are involved in complexation reaction. Kostic *et al*.,(2012) investigated the complexation of humic acid with certain heavy metal ions (Co(II), Ni(II),Cu(II), Zn(II), and Pb(II). The experiment was performed at 25°C, at pH 4.0 and ionic strength of 0.01M. Stability constant of complex between Pb(II) ions and humic acid is greater than stability constants of other investigated metal-humate complexes. Bogata and Sokolowska (2016) analyses the interaction between humic acids from different soils and Zn (II) ions at wide concentration ranges and at pH 5. Studies have showed significant impact of Zn concentration, pH and some properties of humic acids with zinc.But all of these studies were limited to acidic pH range. Therefore, the present study was carried out to determine and compare the stability constants of complexes of metal ions with hydrolysed peat soil humic acid and unhydrolysed peat soil humic under non-acid conditions.

MATERIALS AND METHODS

Analytical grade chemicals used includes hydrochloric acid (HCl), nitric acid (HNO_3), sodium hydroxide (NaOH), lead nitrate $Pb(NO_3)_2$, copper nitrate $Cu(NO_3)_2.3H_2O$, cadmium nitrate $Cd(NO_3)_2.4H_2O$, magnesium nitrate $Mg(NO_3)_2.6H_2O$, potassium nitrate (KNO_3), calcium chloride ($CaCl_2$), (sigma-Aldrich). Dowex 50WX8, (20-50 mesh) from Fluka.

Area of study



Source: Dept. of Geog. BUK (2016)

Figure 1: Map showing the sampling point at Sagamu Town, Ogun State.

Description of Sampling Area

Sagamu has geographical coordinates between 6°50′ north; 3° 38′ east is located in south western region of Nigeria. The region has tropical wet and dry climate with a lengthy wet season and relatively constant temperatures throughout the course of the year. Wet season runs from March to October, November to December forms the region dry season. The vegetation type of the region is savannah which is really grassland with small bushes and occasional big trees. Grassland soils have substantially higher organic matter content than forest soils (Novackova, 2011).

Sample Collection

The Peatsoil samples were collected from four different sampling points (0-10cm depth) in Sagamu into polyethylene bag with plastic spoons. Samples were taken to the laboratory, extraneous materials were removed; the samples were air-dried, crushed and ground to a fine powder in a mortar passed through a 0.20mm sieve. The samples were kept for analysis.

Isolation and purification of humic acid from peat soil sample

Peatsoil sample (100g) was mixed with 1000 cm^3 of 0.1M NaOH solution, shaken for 3hours and left to stand overnight. Dark-coloured supernatant was obtained and decanted from solid residue. The dark-coloured supernatant was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 6 hours. Yellowish brown supernatant and dark-brown precipitate were obtained. The yellowish brown supernatant was decanted followed by centrifuge and discarded. The dark-brown precipitate was mixed with 500$cm^3$of 0.1M NaOH solution followed by passing through dowex resin. The dark-brown solution was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 3 hours. The dark-brown precipitate was washed several times with deionized water. The supernatant was treated with $AgNO_3$ solution until no white precipitate observed. The humic acid was transferred to weighed crucible and dried at 60°C in an oven for 12 hours. The humic acid was cooled and dried in the desiccator, weighed and recorded. The obtained humic acid was dried again at 60°C for additional 6 hours cooled and dried in the desiccator, weighed and recorded constant weight was obtained (Baruah *et al.*, 2015).

FT-IR analysis

FT-IR spectra of humic acid sample was analysed using Carry 630 FT-IR Agilent Technologies.

Unhydrolysed compost humic acid

The unhydrolysed humic acid was obtained after isolation and purification of compost humic acid and kept for investigation.

Acid hydrolysis of Peatsoil acid

Peatsoil humic acid sample (1g) was refluxed for 12 hours at (160°C) with 50cm^3 of 6M HCl. The mixture was allowed to cool, decanted, and centrifuged after hydrolysis. The insoluble residues were washed with distilled water via centrifugation several times, and the supernatant was treated with $AgNO_3$ solution until no white precipitate was observed. The residue was thoroughly dried over $CaCl_2$ in a desiccator at room temperature (Chefetz *et al.*, 2002). Finally, the obtained hydrolysed humic acid was kept for investigation.

Potentiometric Titrations

Potentiometric measurements were carried out using a pH-meter Jenway (model 3510) with combine electrode, the sensitivity of the pH - meter is 0.01 units. The pH meter was switched on half an hour before starting the titration for initial warm up of the instrument. The instrument was calibrated with an aqueous standard buffer solution of pH 4.00 and 10.0 (borate buffer) prepared from a "Qualigens" buffer tablets.

The following sets of solutions were prepared in a 250cm^3 volumetric flask separately for pH metric titrations.

(i) 5 cm^3 0.1 M HCl + 40 cm^3 deionized water
(ii) 5 cm^3 0.1 M HCl + 39 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid
(iii) 5 cm^3 0.1 M HCl + 37 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid + 2 cm^3 0.01 M Cu(II)

The solutions were titrated against standardized 0.110MNaOH separately. The total volume of each mixture was adjusted to 50 cm^3 and the ionic strength of the solutions was maintained constant at by adding appropriate amount of stock solution of 1M KNO$_3$ (Gamal, 2015; Omar and Ali, 2015). A magnetic stirrer was used to achieve thorough mixing of the interacting solutions at 550 rpm. The same set of experimental conditions was applied for potentiometric titration of remaining samples.

Evaluation of pKa of Hydrolysed peat soil Humic Acids

The proton-ligand formation number n$_{\mathbf{A}}$ were calculated by Irving and Rossotti expression (Omar and Ali, 2015).

$$nA = Y - \frac{(V2-V1)(No-Eo)}{(Vo+V1)TcL} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 1$$

Where: Y is number of dissociable proton, (V$_2$-V$_1$) is the measure of displacement of the ligand curve relative to acid curve, N^o and E^o are the resultant concentration of alkali solution, free acid solution, T$_{cL}^o$ is the total ligand concentration, V^o is the total volume of titration solution,V$_1$ is the volume of alkali added to acid solution,V$_2$ is the volume of alkali added to acid solution + ligand solution, acid dissociation constants (pKa - values) of ligand were calculated by algebraic method point wise calculation (Tables 1). The dissociation constants (pKa) were calculated according to the following relation:

$$pKa = pH + \log\left(\frac{nA}{1-nA}\right) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 2$$

Where: pKa is the acid dissociation constant, n$_A$is the Proton-ligand formation number and pH is the pH-values (Omar and Ali, 2015).

Determination of metal-ligand stability constants (log K) of complexes

The potentiometric measurement for the determination of stability constant of a complex in solution is based on the fact that the redox potential of the couple $\frac{M^{+(m-n)}}{M^{+m}}$ is shifted significantly on complexation of the metal ion with the ligand. This method involves change in hydrogen ion concentration [H$^+$] due to the displacement or association of one or more protons taking place during complexation reaction. This change can be found out by titrating the solutions containing free acid, acid with ligand, and acid with ligand and metal ion, individually against a standard alkali solution at a constant ionic strength or temperature. Either ionic strength or temperature may be varied for different sets of solutions. In all the cases, the change in the pH of the solution is measured after each addition of a known amount of alkali to the reaction cell which contains the reaction mixture. The titration curves are then drawn by plotting the measured pH values against the corresponding volume of alkali added and the stability constants of the complexes are determined from the titration curves by employing pH-metric titration technique given by (Irving and Rossoti).

Metal-ligand stability constants (Log K) were determined by using the following relations:

$$\bar{n} = \frac{(V_3 - V_2)(E^0 + N^0)}{(V^0 + V_2)\bar{n}_A T_m^0} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 3$$

and

$$PL = \log_{10}\left\{\frac{1 + \beta_n^H \dfrac{1}{[anti\ \log pH]^n}}{T_L^0 - \bar{n} T_m^0} X \frac{(V^0 + V_3)}{V^0}\right\} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 4$$

Where $T_{L,}$ T^o, E°, and V^ohavethe same significance as in equation (1) above, T_m denotes the total concentration of metal present in solution, V_3 is the volume of metal ions present in solution and β^H is the overall proton ligand stability constant. The metal-ligand stability constants (log K) were determined by employing point wise computational Method (eq. 5 and 6).

$$\mathrm{Log}K_1 = \log\left(\frac{n}{1-n}\right) + pL \qquad \ldots\ldots\ldots\ldots.5$$

$$\mathrm{Log}K_2 = \log\left(\frac{1-n}{2-n}\right) + pL\ldots\ldots\ldots\ldots\ldots\ldots\ldots.6$$

Where: Log K is the metal-ligand stability constant, pL is the Free ligand exponent function, **n** is the Average number of ligand attached with metal ion (Janrao*et al.*, 2014).The results obtained were analyzed by an ORIGIN 2016 program using titration data and then the proton-ligand stability constants (pKa) and Metal-ligand stability constant (LogK) calculated (Omar and Ali, 2015).

RESULTS AND DISCUSSION

Fourier transformed infrared (FT-IR) spectra of isolated humic acid from peat soils Figure 2 had distinct clear absorption bands indicating the presence of major humic acid structural elemental groups such as H bonded OH ($3680 cm^{-1}$ peak), C=O of carbonyl ($1721 cm^{-1}$ peak), functional groups of aliphatic components CH_2 ($2918 cm^{-1}$ peak) and C-O stretching of polysaccharide ($1168 cm^{-1}$ peak). The positions of the absorption bands of the spectra fell within typical major absorption bands of humic acid which is at frequencies 3680, 2918, 1721, 1168 cm^{-1}. The first peak centred in the vicinity of 3680 cm^{-1} region is attributed to phenol OH group bounded by intermolecular H bonds. The $2918 cm^{-1}$ band usually has absorption maximum at 2918 cm^{-1} which is due to C–H stretching of alkane group (CH_2). The next major absorption band is 1721 cm^{-1}. This band has been commonly ascribed to C=O stretching of mainly carboxyl group (COOH) with trace amount of ketones. The last peak was observed at 1168 cm^{-1} due to C–O stretching of polysaccharides and this peak appeared also in the spectra of humic acid from peat soil. The FTIR spectra of the isolated humic acid contained all major characteristic absorption peaks of humic acid. These absorption peaks indicated the presence of the major structural elements of humic acid namely H bonded OH, C=C of aromatic ring, C=O of carbonyl group (both carboxyl and ketonic), CH_2 group. This strongly supports the presence of humic acid.

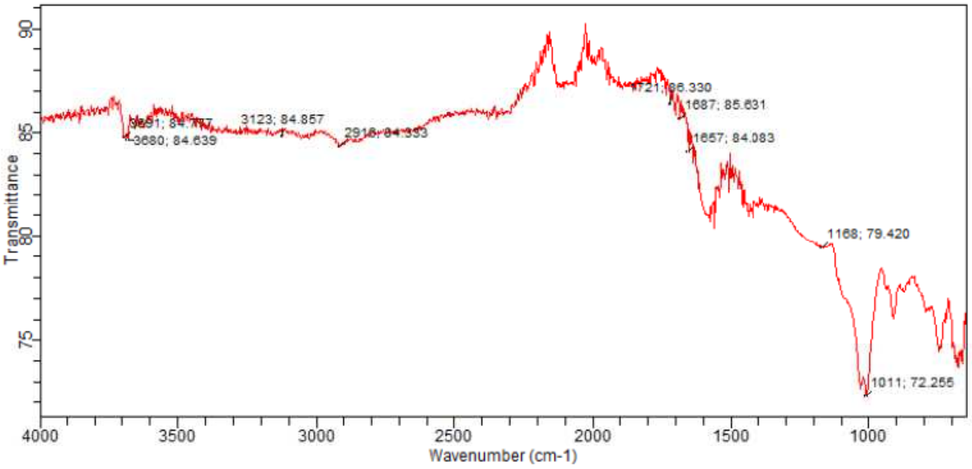


Fig. 2 : FT-IR spectraof peatsoilhumic acid (PSHA)

Evaluation of acid dissociation constant (pka) of acid hydrolysed peat soil humicacid at phenolic group

The value of the dissociation constant of the peat soil humic acid (PSHA) that underwent acidhydrolysis studied was found to be 8.9299 as shown Table 1, which is lower than the literaturevalues reported by Almeida and Szpoganics, (2015), Borges *et al.*, (2005); Badr *et al.*, (2012)and Fernandes *et al*,.(2009) of 9.73, 9.47 and 10.30. The difference between the obtained valuesand the reported values in this study might be probably as a result of acid hydrolysis of humicacid.

Table 1: PKa of (Hydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	log($\frac{nA}{1-nA}$)	pKa
8.50	5.30	6.29	0.99	0.3594	-0.2510	8.2490
8.72	5.35	6.37	1.02	0.3400	-0.2880	8.4320
9.00	5.40	6.46	1.06	0.3141	-0.3391	8.6609
9.22	5.45	6.55	1.10	0.2882	-0.3927	8.8273
9.51	5.50	6.66	1.16	0.2494	-0.4786	9.0314
9.73	5.55	6.78	1.23	0.2041	-0.5910	9.1390
10.00	5.60	6.90	1.30	0.1589	-0.7238	9.2762
10.23	5.65	7.05	1.40	0.0941	-0.9835	9.2465
10.49	5.70	7.10	1.40	0.0941	-0.9835	9.5065

Average pKa = 8.9299 ± 0.4186

Table 2: PKa of (Unhydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	Log($\frac{nA}{1-n}$)	pKa
8.50	5.30	5.81	0.51	0.6619	0.2919	8.7919
8.72	5.35	5.90	0.55	0.6357	0.2418	8.9618
9.00	5.40	6.00	0.60	0.6029	0.1813	9.1813
9.22	5.45	6.10	0.65	0.5701	0.1226	9.3426
9.51	5.50	6.20	0.70	0.5376	0.0654	9.5754
9.73	5.55	6.33	0.78	0.4851	-0.0259	9.7041
10.00	5.60	6.47	0.87	0.4262	-0.1291	9.8709
10.23	5.65	6.62	0.99	0.3609	-0.2481	9.9819
10.49	5.70	6.80	1.10	0.2759	-0.4690	10.0210

Average pKa = 9.4923± 0.4410

Metal-ligand stability constant (Log K)

The stabilityconstants require the accurate values of proton-ligand stability constants (Anil and Maroti, 2008). Metal titration curves crossed over ligand titration curve indicated the formation of complex upon proton release (Santosh, *et al.*, 2011). If the values of n- are within range 0.2-0.8 and 1.2-18 this indicates the formation of 1:1 and 1:2 complexes (Sayyed and Mazahar, 2012).

The metal (II)-humate stepwise stability constants (log k) at phenolic group (Tables 3-18)

Table 3: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n}{1-n}$)	$LogK_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

$LogK_1$ (Average value) = 2.4788± 0.2203

Table 4: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	Log($\frac{n-1}{2-n}$)	$LogK_2$
9.51	5.50	6.66	6.73	0.07	1.3509	1.70	-0.2671	1.4329
9.73	5.55	6.78	6.85	0.07	1.6383	1.51	0.2467	1.7567
10.00	5.60	6.90	6.98	0.08	2.1783	1.31	-0.2158	1.0942
10.23	5.65	7.05	7.13	0.08	4.1904	1.27		
10.49	5.70	7.10	7.19	0.09	4.6920			

$LogK_2$(Average value) = 1.4280 ± 0.3312

Table 5:Point-wise method,Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	$\text{Log}(\frac{n}{n-1})$	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430

$\text{Log}K_1$ **(Average value)** = 2.3059± 0.6153

Table 6:Point-wise method, Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$V_3\text{-}V_2$	n	pL	$\text{Log}(\frac{n-1}{2-n})$	Log K_2
9.73	5.55	6.33	6.42	0.09	0.9000	1.69		
10.00	5.60	6.47	6.58	0.11	1.2578	1.44	-0.4592	0.9808
10.23	5.65	6.62	6.84	0.12	1.6137	1.26	-0.2010	1.4610
10.49	5.70	6.80	6.92	0.12	2.1052	1.03		

$\text{Log}K_2$ **(Average value)** = 1.2209± 0.3398

Table 7:Point-wise method,Pb (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	$\log(\frac{n}{1-n})$	$\text{Log}K_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.60	0.05	0.8333	1.96	0.6989	2.6589

LogK_1 (Average value) = 2.5832 ±0.1614

Table 8:Point-wise method,Pb-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	$\log(\frac{n-1}{2-n})$	$\log K_2$
9.51	5.50	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.83	0.05	1.1702	1.44		
10.00	5.60	6.90	6.90	0.05	1.4864	1.22	-0.0237	1.1963
10.23	5.65	7.05	7.10	0.05	2.0190	1.09		
10.49	5.70	7.10	7.17	0.07	3.6492	1.00		

LogK_2(Average value) = 1.1963

Table 9:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$V_3\text{-}V_2$	n	pL	Log $(\frac{n}{n-1})$	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.5477	2.3123
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	0.0272	2.2072
9.51	5.50	6.20	6.26	0.07	0.6417	1.89	0.2530	2.1430
9.73	5.55	6.40	6.40	0.07	0.7000	1.67	0.3680	2.0380

$\text{Log}K_1$ **(Average value)** = 2.2364 ± 0.1602

Table 10:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$V_3\text{-}V_2$	n	pL	$\text{Log}(\frac{n-1}{2-n})$	Log K_2
10.00	5.60	6.47	6.55	0.08	1.9503	1.41		
10.23	5.65	6.62	6.72	0.11	1.4792	1.26	-0.0361	1.2239

