



Studies of Pb(II) Adsorption onto Local Adsorbent

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Author's contribution

The sole author designed, analyzed and interpreted and prepared the manuscript.

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ABSTRACT

The study was carried out to assess the suitability of a locally sourced clay as potential adsorbent for the removal of Pb(II) ions from aqueous solutions following batch mode of operation. The study investigated the effect of varying contact time, solution pH, adsorbent dose and initial concentration of metal ion on sorption. Batch equilibrium and kinetic experiments were conducted at 25°C, using <0.02 mm particle sizes of clay. The kinetic and equilibrium models were fitted employing the non-linear regression method, using a trial-and-error procedure in the Microsoft Excel solver. In order to determine the best fit isotherm, five error analysis functions were used: hybrid fractional error function, Marquardt's percent standard deviation, average relative error, sum of the errors squared and sum of the absolute errors. However, the sum of normalized error was further employed in order to have a better comparison between the error functions sets for the isotherm models. With the highest R² value of 0.9887 and lowest sum of normalized error value of 0.0108, the Sips isotherm fitted the equilibrium data better than the other isotherm models. The pseudo-second order model gave the best fit to the kinetic data as it had the lowest standard error of the estimates value of 3.22x10⁻⁶ and the highest coefficient of determination, R² values of 0.9887 for the adsorption of Pb(II) onto Ikpoba clay.

Keywords: Clay; heavy metal; error function; isotherm; kinetic studies.

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1. INTRODUCTION

Huge deposits of clay are widely distributed in Africa, especially, Nigeria [1,2]. Clays were used in the past as friendly building materials compared to Portland cements. However, in recent years, Clays have received considerable attention especially as potential adsorbents for environmental research.

The removal of heavy metals from wastewater is important in terms of protecting public health and environment [3]. Many industrial activities such as metal plating and mining operations introduce heavy metals into the environment via their waste effluents [4]. Precipitation, ion-exchange, phytoextraction, ultrafiltration, membrane separation and adsorption are the usual methods for the removal of heavy metal ions from aqueous solutions [5]. Due to its simplicity and easy operational conditions; adsorption is a widely-used process [6].

Activated carbon has been the most employed adsorbent for heavy metal removal from aqueous solution, but it is however expensive. Many reports have appeared on the development of low-cost materials. These include: Modified groundnut (*Arachi hypogea*) husks [7]; clay [8]; sheep hoofs [9].

Many investigators have evaluated natural clay as a low-cost adsorbent due to its adsorption properties for heavy metals including cobalt, cadmium, zinc and chromium ions [10-12].

In this study, clay from Ikpoba in Edo state, Nigeria has been used as adsorbent. For the present study, the Freundlich, Langmuir, Redlich-Peterson, Sips and Radke-Prausnitz adsorption isotherms were examined for lead ion sorption onto Ikpoba clay for their ability to model the equilibrium sorption data at a fixed temperature of 25°C. Also, five different non-linear error functions, hybrid fractional error function (HYBRID), Marquardt's percent standard deviation (MPSD), average relative error (ARE), sum of the errors squared (ERRSQ) and sum of the absolute errors (EABS), were examined and in each case the isotherm parameters were determined by minimising the respective error function across the concentration range studied using the *solver* add-in with Microsoft's spreadsheet, Excel. The kinetic data were fitted to Pseudo-first order, pseudo-second order, Elovich and intraparticle diffusion models.

2. MATERIALS AND METHODS

2.1 Collection of Samples

Clay samples were collected from the clay deposits at Ikpoba river in Benin; and at depths of up to 10 cm with the aid of a plastic shovel and digger and hand-picked to minimize the possibility of contamination. About 2.0 kg of sample was collected and placed in small polythene bag and then dried at 100°C for 24 hr, pulverized and sieved to geometric mean size of <0.02 mm before analysis.

