APPLICATION OF THE LANGMUIR AND FREUNDLICH EQUATIONS FOR THE REMOVAL OF CD^{2+} AND PB^{2+} IONS BY ADSORPTION ON TO NATURAL CLAY MINERALS

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ABSTRACT

Metal ion sorption plays a critical role in mitigating environmental pollution. However, there is a dearth of research data on the sorption characteristics of Cd^{2+} and Pb^{2+} ions on natural clay minerals in Akwa Ibom State, Nigeria. This study aims to investigate the sorption behaviour of Cd^{2+} and Pb^{2+} ions on natural clay minerals using the Langmuir and Freundlich equations. Four samples of natural clay were collected from Ikot Ebom Itam, in Itu and were used for this study. Samples were characterized using standard analytical methods including X-ray fluorescence (XRF), X-ray diffraction (XRD) and Atomic Absorption Spectrophotometry (AAS). Results showed the elemental components to be more of silica and alumina as the predominant constituents, whereas EXRD analysis showed that the patterns of all four samples comprised predominantly crystalline phases of kaolinite ($Al_2Si_2O_5(OH)_4$), and quartz (Si_6O_6) except for sample CSA whose peaks were attributable to goethite (α-FeO(OH)). Results of metal analysis showed Cd, Pb and Fe concentrations (in ppm) ranged from 0.003-0.007, 1.04-1.76 and 0.54-13.54, respectively. The percentage composition of C, H, N and S ranged from 41 to 50%, 3 to 5%, 0 to 1% and 0 to 1% respectively. The EDXRF analysis shows that the clay minerals exhibited greater sorption capacities for Cd^{2+} and Pb^{2+} ions from aqueous solutions due to high levels of Fe and Al oxides. The Langmuir and Freundlich models were applied to study the sorption characteristics using Pearson correlation analysis. The Freundlich isotherm model offered the optimum option for Cd ($R^2 = 0.9548$) sorption and Langmuir model for Pb (0.9940). Results shows that the sorption of these toxic metals on clay minerals which is dependent on pH, initial concentration of adsorbate and type of adsorbent can reduce their concentrations and mobility in aqueous solution and natural environment. Based on the study, it can be said that clay can be used as a less expensive and effective adsorbent in removal of Cd^{2+} and Pb^{2+} ions from aqueous solutions.

KEYWORDS: Adsorption, clay minerals, Langmuir, Freundlich, isotherms

INTRODUCTION

Soil is one of the key elements for all terrestrial ecosystems. It provides the nutrient-bearing environment for plant life and is essentially important for degradation and transfer of biomass. Soil is a very complex heterogeneous medium, which consists of solid phases (the soil matrix) containing minerals and organic matter and fluid phases (the soil water and the soil air), which interact with each other and ions entering the soil system (Alloway, 1995). The ability of soils to adsorb metal ions from aqueous solution is of special interest and has consequences for both agricultural issues such as soil fertility and environmental questions such as remediation of polluted soils and waste deposition. Heavy metal ions such as Cd^{2+}, Cu^{2+}, Fe^{2+} and Pb^{2+} are the most toxic inorganic pollutants which occur in soils and can be of natural or of anthropogenic origin (Siegel, 2002). Some of them are toxic even if their concentration is very low and their toxicity increases with accumulation in water and soils. Adsorption is a major process responsible for accumulation of heavy metals. Therefore, the study of adsorption processes is of utmost importance for the understanding of how heavy metals are transferred from a liquid mobile phase to the surface of a solid phase.

Adsorption of ions at the interface of clay minerals and aqueous solutions is ubiquitous and plays a pivotal role in a wide spectrum of colloidal, chemical, physical, and geological processes, such as the transport and bioavailability of ions, nutrients and contaminants (Jungwirth and Tobias, 2006). Owing to the large surface area, low permeability and high retention capability, clay minerals show outstanding adsorption performances for metal ions. The ability of clays to adsorb or release heavy metal ions has significantly increased in recent years, and, while many aspects have been clarified, much remains to be learnt about relative affinities and the adsorption process. Variety of clay and clay minerals play an important role in the environment and used as an effective adsorbent material for the removal of toxic metal ions from water solution (Crini and Badot, 2010). The use of clays as adsorbent has advantages upon many other commercially available adsorbents in terms of low-cost, an abundant availability, high specific surface area, excellent adsorption properties, non-toxic nature, and large potential for ion exchange (Crini and Badot, 2010; Gupta and Bhattacharyya, 2013; Rao *et al.*, 2015). The porous structure and high surface area of clay minerals provide benefits in the absorption of liquids and the adsorption of heavy metals (El-Maghrabi and Mikhail, 2014).

