ChemSearch Journal 11(2): 82 – 89, December, 2020
Publication of Chemical Society of Nigeria, Kano Chapter

Received: 23/07/2020 Accepted: 08/10/2020
http://www.ajol.info/index.php/csj

Acid Hydrolysis of Compost Humic acid Functional Groups Heterogeniety in Lead (II) Complexes

***[1]Sabo, Y., [1]Jimoh, W. L. O., [1]Shaibu, A. N. and [2]Sholadoye, Q. O.**
[1]Department of Pure and Industrial Chemistry, Bayero University, P.M.B. 3011 BUK, Kano- Nigeria
[2]Department of Chemistry, Nigerian Police Academy, Wudil, Kano-Nigeria
***Correspondence Email:** saboyusuf18@yahoo.com

ABSTRACT

An acid hydrolysis of compost humic acid functional groups heterogeneity in lead (II)-humate complexes was carried out. Humic acid from compost was isolated and its functional groups were characterized by Fourier transformed infrared (FTIR). The dissociation constants (pKa), stepwise stability constants (Log K) and formation constants, (K_f), of the hydrolysed and unhydrolysed humic acids were determined and compared. A potentiometric titration – technique was used to determine the dissociation constants (pKa) and the stepwise stability constants (Log K) of hydrolysed and unhydrolysed humic acids in aqueous solution at carboxyl functional group. The FTIR spectra of isolated humic acid from compost had distinct clear absorption bands indicating the presence of OH (3620cm^{-1}), C=O of carbonyl (1704 cm^{-1}), functional groups aliphatic components CH_2 (2922 cm^{-1}) and C-O of polysaccharide (1023 cm^{-1}). The pKa values of the hydrolysed and unhydrolysed compost humic acids were found to be 5.0107 and 5.4743 at carboxyl groups respectively. The values of the step stability constants were found to be Log K_1 = 11.4772, Log K_2 = 10.3058 and Log K_3 = 9.7251 for lead (II) hydrolysed compost humic acid and Log K_1 = 11.0111 and Log K_2 = 10.0161 for lead (II) unhydrolysed compost humic acid at carboxyl group respectively. The formation constants of the lead (II) complexes were found to be 1.15× 10^3 and 1.102× 10^2 at carboxyl group respectively. Acid hydrolysis causes change of dissociation constants (pKa) at carboxy group of hydrolysed humic acid which was probably the main factor that gave rise to the changes in stepwise stability constants and formation constants of the complexes.

Keywords: Dissociation constant, Humic acid, Potentiometric titration, Stepwise stability constant