2.2 Preparation of Aqueous Solution

The salt used for the preparation of the aqueous solutions was analytical grade Lead nitrate. Other chemicals used were: sodium hydroxide and trioxonitrate (V) acid. All reagents used were of analytical grade. Stock solutions of 1000mg/l each of Pb(II) were prepared by dissolving reagent grade PbNO₃ in appropriate quantity of distilled water. Deionized water was used for preparing stock solutions and dilution.

2.3 Characterization of Clay

The specific surface area of Ikpoba clay was determined from the Brunauer, Emmett and Teller (BET) multipoint method [13] and the pore size distribution were obtained using Barret, Joyner, and Halenda (BJH) method [14]. This was carried out by N₂ adsorption using Micromeritics instrument (Tristar 3000). Also pore volume was determined using the surface area analyzer which utilizes the BET theory for the analysis and plots of each sample data and then presents the results of pore volume (cm³/g). The cation exchange capacity (CEC) of clay was determined by the procedure described by Chapman [15]. Also, X-ray Spectrometer (model PW 4030) was used to determine the chemical composition of the clay.

2.4 Batch Adsorption Studies

Adsorption was performed in batch experiments where 50 mL of aqueous solutions of Pb(II) were mixed with 0.8g of adsorbent (size <0.02 mm) in conical flasks. The pH of each suspension was adjusted in the range of , 3-12 by adding HNO₃ or NaOH aqueous solutions and monitored with pH meter (Suntex, model SP-701). The mixed solutions were shaken in optima mechanical shaker (model 08-752) at 300 rpm and 25°C for

a given time. After the contact time was completed, solution and clay were separated by filtering through a filter paper (Whatmann no. 42). The residual metallic ion concentrations were determined using an Atomic Absorption Spectrophotometer (Buck scientific, model 210 VGP). Adsorption mechanisms were determined according to the predefined procedure with Pb(II) concentrations ranging from 20 to 60 mg l⁻¹. A duplicate was analyzed for every sample to track experimental error and show capability of reproducing results [16].

The adsorbate uptake, q (mg/g) was calculated as:

$$q = \frac{(C_0 - C_e) \cdot V}{m} \quad (1)$$

Where q is the specific uptake in mg/g at equilibrium, C₀ and C_e are the initial and final concentration in mg/l, respectively, V the volume in litres of aqueous solution and m is the mass of adsorbent in grams.

The aqueous samples were taken to preset time intervals and the concentrations of metal ions were similarly measured. The amount of adsorption at time t, q_t (mg/g), was calculated by:

$$q_t = \frac{(C_0 - C_t) \cdot V}{m} \quad (2)$$

Where: C_t (mg/l) is the concentrations of aqueous solution at any time t.

2.5 Kinetic and Equilibrium Studies

The kinetic equations considered are: pseudo first-order [17], pseudo-second order [18], Elovich [19] and intra-particle diffusion model [20]. The equations of the kinetic models are given in Table 1.

Equation (3) is a first-order rate equation to describe the kinetic process of liquid-solid phase adsorption of Pb(II) onto clay, which is believed to be the earliest model pertaining to the adsorption rate based on the adsorption capacity. To distinguish kinetic equations based on adsorption capacity from solution concentration, Lagergren's first order rate equation has been called pseudo-first-order [18].