The study location, Ikot Ebom Itam, Itu Local Government Area of Akwa Ibom State has rich deposits of various forms of clay minerals. This work aims to investigate the sorption behavior of selected toxic metal ions on to natural clay materials. The effect of some adsorption parameters affecting adsorption behaviour of the metals such as the initial solute concentration and solution pH on Cd^{2+} and Pb^{2+} sorption using batch experiments under laboratory conditions have been investigated. The sorption characteristics of the metals on to the natural clay minerals using Langmuir and Freundlich adsorption isotherms have been presented. The adsorbents were characterized using the X-ray fluorescence (XRF), X-ray diffraction (XRD) and Atomic Absorption Spectrophotometer (AAS) methods. The findings of this research will contribute to the understanding of the potential of natural clay from Itu as an effective sorbent for heavy metal removal. Additionally, the results will aid in determining the optimal conditions for efficient sorption and provide insights into the mechanisms involved in the sorption process. The outcomes of this study could have practical implications for environmental remediation strategies, wastewater treatment, and the development of sustainable and cost-effective techniques for heavy metal ion removal. Furthermore, the research may support local communities in Akwa Ibom State by highlighting the potential utilization of natural clay resources for pollution control and environmental protection.

MATERIALS AND METHODS

Preparation of the adsorbent material

Four clay mineral samples from Ikot Ebom Itam in Itu Area (Akwa Ibom) was selected for use as an adsorbent. The clay minerals were air-dried for 5 days, grounded and homogenized with an agate mortar and pestle, sieved through a 2 mm mesh size and then dried at 120 ^{0}C for 4 hours.

Characterization techniques

The clay mineral samples used were identified using different characterization techniques. The chemical composition was determined with XRF using the ‘Epsilon 5’ ED-XRF device, the X-ray tube was activated by applying 25 kV/10 mA power from the HT generator. XRD analyses were carried out using a high-resolution powder X-ray diffractometer (HRPXRD), using Cu-Kα radiation (1.54060 Å) at a goniometer rate of $2\theta = 4°/\text{min}$. The metal analysis of all samples was performed using Atomic Absorption Spectrophotometer (AAS). The elemental analysis for the determination of the total carbon, hydrogen, nitrogen and sulphur was done using the Perkin Elmer 2400 Series II CHNS/O Elemental Analyzer.

Adsorbate

The stock solutions of each metal ion (Cd^{2+} and Pb^{2+}) with concentration ranges of 0 – 40 ppm for Cd and 0 – 500 ppm for Pb were prepared separately by dissolving appropriate amounts of the corresponding metal salts of $Cd(NO_3)_2$ and $Pb(NO_3)_2$ respectively. Serial dilutions (using $C_1V_1 = C_2V_2$) were also done to obtain four other concentrations for each; 30 ppm, 20 ppm, 10 ppm and 5 ppm from the 40-ppm stock solution for Cd and 40 ppm from the 500-ppm stock solution for Pb.

Adsorption Experiments

The adsorption behavior of the different clay mineral samples towards metal ions were studied using batch method under different experimental conditions such as: adsorbent dose (0.1 g for each solution), contact time (0 to 960 mins) which is an important parameter to control the effectiveness of the adsorption, pH of the solution (acidic, basic and neutral). The adsorption of metal ions is a phenomenon that is greatly influenced by pH due to the involvement of mechanisms that are dependent on pH such as ion exchange or retention by electrostatic forces, the acidic, basic and neutral pH were tested for each sample solution and an optimum concentration of 40 ppm for Cd and 100 ppm for Pb by adding two drops of HNO_3 (pH = 4.0) to the solutions labelled “A” and two drops of NaOH (pH = 8.4) to the solutions labelled “B” and also the neutral (pH = 6.7) left the way it is to see which will favor the adsorption more. The initial batch concentration of the adsorbates was 5 to 40 mg L^{-1} for Cd and from 20 to 500 mg L^{-1} for Pb. Following adsorption, the clay samples were separated from the supernatant (liquid phase) by decanting the filtrate out from the solution.


Figure 1: A typical clay mineral pit in the study area

RESULTS AND DISCUSSION

Adsorbent Characterization

The elemental composition analysis of the natural clay samples using the Energy Dispersive X-ray Fluorescence (ED-XRF) showed that silica (SiO_2) and alumina (Al_2O_3) are the predominant constituents in all clay samples (Table 1). They are found in a SiO_2/Al_2O_3 ratio equal to 1.68 in CSA, 1.61 in CSB, 1.76 in CSC and 2.25 in CSD, the relatively high ratio showed an indication of the presence of free quartz in the clay fraction in large proportion (Ouaddari *et al.*, 2018). Also, Fe_2O_3, TiO_2, La_2O_3, MgO and NiO are present in small quantities in the sample. Other oxides such as CuO, MnO, and Cr_2O_3, are present in the sample as impurities. The low CaO content indicates a low amount of calcium carbonate (Sadki *et al.*, 2014). The loss on ignition (LoI) at 1000°C was 4.93% by mass for CSA, 17.62% by mass for CSB, 15.32% by mass for CSC and 10.70% by mass for CSD. It is due to the decomposition of carbonates and dehydroxylation of clay minerals (Ouaddari *et al.*, 2019).