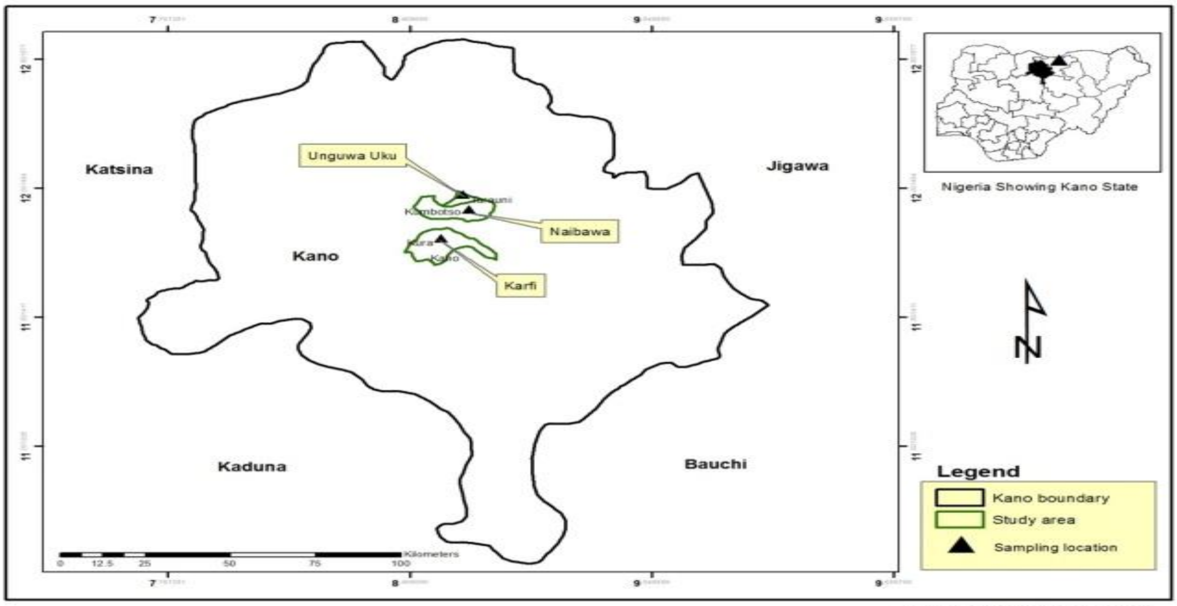
INTRODUCTION

The humic acids are assemblies of large polyfunctional molecules, such as lipids, carbohydrates, aromatics, *etc*. having a great variety of functional groups and metal binding sites (Kostic *et al.*, 2011). Despite the above properties, humic acids have not been widely used in remediation techniques via complexation. The fundamental reason is the extreme structural heterogeneity, which translate into chemical properties that are difficult to control (Perminova *et al.*, 2005). Considering the fact that, the major binding sites of humic acid are attributed to the oxygen-containing functional groups such as carboxylic acid and phenolic groups (Andelkovic *et al.*, 2011). The tools to reduce structural heterogeneity are needed to ensure control over reactive properties of humic acids; hence, to facilitate a use of humic acids in remedial practice (Perminova *et al.*, 2005). Previous investigations involving humic acid modifications such as oxidation, methylation, acetylation, sulphonation and alkaline hydrolysis (Yudov *et al.*, 2005). But, has not yet been used acid hydrolysis method. The hydrolysis of organic compounds is the decomposition of organic compounds by water, with the formation of two or more compounds. Hydrolysis is ordinarily effective in the presence of acids (acid hydrolysis) (Tomson *et al*,. 2017). The aim of the work presented in this paper is to study the influence of acid hydrolysis on dissociation constants (pKa) of compost humic acids and metal-ligand stability constants of Pb(II) with hydrolysed and unhydrolysed compost humic acids.

MATERIALS AND METHODS

Sampling Area

Karfi village is located within 11º27´00.77″north, 9º09´00.16″east in Kura LGA of Kano State. The village is surrounded by some rice mills, small scale processing industries, rice farms, sugar cane and maize markets. Processing of these agricultural which commodities leads to the generation of enormous quantity of wastes, e.g. rice straws and rice husks. Improper disposal of these wastes pollutes the environment. Naibawa village is located within 11. 9247ºN, 8.5446º E in Kumbotso LGA of Kano State. Yan katako (Timber Market) is situated there. This market is surrounded by some Timber mills small scale processing industries, processing of the timber commodities leads to the generation of enormous quantity of wastes, e.g. small and fine saw dusts. Unguwa Uku village is also located 11. 9666^{o}N, 8. 5639^{o}E in Tarauni LGA of Kano State. The village contains some small scale livestock farms and small scale broiler farms. Production of these agricultural commodities leads to the generation of enormous quantity of wastes, e.g. Chicken dung and Cow dung.



Source: Dept. of Geog. BUK (2016)

Figure 1: Sampling Points at Unguwa uku, Naibawa, and Karfi of Kano State, Nigeria

Sample collection

The rice straws were collected from Karfi village located in Kura LGA of Kano State. Fine sawdust was collected from Yan Katako (Timber Market) at Naibawa Village in Kumbotso LGA of Kano State. Chicken dung and cow dung was collected from Unguwa uku in Tarauni LGA of Kano State, Nigeria.

Sample preparation

The rice straws, fine sawdust, chicken dung and cow dung were collected from Karfi, Naibawa, and Unguwa Uku areas of Kano State, Nigeria. Pestle and mortar were used for grinding of samples in order to increase the surface area. Compost was obtained according to the method by Ezue, (2010), the finished compost was then screened, air-dried, crushed, ground to a fine powder in a mortar passed through a 0.20mm sieved and weighed. The sample was kept for analysis.