Based on the linearized form of pseudo first-order model, a linear fit between ln(q_e - q_t) versus contact time (t) indicates that the reaction follows a pseudo-first-order. The pseudo-first-order rate constant k₁, calculated from the slopes of the linear plot. The pseudo-second-order rate equation has been successfully applied to the adsorption of metal ions, dyes, herbicides, oils, and organic substances from aqueous solutions. Based on the linearized form of pseudo second-order model, a linear fit of t/q_t vs t indicates that the reaction follows a pseudo second-order; with q_e equal to the reciprocal of the slope. Elovich's equation is a kinetic equation of chemisorption that was initially used to describe the rate of adsorption of carbon monoxide on manganese dioxide that decreases exponentially with an increase in the amount of gas adsorbed. Elovich's equation has been widely used to describe the adsorption of gas onto solid systems. Recently it has also been applied to describe the adsorption process of pollutants from aqueous solutions, such as cadmium removal from effluents using bone char. The kinetic results will be linear on a q_t versus ln t plot. An excellent fit of data to plot indicates that the rate-determining step is diffusion in nature and that this equation should apply at conditions where desorption rate can be neglected. The constants can be obtained from the slope and the intercept of a straight line plot. In Intraparticle diffusion model, Weber-Morris [20] found that in many adsorption cases, solute uptake varies almost proportionally with t^{1/2} rather than with the contact time t. A plot of q_t vs t^{1/2} should be a straight line with a slope, k_p (the intraparticle diffusion rate constant) when the intraparticle diffusion is a rate-limiting step. Adsorption kinetics may be controlled by film diffusion and intraparticle diffusion simultaneously, thus, the slope is not usually equal to zero. C is a constant related to the thickness of the boundary layer.

Table 1. Kinetic adsorption models

Kinetic Model	Equation
Pseudo first-order [17]	$q_t = q_e [1 - \exp(-k_1 t)]$ (3)
Pseudo-second order [18]	$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t}$ (4)
Elovich [19]	$q_t = \frac{1}{\beta} \ln(\alpha * \beta) + \frac{1}{\beta} \ln(t)$ (5)
Intra-particle diffusion [20]	$q_t = k_p \sqrt{t} + C$ (6)

In addition to using R^2 , the models were evaluated by standard error of the estimates (SEE) which measures the point by point differences of the amount of the divalent metal ions taken up by the adsorbent predicted by the models and the actual q measured experimentally:

$$SEE = \sqrt{\frac{\sum(q_{i,meas} - q_{i,cal})^2}{n-2}} \quad (7)$$

The isotherm equations considered are: Langmuir [21], Freundlich [22], Sips [23] and Redlich-Peterson [24]. The equations of the isotherm models are given in Table 2.

Table 2. Equilibrium isotherm models

Isotherm	Equation
Langmuir	$q_e = \frac{Q_{max}K_L C_e}{1 + K_L C_e}$ (8)
Freundlich	$q_e = K_F C_e^{1/n}$ (9)
Sips	$q_e = \frac{Q_{max}K_S C_e^{1/n}}{1 + K_S C_e^{1/n}}$ (10)
Redlich-Peterson	$q_e = \frac{K_i C_e}{1 + \alpha_L C_e^\beta}$ (11)

Freundlich isotherm model can be applied to nonideal sorption on heterogeneous surfaces as well as multilayer sorption. It is often criticized for lacking a fundamental thermodynamic basis since it does not reduce to Henry's law at low concentrations. K_F characterizes ability of the given surface to adsorb given solute from the mixture with a given solvent. Langmuir model is a theoretical equilibrium isotherm relating the amount of gas sorbed on a surface to the pressure of the gas. The Langmuir model is probably the best known and most widely applied sorption isotherm. At low sorbate concentrations it effectively reduces to a linear isotherm and thus follows Henry's law. Alternatively, at high sorbate concentrations, it predicts a constant – monolayer – sorption capacity. Sips isotherm is a combined form of Langmuir and Freundlich expressions deduced for predicting the heterogeneous adsorption systems and circumventing the limitation of the rising adsorbate concentration associated with Freundlich isotherm model. At low adsorbate concentrations, it reduces to Freundlich isotherm; while at high concentrations, it predicts a monolayer adsorption capacity characteristic of the Langmuir isotherm. Redlich-Peterson isotherm incorporates features of both the Langmuir and Freundlich equations. It can be

described as follows: At low concentrations the Redlich-Peterson isotherm approximates to Henry's law and at high concentrations its behaviour approaches that of the Freundlich isotherm.