$\text{Log}K_2$ **(Average value)** = 1.2239

Table 11:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	$\log(\frac{n}{n-1})$	$\text{Log}K_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4290	2.2110
8.72	5.35	6.37	6.39	0.02	0.2858	2.42	-0.3978	2.0222
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

LogK_1 (Average value)=2.1382**±**0.1046

Table 12:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$\log(\frac{n-1}{2-n})$	$LogK_2$
9.51	5.55	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.84	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.93	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.10		
10.49	5.70	7.10	7.18	0.07	3.6492	0.83		

$LogK_2$(Average value) = 1.5453 **±** 0.3450

Table 13:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$Log(\frac{n}{n-1})$	$Log\ K_1$
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.3477	2.3123
9.00	5.40	6.00	6.04	0.04	0.3236	2.38	-0.3202	2.0598
9.22	5.45	6.10	6.15	0.05	0.4297	2.17	-0.1230	2.0470
9.51	5.50	6.20	6.26	0.06	0.5500	1.89	0.0871	1.9771
9.73	5.55	6.33	6.40	0.07	0.7000	1.67	0.3680	2.0380

$LogK_1$ **(Average value)** = 2.1568 ± 0.2069

Table 14:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$Log(\frac{n-1}{2-n})$	$Log\ K_2$
10.00	5.60	6.47	6.55	0.08	0.9148	1.41		
10.23	5.65	6.62	6.71	0.09	1.2102	1.20	-0.5749	0.6251
10.49	5.70	6.80	6.92	0.09	1.5968	1.03	0.1703	1.2003

$LogK_2$ **(Average value)** = 0.9127± 0.4070

Table15:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$Log(\frac{n}{1-n})$	$LogK_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4210	2.2190
8.72	5.35	6.37	6.40	0.03	0.4286	2.42	-0.1249	2.2951
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.96	0.3010	2.2610
9.51	5.55	6.66	6.70	0.04	0.7720	1.67	0.5297	2.1997

$LogK_1$ (Average value) = 2.2108± 0.0825

Table 16:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$Log(\frac{n-1}{2-n})$	$Log\ K_2$
9.73	5.55	6.78	6.83	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.95	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.09		
10.49	5.70	7.10	7.16	0.06	3.1429	0.89		

$LogK_2$ **(Average value)** = 1.5453± 0.3450

Table 17:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$Log(\frac{n}{n-1})$	$Log\ K_1$
8.50	5.30	5.81	5.86	0.05	0.3717	2.88	-0.2280	2.6520
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.06	0.06	0.4853	2.38	-0.0255	2.3545
9.22	5.45	6.10	6.16	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430
9.73	5.55	6.33	6.41	0.08	0.8000	1.69	0.6020	2.2920

$LogK_1$ **(Average value)** = 2.2516± 0.5380

Table 18:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$\text{Log}(\frac{n-1}{2-n})$	Log K_2
10.00	5.60	6.47	6.57	0.10	1.1434	1.43		
10.23	5.65	6.62	6.72	0.10	1.3448	1.23	-0.2788	0.9512
10.49	5.70	6.80	6.90	0.10	1.7742	1.03	0.5351	1.5651

LogK_2 **(Average value)** = 1.2581± 0.4340

Table 19: Stepwise and overall Stability constants of thehydrolysed and unhydrolysed divalent metal (II) complexes

Chelates	**LogK_1**	**LogK_2**	**Logβ**
[Cu (Hydrolysed PSHA-1)$_2$]	2.4788	1.4280	3.9068
[Pb (Hydrolysed PSHA-1)$_2$]	2.5832	1.1963	3.7795
[Cd (Hydrolysed PSHA-1)$_2$]	2.2108	1.5453	3.7561
[Mg (Hydrolysed PSHA-1)$_2$]	2.1382	1.5453	3.6835
[Cu (Unhydrolysed PSHA-1)$_2$]	2.3059	1.2209	3.5268
[Pb (Unhydrolysed PSHA-1)$_2$]	2.2364	1.2239	3.4603
[Cd (Unhydrolysed PSHA-1)$_2$]	2.2516	1.2581	3.5097
[Mg (Unydrolysed PSHA-1)$_2$]	2.1568	0.9127	3.0695

The results obtained (Table19) shows the stepwise and overall stability constants to be not high indicating low stability of the complexes, because the solubility of most metal ions in the basic pH range is minimal due to metal hydroxide precipitation (Karimi, 2017). In general, the stepwise stability constants (K_1 and K_2) follow the order $K_1 > K_2$ for the copper, lead, magnesium and cadmium complexes respectively. The steady decrease of the values with increasing number of ligands is in agreement with the prediction made by researchers (Na'aliya, 2013). The decrease could be attributed to the fact that as the number of the ligands (Humate ions) that enters the coordination zone increases the aqua molecules available for replacement by the ligands become less. Thus, the metal ions become less electron loving with progressive intake of the ligand and this results in the decrease in the values of the constants (Na'aliya, 2013). Also the stability of the complexes is influenced by the size and number of the chelate rings(Mackay and Mackay,2002).All the complexes form rings in their structure as humate, a bidentate ligand, bond the metal ions in the ratio 1:2 (Boguta and Sokolowska, 2016) forming chelate rings. The values of the overall stability constants (logβ) obtained for humate complexes are not high indicating low stability as the values are not high. LogK values for copper-humates (Table 3 to 6) obtained in this study are lower than those reported for the complexes of humic acids (Pandey *et al*., 2015; Dinu, 2013; Kaschl *et al*., 2010 and Gilbeto and Jorg, 2001). The values of LogK(Table 7 to 10) forlead-humates are lower than those reported for the lead in the literature (Dinu, 2013; Gilbeto and Jorg 2001). Log K values(Table 11 to 14) for magnesium-humates obtained in this study are close to those reported by (Pandey *et al*., 2015). Log K values of cadmium-humates (Table 15 to 18) obtained in this work near to the one reported by (Dinu, 2013 and Pandey *et al*., 2015).The difference between the reported values and the values obtained in this study might be probably as a result of acid hydrolysis of humic acid. The values of the overall stability constants (log β) of the copper humates complexes presented in Table 19 is high than that of other metal humate complexes, show relatively high stability of Cu-HA complexes, show the following order of stability: Cu >Pb> Cd > Mg; which are in close agreement to the findings of (Dinu, 2013 and Pandey *et al*., 2015).The high stability of Cu-humate chelate could be attributed to the existence of coordinate covalent bond between the complexing agents and the Cu^{2+} ions. Since, Cu^{2+} being a metal of the transitional series with $3d^9$ electronic configurations can accept the electrons from the complexing agents. Similarly,the low stabilities of Pb,Cd and Mg -complexes could be explained by that Pb^{2+} with $6s^2$, Cd^{2+} with $4d^{10}$ and Mg^{2+} with $2p^6$ their electronic configuration has a completely filled d,p and s orbitals. Moreover, the stabilities of metal ions with hydrolysed humic acid from peat soil were higher than those with unhydrolysed humic acid from peat soil; which is ascribed to the high content of acidity in hydrolysed humic acid than unhydrolysed humic acid.

CONCLUSION

The values of logK for Cu(II) hydrolysed humic acid complex was higher followed by Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes as compared with metal(II) unhydrolysed humic acid complexes . This indicates acid hydrolysis of humic acid can enhance the complexation behavior of humic acid with metal (II) ions. However, the higher values of logβ for Cu(II), Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes indicates more stable stepwise complexes formed as compared with Cu(II), Pb(II), Cd(II) and Mg(II) unhydrolysed humic acid complexes.

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STABILITY CONSTANTS OF COMPLEXES OF METAL IONS WITH PEATSOIL HUMIC ACIDS UNDER NON-ACID-CONDITIONS

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ABSTRACT

Stability constants of complexes of four divalent metal ions viz. Cu^{2+}, Pb^{2+},Mg^{2+} and Cd^{2+} with humic acids (HA) were determined by potentiometric titration of humic acids with the corresponding salt of the divalent metals in aqueous media under non-acid-condition. The log K (logarithm of the stability constant) ranged from 1.0942 to 2.7471 for metal-humic acid complexes were determined using point-wise computational method. The order of stability constants were obtained as follows: Cu >Pb> Cd > Mg for metal -HA complexes respectively, indicating a higher degree of complexation with Cu metal ion.

Keywords: stability constant, humic acid, potentiometric titration, divalent metals, acid hydrolysis.

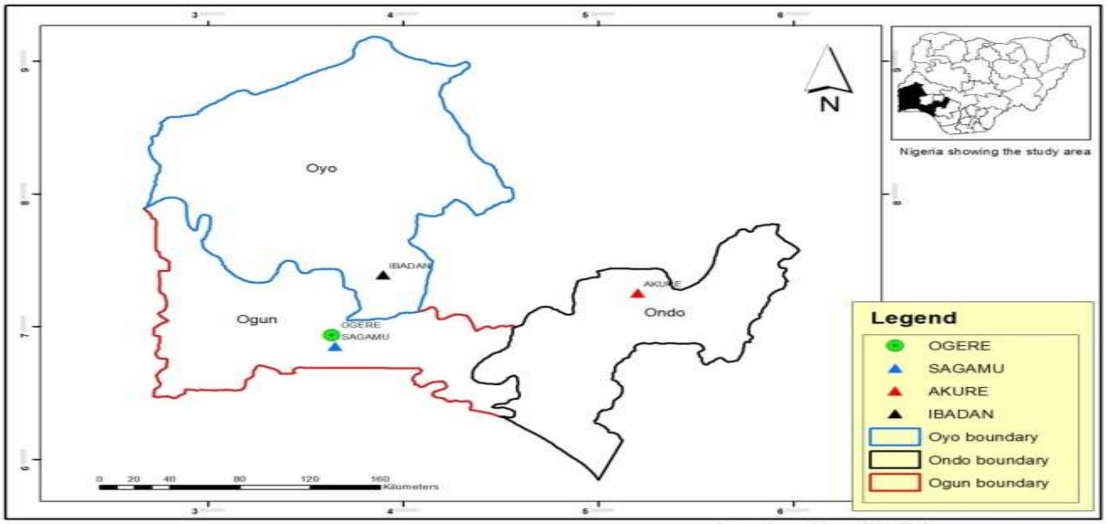
NTRODUCTION

The stability constant of a complex is the numerical expression of its stability and provides a quantitative measure of affinity of the metal ion to the complexing agent. An understanding of the relative stability of metal-complexes helps in predicting the behavior of metal ions in the soil (Ram and Raman, 1982). Extensive researches has been done to determine the stability constants of the complexes formed between humic acid (HA) with a number of metal ions. Ashok *et al.*, (2000) reported that humic acid with hydroxyl, phenoxyl and carboxyl reactive groups can form coordination compound with metal ions at pH 3.5. The stability constants(Log K) for different metal-humic acid complexes indicated the following order of the stabilities of complexes formed between humic acid and metal ion, Cu >Fe >Pb> Ni > Co > Ca > Cd > Zn >Mn> Mg. Andelkovic *et al.*, (2010) investigated the binding of Cd(II) to soil humic acid at pH 6.5 and in 0.1M KNO_3 ionic medium. The stability constant for binding indicating greater stability in the case when carboxyl groups are involved in complexation reaction. Kostic *et al.*,(2012) investigated the complexation of humic acid with certain heavy metal ions (Co(II), Ni(II),Cu(II), Zn(II), and Pb(II). The experiment was performed at 25°C, at pH 4.0 and ionic strength of 0.01M. Stability constant of complex between Pb(II) ions and humic acid is greater than stability constants of other investigated metal-humate complexes. Bogata and Sokolowska (2016) analyses the interaction between humic acids from different soils and Zn (II) ions at wide concentration ranges and at pH 5. Studies have showed significant impact of Zn concentration, pH and some properties of humic acids with zinc.But all of these studies were limited to acidic pH range. Therefore, the present study was carried out to determine and compare the stability constants of complexes of metal ions with hydrolysed peat soil humic acid and unhydrolysed peat soil humic under non-acid conditions.

MATERIALS AND METHODS

Analytical grade chemicals used includes hydrochloric acid (HCl), nitric acid (HNO_3), sodium hydroxide (NaOH), lead nitrate $Pb(NO_3)_2$, copper nitrate $Cu(NO_3)_2.3H_2O$, cadmium nitrate $Cd(NO_3)_2.4H_2O$, magnesium nitrate $Mg(NO_3)_2.6H_2O$, potassium nitrate (KNO_3), calcium chloride ($CaCl_2$), (sigma-Aldrich). Dowex 50WX8, (20-50 mesh) from Fluka.

Area of study



Source: Dept. of Geog. BUK (2016)

Figure 1: Map showing the sampling point at Sagamu Town, Ogun State.

Description of Sampling Area

Sagamu has geographical coordinates between 6°50′ north; 3° 38′ east is located in south western region of Nigeria. The region has tropical wet and dry climate with a lengthy wet season and relatively constant temperatures throughout the course of the year. Wet season runs from March to October, November to December forms the region dry season. The vegetation type of the region is savannah which is really grassland with small bushes and occasional big trees. Grassland soils have substantially higher organic matter content than forest soils (Novackova, 2011).

Sample Collection

The Peatsoil samples were collected from four different sampling points (0-10cm depth) in Sagamu into polyethylene bag with plastic spoons. Samples were taken to the laboratory, extraneous materials were removed; the samples were air-dried, crushed and ground to a fine powder in a mortar passed through a 0.20mm sieve. The samples were kept for analysis.

Isolation and purification of humic acid from peat soil sample

Peatsoil sample (100g) was mixed with 1000 cm^3 of 0.1M NaOH solution, shaken for 3hours and left to stand overnight. Dark-coloured supernatant was obtained and decanted from solid residue. The dark-coloured supernatant was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 6 hours. Yellowish brown supernatant and dark-brown precipitate were obtained. The yellowish brown supernatant was decanted followed by centrifuge and discarded. The dark-brown precipitate was mixed with $500cm^3$of 0.1M NaOH solution followed by passing through dowex resin. The dark-brown solution was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 3 hours. The dark-brown precipitate was washed several times with deionized water. The supernatant was treated with $AgNO_3$ solution until no white precipitate observed. The humic acid was transferred to weighed crucible and dried at 60°C in an oven for 12 hours. The humic acid was cooled and dried in the desiccator, weighed and recorded. The obtained humic acid was dried again at 60°C for additional 6 hours cooled and dried in the desiccator, weighed and recorded constant weight was obtained (Baruah *et al*., 2015).

FT-IR analysis

FT-IR spectra of humic acid sample was analysed using Carry 630 FT-IR Agilent Technologies.

Unhydrolysed compost humic acid

The unhydrolysed humic acid was obtained after isolation and purification of compost humic acid and kept for investigation.

Acid hydrolysis of Peatsoil acid

Peatsoil humic acid sample (1g) was refluxed for 12 hours at (160°C) with $50cm^3$ of 6M HCl. The mixture was allowed to cool, decanted, and centrifuged after hydrolysis. The insoluble residues were washed with distilled water via centrifugation several times, and the supernatant was treated with $AgNO_3$ solution until no white precipitate was observed. The residue was thoroughly dried over $CaCl_2$ in a desiccator at room temperature (Chefetz *et al*., 2002). Finally, the obtained hydrolysed humic acid was kept for investigation.

Potentiometric Titrations

Potentiometric measurements were carried out using a pH-meter Jenway (model 3510) with combine electrode, the sensitivity of the pH - meter is 0.01 units. The pH meter was switched on half an hour before starting the titration for initial warm up of the instrument. The instrument was calibrated with an aqueous standard buffer solution of pH 4.00 and 10.0 (borate buffer) prepared from a "Qualigens" buffer tablets.

The following sets of solutions were prepared in a 250cm^3 volumetric flask separately for pH metric titrations.

(i) 5 cm^3 0.1 M HCl + 40 cm^3 deionized water
(ii) 5 cm^3 0.1 M HCl + 39 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid
(iii) 5 cm^3 0.1 M HCl + 37 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid + 2 cm^3 0.01 M Cu(II)

The solutions were titrated against standardized 0.110MNaOH separately. The total volume of each mixture was adjusted to 50 cm^3 and the ionic strength of the solutions was maintained constant at by adding appropriate amount of stock solution of 1M KNO$_3$ (Gamal, 2015; Omar and Ali, 2015). A magnetic stirrer was used to achieve thorough mixing of the interacting solutions at 550 rpm. The same set of experimental conditions was applied for potentiometric titration of remaining samples.

Evaluation of pKa of Hydrolysed peat soil Humic Acids

The proton-ligand formation number n$_{\mathbf{A}}$ were calculated by Irving and Rossotti expression (Omar and Ali, 2015).

$$nA = Y- \frac{(V2-V1)(No-Eo)}{(Vo+V1)TcL} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots 1$$

Where: Y is number of dissociable proton, (V$_2$-V$_1$) is the measure of displacement of the ligand curve relative to acid curve, N^o and E^o are the resultant concentration of alkali solution, free acid solution, T_{cL}^{o} is the total ligand concentration, V^o is the total volume of titration solution,V$_1$ is the volume of alkali added to acid solution,V$_2$ is the volume of alkali added to acid solution + ligand solution, acid dissociation constants (pKa - values) of ligand were calculated by algebraic method point wise calculation (Tables 1). The dissociation constants (pKa) were calculated according to the following relation:

$$pKa = pH + \log(\frac{nA}{1-nA}) \quad \ldots\ldots\ldots\ldots\ldots 2$$

Where: pKa is the acid dissociation constant, n$_A$is the Proton-ligand formation number and pH is the pH-values (Omar and Ali, 2015).