Analytical grade chemicals were used, hydrochloric acid (HCl), nitric acid (HNO_3), sodium hydroxide (NaOH), lead nitrate ($Pb(NO_3)_2$), potassium nitrate (KNO_3), calcium chloride ($CaCl_2$), (sigma-Aldrich). Dowex 50WX8, (20-50 mesh) was from Fluka. All glasswares and plastic containers were washed with detergents, rinsed with distilled water and then soaked in a 10% HNO_3 solution for 24hrs. They were then washed with deionised water and dried in an oven for 24hrs at 80^{o}C (Ibrahim, 2011).

FT-IR analysis

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

Isolation and purification of humic acid from compost sample

Compost 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).

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 Compost Humic acid

Compost humic acid sample (1g) was refluxed for 12 hours at (160ºC) 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 Pb(II)

The above sets of solutions were titrated against standardized 0.110M NaOH 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 1.0 M KNO_3 (Gamal, 2014; 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 unhydrolysed compost humic acid.

Evaluation of pKa of Hydrolysed and Unhydrolysed Humic Acids

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

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

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. The dissociation constants (pKa) were calculated according to equation 2.

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

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

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

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

and

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

Where T_L, T^o, E°, and V^o have the 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 (equations. 5, 6, and 7).

$$LogK_1 = \log\left(\frac{n}{1-n}\right) + pL \qquad (5)$$

$$LogK_2 = \log\left(\frac{1-n}{2-n}\right) + pL \qquad (6)$$

$$LogK_3 = \log\left(\frac{2-n}{3-n}\right) + pL \qquad (7)$$

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 compost Figure 2 had distinct clear absorption bands indicating the presence of major humic acid structural elemental groups such as H bonded OH (3620cm^{-1} peak), C=O of carbonyl (1704cm^{-1} peak), functional groups of aliphatic components CH_2 (2922cm^{-1} peak) and C=O stretching of polysaccharide (1123cm^{-1} peak).The positions of the absorption bands of the spectra fell within typical major absorption bands of humic acid which is at frequencies 3620–3578, 2922, 1704, 1123 cm^{-1}. The first peak centred in the vicinity of 3620 cm^{-1} region is attributed to phenolic OH group bonded by intermolecular H bonds. The absorption maximum at 2922 cm^{-1} which is due to C–H stretching of alkane group (CH_2). The next major absorption band is 1704 cm^{-1}. This band has been commonly ascribed to C=O stretching of mainly carboxyl group (COOH) with trace amount of ketones. Peak nearest to 1700 cm^{-1} indicates highly protonated carboxyl group. The last peak was observed at 1123 cm^{-1} due to C–O stretching of polysaccharides and this peak appeared also in the spectra of humic acid from compost. It is likely that during composting of the agricultural wastes biomass, not all the polysaccharides had been degraded. 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 indicates that the humic acid is authentic.