The mineralogical composition of all samples was determined from the X-ray diffractogram represented in Figure 1 and 2. The XRD spectra of CSA, CSB, CSC and CSD provide rich information on the phase identity, crystallinity and average grain size of the different clay

minerals. The XRD patterns of all the samples showed the clay minerals comprised predominantly of crystalline phases of kaolinite ($Al_2Si_2O_5(OH)_4$), and quartz (Si_6O_6) except for CSA whose peaks were attributable to goethite (α-FeO(OH))

Table 1. Chemical composition of the clay samples

Parameters	Samples			
	CSA	**CSB**	**CSC**	**CSD**
Elemental composition (% weight)				
SiO_2	37.470	41.990	45.520	52.150
Al_2O_3	22.280	25.950	25.890	23.180
Fe_2O_3	12.353	2.389	2.087	1.320
TiO_2	10.385	1.078	1.099	1.208
La_2O_3	4.311	3.455	3.599	3.774
MgO	4.098	5.099	4.009	5.099
CdO	2.009	0.500	0.500	0.610
NiO	1.605	1.617	1.626	1.616
K_2O	0.470	0.230	0.260	0.300
CaO	0.043	0.031	0.014	0.010
Cr_2O_3	0.024	0.016	0.014	0.011
CuO	0.015	0.014	0.040	0.009
MnO	0.007	0.012	0.025	0.019
CHNS (%)				
Carbon	41.06	44.38	46.68	49.85
Hydrogen	4.77	3.67	4.97	4.94
Nitrogen	1.09	1.74	0.77	0.51
Sulphur	0.23	0.63	0.89	0.78
Metal concentration				
Cadmium (ppm)	0.003±0.001	0.003±0.001	0.007±0.000	0.006±0.001
Lead (ppm)	1.56±0.003	1.76±0.002	1.26±0.003	1.04±0.004

Table 2. Crystallographic parameters for Quartz and Kaolinite clay samples

Crystallographic parameters	**Quartz (Si_6O_6)**				**Kaolinite ($Al_2Si_2O_9H_4$)**			
	CSA	CSB	CSC	CSD	CSA	CSB	CSC	CSD
Crystal system	An	An	An	An	Hex	Hex	Hex	Hex
a (Å)	4.930	4.912	4.930	4.913	5.152	5.152	5.155	5.153
b (Å)	4.930	4.912	4.930	4.913	5.154	5.154	5.155	5.153
c (Å)	5.415	5.404	5.415	5.405	7.391	7.391	7.405	7.406
Alpha (°)	90.00	90.00	90.00	90.00	74.954	74.954	84.116	84.118
Beta (°)	90.00	90.00	90.00	90.00	84.223	84.223	75.138	75.136
Gamma (°)	120.00	120.00	120.00	120.00	60.196	60.196	60.176	60.186
Calculated density (g/cm^3)	3.85	2.65	3.85	2.65	2.61	2.61	2.56	2.57
Volume of cell (10^{6}pm^3)	113.98	112.92	113.98	112.98	164.37	164.37	164.93	164.83
RIR	1.96	3.16	1.96	3.14	1.07	1.07	1.18	1.17

An = Anorthic, Hex = Hexagonal

The mineralogical composition of all samples was determined from the X-ray diffractogram represented in Figures 2 and 3. The XRD spectra of CSA, CSB, CSC and CSD provide rich information on the phase identity, crystallinity and average grain size of the different clay minerals. The XRD patterns of all the samples showed the clay minerals comprised predominantly of crystalline phases of kaolinite ($Al_2Si_2O_5(OH)_4$), and quartz (Si_6O_6) except for CSA whose peaks were attributable to goethite (α-FeO(OH)). The quartz and kaolinite phases in all the samples had hexagonal and anorthic crystal system respectively. The calculated density of the major mineral phases - quartz and kaolinite were respectively given as 3.85 and 2.61 g/cm^3 (for CSA), 2.65 and 2.61 g/cm^3 (for CSB), 3.85 and 2.56 g/cm^3 (for CSC) 2.57 and 2.65 g/cm^3 (for CSD) (Table 2). Also, the presence of broad and low-intensity peaks around 2Ɵ value of 50° and 60° in all samples and except for CSA which was between 30° and 40° revealing the amorphosity of the kaolinite, quartz and goethite phases attributable to the presence of organic matter (Fazlzadeh *et al.*, 2017). Similarly, all four samples showed amorphous features of quartz and kaolinite around 60-70°.

The results of metal analysis in the four natural clay samples under study showed that for all soil samples, Cd^{2+} was present in low concentrations and previous report revealed that cadmium was more mobile and bioavailable (ability to be absorbed by living organisms) than other metals, hence, its low concentrations. Lead ion (Pb^{2+}) showed moderate concentrations in all soil samples. The high carbon content (Table 1) predicts that all samples were good sources of nutrients through mineralization, which helps to aggregate soil particles (structure) to provide resilience to physical degradation, increasing microbial activity, water storage and availability to plants, and protecting the soil from erosion.