Determination of metal-ligand stability constants (log K) of complexes

The potentiometric measurement for the determination of stability constant of a complex in solution is based on the fact that the redox potential of the couple $\frac{M^{+(m-n)}}{M^{+m}}$ is shifted significantly on complexation of the metal ion with the ligand. This method involves change in hydrogen ion concentration [H$^+$] due to the displacement or association of one or more protons taking place during complexation reaction. This change can be found out by titrating the solutions containing free acid, acid with ligand, and acid with ligand and metal ion, individually against a standard alkali solution at a constant ionic strength or temperature. Either ionic strength or temperature may be varied for different sets of solutions. In all the cases, the change in the pH of the solution is measured after each addition of a known amount of alkali to the reaction cell which contains the reaction mixture. The titration curves are then drawn by plotting the measured pH values against the corresponding volume of alkali added and the stability constants of the complexes are determined from the titration curves by employing pH-metric titration technique given by (Irving and Rossoti).

Metal-ligand stability constants (Log K) were determined by using the following relations:

$$\bar{n} = \frac{(V_3 - V_2)(E^0 + N^0)}{(V^0 + V_2)\bar{n}_A T_m^0} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 3$$

and

$$PL = \log_{10}\{\frac{1 + \beta_n^H \frac{1}{[anti\ \log pH]^n}}{T_L^0 - \bar{n}T_m^0} X \frac{(V^0 + V_3)}{V^0}\} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots 4$$

Where $T_{L,}$ T^o, E°, and V^ohavethe same significance as in equation (1) above, T_m denotes the total concentration of metal present in solution, V_3 is the volume of metal ions present in solution and β^H is the overall proton ligand stability constant. The metal-ligand stability constants (log K) were determined by employing point wise computational Method (eq. 5 and 6).

$LogK_1 = \log\left(\frac{n}{1-n}\right) + pL$ 5

$LogK_2 = \log\left(\frac{1-n}{2-n}\right) + pL$.......................6

Where: Log K is the metal-ligand stability constant, pL is the Free ligand exponent function, **n** is the Average number of ligand attached with metal ion (Janrao*et al.*, 2014).The results obtained were analyzed by an ORIGIN 2016 program using titration data and then the proton-ligand stability constants (pKa) and Metal-ligand stability constant (LogK) calculated (Omar and Ali, 2015).

RESULTS AND DISCUSSION

Fourier transformed infrared (FT-IR) spectra of isolated humic acid from peat soils Figure 2 had distinct clear absorption bands indicating the presence of major humic acid structural elemental groups such as H bonded OH ($3680cm^{-1}$ peak), C=O of carbonyl ($1721cm^{-1}$ peak), functional groups of aliphatic components CH_2 ($2918cm^{-1}$ peak) and C-O stretching of polysaccharide ($1168cm^{-1}$ peak). The positions of the absorption bands of the spectra fell within typical major absorption bands of humic acid which is at frequencies 3680, 2918, 1721, 1168 cm^{-1}. The first peak centred in the vicinity of 3680 cm^{-1} region is attributed to phenol OH group bounded by intermolecular H bonds. The $2918cm^{-1}$ band usually has absorption maximum at 2918 cm^{-1} which is due to C–H stretching of alkane group (CH_2). The next major absorption band is 1721 cm^{-1}. This band has been commonly ascribed to C=O stretching of mainly carboxyl group (COOH) with trace amount of ketones. The last peak was observed at 1168 cm^{-1} due to C–O stretching of polysaccharides and this peak appeared also in the spectra of humic acid from peat soil. The FTIR spectra of the isolated humic acid contained all major characteristic absorption peaks of humic acid. These absorption peaks indicated the presence of the major structural elements of humic acid namely H bonded OH, C=C of aromatic ring, C=O of carbonyl group (both carboxyl and ketonic), CH_2 group. This strongly supports the presence of humic acid.

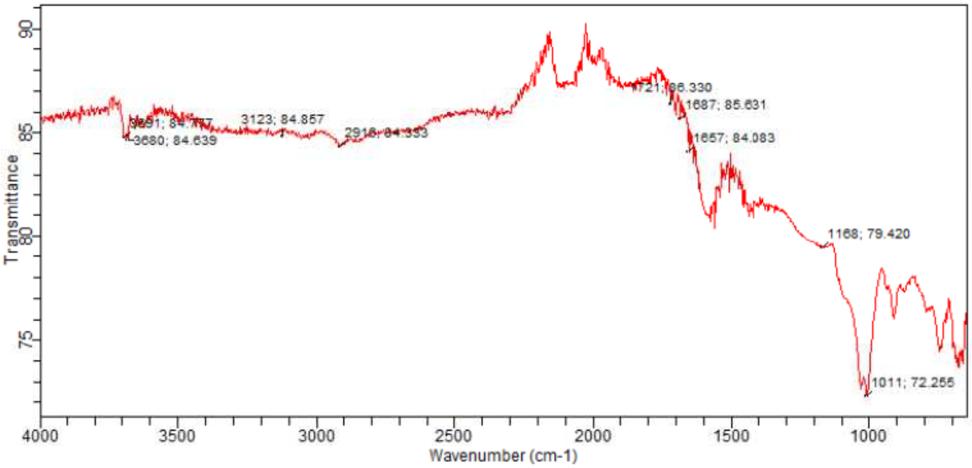


Fig. 2 : FT-IR spectraof peatsoilhumic acid (PSHA)

Evaluation of acid dissociation constant (pka) of acid hydrolysed peat soil humicacid at phenolic group

The value of the dissociation constant of the peat soil humic acid (PSHA) that underwent acidhydrolysis studied was found to be 8.9299 as shown Table 1, which is lower than the literaturevalues reported by Almeida and Szpoganics, (2015), Borges *et al.*, (2005); Badr *et al.*, (2012)and Fernandes *et al*,.(2009) of 9.73, 9.47 and 10.30. The difference between the obtained valuesand the reported values in this study might be probably as a result of acid hydrolysis of humicacid.

Table 1: PKa of (Hydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	$\log(\frac{nA}{1-nA})$	pKa
8.50	5.30	6.29	0.99	0.3594	-0.2510	8.2490
8.72	5.35	6.37	1.02	0.3400	-0.2880	8.4320
9.00	5.40	6.46	1.06	0.3141	-0.3391	8.6609
9.22	5.45	6.55	1.10	0.2882	-0.3927	8.8273
9.51	5.50	6.66	1.16	0.2494	-0.4786	9.0314
9.73	5.55	6.78	1.23	0.2041	-0.5910	9.1390
10.00	5.60	6.90	1.30	0.1589	-0.7238	9.2762
10.23	5.65	7.05	1.40	0.0941	-0.9835	9.2465
10.49	5.70	7.10	1.40	0.0941	-0.9835	9.5065

Average pKa = 8.9299 ± 0.4186

Table 2: PKa of (Unhydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	$\mathrm{Log}(\frac{nA}{1-n})$	pKa
8.50	5.30	5.81	0.51	0.6619	0.2919	8.7919
8.72	5.35	5.90	0.55	0.6357	0.2418	8.9618
9.00	5.40	6.00	0.60	0.6029	0.1813	9.1813
9.22	5.45	6.10	0.65	0.5701	0.1226	9.3426
9.51	5.50	6.20	0.70	0.5376	0.0654	9.5754
9.73	5.55	6.33	0.78	0.4851	-0.0259	9.7041
10.00	5.60	6.47	0.87	0.4262	-0.1291	9.8709
10.23	5.65	6.62	0.99	0.3609	-0.2481	9.9819
10.49	5.70	6.80	1.10	0.2759	-0.4690	10.0210

Average pKa = 9.4923± 0.4410

Metal-ligand stability constant (Log K)

The stabilityconstants require the accurate values of proton-ligand stability constants (Anil and Maroti, 2008). Metal titration curves crossed over ligand titration curve indicated the formation of complex upon proton release (Santosh, *et al.*, 2011). If the values of n- are within range 0.2-0.8 and 1.2-18 this indicates the formation of 1:1 and 1:2 complexes (Sayyed and Mazahar, 2012).

The metal (II)-humate stepwise stability constants (log k) at phenolic group (Tables 3-18)

Table 3: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$\log(\frac{n}{1-n})$	LogK_1
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

$\mathbf{LogK_1}$ (Average value) = 2.4788± 0.2203

Table 4: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$\mathrm{Log}(\frac{n-1}{2-n})$	LogK_2
9.51	5.50	6.66	6.73	0.07	1.3509	1.70	-0.2671	1.4329
9.73	5.55	6.78	6.85	0.07	1.6383	1.51	0.2467	1.7567
10.00	5.60	6.90	6.98	0.08	2.1783	1.31	-0.2158	1.0942
10.23	5.65	7.05	7.13	0.08	4.1904	1.27		
10.49	5.70	7.10	7.19	0.09	4.6920			

$\mathbf{LogK_2}$(Average value) = 1.4280 ± 0.3312

Table 5:Point-wise method,Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	Log($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430

$LogK_1$ **(Average value)** = 2.3059± 0.6153

Table 6:Point-wise method, Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
9.73	5.55	6.33	6.42	0.09	0.9000	1.69		
10.00	5.60	6.47	6.58	0.11	1.2578	1.44	-0.4592	0.9808
10.23	5.65	6.62	6.84	0.12	1.6137	1.26	-0.2010	1.4610
10.49	5.70	6.80	6.92	0.12	2.1052	1.03		

$LogK_2$ **(Average value)** = 1.2209± 0.3398

Table 7:Point-wise method,Pb (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n}{1-n}$)	$LogK_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.60	0.05	0.8333	1.96	0.6989	2.6589

$LogK_1$ (Average value) = 2.5832 ±0.1614

Table 8:Point-wise method,Pb-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n-1}{2-n}$)	$logK_2$
9.51	5.50	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.83	0.05	1.1702	1.44		
10.00	5.60	6.90	6.90	0.05	1.4864	1.22	-0.0237	1.1963
10.23	5.65	7.05	7.10	0.05	2.0190	1.09		
10.49	5.70	7.10	7.17	0.07	3.6492	1.00		

$LogK_2$(Average value) = 1.1963

Table 9:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log ($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.5477	2.3123
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	0.0272	2.2072
9.51	5.50	6.20	6.26	0.07	0.6417	1.89	0.2530	2.1430
9.73	5.55	6.40	6.40	0.07	0.7000	1.67	0.3680	2.0380

$LogK_1$ **(Average value)** = 2.2364 ± 0.1602

Table 10:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
10.00	5.60	6.47	6.55	0.08	1.9503	1.41		
10.23	5.65	6.62	6.72	0.11	1.4792	1.26	-0.0361	1.2239

$LogK_2$ **(Average value)** = 1.2239

Table 11:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n}{n-1}$)	$LogK_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4290	2.2110
8.72	5.35	6.37	6.39	0.02	0.2858	2.42	-0.3978	2.0222
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

$LogK_1$ (Average value)=2.1382**±**0.1046

Table 12:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	log($\frac{n-1}{2-n}$)	LogK$_2$
9.51	5.55	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.84	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.93	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.10		
10.49	5.70	7.10	7.18	0.07	3.6492	0.83		

LogK$_2$(Average value) = 1.5453 **±** 0.3450

Table 13:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	V$_3$-V$_2$	n	pL	Log($\frac{n}{n-1}$)	Log K$_1$
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.3477	2.3123
9.00	5.40	6.00	6.04	0.04	0.3236	2.38	-0.3202	2.0598
9.22	5.45	6.10	6.15	0.05	0.4297	2.17	-0.1230	2.0470
9.51	5.50	6.20	6.26	0.06	0.5500	1.89	0.0871	1.9771
9.73	5.55	6.33	6.40	0.07	0.7000	1.67	0.3680	2.0380

LogK$_1$ **(Average value)** = 2.1568 ± 0.2069

Table 14:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	V$_3$-V$_2$	n	pL	Log($\frac{n-1}{2-n}$)	Log K$_2$
10.00	5.60	6.47	6.55	0.08	0.9148	1.41		
10.23	5.65	6.62	6.71	0.09	1.2102	1.20	-0.5749	0.6251
10.49	5.70	6.80	6.92	0.09	1.5968	1.03	0.1703	1.2003

LogK$_2$ **(Average value)** = 0.9127± 0.4070

Table15:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	Log($\frac{n}{1-n}$)	LogK$_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4210	2.2190
8.72	5.35	6.37	6.40	0.03	0.4286	2.42	-0.1249	2.2951
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.96	0.3010	2.2610
9.51	5.55	6.66	6.70	0.04	0.7720	1.67	0.5297	2.1997

LogK$_1$ (Average value) = 2.2108± 0.0825

Table 16:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	(V$_3$-V$_2$)	n	pL	Log($\frac{n-1}{2-n}$)	Log K$_2$
9.73	5.55	6.78	6.83	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.95	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.09		
10.49	5.70	7.10	7.16	0.06	3.1429	0.89		

LogK$_2$ **(Average value)** = 1.5453± 0.3450

Table 17:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV$_1$	BV$_2$	BV$_3$	V$_3$-V$_2$	n	pL	Log($\frac{n}{n-1}$)	Log K$_1$
8.50	5.30	5.81	5.86	0.05	0.3717	2.88	-0.2280	2.6520
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.06	0.06	0.4853	2.38	-0.0255	2.3545
9.22	5.45	6.10	6.16	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430
9.73	5.55	6.33	6.41	0.08	0.8000	1.69	0.6020	2.2920

LogK$_1$ **(Average value)** = 2.2516± 0.5380

Table 18:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$\text{Log}(\frac{n-1}{2-n})$	Log K_2
10.00	5.60	6.47	6.57	0.10	1.1434	1.43		
10.23	5.65	6.62	6.72	0.10	1.3448	1.23	-0.2788	0.9512
10.49	5.70	6.80	6.90	0.10	1.7742	1.03	0.5351	1.5651

LogK_2 **(Average value)** = 1.2581± 0.4340

Table 19: Stepwise and overall Stability constants of thehydrolysed and unhydrolysed divalent metal (II) complexes

Chelates	**LogK_1**	**LogK_2**	**Logβ**
[Cu (Hydrolysed PSHA-1)$_2$]	2.4788	1.4280	3.9068
[Pb (Hydrolysed PSHA-1)$_2$]	2.5832	1.1963	3.7795
[Cd (Hydrolysed PSHA-1)$_2$]	2.2108	1.5453	3.7561
[Mg (Hydrolysed PSHA-1)$_2$]	2.1382	1.5453	3.6835
[Cu (Unhydrolysed PSHA-1)$_2$]	2.3059	1.2209	3.5268
[Pb (Unhydrolysed PSHA-1)$_2$]	2.2364	1.2239	3.4603
[Cd (Unhydrolysed PSHA-1)$_2$]	2.2516	1.2581	3.5097
[Mg (Unydrolysed PSHA-1)$_2$]	2.1568	0.9127	3.0695

The results obtained (Table19) shows the stepwise and overall stability constants to be not high indicating low stability of the complexes, because the solubility of most metal ions in the basic pH range is minimal due to metal hydroxide precipitation (Karimi, 2017). In general, the stepwise stability constants (K_1 and K_2) follow the order $K_1 > K_2$ for the copper, lead, magnesium and cadmium complexes respectively. The steady decrease of the values with increasing number of ligands is in agreement with the prediction made by researchers (Na'aliya, 2013). The decrease could be attributed to the fact that as the number of the ligands (Humate ions) that enters the coordination zone increases the aqua molecules available for replacement by the ligands become less. Thus, the metal ions become less electron loving with progressive intake of the ligand and this results in the decrease in the values of the constants (Na'aliya, 2013). Also the stability of the complexes is influenced by the size and number of the chelate rings(Mackay and Mackay,2002).All the complexes form rings in their structure as humate, a bidentate ligand, bond the metal ions in the ratio 1:2 (Boguta and Sokolowska, 2016) forming chelate rings. The values of the overall stability constants (logβ) obtained for humate complexes are not high indicating low stability as the values are not high. LogK values for copper-humates (Table 3 to 6) obtained in this study are lower than those reported for the complexes of humic acids (Pandey *et al.*, 2015; Dinu, 2013; Kaschl *et al.*, 2010 and Gilbeto and Jorg, 2001). The values of LogK(Table 7 to 10) forlead-humates are lower than those reported for the lead in the literature (Dinu, 2013; Gilbeto and Jorg 2001). Log K values(Table 11 to 14) for magnesium-humates obtained in this study are close to those reported by (Pandey *et al.*, 2015). Log K values of cadmium-humates (Table 15 to 18) obtained in this work near to the one reported by (Dinu, 2013 and Pandey *et al.*, 2015).The difference between the reported values and the values obtained in this study might be probably as a result of acid hydrolysis of humic acid. The values of the overall stability constants (log β) of the copper humates complexes presented in Table 19 is high than that of other metal humate complexes, show relatively high stability of Cu-HA complexes, show the following order of stability: Cu >Pb> Cd > Mg; which are in close agreement to the findings of (Dinu, 2013 and Pandey *et al.*, 2015).The high stability of Cu-humate chelate could be attributed to the existence of coordinate covalent bond between the complexing agents and the Cu^{2+} ions. Since, Cu^{2+} being a metal of the transitional series with $3d^9$ electronic configurations can accept the electrons from the complexing agents. Similarly,the low stabilities of Pb,Cd and Mg -complexes could be explained by that Pb^{2+} with $6s^2$, Cd^{2+} with $4d^{10}$ and Mg^{2+} with $2p^6$ their electronic configuration has a completely filled d,p and s orbitals. Moreover, the stabilities of metal ions with hydrolysed humic acid from peat soil were higher than those with unhydrolysed humic acid from peat soil; which is ascribed to the high content of acidity in hydrolysed humic acid than unhydrolysed humic acid.