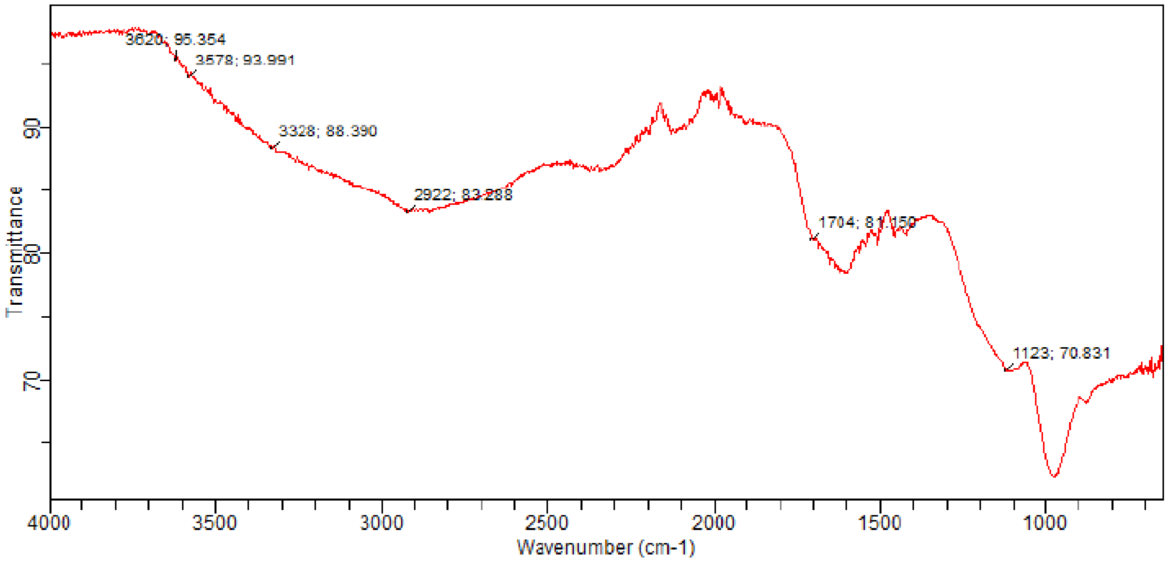


Figure 2: Infrared Spectra of Compost Humic Acid

Evaluation of acid dissociation constant (pka) of acid hydrolysed and unhydrolysed compost humic acids at carboxyl group

The dissociation constants pKa of humic acids were evaluated and reported as pKa (Badr *et al.*, 2012; Baruah *et al.*, 2012; Klucakova and Kolajova 2014; Fernandes *et al.*, 2009; Borges et al., 2005; Almeida and Szpoganicz, 2015). The value of the dissociation constant of the compost humic acid (CHA) that underwent acid hydrolysis studied was found to be 5.0187 as revealed in Table 1. Also, the value of the dissociation constant of the CHA that does not undergone acid hydrolysis was found to be 5.4743 as shown in Table 2. The pKa value of 5.4743 from unhydrolysed CHA Table 2 is lower to the values 6.25 and 6.50 reported by Almeida and Szponics, (2015) and Badr *et al.*, (2012). On the other hand, the pKa value from hydrolysed CHA 5.0187 in Table 1 is lowest to the values 6.25 and 6.50 reported by Almeida and Szponics, (2015) and Badr *et al.*, (2012). It observed that, acid hydrolysis brings about the change of dissociation properties between unhydrolysed humic acid and hydrolysed compost humic acid at their carboxyl groups. This change may be due to the removal of esters, amides, carbohydrates and some of the N-containing compounds from the humic acid molecules, causing intensity of the high molecular size (MS) fraction decreased in hydrolysed compost humic acid molecules, because their chemical characteristics showed that carboxyl group acidity increased after hydrolysis, this favour the ionization degree of the carboxy functional groups under acid medium to ionize and dissociates readily compared to unhydrolysed compost humic acid molecules.

Dissociation constants of the hydrolysed and unhydrolysed (CHA) were calculated as follows:

Table 1: pKa of Hydrolysed CHA

pH	BV_1	BV_2	$(V_2\text{-}V_1)$	n_A	$\log\left(\frac{nA}{1-nA}\right)$	pKa
2.58	1.40	1.42	0.02	0.9857	1.8384	4.4184
2.78	1.60	1.62	0.02	0.9858	1.8415	4.6215
2.98	1.80	1.83	0.03	0.9788	1.6643	4.6443
3.18	2.00	2.06	0.06	0.9577	1.3549	4.5349
3.39	2.20	2.28	0.08	0.9438	1.2251	4.6151
3.60	2.40	2.51	0.11	0.9230	1.0787	4.6787
3.81	2.60	2.76	0.16	0.8885	0.9013	4.7113
4.02	2.80	3.02	0.22	0.8472	0.7439	4.7636
4.23	3.00	3.30	0.30	0.7924	0.5817	4.8117
4.45	3.20	3.55	0.35	0.7588	0.4978	4.9478
4.67	3.40	3.82	0.42	0.7116	0.3922	5.0622
4.89	3.60	4.10	0.50	0.6580	0.2841	5.1741
5.11	3.80	4.38	0.58	0.6047	0.1846	5.2946
5.33	4.00	4.69	0.69	0.5314	0.0546	5.3846
5.56	4.20	5.00	0.80	0.4588	-0.0717	5.4883
5.80	4.40	5.30	0.90	0.3933	-0.1882	5.6118
6.05	4.60	5.60	1.00	0.3284	-0.3107	5.7393
6.31	4.80	5.92	1.12	0.2506	-0.4757	5.8343