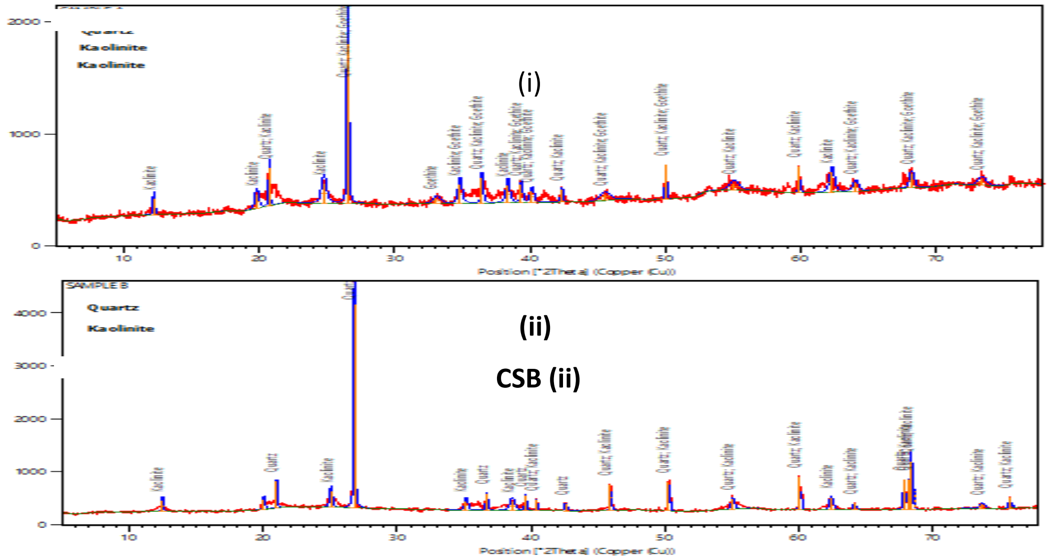

Figure 2. X-ray diffraction pattern of sample CSA (i) and CSB (ii)

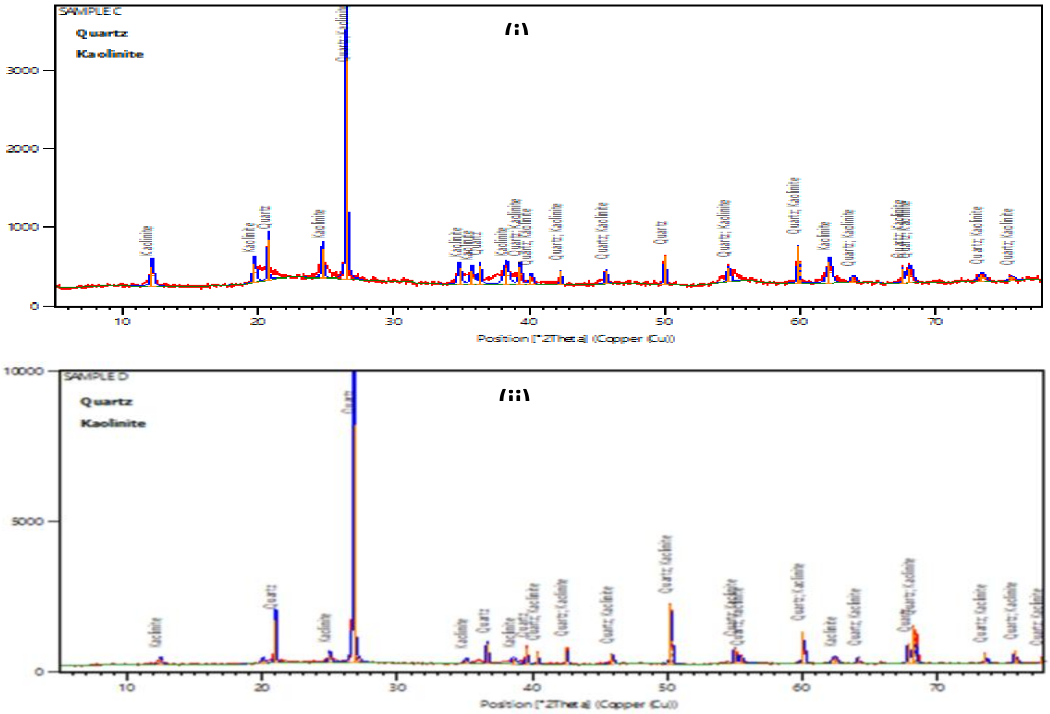

Figure 3. X-ray diffraction pattern of sample CSC (i) and CSD (ii)

Adsorption Analysis

Effect of initial concentration

The initial concentration serves as a crucial driving force to get through all of the molecules' mass transfer barriers between the aqueous and solid phases (Kadiri *et al*, 2018; Lebkiri *et al.*, 2019; Donmez and Aksu, 2002). The efficiency of the current adsorption system with metal solutions of different concentrations may be determined by the research of the initial concentration impact. Additionally, it will enable the investigation of the underlying process using several adsorption isotherms. In this study, the effect of the initial concentration of metal solutions on the amount adsorbed (mg/g) per clay sample was investigated over a range of initial concentrations from 0 to 120 mg L^{-1}. The adsorption capabilities of metal solutions are shown in Figures 4 (a & b).