CONCLUSION

The values of logK for Cu(II) hydrolysed humic acid complex was higher followed by Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes as compared with metal(II) unhydrolysed humic acid complexes . This indicates acid hydrolysis of humic acid can enhance the complexation behavior of humic acid with metal (II) ions. However, the higher values of logβ for Cu(II), Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes indicates more stable stepwise complexes formed as compared with Cu(II), Pb(II), Cd(II) and Mg(II) unhydrolysed humic acid complexes.

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STABILITY CONSTANTS OF COMPLEXES OF METAL IONS WITH PEATSOIL HUMIC ACIDS UNDER NON-ACID-CONDITIONS

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ABSTRACT

Stability constants of complexes of four divalent metal ions viz. Cu^{2+}, Pb^{2+},Mg^{2+} and Cd^{2+} with humic acids (HA) were determined by potentiometric titration of humic acids with the corresponding salt of the divalent metals in aqueous media under non-acid-condition. The log K (logarithm of the stability constant) ranged from 1.0942 to 2.7471 for metal-humic acid complexes were determined using point-wise computational method. The order of stability constants were obtained as follows: Cu >Pb> Cd > Mg for metal -HA complexes respectively, indicating a higher degree of complexation with Cu metal ion.

Keywords: stability constant, humic acid, potentiometric titration, divalent metals, acid hydrolysis.

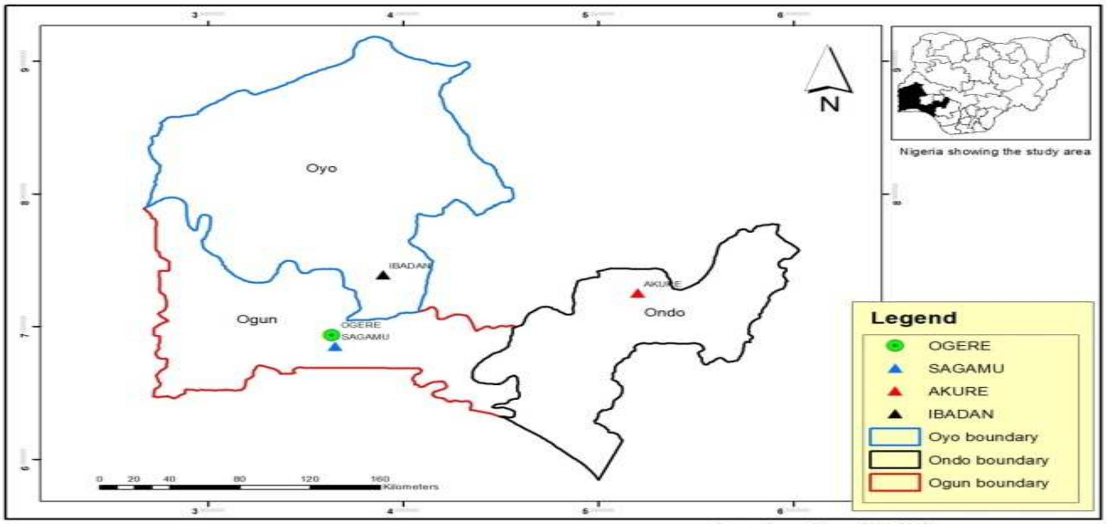
NTRODUCTION

The stability constant of a complex is the numerical expression of its stability and provides a quantitative measure of affinity of the metal ion to the complexing agent. An understanding of the relative stability of metal-complexes helps in predicting the behavior of metal ions in the soil (Ram and Raman, 1982). Extensive researches has been done to determine the stability constants of the complexes formed between humic acid (HA) with a number of metal ions. Ashok *et al*., (2000) reported that humic acid with hydroxyl, phenoxyl and carboxyl reactive groups can form coordination compound with metal ions at pH 3.5. The stability constants(Log K) for different metal-humic acid complexes indicated the following order of the stabilities of complexes formed between humic acid and metal ion, Cu >Fe >Pb> Ni > Co > Ca > Cd > Zn >Mn> Mg. Andelkovic *et al*., (2010) investigated the binding of Cd(II) to soil humic acid at pH 6.5 and in 0.1M KNO_3 ionic medium. The stability constant for binding indicating greater stability in the case when carboxyl groups are involved in complexation reaction. Kostic *et al*.,(2012) investigated the complexation of humic acid with certain heavy metal ions (Co(II), Ni(II),Cu(II), Zn(II), and Pb(II). The experiment was performed at 25°C, at pH 4.0 and ionic strength of 0.01M. Stability constant of complex between Pb(II) ions and humic acid is greater than stability constants of other investigated metal-humate complexes. Bogata and Sokolowska (2016) analyses the interaction between humic acids from different soils and Zn (II) ions at wide concentration ranges and at pH 5. Studies have showed significant impact of Zn concentration, pH and some properties of humic acids with zinc.But all of these studies were limited to acidic pH range. Therefore, the present study was carried out to determine and compare the stability constants of complexes of metal ions with hydrolysed peat soil humic acid and unhydrolysed peat soil humic under non-acid conditions.

MATERIALS AND METHODS

Analytical grade chemicals used includes hydrochloric acid (HCl), nitric acid (HNO_3), sodium hydroxide (NaOH), lead nitrate $Pb(NO_3)_2$, copper nitrate $Cu(NO_3)_2.3H_2O$, cadmium nitrate $Cd(NO_3)_2.4H_2O$, magnesium nitrate $Mg(NO_3)_2.6H_2O$, potassium nitrate (KNO_3), calcium chloride ($CaCl_2$), (sigma-Aldrich). Dowex 50WX8, (20-50 mesh) from Fluka.

Area of study



Source: Dept. of Geog. BUK (2016)

Figure 1: Map showing the sampling point at Sagamu Town, Ogun State.

Description of Sampling Area

Sagamu has geographical coordinates between 6°50′ north; 3° 38′ east is located in south western region of Nigeria. The region has tropical wet and dry climate with a lengthy wet season and relatively constant temperatures throughout the course of the year. Wet season runs from March to October, November to December forms the region dry season. The vegetation type of the region is savannah which is really grassland with small bushes and occasional big trees. Grassland soils have substantially higher organic matter content than forest soils (Novackova, 2011).

Sample Collection

The Peatsoil samples were collected from four different sampling points (0-10cm depth) in Sagamu into polyethylene bag with plastic spoons. Samples were taken to the laboratory, extraneous materials were removed; the samples were air-dried, crushed and ground to a fine powder in a mortar passed through a 0.20mm sieve. The samples were kept for analysis.

Isolation and purification of humic acid from peat soil sample

Peatsoil sample (100g) was mixed with 1000 cm^3 of 0.1M NaOH solution, shaken for 3hours and left to stand overnight. Dark-coloured supernatant was obtained and decanted from solid residue. The dark-coloured supernatant was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 6 hours. Yellowish brown supernatant and dark-brown precipitate were obtained. The yellowish brown supernatant was decanted followed by centrifuge and discarded. The dark-brown precipitate was mixed with $500cm^3$of 0.1M NaOH solution followed by passing through dowex resin. The dark-brown solution was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 3 hours. The dark-brown precipitate was washed several times with deionized water. The supernatant was treated with $AgNO_3$ solution until no white precipitate observed. The humic acid was transferred to weighed crucible and dried at 60^oC in an oven for 12 hours. The humic acid was cooled and dried in the desiccator, weighed and recorded. The obtained humic acid was dried again at 60^oC for additional 6 hours cooled and dried in the desiccator, weighed and recorded constant weight was obtained (Baruah *et al*., 2015).

FT-IR analysis

FT-IR spectra of humic acid sample was analysed using Carry 630 FT-IR Agilent Technologies.

Unhydrolysed compost humic acid

The unhydrolysed humic acid was obtained after isolation and purification of compost humic acid and kept for investigation.

Acid hydrolysis of Peatsoil acid

Peatsoil humic acid sample (1g) was refluxed for 12 hours at (160^oC) with $50cm^3$ of 6M HCl. The mixture was allowed to cool, decanted, and centrifuged after hydrolysis. The insoluble residues were washed with distilled water via centrifugation several times, and the supernatant was treated with $AgNO_3$ solution until no white precipitate was observed. The residue was thoroughly dried over $CaCl_2$ in a desiccator at room temperature (Chefetz *et al*., 2002). Finally, the obtained hydrolysed humic acid was kept for investigation.

Potentiometric Titrations

Potentiometric measurements were carried out using a pH-meter Jenway (model 3510) with combine electrode, the sensitivity of the pH - meter is 0.01 units. The pH meter was switched on half an hour before starting the titration for initial warm up of the instrument. The instrument was calibrated with an aqueous standard buffer solution of pH 4.00 and 10.0 (borate buffer) prepared from a "Qualigens" buffer tablets.

The following sets of solutions were prepared in a 250cm^3 volumetric flask separately for pH metric titrations.

(i) 5 cm^3 0.1 M HCl + 40 cm^3 deionized water

(ii) 5 cm^3 0.1 M HCl + 39 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid

(iii) 5 cm^3 0.1 M HCl + 37 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid + 2 cm^3 0.01 M Cu(II)

The solutions were titrated against standardized 0.110MNaOH separately. The total volume of each mixture was adjusted to 50 cm^3 and the ionic strength of the solutions was maintained constant at by adding appropriate amount of stock solution of 1M KNO$_3$ (Gamal, 2015; Omar and Ali, 2015). A magnetic stirrer was used to achieve thorough mixing of the interacting solutions at 550 rpm. The same set of experimental conditions was applied for potentiometric titration of remaining samples.

Evaluation of pKa of Hydrolysed peat soil Humic Acids

The proton-ligand formation number n_A were calculated by Irving and Rossotti expression (Omar and Ali, 2015).

$$nA = Y - \frac{(V2-V1)(No-Eo)}{(Vo+V1)TcL} \quad \text{.................................1}$$

Where: Y is number of dissociable proton, $(V_2\text{-}V_1)$ is the measure of displacement of the ligand curve relative to acid curve, N^o and E^o are the resultant concentration of alkali solution, free acid solution, $T_{cL}{}^o$ is the total ligand concentration, V^o is the total volume of titration solution,V_1 is the volume of alkali added to acid solution,V_2 is the volume of alkali added to acid solution + ligand solution, acid dissociation constants (pKa - values) of ligand were calculated by algebraic method point wise calculation (Tables 1). The dissociation constants (pKa) were calculated according to the following relation:

$$pKa = pH + \log\left(\frac{nA}{1-nA}\right) \quad \text{............................2}$$

Where: pKa is the acid dissociation constant, $n_A$is the Proton-ligand formation number and pH is the pH-values (Omar and Ali, 2015).

Determination of metal-ligand stability constants (log K) of complexes

The potentiometric measurement for the determination of stability constant of a complex in solution is based on the fact that the redox potential of the couple $\frac{M^{+(m-n)}}{M^{+m}}$ is shifted significantly on complexation of the metal ion with the ligand. This method involves change in hydrogen ion concentration [H$^+$] due to the displacement or association of one or more protons taking place during complexation reaction. This change can be found out by titrating the solutions containing free acid, acid with ligand, and acid with ligand and metal ion, individually against a standard alkali solution at a constant ionic strength or temperature. Either ionic strength or temperature may be varied for different sets of solutions. In all the cases, the change in the pH of the solution is measured after each addition of a known amount of alkali to the reaction cell which contains the reaction mixture. The titration curves are then drawn by plotting the measured pH values against the corresponding volume of alkali added and the stability constants of the complexes are determined from the titration curves by employing pH-metric titration technique given by (Irving and Rossoti).

Metal-ligand stability constants (Log K) were determined by using the following relations:

$$\bar{n} = \frac{(V_3 - V_2)(E^0 + N^0)}{(V^0 + V_2)\bar{n}_A T_m^0} \quad \text{...3}$$

and

$$PL = \log_{10}\left\{\frac{1+\beta_n^H \dfrac{1}{[anti\ \log pH]^n}}{T_L^0 - \bar{n}T_m^0} X \frac{(V^0+V_3)}{V^0}\right\} \quad \text{...4}$$

Where $T_{L,}$ T^{o}, E°, and V^{o}havethe same significance as in equation (1) above, T_m denotes the total concentration of metal present in solution, V_3 is the volume of metal ions present in solution and β^{H} is the overall proton ligand stability constant. The metal-ligand stability constants (log K) were determined by employing point wise computational Method (eq. 5 and 6).

$$\mathrm{LogK}_1 = \log\left(\frac{n}{1-n}\right) + \mathrm{pL} \qquad \text{.............}5$$

$$\mathrm{LogK}_2 = \log\left(\frac{1-n}{2-n}\right) + \mathrm{pL}\text{.......................}6$$

Where: Log K is the metal-ligand stability constant, pL is the Free ligand exponent function, **n** is the Average number of ligand attached with metal ion (Janrao*et al.*, 2014).The results obtained were analyzed by an ORIGIN 2016 program using titration data and then the proton-ligand stability constants (pKa) and Metal-ligand stability constant (LogK) calculated (Omar and Ali, 2015).

RESULTS AND DISCUSSION

Fourier transformed infrared (FT-IR) spectra of isolated humic acid from peat soils Figure 2 had distinct clear absorption bands indicating the presence of major humic acid structural elemental groups such as H bonded OH ($3680cm^{-1}$ peak), C=O of carbonyl ($1721cm^{-1}$ peak), functional groups of aliphatic components CH_2 ($2918cm^{-1}$ peak) and C-O stretching of polysaccharide ($1168cm^{-1}$ peak). The positions of the absorption bands of the spectra fell within typical major absorption bands of humic acid which is at frequencies 3680, 2918, 1721, 1168 cm^{-1}. The first peak centred in the vicinity of 3680 cm^{-1} region is attributed to phenol OH group bounded by intermolecular H bonds. The $2918cm^{-1}$ band usually has absorption maximum at 2918 cm^{-1} which is due to C–H stretching of alkane group (CH_2). The next major absorption band is 1721 cm^{-1}. This band has been commonly ascribed to C=O stretching of mainly carboxyl group (COOH) with trace amount of ketones. The last peak was observed at 1168 cm^{-1} due to C–O stretching of polysaccharides and this peak appeared also in the spectra of humic acid from peat soil. The FTIR spectra of the isolated humic acid contained all major characteristic absorption peaks of humic acid. These absorption peaks indicated the presence of the major structural elements of humic acid namely H bonded OH, C=C of aromatic ring, C=O of carbonyl group (both carboxyl and ketonic), CH_2 group. This strongly supports the presence of humic acid.

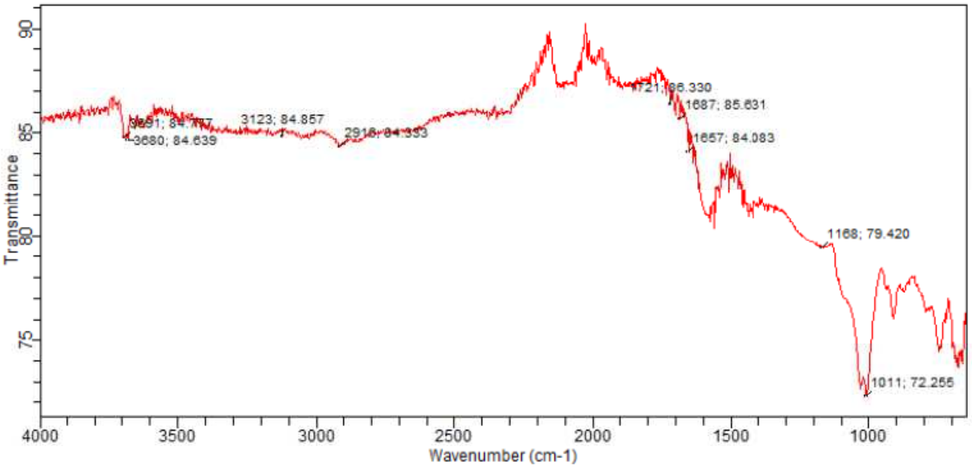


Fig. 2 : FT-IR spectraof peatsoilhumic acid (PSHA)

Evaluation of acid dissociation constant (pka) of acid hydrolysed peat soil humicacid at phenolic group

The value of the dissociation constant of the peat soil humic acid (PSHA) that underwent acidhydrolysis studied was found to be 8.9299 as shown Table 1, which is lower than the literaturevalues reported by Almeida and Szpoganics, (2015), Borges *et al.*, (2005); Badr *et al.*, (2012)and Fernandes *et al*,.(2009) of 9.73, 9.47 and 10.30. The difference between the obtained valuesand the reported values in this study might be probably as a result of acid hydrolysis of humicacid.

Table 1: PKa of (Hydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	log($\frac{nA}{1-nA}$)	pKa
8.50	5.30	6.29	0.99	0.3594	-0.2510	8.2490
8.72	5.35	6.37	1.02	0.3400	-0.2880	8.4320
9.00	5.40	6.46	1.06	0.3141	-0.3391	8.6609
9.22	5.45	6.55	1.10	0.2882	-0.3927	8.8273
9.51	5.50	6.66	1.16	0.2494	-0.4786	9.0314
9.73	5.55	6.78	1.23	0.2041	-0.5910	9.1390
10.00	5.60	6.90	1.30	0.1589	-0.7238	9.2762
10.23	5.65	7.05	1.40	0.0941	-0.9835	9.2465
10.49	5.70	7.10	1.40	0.0941	-0.9835	9.5065

Average pKa = 8.9299 ± 0.4186

Table 2: PKa of (Unhydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	Log($\frac{nA}{1-n}$)	pKa
8.50	5.30	5.81	0.51	0.6619	0.2919	8.7919
8.72	5.35	5.90	0.55	0.6357	0.2418	8.9618
9.00	5.40	6.00	0.60	0.6029	0.1813	9.1813
9.22	5.45	6.10	0.65	0.5701	0.1226	9.3426
9.51	5.50	6.20	0.70	0.5376	0.0654	9.5754
9.73	5.55	6.33	0.78	0.4851	-0.0259	9.7041
10.00	5.60	6.47	0.87	0.4262	-0.1291	9.8709
10.23	5.65	6.62	0.99	0.3609	-0.2481	9.9819
10.49	5.70	6.80	1.10	0.2759	-0.4690	10.0210

Average pKa = 9.4923± 0.4410

Metal-ligand stability constant (Log K)

The stabilityconstants require the accurate values of proton-ligand stability constants (Anil and Maroti, 2008). Metal titration curves crossed over ligand titration curve indicated the formation of complex upon proton release (Santosh, *et al.*, 2011). If the values of n- are within range 0.2-0.8 and 1.2-18 this indicates the formation of 1:1 and 1:2 complexes (Sayyed and Mazahar, 2012).