Average pKa =5.0187 ± 0.4453

Table 2: pKa of Unhydrolysed CHA

pH	BV_1	BV_2	$(V_2\text{-}V_1)$	n_A	$\log\left(\frac{nA}{1-nA}\right)$	pKa
2.58	1.40	1.41	0.01	0.9929	2.1457	4.7257
2.78	1.60	1.61	0.01	0.9929	2.1457	4.9257
2.98	1.80	1.81	0.01	0.9930	2.1519	4.1319
3.18	2.00	2.01	0.01	0.9930	2.1519	4.3319
3.39	2.20	2.22	0.02	0.9860	1.8478	4.2378
3.60	2.40	2.42	0.02	0.9860	1.8478	4.4478
3.81	2.60	2.65	0.05	0.9651	1.4418	5.2518
4.02	2.80	2.88	0.08	0.9444	1.2300	5.2500
4.23	3.00	3.10	0.10	0.9309	1.1294	5.3594
4.45	3.20	3.35	0.15	0.8967	0.9386	5.3886
4.67	3.40	3.60	0.20	0.8627	0.7981	5.4681
4.89	3.60	3.87	0.27	0.8153	0.6449	5.5349
5.11	3.80	4.14	0.34	0.7682	0.5203	5.6303
5.33	4.00	4.42	0.42	0.7149	0.3992	5.7292
5.56	4.20	4.69	0.49	0.6686	0.3049	5.8649
5.80	4.40	4.99	0.59	0.6023	0.1802	5.9802
6.05	4.60	5.30	0.70	0.5300	-0.0521	6.1021
6.31	4.80	5.66	0.86	0.4246	-0.1320	6.1780

Average pKa = 5.4743 ± 0.6887

Metal-ligand stability constant

Determination of metal-ligand stability constants requires 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), also if the values of n- are within range 2.2- 2.8, this indicates the formation of 1:3 complexes (Omar and Ali, 2015).

In this investigation Pb (II) hydrolysed humic acid, n- ranges from 0.2200 to 2.8630 indicating the formation of ML, ML_2 and ML_3 complex species and the pH range of 3.58 to 6.31 showed that complexes are stable in acidic medium (Tables 3 to 5 and Fig.3).

Table 3: Point-wise method, Pb-Hydrolysed CHA

pH	BV_1	BV_2	BV_3	(V_3-V_2)	N	pL	$\log(\frac{n}{1-n})$	$LogK_1$
2.58	1.40	1.42	1.46	0.04	0.2200	12.55	-0.5497	12.0003
2.78	1.60	1.62	1.67	0.05	0.2750	12.35	-0.4210	11.9290
2.98	1.80	1.82	1.88	0.05	0.2750	12.16	-0.4210	11.7390
3.18	2.00	2.06	2.12	0.06	0.3300	11.96	-0.3016	11.6624
3.39	2.20	2.28	2.34	0.06	0.3300	11.75	-0.3016	11.4424
3.60	2.40	2.51	2.58	0.07	0.3850	11.55	-0.2034	11.3466
3.81	2.60	2.76	2.84	0.08	0.4631	11.33	-0.0642	11.2658
4.02	2.80	3.02	3.11	0.09	0.5500	11.14	-0.0871	11.2271
4.23	3.00	3.30	3.40	0.10	0.6470	10.93	0.2631	11.1931
4.45	3.20	3.55	3.67	0.12	0.7764	10.73	0.5406	10.2706
4.67	3.40	3.82	3.94	0.12	0.7764	10.51	0.6734	10.1834
4.89	3.60	4.10	4.23	0.13	1.0214	10.31		

$LogK_1$ (Average Value = 11.4772 ± 0.2679)

Table 4: Point-wise method, Pb-Hydrolysed CHA

pH	BV_1	BV_2	BV_3	(V_3-V_2)	N	pL	$\log(\frac{n-1}{2-n})$	$LogK_2$
5.11	3.80	4.38	4.52	0.14	1.1846	10.09		
5.33	4.00	4.69	4.85	0.16	1.6000	9.91	0.1760	10.0860
5.56	4.20	5.00	5.17	0.17	1.8700	9.70	0.8256	10.5256