The adsorption pattern of Cd in the four studied soil samples with initial concentrations ranging from 5 – 40 mg L^{-1} is shown in Figure 4 (a). Results obtained showed increased concentration for sorbed Cd ions with increasing levels of added Cd ions and highest at an initial concentration of 40 mgL^{-1} with % sorption 97.0, 96.9, 96.5 and 96.4 percent for samples CSA, CSB, CSD and CSC respectively (Table 3). The highest mean sorbed Cd concentration, 16.6±15.1 mg L^{-1} (76.5±37.9 %) was recorded at CSB. Among the four studied soil samples, CSC showed the least Cd ion sorption with mean value, 16.4±15.0 mg L^{-1} (75.1±37.5 %). The adsorption pattern for Pb with initial concentrations ranging from 40 – 120 mg L^{-1} in the four samples are shown in Figure 5 (b). Results showed increased concentration for sorbed Pb^{2+} ions with increasing levels of added metal ions. Among the four studied clay samples, sample CSC and CSD showed highest percentage sorption values of 98.8% and 97.3% with initial Pb concentration of 100 mgL^{-1}, while sample CSA showed maximum sorption value of 111.7 mgL^{-1} with initial Pb concentration of 120 mgL^{-1}, giving 93.0% sorption (Table 3). 64.1±41.5 mg L^{-1} (80.1±39.3%) while CSB showed the least Pb sorption with mean value, 45.2±25.5 mg L^{-1} (61.5±36.4%) (Figure 4 (b)).

Effect of solution pH on adsorption

The adsorption of metal ions is a phenomenon that is strongly influenced by pH. This is due to the involvement of mechanisms that are dependent on pH such as ion exchange or retention by electrostatic forces (Brahim *et al.*, 2020). The adsorption Cd and Pb ions on the four clay samples at the three different pH levels (4.0, 6.7 and 8.4) are shown in Figure 5. Adsorption efficiency for cadmium in all four clay samples are relatively low across all three pH levels ranging between 30% and 34%. This may be due to electrostatic repulsion; adsorbent surface and the adsorbate having like charges, causing repulsion. Another reason could be due to low concentration of the metal compared to other metals. Lead also showed high adsorption at pH 8.4, due to the presence of hydroxide ions (OH^{-}) in basic solutions with values ranging between 93% and 98%. Adsorption is enhanced because of the formation of metal hydroxide complexes.

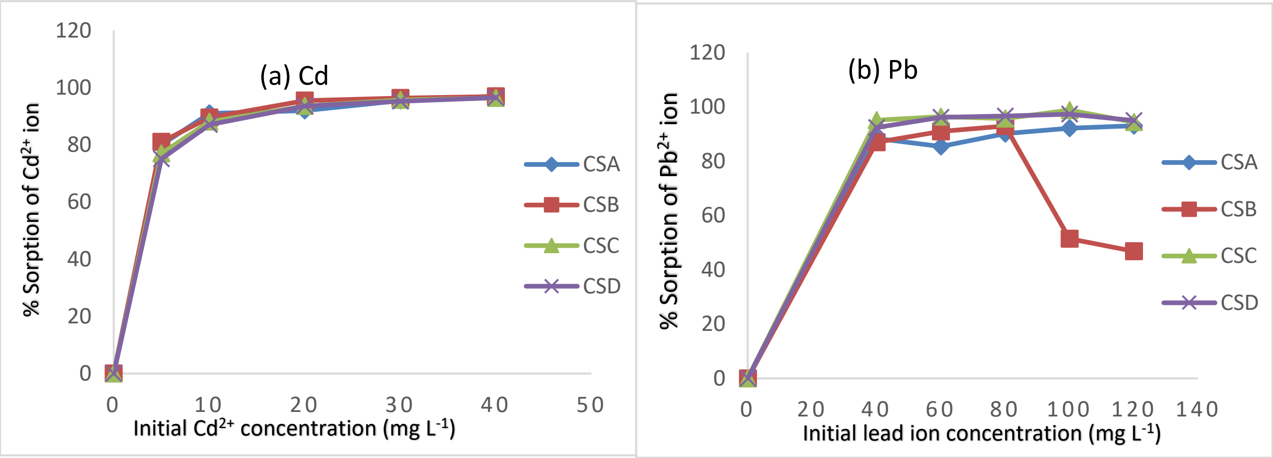

Figure 4. Variation in the adsorption capacity of Cd^{2+}and Pb^{2+} as a function of initial concentration