The metal (II)-humate stepwise stability constants (log k) at phenolic group (Tables 3-18)

Table 3: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n}{1-n}$)	LogK_1
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

LogK_1 (Average value) = 2.4788± 0.2203

Table 4: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	Log($\frac{n-1}{2-n}$)	LogK_2
9.51	5.50	6.66	6.73	0.07	1.3509	1.70	-0.2671	1.4329
9.73	5.55	6.78	6.85	0.07	1.6383	1.51	0.2467	1.7567
10.00	5.60	6.90	6.98	0.08	2.1783	1.31	-0.2158	1.0942
10.23	5.65	7.05	7.13	0.08	4.1904	1.27		
10.49	5.70	7.10	7.19	0.09	4.6920			

LogK_2(Average value) = 1.4280 ± 0.3312

Table 5:Point-wise method,Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$\text{Log}(\frac{n}{n-1})$	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430

$\text{Log}K_1$ **(Average value)** = 2.3059± 0.6153

Table 6:Point-wise method, Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$\text{Log}(\frac{n-1}{2-n})$	Log K_2
9.73	5.55	6.33	6.42	0.09	0.9000	1.69		
10.00	5.60	6.47	6.58	0.11	1.2578	1.44	-0.4592	0.9808
10.23	5.65	6.62	6.84	0.12	1.6137	1.26	-0.2010	1.4610
10.49	5.70	6.80	6.92	0.12	2.1052	1.03		

$\text{Log}K_2$ **(Average value)** = 1.2209± 0.3398

Table 7:Point-wise method,Pb (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$\log(\frac{n}{1-n})$	$\text{Log}K_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.60	0.05	0.8333	1.96	0.6989	2.6589

$\text{Log}K_1$ (Average value) = 2.5832 ±0.1614

Table 8:Point-wise method,Pb-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$\log(\frac{n-1}{2-n})$	$\log K_2$
9.51	5.50	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.83	0.05	1.1702	1.44		
10.00	5.60	6.90	6.90	0.05	1.4864	1.22	-0.0237	1.1963
10.23	5.65	7.05	7.10	0.05	2.0190	1.09		
10.49	5.70	7.10	7.17	0.07	3.6492	1.00		

$\text{Log}K_2$(Average value) = 1.1963

Table 9:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log $(\frac{n}{n-1})$	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.5477	2.3123
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	0.0272	2.2072
9.51	5.50	6.20	6.26	0.07	0.6417	1.89	0.2530	2.1430
9.73	5.55	6.40	6.40	0.07	0.7000	1.67	0.3680	2.0380

$\text{Log}K_1$ **(Average value)** = 2.2364 ± 0.1602

Table 10:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$\text{Log}(\frac{n-1}{2-n})$	Log K_2
10.00	5.60	6.47	6.55	0.08	1.9503	1.41		
10.23	5.65	6.62	6.72	0.11	1.4792	1.26	-0.0361	1.2239

$\text{Log}K_2$ **(Average value)** = 1.2239

Table 11:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$\log(\frac{n}{n-1})$	$\text{Log}K_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4290	2.2110
8.72	5.35	6.37	6.39	0.02	0.2858	2.42	-0.3978	2.0222
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

$\text{Log}K_1$ (Average value)=2.1382**±**0.1046

Table 12:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log$(\frac{n-1}{2-n})$	$LogK_2$
9.51	5.55	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.84	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.93	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.10		
10.49	5.70	7.10	7.18	0.07	3.6492	0.83		

$LogK_2$(Average value) = 1.5453 **±** 0.3450

Table 13:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log$(\frac{n}{n-1})$	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.3477	2.3123
9.00	5.40	6.00	6.04	0.04	0.3236	2.38	-0.3202	2.0598
9.22	5.45	6.10	6.15	0.05	0.4297	2.17	-0.1230	2.0470
9.51	5.50	6.20	6.26	0.06	0.5500	1.89	0.0871	1.9771
9.73	5.55	6.33	6.40	0.07	0.7000	1.67	0.3680	2.0380

$LogK_1$ **(Average value)** = 2.1568 ± 0.2069

Table 14:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log$(\frac{n-1}{2-n})$	Log K_2
10.00	5.60	6.47	6.55	0.08	0.9148	1.41		
10.23	5.65	6.62	6.71	0.09	1.2102	1.20	-0.5749	0.6251
10.49	5.70	6.80	6.92	0.09	1.5968	1.03	0.1703	1.2003

$LogK_2$ **(Average value)** = 0.9127± 0.4070

Table15:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	Log$(\frac{n}{1-n})$	$LogK_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4210	2.2190
8.72	5.35	6.37	6.40	0.03	0.4286	2.42	-0.1249	2.2951
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.96	0.3010	2.2610
9.51	5.55	6.66	6.70	0.04	0.7720	1.67	0.5297	2.1997

$LogK_1$ (Average value) = 2.2108± 0.0825

Table 16:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	Log$(\frac{n-1}{2-n})$	Log K_2
9.73	5.55	6.78	6.83	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.95	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.09		
10.49	5.70	7.10	7.16	0.06	3.1429	0.89		

$LogK_2$ **(Average value)** = 1.5453± 0.3450

Table 17:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log$(\frac{n}{n-1})$	Log K_1
8.50	5.30	5.81	5.86	0.05	0.3717	2.88	-0.2280	2.6520
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.06	0.06	0.4853	2.38	-0.0255	2.3545
9.22	5.45	6.10	6.16	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430
9.73	5.55	6.33	6.41	0.08	0.8000	1.69	0.6020	2.2920

$LogK_1$ **(Average value)** = 2.2516± 0.5380

Table 18:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$\text{Log}(\frac{n-1}{2-n})$	Log K_2
10.00	5.60	6.47	6.57	0.10	1.1434	1.43		
10.23	5.65	6.62	6.72	0.10	1.3448	1.23	-0.2788	0.9512
10.49	5.70	6.80	6.90	0.10	1.7742	1.03	0.5351	1.5651

LogK_2 **(Average value)** = 1.2581± 0.4340

Table 19: Stepwise and overall Stability constants of thehydrolysed and unhydrolysed divalent metal (II) complexes

Chelates	**LogK_1**	**LogK_2**	**Logβ**
[Cu (Hydrolysed PSHA-1)$_2$]	2.4788	1.4280	3.9068
[Pb (Hydrolysed PSHA-1)$_2$]	2.5832	1.1963	3.7795
[Cd (Hydrolysed PSHA-1)$_2$]	2.2108	1.5453	3.7561
[Mg (Hydrolysed PSHA-1)$_2$]	2.1382	1.5453	3.6835
[Cu (Unhydrolysed PSHA-1)$_2$]	2.3059	1.2209	3.5268
[Pb (Unhydrolysed PSHA-1)$_2$]	2.2364	1.2239	3.4603
[Cd (Unhydrolysed PSHA-1)$_2$]	2.2516	1.2581	3.5097
[Mg (Unydrolysed PSHA-1)$_2$]	2.1568	0.9127	3.0695

The results obtained (Table19) shows the stepwise and overall stability constants to be not high indicating low stability of the complexes, because the solubility of most metal ions in the basic pH range is minimal due to metal hydroxide precipitation (Karimi, 2017). In general, the stepwise stability constants (K_1 and K_2) follow the order $K_1 > K_2$ for the copper, lead, magnesium and cadmium complexes respectively. The steady decrease of the values with increasing number of ligands is in agreement with the prediction made by researchers (Na'aliya, 2013). The decrease could be attributed to the fact that as the number of the ligands (Humate ions) that enters the coordination zone increases the aqua molecules available for replacement by the ligands become less. Thus, the metal ions become less electron loving with progressive intake of the ligand and this results in the decrease in the values of the constants (Na'aliya, 2013). Also the stability of the complexes is influenced by the size and number of the chelate rings(Mackay and Mackay,2002).All the complexes form rings in their structure as humate, a bidentate ligand, bond the metal ions in the ratio 1:2 (Boguta and Sokolowska, 2016) forming chelate rings. The values of the overall stability constants (logβ) obtained for humate complexes are not high indicating low stability as the values are not high. LogK values for copper-humates (Table 3 to 6) obtained in this study are lower than those reported for the complexes of humic acids (Pandey *et al.*, 2015; Dinu, 2013; Kaschl *et al.*, 2010 and Gilbeto and Jorg, 2001). The values of LogK(Table 7 to 10) forlead-humates are lower than those reported for the lead in the literature (Dinu, 2013; Gilbeto and Jorg 2001). Log K values(Table 11 to 14) for magnesium-humates obtained in this study are close to those reported by (Pandey *et al.*, 2015). Log K values of cadmium-humates (Table 15 to 18) obtained in this work near to the one reported by (Dinu, 2013 and Pandey *et al.*, 2015).The difference between the reported values and the values obtained in this study might be probably as a result of acid hydrolysis of humic acid. The values of the overall stability constants (log β) of the copper humates complexes presented in Table 19 is high than that of other metal humate complexes, show relatively high stability of Cu-HA complexes, show the following order of stability: Cu >Pb> Cd > Mg; which are in close agreement to the findings of (Dinu, 2013 and Pandey *et al.*, 2015).The high stability of Cu-humate chelate could be attributed to the existence of coordinate covalent bond between the complexing agents and the Cu^{2+} ions. Since, Cu^{2+} being a metal of the transitional series with $3d^9$ electronic configurations can accept the electrons from the complexing agents. Similarly,the low stabilities of Pb,Cd and Mg -complexes could be explained by that Pb^{2+} with $6s^2$, Cd^{2+} with $4d^{10}$ and Mg^{2+} with $2p^6$ their electronic configuration has a completely filled d,p and s orbitals. Moreover, the stabilities of metal ions with hydrolysed humic acid from peat soil were higher than those with unhydrolysed humic acid from peat soil; which is ascribed to the high content of acidity in hydrolysed humic acid than unhydrolysed humic acid.

CONCLUSION

The values of logK for Cu(II) hydrolysed humic acid complex was higher followed by Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes as compared with metal(II) unhydrolysed humic acid complexes . This indicates acid hydrolysis of humic acid can enhance the complexation behavior of humic acid with metal (II) ions. However, the higher values of logβ for Cu(II), Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes indicates more stable stepwise complexes formed as compared with Cu(II), Pb(II), Cd(II) and Mg(II) unhydrolysed humic acid complexes.

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STABILITY CONSTANTS OF COMPLEXES OF METAL IONS WITH PEATSOIL HUMIC ACIDS UNDER NON-ACID-CONDITIONS

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ABSTRACT

Stability constants of complexes of four divalent metal ions viz. Cu^{2+}, Pb^{2+},Mg^{2+} and Cd^{2+} with humic acids (HA) were determined by potentiometric titration of humic acids with the corresponding salt of the divalent metals in aqueous media under non-acid-condition. The log K (logarithm of the stability constant) ranged from 1.0942 to 2.7471 for metal-humic acid complexes were determined using point-wise computational method. The order of stability constants were obtained as follows: Cu >Pb> Cd > Mg for metal -HA complexes respectively, indicating a higher degree of complexation with Cu metal ion.

Keywords: stability constant, humic acid, potentiometric titration, divalent metals, acid hydrolysis.

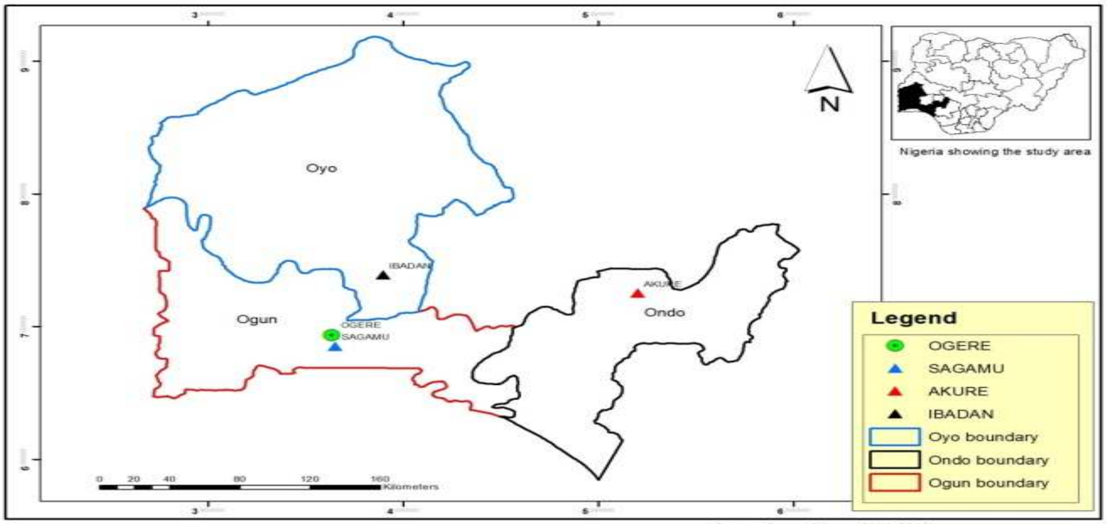
NTRODUCTION

The stability constant of a complex is the numerical expression of its stability and provides a quantitative measure of affinity of the metal ion to the complexing agent. An understanding of the relative stability of metal-complexes helps in predicting the behavior of metal ions in the soil (Ram and Raman, 1982). Extensive researches has been done to determine the stability constants of the complexes formed between humic acid (HA) with a number of metal ions. Ashok *et al*., (2000) reported that humic acid with hydroxyl, phenoxyl and carboxyl reactive groups can form coordination compound with metal ions at pH 3.5. The stability constants(Log K) for different metal-humic acid complexes indicated the following order of the stabilities of complexes formed between humic acid and metal ion, Cu >Fe >Pb> Ni > Co > Ca > Cd > Zn >Mn> Mg. Andelkovic *et al*., (2010) investigated the binding of Cd(II) to soil humic acid at pH 6.5 and in 0.1M KNO_3 ionic medium. The stability constant for binding indicating greater stability in the case when carboxyl groups are involved in complexation reaction. Kostic *et al*.,(2012) investigated the complexation of humic acid with certain heavy metal ions (Co(II), Ni(II),Cu(II), Zn(II), and Pb(II). The experiment was performed at 25°C, at pH 4.0 and ionic strength of 0.01M. Stability constant of complex between Pb(II) ions and humic acid is greater than stability constants of other investigated metal-humate complexes. Bogata and Sokolowska (2016) analyses the interaction between humic acids from different soils and Zn (II) ions at wide concentration ranges and at pH 5. Studies have showed significant impact of Zn concentration, pH and some properties of humic acids with zinc.But all of these studies were limited to acidic pH range. Therefore, the present study was carried out to determine and compare the stability constants of complexes of metal ions with hydrolysed peat soil humic acid and unhydrolysed peat soil humic under non-acid conditions.

MATERIALS AND METHODS

Analytical grade chemicals used includes hydrochloric acid (HCl), nitric acid (HNO_3), sodium hydroxide (NaOH), lead nitrate $Pb(NO_3)_2$, copper nitrate $Cu(NO_3)_2.3H_2O$, cadmium nitrate $Cd(NO_3)_2.4H_2O$, magnesium nitrate $Mg(NO_3)_2.6H_2O$, potassium nitrate (KNO_3), calcium chloride ($CaCl_2$), (sigma-Aldrich). Dowex 50WX8, (20-50 mesh) from Fluka.

Area of study



Source: Dept. of Geog. BUK (2016)

Figure 1: Map showing the sampling point at Sagamu Town, Ogun State.

Description of Sampling Area

Sagamu has geographical coordinates between 6°50′ north; 3° 38′ east is located in south western region of Nigeria. The region has tropical wet and dry climate with a lengthy wet season and relatively constant temperatures throughout the course of the year. Wet season runs from March to October, November to December forms the region dry season. The vegetation type of the region is savannah which is really grassland with small bushes and occasional big trees. Grassland soils have substantially higher organic matter content than forest soils (Novackova, 2011).

Sample Collection

The Peatsoil samples were collected from four different sampling points (0-10cm depth) in Sagamu into polyethylene bag with plastic spoons. Samples were taken to the laboratory, extraneous materials were removed; the samples were air-dried, crushed and ground to a fine powder in a mortar passed through a 0.20mm sieve. The samples were kept for analysis.