$LogK_2$ (Average Value = 10.3058 ± 0.3109)

Table 5: Point-wise method, Pb-Hydrolysed CHA

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$\log(\frac{n-2}{3-n})$	$LogK_3$
5.80	4.40	5.30	5.48	0.18	2.2759	9.77	-0.4190	9.3510
6.05	4.60	5.60	5.79	0.19	2.8630	9.30	0.7992	10.0992
6.31	4.80	5.92	6.12	0.20	3.9286	9.18		

$LogK_3$ (Average Value = 9.7251 ± 0.5291)

$K_f = LogK_1 \times LogK_2 \times LogK_3$

$K_f = 11.4772 \times 10.3058 \times 9.7251 = 1.150 \times 10^3$

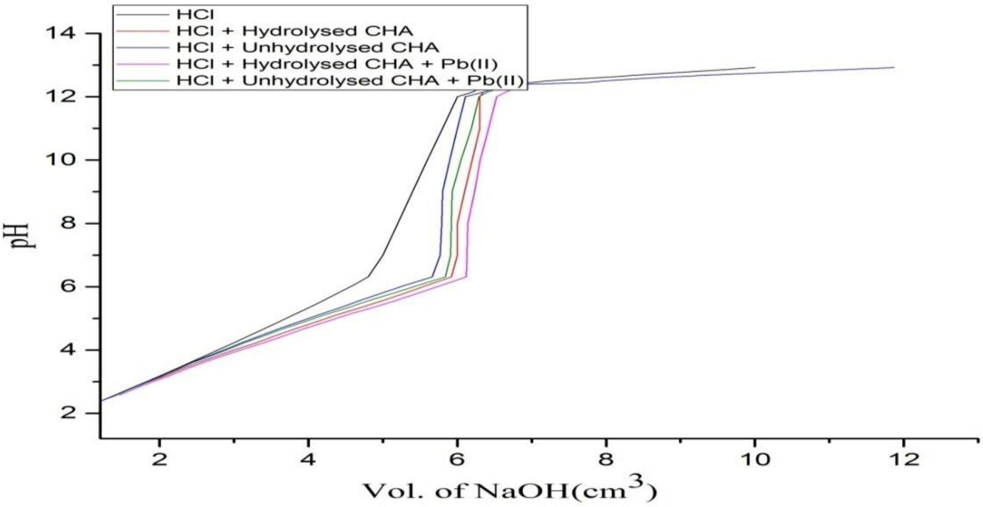


Fig. 3: Potentiometric titration curves of alkali solution versus three sets of solutions (HCl), (HCl + Hydrolysed CHA), (HCl + Unhydrolysed CHA), (HCl + Hydrolysed CHA + Pb(II) and (HCl + Unhydrolysed CHA + Pb(II).

For Pb (II) hydrolysed humic acid titration curve crossed over the hydrolysed CHA titration curve at pH 3.58 to 6.31 indicating formation of the chelate (Omar and Ali, 2015). However, Pb (II) unhydrolysed humic acid, n- extends between 0.2202 and 1.6780 indicating the formation of chelate species ML and ML_2 (Tables 6 and 7). Pb (II) unhydrolysed humic acid titration curve crossed over the unhydrolysed CHA titration curve at pH 3.58 to 6.31 (Fig.3), showing formation of the chelate (Omar and Ali, 2015). The higher values of $\log K_1$, $\log K_2$ and $\log K_3$ showed that the ligand is strongest chelating agent (Anil and Maroti, 2008). The average values were taken as correct value of $\log K_1$ $\log K_2$ and $\log K_3$. The obtained results above indicate that the acid hydrolysis likely produced transformation in the humic molecules, inducing depolymerization which minimizing steric effects, increases dissociation degree of reactive functional group hence increases the acidic constants, thus favours the stability constants and formation constants (K_f) of lead (II) hydrolysed humate complexes than lead(II) unhydrolysed humate complexes.