Table 3: Levels of adsorbed Cd^{2+} and Pb^{2+} adsorbed (mg L^{-1}) with initial concentration

Sample	Cd concentration (mg L^{-1})					Range
	5	10	20	30	40	
CS1	4.00(80.0)	9.10(91.0)	18.4(92.0)	28.7(95.5)	38.8(97.0)	4.00-38.8(80.0-97.0)
CS2	4.05(81.0)	8.95(89.5)	19.1(95.5)	28.9(96.3)	38.8(96.9)	4.05-38.8(81.0-96.9)
CS3	3.85(77.0)	8.80(88.0)	18.7(93.5)	28.7(95.7)	38.6(96.4)	3.85-38.6(77.0-96.4)
CS4	3.75(75.0)	8.70(87.0)	18.7(93.5)	28.6(95.2)	38.6(96.5)	3.75-38.6(75.0-96.5)
	Pb concentration (mg L^{-1})					
	40	60	80	100	120	
CS1	35.4(88.4)	51.3(85.4)	72.1(90.1)	92.1(92.1)	111.7(93.0)	35.4-111.7(85.4-93.0)
CS2	34.8(87.0)	54.6(91.0)	74.4(92.9)	51.4(51.4)	56.3(46.9)	34.8-74.4(46.9-92.9)
CS3	38.1(95.1)	57.9(96.4)	76.6(95.7)	98.8(98.8)	113.2(94.3)	38.1-113.2(94.3-98.8)
CS4	37.0(92.4)	57.7(96.2)	77.3(96.6)	97.3(97.3)	114.0(95.0)	37.0-114.0(92.4-97.3)

Values in parentheses are percentages of metal ion adsorbed (% S)

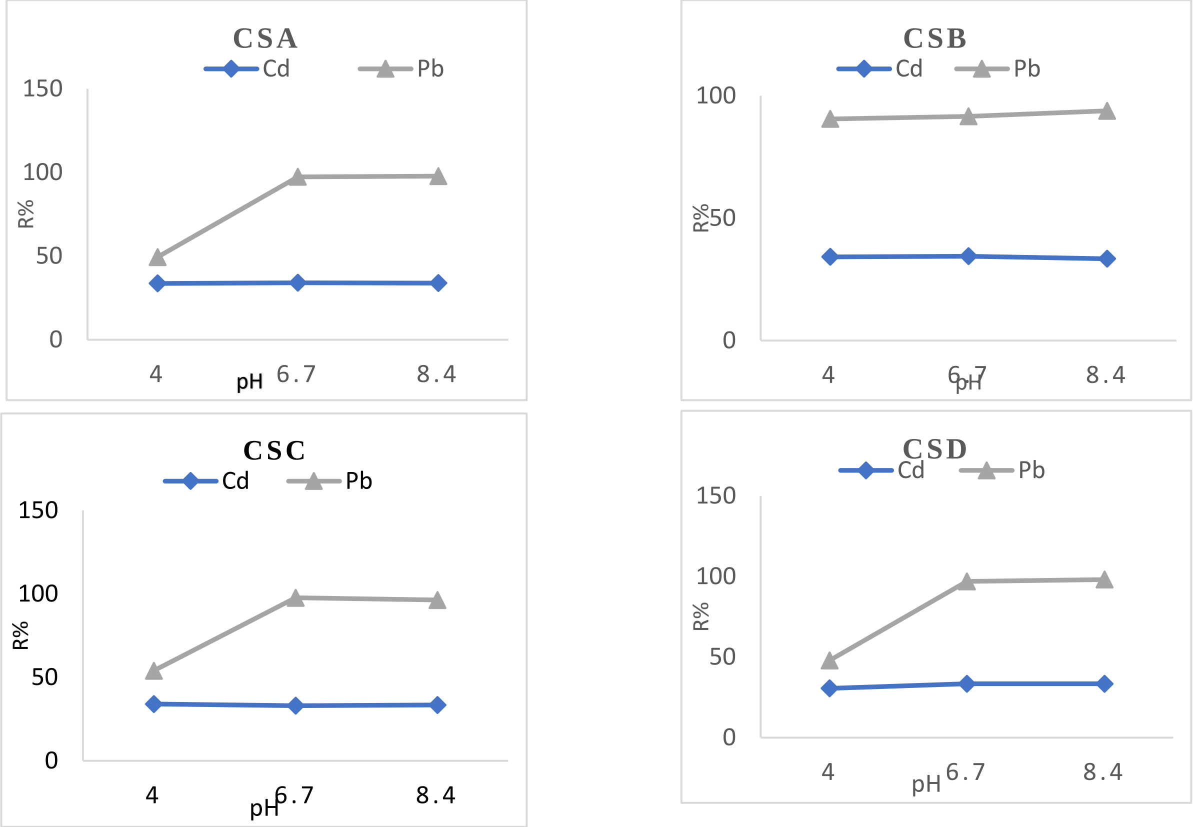

Figure 5. Variation of sorption efficiency of heavy metals as a function of solution pH in samples CSA, CSB, CSC and CSD.