Isolation and purification of humic acid from peat soil sample

Peatsoil sample (100g) was mixed with 1000 cm^3 of 0.1M NaOH solution, shaken for 3hours and left to stand overnight. Dark-coloured supernatant was obtained and decanted from solid residue. The dark-coloured supernatant was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 6 hours. Yellowish brown supernatant and dark-brown precipitate were obtained. The yellowish brown supernatant was decanted followed by centrifuge and discarded. The dark-brown precipitate was mixed with 500$cm^3$of 0.1M NaOH solution followed by passing through dowex resin. The dark-brown solution was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 3 hours. The dark-brown precipitate was washed several times with deionized water. The supernatant was treated with $AgNO_3$ solution until no white precipitate observed. The humic acid was transferred to weighed crucible and dried at 60°C in an oven for 12 hours. The humic acid was cooled and dried in the desiccator, weighed and recorded. The obtained humic acid was dried again at 60°C for additional 6 hours cooled and dried in the desiccator, weighed and recorded constant weight was obtained (Baruah *et al*., 2015).

FT-IR analysis

FT-IR spectra of humic acid sample was analysed using Carry 630 FT-IR Agilent Technologies.

Unhydrolysed compost humic acid

The unhydrolysed humic acid was obtained after isolation and purification of compost humic acid and kept for investigation.

Acid hydrolysis of Peatsoil acid

Peatsoil humic acid sample (1g) was refluxed for 12 hours at (160°C) with 50cm^3 of 6M HCl. The mixture was allowed to cool, decanted, and centrifuged after hydrolysis. The insoluble residues were washed with distilled water via centrifugation several times, and the supernatant was treated with $AgNO_3$ solution until no white precipitate was observed. The residue was thoroughly dried over $CaCl_2$ in a desiccator at room temperature (Chefetz *et al*., 2002). Finally, the obtained hydrolysed humic acid was kept for investigation.

Potentiometric Titrations

Potentiometric measurements were carried out using a pH-meter Jenway (model 3510) with combine electrode, the sensitivity of the pH - meter is 0.01 units. The pH meter was switched on half an hour before starting the titration for initial warm up of the instrument. The instrument was calibrated with an aqueous standard buffer solution of pH 4.00 and 10.0 (borate buffer) prepared from a "Qualigens" buffer tablets.

The following sets of solutions were prepared in a 250cm^3 volumetric flask separately for pH metric titrations.

(i) 5 cm^3 0.1 M HCl + 40 cm^3 deionized water

(ii) 5 cm^3 0.1 M HCl + 39 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid

(iii) 5 cm^3 0.1 M HCl + 37 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid + 2 cm^3 0.01 M Cu(II)

The solutions were titrated against standardized 0.110MNaOH separately. The total volume of each mixture was adjusted to 50 cm^3 and the ionic strength of the solutions was maintained constant at by adding appropriate amount of stock solution of 1M KNO_3 (Gamal, 2015; Omar and Ali, 2015). A magnetic stirrer was used to achieve thorough mixing of the interacting solutions at 550 rpm. The same set of experimental conditions was applied for potentiometric titration of remaining samples.

Evaluation of pKa of Hydrolysed peat soil Humic Acids

The proton-ligand formation number n$_{\mathbf{A}}$ were calculated by Irving and Rossotti expression (Omar and Ali, 2015).

$$nA = Y- \frac{(V2-V1)(No-Eo)}{(Vo+V1)TcL} \quad \text{....................................1}$$

Where: Y is number of dissociable proton, (V_2-V_1) is the measure of displacement of the ligand curve relative to acid curve, N^o and E^o are the resultant concentration of alkali solution, free acid solution, $T_{cL}{}^o$ is the total ligand concentration, V^o is the total volume of titration solution,V_1 is the volume of alkali added to acid solution,V_2 is the volume of alkali added to acid solution + ligand solution, acid dissociation constants (pKa - values) of ligand were calculated by algebraic method point wise calculation (Tables 1). The dissociation constants (pKa) were calculated according to the following relation:

$$pKa = pH + \log(\frac{nA}{1-nA}) \quad \text{..............................2}$$

Where: pKa is the acid dissociation constant, $n_A$is the Proton-ligand formation number and pH is the pH-values (Omar and Ali, 2015).

Determination of metal-ligand stability constants (log K) of complexes

The potentiometric measurement for the determination of stability constant of a complex in solution is based on the fact that the redox potential of the couple $\frac{M^{+(m-n)}}{M^{+m}}$ is shifted significantly on complexation of the metal ion with the ligand. This method involves change in hydrogen ion concentration [H$^+$] due to the displacement or association of one or more protons taking place during complexation reaction. This change can be found out by titrating the solutions containing free acid, acid with ligand, and acid with ligand and metal ion, individually against a standard alkali solution at a constant ionic strength or temperature. Either ionic strength or temperature may be varied for different sets of solutions. In all the cases, the change in the pH of the solution is measured after each addition of a known amount of alkali to the reaction cell which contains the reaction mixture. The titration curves are then drawn by plotting the measured pH values against the corresponding volume of alkali added and the stability constants of the complexes are determined from the titration curves by employing pH-metric titration technique given by (Irving and Rossoti).

Metal-ligand stability constants (Log K) were determined by using the following relations:

$$\bar{n} = \frac{(V_3 - V_2)(E^0 + N^0)}{(V^0 + V_2)\bar{n}_A T_m^0} \quad \text{..3}$$

and

$$PL = \log_{10}\{\frac{1+\beta_n^H \frac{1}{[anti\ \log pH]^n}}{T_L^0 - \bar{n}T_m^0} X \frac{(V^0+V_3)}{V^0}\} \quad \text{...4}$$

Where $T_{L,}$ T^o, $E°$, and V^ohavethe same significance as in equation (1) above, T_m denotes the total concentration of metal present in solution, V_3 is the volume of metal ions present in solution and β^H is the overall proton ligand stability constant. The metal-ligand stability constants (log K) were determined by employing point wise computational Method (eq. 5 and 6).

$\text{LogK}_1 = \log\left(\frac{n}{1-n}\right) + pL$ ………….5

$\text{LogK}_2 = \log\left(\frac{1-n}{2-n}\right) + pL$……………………6

Where: Log K is the metal-ligand stability constant, pL is the Free ligand exponent function, **n** is the Average number of ligand attached with metal ion (Janrao*et al.*, 2014).The results obtained were analyzed by an ORIGIN 2016 program using titration data and then the proton-ligand stability constants (pKa) and Metal-ligand stability constant (LogK) calculated (Omar and Ali, 2015).

RESULTS AND DISCUSSION

Fourier transformed infrared (FT-IR) spectra of isolated humic acid from peat soils Figure 2 had distinct clear absorption bands indicating the presence of major humic acid structural elemental groups such as H bonded OH ($3680cm^{-1}$ peak), C=O of carbonyl ($1721cm^{-1}$ peak), functional groups of aliphatic components CH_2 ($2918cm^{-1}$ peak) and C-O stretching of polysaccharide ($1168cm^{-1}$ peak). The positions of the absorption bands of the spectra fell within typical major absorption bands of humic acid which is at frequencies 3680, 2918, 1721, 1168 cm^{-1}. The first peak centred in the vicinity of 3680 cm^{-1} region is attributed to phenol OH group bounded by intermolecular H bonds. The $2918cm^{-1}$ band usually has absorption maximum at 2918 cm^{-1} which is due to C–H stretching of alkane group (CH_2). The next major absorption band is 1721 cm^{-1}. This band has been commonly ascribed to C=O stretching of mainly carboxyl group (COOH) with trace amount of ketones. The last peak was observed at 1168 cm^{-1} due to C–O stretching of polysaccharides and this peak appeared also in the spectra of humic acid from peat soil. The FTIR spectra of the isolated humic acid contained all major characteristic absorption peaks of humic acid. These absorption peaks indicated the presence of the major structural elements of humic acid namely H bonded OH, C=C of aromatic ring, C=O of carbonyl group (both carboxyl and ketonic), CH_2 group. This strongly supports the presence of humic acid.

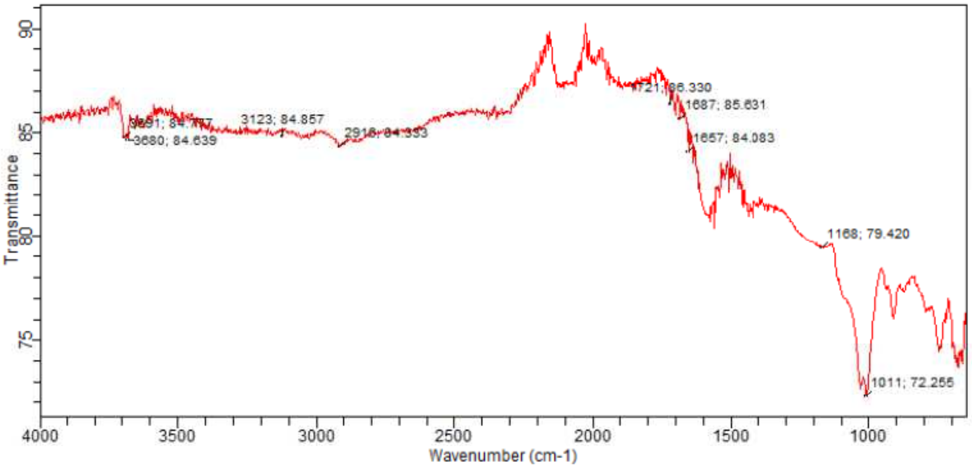


Fig. 2 : FT-IR spectraof peatsoilhumic acid (PSHA)

Evaluation of acid dissociation constant (pka) of acid hydrolysed peat soil humicacid at phenolic group

The value of the dissociation constant of the peat soil humic acid (PSHA) that underwent acidhydrolysis studied was found to be 8.9299 as shown Table 1, which is lower than the literaturevalues reported by Almeida and Szpoganics, (2015), Borges *et al.*, (2005); Badr *et al.*, (2012)and Fernandes *et al*,.(2009) of 9.73, 9.47 and 10.30. The difference between the obtained valuesand the reported values in this study might be probably as a result of acid hydrolysis of humicacid.

Table 1: PKa of (Hydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	log($\frac{nA}{1-nA}$)	pKa
8.50	5.30	6.29	0.99	0.3594	-0.2510	8.2490
8.72	5.35	6.37	1.02	0.3400	-0.2880	8.4320
9.00	5.40	6.46	1.06	0.3141	-0.3391	8.6609
9.22	5.45	6.55	1.10	0.2882	-0.3927	8.8273
9.51	5.50	6.66	1.16	0.2494	-0.4786	9.0314
9.73	5.55	6.78	1.23	0.2041	-0.5910	9.1390
10.00	5.60	6.90	1.30	0.1589	-0.7238	9.2762
10.23	5.65	7.05	1.40	0.0941	-0.9835	9.2465
10.49	5.70	7.10	1.40	0.0941	-0.9835	9.5065

Average pKa = 8.9299 ± 0.4186

Table 2: PKa of (Unhydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	Log($\frac{nA}{1-n}$)	pKa
8.50	5.30	5.81	0.51	0.6619	0.2919	8.7919
8.72	5.35	5.90	0.55	0.6357	0.2418	8.9618
9.00	5.40	6.00	0.60	0.6029	0.1813	9.1813
9.22	5.45	6.10	0.65	0.5701	0.1226	9.3426
9.51	5.50	6.20	0.70	0.5376	0.0654	9.5754
9.73	5.55	6.33	0.78	0.4851	-0.0259	9.7041
10.00	5.60	6.47	0.87	0.4262	-0.1291	9.8709
10.23	5.65	6.62	0.99	0.3609	-0.2481	9.9819
10.49	5.70	6.80	1.10	0.2759	-0.4690	10.0210

Average pKa = 9.4923± 0.4410

Metal-ligand stability constant (Log K)

The stabilityconstants require the accurate values of proton-ligand stability constants (Anil and Maroti, 2008). Metal titration curves crossed over ligand titration curve indicated the formation of complex upon proton release (Santosh, *et al.*, 2011). If the values of n- are within range 0.2-0.8 and 1.2-18 this indicates the formation of 1:1 and 1:2 complexes (Sayyed and Mazahar, 2012).

The metal (II)-humate stepwise stability constants (log k) at phenolic group (Tables 3-18)

Table 3: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	log($\frac{n}{1-n}$)	$LogK_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

$LogK_1$ (Average value) = 2.4788± 0.2203

Table 4: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	Log($\frac{n-1}{2-n}$)	$LogK_2$
9.51	5.50	6.66	6.73	0.07	1.3509	1.70	-0.2671	1.4329
9.73	5.55	6.78	6.85	0.07	1.6383	1.51	0.2467	1.7567
10.00	5.60	6.90	6.98	0.08	2.1783	1.31	-0.2158	1.0942
10.23	5.65	7.05	7.13	0.08	4.1904	1.27		
10.49	5.70	7.10	7.19	0.09	4.6920			

$LogK_2$(Average value) = 1.4280 ± 0.3312

Table 5:Point-wise method,Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	Log($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430

$LogK_1$ **(Average value)** = 2.3059± 0.6153

Table 6:Point-wise method, Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$V_3\text{-}V_2$	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
9.73	5.55	6.33	6.42	0.09	0.9000	1.69		
10.00	5.60	6.47	6.58	0.11	1.2578	1.44	-0.4592	0.9808
10.23	5.65	6.62	6.84	0.12	1.6137	1.26	-0.2010	1.4610
10.49	5.70	6.80	6.92	0.12	2.1052	1.03		

$LogK_2$ **(Average value)** = 1.2209± 0.3398

Table 7:Point-wise method,Pb (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	log($\frac{n}{1-n}$)	$LogK_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.60	0.05	0.8333	1.96	0.6989	2.6589

$LogK_1$ (Average value) = 2.5832 ±0.1614

Table 8:Point-wise method,Pb-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	log($\frac{n-1}{2-n}$)	$logK_2$
9.51	5.50	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.83	0.05	1.1702	1.44		
10.00	5.60	6.90	6.90	0.05	1.4864	1.22	-0.0237	1.1963
10.23	5.65	7.05	7.10	0.05	2.0190	1.09		
10.49	5.70	7.10	7.17	0.07	3.6492	1.00		

$LogK_2$(Average value) = 1.1963

Table 9:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$V_3\text{-}V_2$	n	pL	Log ($\frac{n}{n-1}$)	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.5477	2.3123
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	0.0272	2.2072
9.51	5.50	6.20	6.26	0.07	0.6417	1.89	0.2530	2.1430
9.73	5.55	6.40	6.40	0.07	0.7000	1.67	0.3680	2.0380

$LogK_1$ **(Average value)** = 2.2364 ± 0.1602

Table 10:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$V_3\text{-}V_2$	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
10.00	5.60	6.47	6.55	0.08	1.9503	1.41		
10.23	5.65	6.62	6.72	0.11	1.4792	1.26	-0.0361	1.2239

$LogK_2$ **(Average value)** = 1.2239

Table 11:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	log($\frac{n}{n-1}$)	$LogK_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4290	2.2110
8.72	5.35	6.37	6.39	0.02	0.2858	2.42	-0.3978	2.0222
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

$LogK_1$ (Average value)=2.1382**±**0.1046

Table 12:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$\log(\frac{n-1}{2-n})$	$LogK_2$
9.51	5.55	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.84	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.93	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.10		
10.49	5.70	7.10	7.18	0.07	3.6492	0.83		

$LogK_2$(Average value) = 1.5453 **±** 0.3450

Table 13:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$Log(\frac{n}{n-1})$	$Log K_1$
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.3477	2.3123
9.00	5.40	6.00	6.04	0.04	0.3236	2.38	-0.3202	2.0598
9.22	5.45	6.10	6.15	0.05	0.4297	2.17	-0.1230	2.0470
9.51	5.50	6.20	6.26	0.06	0.5500	1.89	0.0871	1.9771
9.73	5.55	6.33	6.40	0.07	0.7000	1.67	0.3680	2.0380

$LogK_1$ **(Average value)** = 2.1568 ± 0.2069

Table 14:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$Log(\frac{n-1}{2-n})$	$Log K_2$
10.00	5.60	6.47	6.55	0.08	0.9148	1.41		
10.23	5.65	6.62	6.71	0.09	1.2102	1.20	-0.5749	0.6251
10.49	5.70	6.80	6.92	0.09	1.5968	1.03	0.1703	1.2003

$LogK_2$ **(Average value)** = 0.9127± 0.4070

Table15:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$Log(\frac{n}{1-n})$	$LogK_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4210	2.2190
8.72	5.35	6.37	6.40	0.03	0.4286	2.42	-0.1249	2.2951
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.96	0.3010	2.2610
9.51	5.55	6.66	6.70	0.04	0.7720	1.67	0.5297	2.1997

$LogK_1$ (Average value) = 2.2108± 0.0825

Table 16:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$Log(\frac{n-1}{2-n})$	$Log K_2$
9.73	5.55	6.78	6.83	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.95	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.09		
10.49	5.70	7.10	7.16	0.06	3.1429	0.89		

$LogK_2$ **(Average value)** = 1.5453± 0.3450

Table 17:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$Log(\frac{n}{n-1})$	$Log K_1$
8.50	5.30	5.81	5.86	0.05	0.3717	2.88	-0.2280	2.6520
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.06	0.06	0.4853	2.38	-0.0255	2.3545
9.22	5.45	6.10	6.16	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430
9.73	5.55	6.33	6.41	0.08	0.8000	1.69	0.6020	2.2920

$LogK_1$ **(Average value)** = 2.2516± 0.5380

Table 18:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	$\mathrm{Log}(\frac{n-1}{2-n})$	Log K_2
10.00	5.60	6.47	6.57	0.10	1.1434	1.43		
10.23	5.65	6.62	6.72	0.10	1.3448	1.23	-0.2788	0.9512
10.49	5.70	6.80	6.90	0.10	1.7742	1.03	0.5351	1.5651

LogK_2 **(Average value)** = 1.2581± 0.4340

Table 19: Stepwise and overall Stability constants of thehydrolysed and unhydrolysed divalent metal (II) complexes