Table 6: Point-wise method, Pb-Unhydrolysed CHA

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$\log\left(\frac{n}{1-n}\right)$	LogK_1
2.58	1.40	1.41	1.42	0.01	0.0540	13.23		
2.78	1.60	1.61	1.62	0.01	0.0537	13.03		
2.98	1.80	1.81	1.83	0.02	0.1068	12.83		
3.18	2.00	2.01	2.03	0.02	0.1062	12.63		
3.39	2.20	2.22	2.24	0.02	0.1068	12.42		
3.60	2.40	2.42	2.44	0.02	0.1062	12.22		
3.81	2.60	2.65	2.68	0.03	0.1626	12.01		
4.02	2.80	2.88	2.92	0.04	0.2202	11.81	-0.5491	11.2609
4.23	3.00	3.10	3.14	0.04	0.2222	11.60	-0.5441	11.0559
4.45	3.20	3.35	4.40	0.05	0.2880	11.39	-0.3930	10.9970
4..67	3.40	3.60	3.66	0.06	0.3568	11.18	-0.2560	10.9240
4.89	3.60	4.87	3.94	0.07	0.4375	10.97	-0.1091	10.8609
5.11	3.80	4.14	4.22	0.08	0.5270	10.75	0.0470	10.7970
5.33	4.00	4.42	4.52	0.10	0.7051	10.54	0.3786	10.9186
5.56	4.20	4.69	4.81	0.12	0.8980	10.33	0.9447	10.2747

LogK_1 (Average Value= 11.0111 ± 0.1767)

Table 7: Point-wise method, Pb-Unhydrolysed CHA

pH	BV_1	BV_2	BV_3	(V_3-V_2)	n	pL	$\log\left(\frac{n-1}{2-n}\right)$	LogK_2
5.80	4.40	4.99	5.15	0.16	1.3333	10.11	-0.3010	9.8090
6.05	4.60	5.30	5.48	0.18	1.6780	9.90	0.3233	10.2233
6.31	4.80	5.66	5.84	0.18	2.0930	9.68		

LogK_2 (Average Value= 10.0161 ± 0.2930)

$K_f = \text{LogK}_1 \times \text{LogK}_2$

$K_f = 11.0111 \times 10.016151 = 110.2889$

CONCLUSION

From the results obtained, the acidic nature of the hydrolysed and unhydrolysed compost humic acids were not exactly alike as these have different pKa- values, suggesting that the acid hydrolysis brings about the change of dissociation properties between unhydrolysed and hydrolysed compost humic acid at carboxyl group. Lead (II) used in this study showed a tendency to preferably association with hydrolysed humic acid, due to its higher acidity at carboxyl group. The stepwise stability constants and formation constants have been found to vary between hydrolysed and unhydrolysed humic acids, indicated that the acid hydrolysis likely produced transformation in the humic molecules, inducing depolymerization which minimizing steric effects, increases dissociation degree of reactive functional group hence increases the stability constants of hydrolysed compost humic acid than unhydrolysed compost humic acid.

REFERENCES

Almeida, V.R. and Szpoganicz, B. (2015). Humic Acid Potentiometric Response Patterns: Out- of Equilibrium Properties and Species Distribution Modelling. *Chemical. Biol. Technol. Agric.* 2: 17.

Anđelković, T., Nikolić, R., Bojić, A., Purenović, M., Blagojević, S., and Kostić, I. (2011). Copper(II) and Lead(II) Complexation by Humic acid and Humic-like Ligands. *J Serb Chem Soc.*76 (9): 1325–1336.

Anil, B. N. and Maroti, N. (2008). Studies on Influence of Die-Lectric Constants on Complex Equilibria between Substituted Py-Razalines and Lanthanide Metal Ions pH-Metrically. Amer.-Euras. sci-ent. *Res*. 3(2): 212-216.

Badr, M. H., El-Halafawi, M. H. and Abd El-al Zeid, E. R. (2012). Comparison Between the Effect of Ionic Strength on Acidity and Dissociation Constants of Humic Acids Extracted from Sewage Sludge and Nile Water Hyacinth Composts. *Global Journal of Environmental Research* 6 (1): 36-43.

Baruah, M.K., Borah, D., Saikia, P.P., Paul, S., Sharma, T. (2015). Evaluation of pKa Values of Soil Humic Acids and their Complexation Properties. *International Journal of Plant & Soil Science* 6(4): 218-228.