Adsorption isotherms

The regression coefficient (R^2) values for the Langmuir and Freundlich isotherm models were applied to study the adsorption pattern for Cd^{2+} and Pb^{2+} ions in the four different clay minerals (CSA, CSB, CSC, and CSD). The R^2 values represent the goodness of fit for each isotherm model, indicating how well the model fits the experimental data. The Langmuir model showed highest data, $R^2 = 0.9940$ for Pb as shown in sample CSB, whereas, the Freundlich isotherm showed highest $R^2 = 0.9548$ for Cd in sample CSD (Table 4). This, therefore, indicates that the Langmuir and Freundlich model provided the best fit data for Pb and Cd depending on the nature of the sample. The Freundlich model is known for its versatility and ability to describe multilayer adsorption on heterogeneous surfaces, making it suitable for complex adsorption processes involving clay samples and heavy metals (Andy and Toro-Vazquez, 2009). The Langmuir isotherm assumes a monolayer adsorption with a limited number of identical sites. Inconsistencies in their performance may be attributed to variations in the surface characteristics and adsorption mechanisms of the clay samples and heavy metals (Seda and Ilknur, 2018).

Table 4. Regression coefficient (R^2) values for four different isotherm models

Isotherm models	Metals	Regression coefficient (R^2) values for different isotherm models			
		CSA	CSB	CSC	CSD
Langmuir	Cd	0.0616	0.0984	0.0855	0.1108
	Pb	0.4923	0.9940	0.6678	0.3941
Freundlich	Cd	0.2444	0.1165	0.8702	0.9548
	Pb	0.9599	0.4708	0.3475	0.7115

The adsorption capacity for the different metals showed that Pb was greater than Cd. The variability of the R^2 may be attributed to the differences in the physical and chemical properties of the clay samples, such as surface area, pore size distribution, and composition. Additionally, the presence of various functional groups on the clay surfaces can influence the adsorption behavior of heavy metals differently (Esra *et al.*, 2022).

Overall, the significant performance of the Freundlich isotherm model suggests that its non-linear nature is better suited to describe the complex adsorption phenomena occurring on the clay samples. In contrast, the mixed performance of the Langmuir isotherms highlights the importance of considering the specific characteristics of the clay samples and heavy metals when selecting an appropriate adsorption model.

Equilibrium Modelling for Cadmium and Lead Ions

The non-linear Langmuir and Freundlich adsorption isotherm demonstrated the relationship between the equilibrium concentration (C_e) and the amount of solute (Q_e) on clay adsorbent in the aqueous phase. The sorption capacities of Cd^{2+} and Pb^{2+} in the different clay minerals at chosen concentrations and soil-solution pH, was evaluated by examining the equilibrium adsorption of Cd^{2+} and Pb^{2+} as a function of their concentration and the adsorption isotherms. The experimental data were fitted in to the different adsorption isotherm equations. Results obtained for Cd^{2+} and Pb^{2+} sorption are presented in Table 5. Since equilibrium constant, Kc, of adsorption depends on the thermodynamic parameters which relates to standard free energy change (ΔG),

$$K_c = \frac{Q_e}{C_e}\ ;\ \Delta G^o = RT\ ln\ K_c \qquad [1]$$

Where, Q_e = the amount of solute adsorbed at equilibrium (mg g^{-1}),

C_e = equilibrium concentration of solute (mg L^{-1})
ΔG^o = standard free energy change of adsorption.
R = gas constant (0.008314 $kJmol^{-1}K^{-1}$)
T = temperature in Kelvin (K).

Therefore, plotting $ln\ K_c = ln\ \frac{Q_e}{C_e}$ versus *ln* C_e showed a linear relation with R^2 significantly better than that of the Freundlich isotherm (Bhatt *et al*., 2012).

Equilibrium Modelling for Cadmium and Lead Adsorption

To understand the estimation of Cd^{2+} sorption capacities for the four soil samples studied at different concentrations (5, 10, 20, 30 and 40 mg Cd^{2+} L^{-1}), the experimental data obtained were fitted into the Langmuir and Freundlich isotherm equations.

The Langmuir equilibrium adsorption model is expressed according to equation [2]:

$$\frac{C_e}{Q_e} = \frac{1}{Q_{max}K_L} + {C_e}/{Q_{\max}} \qquad --[2]$$

Where Q_{max} and K_L are the Langmuir constant relating the sorption capacity of the adsorbent and the energy of the sorption process respectively.