Chelates	**LogK_1**	**LogK_2**	**Logβ**
[Cu (Hydrolysed PSHA-1)$_2$]	2.4788	1.4280	3.9068
[Pb (Hydrolysed PSHA-1)$_2$]	2.5832	1.1963	3.7795
[Cd (Hydrolysed PSHA-1)$_2$]	2.2108	1.5453	3.7561
[Mg (Hydrolysed PSHA-1)$_2$]	2.1382	1.5453	3.6835
[Cu (Unhydrolysed PSHA-1)$_2$]	2.3059	1.2209	3.5268
[Pb (Unhydrolysed PSHA-1)$_2$]	2.2364	1.2239	3.4603
[Cd (Unhydrolysed PSHA-1)$_2$]	2.2516	1.2581	3.5097
[Mg (Unydrolysed PSHA-1)$_2$]	2.1568	0.9127	3.0695

The results obtained (Table19) shows the stepwise and overall stability constants to be not high indicating low stability of the complexes, because the solubility of most metal ions in the basic pH range is minimal due to metal hydroxide precipitation (Karimi, 2017). In general, the stepwise stability constants (K_1 and K_2) follow the order $K_1 > K_2$ for the copper, lead, magnesium and cadmium complexes respectively. The steady decrease of the values with increasing number of ligands is in agreement with the prediction made by researchers (Na'aliya, 2013). The decrease could be attributed to the fact that as the number of the ligands (Humate ions) that enters the coordination zone increases the aqua molecules available for replacement by the ligands become less. Thus, the metal ions become less electron loving with progressive intake of the ligand and this results in the decrease in the values of the constants (Na'aliya, 2013). Also the stability of the complexes is influenced by the size and number of the chelate rings(Mackay and Mackay,2002).All the complexes form rings in their structure as humate, a bidentate ligand, bond the metal ions in the ratio 1:2 (Boguta and Sokolowska, 2016) forming chelate rings. The values of the overall stability constants (logβ) obtained for humate complexes are not high indicating low stability as the values are not high. LogK values for copper-humates (Table 3 to 6) obtained in this study are lower than those reported for the complexes of humic acids (Pandey *et al.*, 2015; Dinu, 2013; Kaschl *et al.*, 2010 and Gilbeto and Jorg, 2001). The values of LogK(Table 7 to 10) forlead-humates are lower than those reported for the lead in the literature (Dinu, 2013; Gilbeto and Jorg 2001). Log K values(Table 11 to 14) for magnesium-humates obtained in this study are close to those reported by (Pandey *et al.*, 2015). Log K values of cadmium-humates (Table 15 to 18) obtained in this work near to the one reported by (Dinu, 2013 and Pandey *et al.*, 2015).The difference between the reported values and the values obtained in this study might be probably as a result of acid hydrolysis of humic acid. The values of the overall stability constants (log β) of the copper humates complexes presented in Table 19 is high than that of other metal humate complexes, show relatively high stability of Cu-HA complexes, show the following order of stability: Cu >Pb> Cd > Mg; which are in close agreement to the findings of (Dinu, 2013 and Pandey *et al.*, 2015).The high stability of Cu-humate chelate could be attributed to the existence of coordinate covalent bond between the complexing agents and the Cu^{2+} ions. Since, Cu^{2+} being a metal of the transitional series with $3d^9$ electronic configurations can accept the electrons from the complexing agents. Similarly,the low stabilities of Pb,Cd and Mg -complexes could be explained by that Pb^{2+} with $6s^2$, Cd^{2+} with $4d^{10}$ and Mg^{2+} with $2p^6$ their electronic configuration has a completely filled d,p and s orbitals. Moreover, the stabilities of metal ions with hydrolysed humic acid from peat soil were higher than those with unhydrolysed humic acid from peat soil; which is ascribed to the high content of acidity in hydrolysed humic acid than unhydrolysed humic acid.

CONCLUSION

The values of logK for Cu(II) hydrolysed humic acid complex was higher followed by Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes as compared with metal(II) unhydrolysed humic acid complexes . This indicates acid hydrolysis of humic acid can enhance the complexation behavior of humic acid with metal (II) ions. However, the higher values of logβ for Cu(II), Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes indicates more stable stepwise complexes formed as compared with Cu(II), Pb(II), Cd(II) and Mg(II) unhydrolysed humic acid complexes.

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STABILITY CONSTANTS OF COMPLEXES OF METAL IONS WITH PEATSOIL HUMIC ACIDS UNDER NON-ACID-CONDITIONS

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ABSTRACT

Stability constants of complexes of four divalent metal ions viz. Cu^{2+}, Pb^{2+},Mg^{2+} and Cd^{2+} with humic acids (HA) were determined by potentiometric titration of humic acids with the corresponding salt of the divalent metals in aqueous media under non-acid-condition. The log K (logarithm of the stability constant) ranged from 1.0942 to 2.7471 for metal-humic acid complexes were determined using point-wise computational method. The order of stability constants were obtained as follows: Cu >Pb> Cd > Mg for metal -HA complexes respectively, indicating a higher degree of complexation with Cu metal ion.

Keywords: stability constant, humic acid, potentiometric titration, divalent metals, acid hydrolysis.

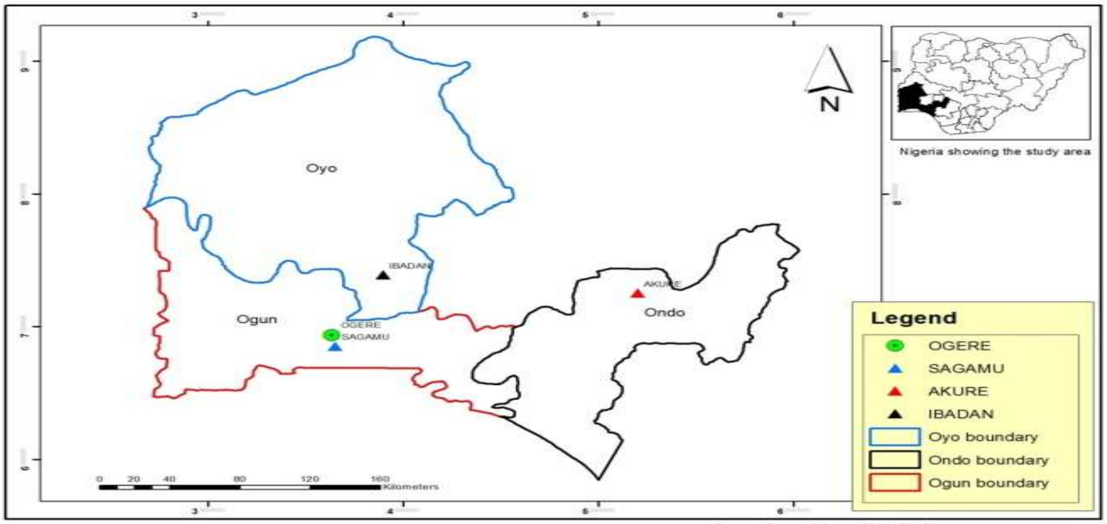
NTRODUCTION

The stability constant of a complex is the numerical expression of its stability and provides a quantitative measure of affinity of the metal ion to the complexing agent. An understanding of the relative stability of metal-complexes helps in predicting the behavior of metal ions in the soil (Ram and Raman, 1982). Extensive researches has been done to determine the stability constants of the complexes formed between humic acid (HA) with a number of metal ions. Ashok *et al*., (2000) reported that humic acid with hydroxyl, phenoxyl and carboxyl reactive groups can form coordination compound with metal ions at pH 3.5. The stability constants(Log K) for different metal-humic acid complexes indicated the following order of the stabilities of complexes formed between humic acid and metal ion, Cu >Fe >Pb> Ni > Co > Ca > Cd > Zn >Mn> Mg. Andelkovic *et al*., (2010) investigated the binding of Cd(II) to soil humic acid at pH 6.5 and in 0.1M KNO_3 ionic medium. The stability constant for binding indicating greater stability in the case when carboxyl groups are involved in complexation reaction. Kostic *et al*.,(2012) investigated the complexation of humic acid with certain heavy metal ions (Co(II), Ni(II),Cu(II), Zn(II), and Pb(II). The experiment was performed at 25°C, at pH 4.0 and ionic strength of 0.01M. Stability constant of complex between Pb(II) ions and humic acid is greater than stability constants of other investigated metal-humate complexes. Bogata and Sokolowska (2016) analyses the interaction between humic acids from different soils and Zn (II) ions at wide concentration ranges and at pH 5. Studies have showed significant impact of Zn concentration, pH and some properties of humic acids with zinc.But all of these studies were limited to acidic pH range. Therefore, the present study was carried out to determine and compare the stability constants of complexes of metal ions with hydrolysed peat soil humic acid and unhydrolysed peat soil humic under non-acid conditions.

MATERIALS AND METHODS

Analytical grade chemicals used includes hydrochloric acid (HCl), nitric acid (HNO_3), sodium hydroxide (NaOH), lead nitrate $Pb(NO_3)_2$, copper nitrate $Cu(NO_3)_2.3H_2O$, cadmium nitrate $Cd(NO_3)_2.4H_2O$, magnesium nitrate $Mg(NO_3)_2.6H_2O$, potassium nitrate (KNO_3), calcium chloride ($CaCl_2$), (sigma-Aldrich). Dowex 50WX8, (20-50 mesh) from Fluka.

Area of study



Source: Dept. of Geog. BUK (2016)

Figure 1: Map showing the sampling point at Sagamu Town, Ogun State.

Description of Sampling Area

Sagamu has geographical coordinates between 6°50′ north; 3° 38′ east is located in south western region of Nigeria. The region has tropical wet and dry climate with a lengthy wet season and relatively constant temperatures throughout the course of the year. Wet season runs from March to October, November to December forms the region dry season. The vegetation type of the region is savannah which is really grassland with small bushes and occasional big trees. Grassland soils have substantially higher organic matter content than forest soils (Novackova, 2011).

Sample Collection

The Peatsoil samples were collected from four different sampling points (0-10cm depth) in Sagamu into polyethylene bag with plastic spoons. Samples were taken to the laboratory, extraneous materials were removed; the samples were air-dried, crushed and ground to a fine powder in a mortar passed through a 0.20mm sieve. The samples were kept for analysis.

Isolation and purification of humic acid from peat soil sample

Peatsoil sample (100g) was mixed with 1000 cm^3 of 0.1M NaOH solution, shaken for 3hours and left to stand overnight. Dark-coloured supernatant was obtained and decanted from solid residue. The dark-coloured supernatant was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 6 hours. Yellowish brown supernatant and dark-brown precipitate were obtained. The yellowish brown supernatant was decanted followed by centrifuge and discarded. The dark-brown precipitate was mixed with $500cm^3$of 0.1M NaOH solution followed by passing through dowex resin. The dark-brown solution was acidified to (pH= 1.0) with 6M HCl stirred and allowed to stand for 3 hours. The dark-brown precipitate was washed several times with deionized water. The supernatant was treated with $AgNO_3$ solution until no white precipitate observed. The humic acid was transferred to weighed crucible and dried at 60°C in an oven for 12 hours. The humic acid was cooled and dried in the desiccator, weighed and recorded. The obtained humic acid was dried again at 60°C for additional 6 hours cooled and dried in the desiccator, weighed and recorded constant weight was obtained (Baruah *et al.*, 2015).

FT-IR analysis

FT-IR spectra of humic acid sample was analysed using Carry 630 FT-IR Agilent Technologies.

Unhydrolysed compost humic acid

The unhydrolysed humic acid was obtained after isolation and purification of compost humic acid and kept for investigation.

Acid hydrolysis of Peatsoil acid

Peatsoil humic acid sample (1g) was refluxed for 12 hours at (160°C) with $50cm^3$ of 6M HCl. The mixture was allowed to cool, decanted, and centrifuged after hydrolysis. The insoluble residues were washed with distilled water via centrifugation several times, and the supernatant was treated with $AgNO_3$ solution until no white precipitate was observed. The residue was thoroughly dried over $CaCl_2$ in a desiccator at room temperature (Chefetz *et al.*, 2002). Finally, the obtained hydrolysed humic acid was kept for investigation.

Potentiometric Titrations

Potentiometric measurements were carried out using a pH-meter Jenway (model 3510) with combine electrode, the sensitivity of the pH - meter is 0.01 units. The pH meter was switched on half an hour before starting the titration for initial warm up of the instrument. The instrument was calibrated with an aqueous standard buffer solution of pH 4.00 and 10.0 (borate buffer) prepared from a "Qualigens" buffer tablets.

The following sets of solutions were prepared in a 250cm^3 volumetric flask separately for pH metric titrations.

(i) 5 cm^3 0.1 M HCl + 40 cm^3 deionized water

(ii) 5 cm^3 0.1 M HCl + 39 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid

(iii) 5 cm^3 0.1 M HCl + 37 cm^3 deionized water + 1 cm^3 0.15gcm^{-3}humic acid + 2 cm^3 0.01 M Cu(II)

The solutions were titrated against standardized 0.110MNaOH separately. The total volume of each mixture was adjusted to 50 cm^3 and the ionic strength of the solutions was maintained constant at by adding appropriate amount of stock solution of 1M KNO_3 (Gamal, 2015; Omar and Ali, 2015). A magnetic stirrer was used to achieve thorough mixing of the interacting solutions at 550 rpm. The same set of experimental conditions was applied for potentiometric titration of remaining samples.

Evaluation of pKa of Hydrolysed peat soil Humic Acids

The proton-ligand formation number n_A were calculated by Irving and Rossotti expression (Omar and Ali, 2015).

$$nA = Y - \frac{(V2-V1)(No-Eo)}{(Vo+V1)TcL} \quad \text{....................................1}$$

Where: Y is number of dissociable proton, (V_2-V_1) is the measure of displacement of the ligand curve relative to acid curve, N^o and E^o are the resultant concentration of alkali solution, free acid solution, $T_{cL}{}^o$ is the total ligand concentration, V^o is the total volume of titration solution,V_1 is the volume of alkali added to acid solution,V_2 is the volume of alkali added to acid solution + ligand solution, acid dissociation constants (pKa - values) of ligand were calculated by algebraic method point wise calculation (Tables 1). The dissociation constants (pKa) were calculated according to the following relation:

$$pKa = pH + \log(\frac{nA}{1-nA}) \quad \text{.............................2}$$

Where: pKa is the acid dissociation constant, $n_A$is the Proton-ligand formation number and pH is the pH-values (Omar and Ali, 2015).

Determination of metal-ligand stability constants (log K) of complexes

The potentiometric measurement for the determination of stability constant of a complex in solution is based on the fact that the redox potential of the couple $\frac{M^{+(m-n)}}{M^{+m}}$ is shifted significantly on complexation of the metal ion with the ligand. This method involves change in hydrogen ion concentration [H$^+$] due to the displacement or association of one or more protons taking place during complexation reaction. This change can be found out by titrating the solutions containing free acid, acid with ligand, and acid with ligand and metal ion, individually against a standard alkali solution at a constant ionic strength or temperature. Either ionic strength or temperature may be varied for different sets of solutions. In all the cases, the change in the pH of the solution is measured after each addition of a known amount of alkali to the reaction cell which contains the reaction mixture. The titration curves are then drawn by plotting the measured pH values against the corresponding volume of alkali added and the stability constants of the complexes are determined from the titration curves by employing pH-metric titration technique given by (Irving and Rossoti).

Metal-ligand stability constants (Log K) were determined by using the following relations:

$$\bar{n} = \frac{(V_3 - V_2)(E^0 + N^0)}{(V^0 + V_2)\bar{n}_A T_m^0} \quad \text{...3}$$

and

$$PL = \log_{10}\{\frac{1+\beta_n^H \frac{1}{[anti\ \log pH]^n}}{T_L^0 - \bar{n}T_m^0} X \frac{(V^0+V_3)}{V^0}\} \quad \text{..4}$$

Where $T_{L,}$ T^o, E°, and V^ohavethe same significance as in equation (1) above, T_m denotes the total concentration of metal present in solution, V_3 is the volume of metal ions present in solution and β^H is the overall proton ligand stability constant. The metal-ligand stability constants (log K) were determined by employing point wise computational Method (eq. 5 and 6).

$$\mathrm{Log}K_1 = \log\left(\frac{n}{1-n}\right) + pL \qquad ....5$$

$$\mathrm{Log}K_2 = \log\left(\frac{1-n}{2-n}\right) + pL.......................6$$

Where: Log K is the metal-ligand stability constant, pL is the Free ligand exponent function, **n** is the Average number of ligand attached with metal ion (Janrao*et al.*, 2014).The results obtained were analyzed by an ORIGIN 2016 program using titration data and then the proton-ligand stability constants (pKa) and Metal-ligand stability constant (LogK) calculated (Omar and Ali, 2015).

RESULTS AND DISCUSSION

Fourier transformed infrared (FT-IR) spectra of isolated humic acid from peat soils Figure 2 had distinct clear absorption bands indicating the presence of major humic acid structural elemental groups such as H bonded OH ($3680cm^{-1}$ peak), C=O of carbonyl ($1721cm^{-1}$ peak), functional groups of aliphatic components CH_2 ($2918cm^{-1}$ peak) and C-O stretching of polysaccharide ($1168cm^{-1}$ peak). The positions of the absorption bands of the spectra fell within typical major absorption bands of humic acid which is at frequencies 3680, 2918, 1721, 1168 cm^{-1}. The first peak centred in the vicinity of 3680 cm^{-1} region is attributed to phenol OH group bounded by intermolecular H bonds. The $2918cm^{-1}$ band usually has absorption maximum at 2918 cm^{-1} which is due to C–H stretching of alkane group (CH_2). The next major absorption band is 1721 cm^{-1}. This band has been commonly ascribed to C=O stretching of mainly carboxyl group (COOH) with trace amount of ketones. The last peak was observed at 1168 cm^{-1} due to C–O stretching of polysaccharides and this peak appeared also in the spectra of humic acid from peat soil. The FTIR spectra of the isolated humic acid contained all major characteristic absorption peaks of humic acid. These absorption peaks indicated the presence of the major structural elements of humic acid namely H bonded OH, C=C of aromatic ring, C=O of carbonyl group (both carboxyl and ketonic), CH_2 group. This strongly supports the presence of humic acid.