Borges, F., Guimaraes, C., Lima, L.F.C., Pinto, I. and Reis, S.(2005). Potentiometric Studies on the Complexation of Copper(II) by Phenolic Acids as Discrete Ligand Models of Humic Substances Talanta 66 (2005) 670–673.

Chefetz, B., Salloum, M. J., Deshmulkin, A. P. and Hatcher, P. (2002). Structural Components of Humic Acids as Determined by Chemical Modifications and Carbon-13 NMR, Pyrolysis, and Thermochemolysis-Gas Chromatography/Mass Spectrometry. *Soil Science Society of American journal Abstract Division S-2- Soil Chemistry* Vol. 66. P 1159-1171.

Ezue, C.P. (2010). Studies on the Composting Garden and Kitchen Wastes. (Unpublished Masters Thesis) Nnamdi Azikiwe University Awka. Nigeria.

Fernandes, A.N., Giacomelli, C., Giovanela, M. Vaz, D.V. Szpoganicz, B. and Maria M. D. (2009). Potentiometric Acidity Determination in Humic Substances Influenced By Different Analytical Procedures. *J. Braz. Chem. Soc*.20(9):1-4.

Gamal, A. H. (2015). Stability Constants of Rhenium (V) Metal Complexes with Selected Drugs. *Pyrex Journal of Research in Environmental Studies.* Vol. 2(2). Pp 006-014.

Ibrahim, M.B. (2011): Removal of Toxic Metals from Aqueous Solution by Saw dust. Bayero Journal of Pure and Applied Sciences, 4(1): 88-93.

Janrao, D. M., Pathan, J., Kayande, D.D., and Mulla, J.J. (2014). An Over View of Potentiometric Determination of Stability Constants of Metal Complexes. Sci. Revs. Chem. Commun.: 4(1), 2014, 11-24.

Klučáková, M. and Nováčková, K. (2014). Comparison of Thermal and Chemical Stability of Cu-Humic Complexes. In: Xu J., Wu J., He Y. (eds) Functions of Natural Organic Matter in Changing Environment. Springer, Dordrecht.14(12): 29-34.

Kostić I, Anđelković T, Nikolić R, Bojić A, Purenović M, Blagojević S, (2011). Copper(II) and Lead(II) Complexation by Humic Acid and Humic-Like Ligands. *J Serb Chem Soc*. 76 (9): 1325–1336.

Omar, A. A. and Ali, E. A. (2015). Potentiometric Studies on Complexes of Cr (III) and Zr (IV) with some Carboxylic Acids. *International Journal of Advanced Chemistry*, 3(1) pp25-37.

Perminova, I. V. and Hatfield, K. (2005). Remediation Chemistry of Humic Substances.Theory and Implications for Technology.In: use of humic substances to remediate polluted environments: from theory to practice, Perminova, I. V., Hatfield, K., Herkorn N. (Eds.), NATO Science Series, Vol. 52, Springer, Dordrecht, The Netherlands. Pp3-36.

Santosh, D. D., Ashok, B. K., Vijay, J. T., Shivraj, G. W. and Vinay, V. W. (2011). Potentiometric Studies of Elec-Trolyte Effects on Complex Equilibria of Some Substituted 5-(2-hydroxy Phenyl) Pyrazoles. Der pharm. 3 (6): 75-83.

Sayyed, H. and Abdul Rahim, M. F. (2012). Studies of Binary Complexes of Metal Ions with Mandelic Acid by Potentiometry. *Chem. J.* 02 (6): 206-209.

Tomson, A.E., Naumova, G.V., and Zhmakova, N.A., (2017). Studies on the Oxidative and Hydrolytic Destruction of Peat. Solid Fuel Chemistry. Vol. 51, Pp 315-320.

Yudov, M.V., Zhilin, D.M., Pankova, A.P., Rusanova, A.G., Perminova, I.V., Petrosyan, V.S., and Matorin D.N. (2005). Synthesis, Metal-binding properties and Detoxifying Ability of Sulphonated Humic Acids. Earth and Environmental Sciences. Vol. 52, Springer, Dordrech. The Netherlands, Pp 485-498.