The Cd^{2+} sorption parameters obtained for all isotherm models for the four studied soil samples are presented in Table 5, plotting C_e/Q_s against C_e (Langmuir), *ln* Q_s against *ln* C_e (Freundlich), was applied to find the best adsorption isotherm that could best describe the experimental data. The sorption parameters, Q_{max} and the Langmuir constant, K_L, values for each soil sample calculated from the slope and intercept of each plot are indicated (Table 5).

Results obtained showed that the Langmuir equation characterized Cd^{2+} sorption data for all soil samples poorly with regression coefficient (R^2) values ranging between 0.0616 and 0.1108 for all four clay minerals under study. The experimental data were fitted to the Freundlich isotherm according to the equation [3]:

$$ln\ Q_s = ln\ K_F + 1/n_F\ (ln\ C_e) \qquad [3]$$

Where, K_F and n_F are empirical constants indicating the adsorption capacity and adsorption intensity respectively. A plot of *ln* Q_s against *ln* C_e for all four studied soils helps in determining the constant, K_F and n_F, from the slope and intercept of the graph respectively for both Cd and Pb ion (Table 5).

Table 5: Langmuir and Freundlich adsorption constants for Cd^{2+} and Pb^{2+} sorption values

Isotherm	Cd^{2+} sorption values					Pb^{2+} sorption values				
Parameters	CSA	CSB	CSC	CSD	Mean	CSA	CSB	CSC	CSD	Mean
Langmuir isotherm										
R^2	0.0616	0.0984	0.0855	0.1108	0.0891	0.4923	0.9940	0.6678	0.3941	0.6371
r	0.2482	0.3137	0.2924	0.3329	0.2968	0.7016	0.9970	0.8172	0.6278	0.7859
Q_{max}	434.8	769.2	588.2	833.3	656.4	1000	2000	1429	1429	1464
K_L	1.150	0.433	0.567	0.324	0.6186	1.67	0.56	1.75	1.75	1.43
Q_{max}*K_L	500.0	333.3	333.3	270.3	359.2	1667	1111	2500	2500	1944
R_L	0.02	0.05	0.04	0.07	0.04	0.0050	0.0148	0.0047	0.0047	0.0073
Freundlich isotherm										
R^2	0.2444	0.1165	0.8702	0.9548	0.5465	0.9599	0.4708	0.3475	0.7115	0.6224
r	0.4944	0.3413	0.9328	0.9771	0.6864	0.9797	0.6861	0.5895	0.8435	0.7747
n_F	0.1780	0.1379	0.0553	0.0542	0.1064	0.2908	0.8008	0.3992	0.2281	0.4297
$1/n_F$	5.62	7.25	18.08	18.45	12.35	3.44	1.25	2.50	4.38	2.89
K_F	52.29	90.21	2.91	1.29	36.68	1.336	21.617	58.224	6.464	21.91

Q_{max} = maximum adsorption capacity (mg g^{-1}); K_L = Langmuir adsorption constant (L mg^{-1}); Q_{max}*K_L = maximum buffering capacity (L g^{-1}); n_F = heterogeneity factor of adsorption sites (dimensionless); K_F = Freundlich constant (L g^{-1}).

The Pb sorption for the studied clay samples with initial lead concentration which varied from 40 to 120 mg Pb^{2+} L^{-1} are presented in Table 5. The regression coefficient (R^2) values calculated from the Langmuir adsorption isotherm for the four studied clay samples ranged from 0.3941 to 0.9940 ($\overline{R}^2$= 0.6371) with CSB and CSD having the highest and least regression coefficient (R^2) values of 0.9940 and 0.3941 respectively. Whereas, CSA recorded the highest regression coefficient (R^2) value of 0.9599 from the Freundlich model and CSD having the least highest regression coefficient (R^2) value of 0.3475.

CONCLUSION

In conclusion, this study examined the adsorption behavior of some heavy metals – Cd and Pb on four samples of clay minerals from Ikot Ebom Itam, in Itu LGA of Akwa Ibom State, at varying pH levels. The adsorption capacity and efficiency of each metal ion in the samples were critically analyzed using the Langmuir and Freundlich isotherm models. The adsorption capacity order obtained, based on the R^2 values, showed that Pb was greater than Cd. Results also revealed that Cd exhibited relatively low adsorption efficiency across all four clay samples, while Pb displayed substantial adsorption efficiency, particularly at pH = 8.4. The results indicated increased sorbed metal ion concentrations with higher levels of added metal ions. CSB exhibited the highest mean sorbed concentrations for Cd while CSC recorded the highest mean sorbed concentration for Pb. The background metal levels determined by AAS provided valuable baseline data for assessing potential contamination levels in the clay materials. By elucidating the adsorption mechanisms and providing valuable data on metal background levels, this research contributes to the broader understanding of metal behavior in natural clay minerals from the studied area. In conclusion, the study provides valuable research data and guidance for environmental applications which underscores the importance of continued research in understanding metal adsorption behavior and its implications for environmental management and sustainability.

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