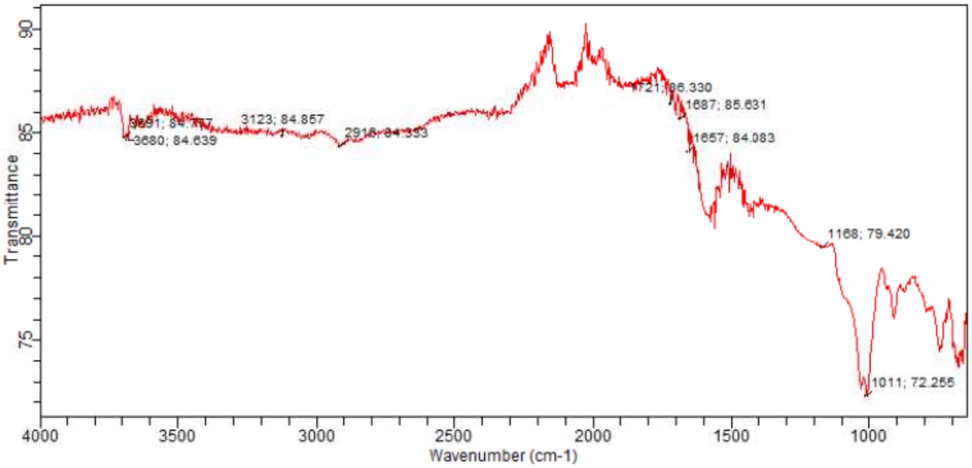


Fig. 2 : FT-IR spectraof peatsoilhumic acid (PSHA)

Evaluation of acid dissociation constant (pka) of acid hydrolysed peat soil humicacid at phenolic group

The value of the dissociation constant of the peat soil humic acid (PSHA) that underwent acidhydrolysis studied was found to be 8.9299 as shown Table 1, which is lower than the literaturevalues reported by Almeida and Szpoganics, (2015), Borges *et al.*, (2005); Badr *et al.*, (2012)and Fernandes *et al*,.(2009) of 9.73, 9.47 and 10.30. The difference between the obtained valuesand the reported values in this study might be probably as a result of acid hydrolysis of humicacid.

Table 1: PKa of (Hydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	$\log(\frac{nA}{1-nA})$	pKa
8.50	5.30	6.29	0.99	0.3594	-0.2510	8.2490
8.72	5.35	6.37	1.02	0.3400	-0.2880	8.4320
9.00	5.40	6.46	1.06	0.3141	-0.3391	8.6609
9.22	5.45	6.55	1.10	0.2882	-0.3927	8.8273
9.51	5.50	6.66	1.16	0.2494	-0.4786	9.0314
9.73	5.55	6.78	1.23	0.2041	-0.5910	9.1390
10.00	5.60	6.90	1.30	0.1589	-0.7238	9.2762
10.23	5.65	7.05	1.40	0.0941	-0.9835	9.2465
10.49	5.70	7.10	1.40	0.0941	-0.9835	9.5065

Average pKa = 8.9299 ± 0.4186

Table 2: PKa of (Unhydrolysed PSHA)

pH	BV_1	BV_2	V_2-V_1	nA	$\mathrm{Log}(\frac{nA}{1-n})$	pKa
8.50	5.30	5.81	0.51	0.6619	0.2919	8.7919
8.72	5.35	5.90	0.55	0.6357	0.2418	8.9618
9.00	5.40	6.00	0.60	0.6029	0.1813	9.1813
9.22	5.45	6.10	0.65	0.5701	0.1226	9.3426
9.51	5.50	6.20	0.70	0.5376	0.0654	9.5754
9.73	5.55	6.33	0.78	0.4851	-0.0259	9.7041
10.00	5.60	6.47	0.87	0.4262	-0.1291	9.8709
10.23	5.65	6.62	0.99	0.3609	-0.2481	9.9819
10.49	5.70	6.80	1.10	0.2759	-0.4690	10.0210

Average pKa = 9.4923± 0.4410

Metal-ligand stability constant (Log K)

The stabilityconstants require the accurate values of proton-ligand stability constants (Anil and Maroti, 2008). Metal titration curves crossed over ligand titration curve indicated the formation of complex upon proton release (Santosh, *et al.*, 2011). If the values of n- are within range 0.2-0.8 and 1.2-18 this indicates the formation of 1:1 and 1:2 complexes (Sayyed and Mazahar, 2012).

The metal (II)-humate stepwise stability constants (log k) at phenolic group (Tables 3-18)

Table 3: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$\log(\frac{n}{1-n})$	$\mathrm{Log}K_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

LogK_1 (Average value) = 2.4788± 0.2203

Table 4: Point-wise method,Cu-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$\mathrm{Log}(\frac{n-1}{2-n})$	$\mathrm{Log}K_2$
9.51	5.50	6.66	6.73	0.07	1.3509	1.70	-0.2671	1.4329
9.73	5.55	6.78	6.85	0.07	1.6383	1.51	0.2467	1.7567
10.00	5.60	6.90	6.98	0.08	2.1783	1.31	-0.2158	1.0942
10.23	5.65	7.05	7.13	0.08	4.1904	1.27		
10.49	5.70	7.10	7.19	0.09	4.6920			

LogK_2(Average value) = 1.4280 ± 0.3312

Table 5:Point-wise method,Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	Log$(\frac{n}{n-1})$	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430

$LogK_1$ **(Average value)** = 2.3059± 0.6153

Table 6:Point-wise method, Cu (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$V_3\text{-}V_2$	n	pL	Log$(\frac{n-1}{2-n})$	Log K_2
9.73	5.55	6.33	6.42	0.09	0.9000	1.69		
10.00	5.60	6.47	6.58	0.11	1.2578	1.44	-0.4592	0.9808
10.23	5.65	6.62	6.84	0.12	1.6137	1.26	-0.2010	1.4610
10.49	5.70	6.80	6.92	0.12	2.1052	1.03		

$LogK_2$ **(Average value)** = 1.2209± 0.3398

Table 7:Point-wise method,Pb (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	log$(\frac{n}{1-n})$	$LogK_1$
8.50	5.30	6.29	6.33	0.04	0.5500	2.66	0.0871	2.7471
8.72	5.35	6.37	6.41	0.04	0.5714	2.43	0.1249	2.5549
9.00	5.40	6.46	6.50	0.04	0.6198	2.16	0.2122	2.3722
9.22	5.45	6.55	6.60	0.05	0.8333	1.96	0.6989	2.6589

$\mathbf{LogK_1}$ **(Average value)** = 2.5832 ±0.1614

Table 8:Point-wise method,Pb-(Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	log$(\frac{n-1}{2-n})$	$logK_2$
9.51	5.50	6.66	6.71	0.05	0.9650	1.67	-0.0237	1.1963
9.73	5.55	6.78	6.83	0.05	1.1702	1.44		
10.00	5.60	6.90	6.90	0.05	1.4864	1.22		
10.23	5.65	7.05	7.10	0.05	2.0190	1.09		
10.49	5.70	7.10	7.17	0.07	3.6492	1.00		

$\mathbf{LogK_2}$**(Average value)** = 1.1963

Table 9:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$V_3\text{-}V_2$	n	pL	Log $(\frac{n}{n-1})$	Log K_1
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.5477	2.3123
9.00	5.40	6.00	6.05	0.05	0.4044	2.38	-0.1681	2.2119
9.22	5.45	6.10	6.15	0.06	0.5157	2.18	0.0272	2.2072
9.51	5.50	6.20	6.26	0.07	0.6417	1.89	0.2530	2.1430
9.73	5.55	6.40	6.40	0.07	0.7000	1.67	0.3680	2.0380

$LogK_1$ **(Average value)** = 2.2364 ± 0.1602

Table 10:Point-wise method,Pb (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$V_3\text{-}V_2$	n	pL	Log$(\frac{n-1}{2-n})$	Log K_2
10.00	5.60	6.47	6.55	0.08	1.9503	1.41		
10.23	5.65	6.62	6.72	0.11	1.4792	1.26	-0.0361	1.2239

$LogK_2$ **(Average value)** = 1.2239

Table 11:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	log$(\frac{n}{n-1})$	$LogK_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4290	2.2110
8.72	5.35	6.37	6.39	0.02	0.2858	2.42	-0.3978	2.0222
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.94	0.3010	2.2410

$\mathbf{LogK_1}$ **(Average value)=**2.1382**±**0.1046

Table 12:Point-wise method,Mg (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	$\log(\frac{n-1}{2-n})$	$LogK_2$
9.51	5.55	6.66	6.71	0.05	0.9650	1.67		
9.73	5.55	6.78	6.84	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.93	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.10		
10.49	5.70	7.10	7.18	0.07	3.6492	0.83		

$LogK_2$(Average value) = 1.5453 **±** 0.3450

Table 13:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$V_3\text{-}V_2$	n	pL	$Log(\frac{n}{n-1})$	$Log\ K_1$
8.50	5.30	5.81	5.85	0.04	0.2973	2.88	-0.3736	2.5064
8.72	5.35	5.90	5.94	0.04	0.3099	2.66	-0.3477	2.3123
9.00	5.40	6.00	6.04	0.04	0.3236	2.38	-0.3202	2.0598
9.22	5.45	6.10	6.15	0.05	0.4297	2.17	-0.1230	2.0470
9.51	5.50	6.20	6.26	0.06	0.5500	1.89	0.0871	1.9771
9.73	5.55	6.33	6.40	0.07	0.7000	1.67	0.3680	2.0380

$LogK_1$ **(Average value)** = 2.1568 ± 0.2069

Table 14:Point-wise method, Mg (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$V_3\text{-}V_2$	n	pL	$Log(\frac{n-1}{2-n})$	$Log\ K_2$
10.00	5.60	6.47	6.55	0.08	0.9148	1.41		
10.23	5.65	6.62	6.71	0.09	1.2102	1.20	-0.5749	0.6251
10.49	5.70	6.80	6.92	0.09	1.5968	1.03	0.1703	1.2003

$LogK_2$ **(Average value)** = 0.9127± 0.4070

Table15:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	$Log(\frac{n}{1-n})$	$LogK_1$
8.50	5.30	6.29	6.31	0.02	0.2750	2.64	-0.4210	2.2190
8.72	5.35	6.37	6.40	0.03	0.4286	2.42	-0.1249	2.2951
9.00	5.40	6.46	6.49	0.03	0.4648	2.14	-0.0612	2.0788
9.22	5.45	6.55	6.59	0.04	0.6667	1.96	0.3010	2.2610
9.51	5.55	6.66	6.70	0.04	0.7720	1.67	0.5297	2.1997

$LogK_1$ (Average value) = 2.2108± 0.0825

Table 16:Point-wise method, Cd (Hydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$(V_3\text{-}V_2)$	n	pL	$Log(\frac{n-1}{2-n})$	$Log\ K_2$
9.73	5.55	6.78	6.83	0.06	1.4042	1.47	-0.1686	1.3014
10.00	5.60	6.90	6.95	0.06	1.7838	1.23	0.5593	1.7893
10.23	5.65	7.05	7.10	0.06	3.1429	1.09		
10.49	5.70	7.10	7.16	0.06	3.1429	0.89		

$LogK_2$ **(Average value)** = 1.5453± 0.3450

Table 17:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	$V_3\text{-}V_2$	n	pL	$Log(\frac{n}{n-1})$	$Log\ K_1$
8.50	5.30	5.81	5.86	0.05	0.3717	2.88	-0.2280	2.6520
8.72	5.35	5.90	5.95	0.05	0.3873	2.66	-0.1992	2.4608
9.00	5.40	6.00	6.06	0.06	0.4853	2.38	-0.0255	2.3545
9.22	5.45	6.10	6.16	0.06	0.5157	2.18	-0.0272	2.2072
9.51	5.50	6.20	6.27	0.07	0.6417	1.89	0.2530	1.1430
9.73	5.55	6.33	6.41	0.08	0.8000	1.69	0.6020	2.2920

$LogK_1$ **(Average value)** = 2.2516± 0.5380

Table 18:Point-wise method, Cd (Unhydrolysed PSHA)

pH	BV_1	BV_2	BV_3	V_3-V_2	n	pL	Log($\frac{n-1}{2-n}$)	Log K_2
10.00	5.60	6.47	6.57	0.10	1.1434	1.43		
10.23	5.65	6.62	6.72	0.10	1.3448	1.23	-0.2788	0.9512
10.49	5.70	6.80	6.90	0.10	1.7742	1.03	0.5351	1.5651

LogK_2 **(Average value)** = 1.2581± 0.4340

Table 19: Stepwise and overall Stability constants of thehydrolysed and unhydrolysed divalent metal (II) complexes

Chelates	**LogK_1**	**LogK_2**	**Logβ**
[Cu (Hydrolysed PSHA-1)$_2$]	2.4788	1.4280	3.9068
[Pb (Hydrolysed PSHA-1)$_2$]	2.5832	1.1963	3.7795
[Cd (Hydrolysed PSHA-1)$_2$]	2.2108	1.5453	3.7561
[Mg (Hydrolysed PSHA-1)$_2$]	2.1382	1.5453	3.6835
[Cu (Unhydrolysed PSHA-1)$_2$]	2.3059	1.2209	3.5268
[Pb (Unhydrolysed PSHA-1)$_2$]	2.2364	1.2239	3.4603
[Cd (Unhydrolysed PSHA-1)$_2$]	2.2516	1.2581	3.5097
[Mg (Unydrolysed PSHA-1)$_2$]	2.1568	0.9127	3.0695

The results obtained (Table19) shows the stepwise and overall stability constants to be not high indicating low stability of the complexes, because the solubility of most metal ions in the basic pH range is minimal due to metal hydroxide precipitation (Karimi, 2017). In general, the stepwise stability constants (K_1 and K_2) follow the order $K_1 > K_2$ for the copper, lead, magnesium and cadmium complexes respectively. The steady decrease of the values with increasing number of ligands is in agreement with the prediction made by researchers (Na'aliya, 2013). The decrease could be attributed to the fact that as the number of the ligands (Humate ions) that enters the coordination zone increases the aqua molecules available for replacement by the ligands become less. Thus, the metal ions become less electron loving with progressive intake of the ligand and this results in the decrease in the values of the constants (Na'aliya, 2013). Also the stability of the complexes is influenced by the size and number of the chelate rings(Mackay and Mackay,2002).All the complexes form rings in their structure as humate, a bidentate ligand, bond the metal ions in the ratio 1:2 (Boguta and Sokolowska, 2016) forming chelate rings. The values of the overall stability constants (logβ) obtained for humate complexes are not high indicating low stability as the values are not high. LogK values for copper-humates (Table 3 to 6) obtained in this study are lower than those reported for the complexes of humic acids (Pandey *et al.*, 2015; Dinu, 2013; Kaschl *et al.*, 2010 and Gilbeto and Jorg, 2001). The values of LogK(Table 7 to 10) forlead-humates are lower than those reported for the lead in the literature (Dinu, 2013; Gilbeto and Jorg 2001). Log K values(Table 11 to 14) for magnesium-humates obtained in this study are close to those reported by (Pandey *et al.*, 2015). Log K values of cadmium-humates (Table 15 to 18) obtained in this work near to the one reported by (Dinu, 2013 and Pandey *et al.*, 2015).The difference between the reported values and the values obtained in this study might be probably as a result of acid hydrolysis of humic acid. The values of the overall stability constants (log β) of the copper humates complexes presented in Table 19 is high than that of other metal humate complexes, show relatively high stability of Cu-HA complexes, show the following order of stability: Cu >Pb> Cd > Mg; which are in close agreement to the findings of (Dinu, 2013 and Pandey *et al.*, 2015).The high stability of Cu-humate chelate could be attributed to the existence of coordinate covalent bond between the complexing agents and the Cu^{2+} ions. Since, Cu^{2+} being a metal of the transitional series with $3d^9$ electronic configurations can accept the electrons from the complexing agents. Similarly,the low stabilities of Pb,Cd and Mg - complexes could be explained by that Pb^{2+} with $6s^2$, Cd^{2+} with $4d^{10}$ and Mg^{2+} with $2p^6$ their electronic configuration has a completely filled d,p and s orbitals. Moreover, the stabilities of metal ions with hydrolysed humic acid from peat soil were higher than those with unhydrolysed humic acid from peat soil; which is ascribed to the high content of acidity in hydrolysed humic acid than unhydrolysed humic acid.

CONCLUSION

The values of logK for Cu(II) hydrolysed humic acid complex was higher followed by Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes as compared with metal(II) unhydrolysed humic acid complexes . This indicates acid hydrolysis of humic acid can enhance the complexation behavior of humic acid with metal (II) ions. However, the higher values of logβ for Cu(II), Pb(II), Cd(II) and Mg(II) hydrolysed humic acid complexes indicates more stable stepwise complexes formed as compared with Cu(II), Pb(II), Cd(II) and Mg(II) unhydrolysed humic acid complexes.

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