2.5.1 Validity of adsorption isotherm-error functions

A trial-and-error procedure was used for nonlinear regression to minimize or maximize the objective function using the solver add-in function, Microsoft Excel, Microsoft Corporation. The models parameters were evaluated by some error functions, namely HYBRID, MPSD, ERRSQ, ARE and EABS. Contrary to the linearization models, nonlinear regression usually involves the minimization of error distribution (between the experimental data and the predicted isotherm) based on its convergence criteria [25]. As each of the error criteria is likely to produce a different set of isotherm parameters, an overall optimum parameter set is difficult to identify directly. Hence, in order to try to make a meaningful comparison between the parameter sets, a procedure of normalizing and combining the error results was adopted producing a so-called 'sum of the normalized errors' for each parameter set for each isotherm [26]. Below is a list of error functions used and their definitions:

3. RESULTS AND DISCUSSION

Table 4 shows the surface area, average pore diameter and pore volume for the adsorbent used for this study. The Specific surface area using the BET method was 8.6932m²/g, the average pore diameter was 26.22612nm and pore volume was 0.101267 cm³/g. As observed, the surface area for the clay is relatively low; below the range of 10 to 20 m²/g established for kaolinite [32]. This may be due to the high quartz content of the clay. The CEC was also observed to be low (4.8 meq/100 g). This is however within the range of values of 3 and 15 meq/100 g for Kaolinite given elsewhere [33]. With a pore diameter of 26.22612nm, the clay sample is mesoporous based on IUPAC classification [34].

From the XRF results in Table 5 it is seen that SiO₂ had the highest composition of 78.65, Al₂O₃ was next with a percentage of 15.17; while the lowest oxide present was Cr₂O₃ with a percentage of 0.01 in the clay sample.

Table 3. List of error functions

Error function	Definition/expression	Reference
Sum squares errors (ERRSQ)	$\sum_{i=1}^p (q_{e,meas} - q_{e,calc})_i^2$	[25]
Hybrid fractional error function (HYBRID)	$\frac{100}{n-p} \sum_{i=1}^n \left[\frac{(q_{e,meas} - q_{e,calc})^2}{q_{e,meas}} \right]_i$	[27]
Average relative error (ARE)	$\frac{100}{n} \sum_{i=1}^n \left \frac{q_{e,meas} - q_{e,calc}}{q_{e,meas}} \right $	[28]
Marquardt's percent standard deviation (MPSD)	$100 * \sum_{i=1}^p \left(\frac{q_{e,meas} - q_{e,calc}}{q_{e,meas}} \right)_i^2$	[29]
Coefficient of determination (R ²)	$\frac{\sum (q_{e,meas} - \bar{q}_{e,calc})^2}{\sum (q_{e,meas} - \bar{q}_{e,calc})^2 + \sum (q_{e,meas} - q_{e,calc})^2}$	[30]
sum of the absolute errors (EABS)	$\sum_{i=1}^n q_{e,meas} - q_{e,calc} _i$	[27]
Sum of Normalized error (SNE)	-	[31]

Where $q_{e,calc}$ is the equilibrium capacity obtained from the isotherm model, $q_{e,meas}$ is the equilibrium capacity obtained from experiment, and \bar{q}_e is the average of q_e , n is number of data points and p is number of parameters within the isotherm.

Table 4. Physico-chemical properties of Ikpoba clay

Parameter	Value
CEC (meq/100 g)	4.8
Specific surface area - BET (m ² /g)	8.6932
Average Pore Diameter Range (nm)	26.22612
Pore Volume (cm ³ /g)	0.101267

Fig. 1 shows increase in percentage removal of Pb(II) as pH increases from 3 to 11 and thereafter decreases. This trend in the percent removal is in agreement with researches elsewhere [35]. As reported elsewhere [36] metal adsorption is pH-dependent and that the intensity of the phenomenon increases drastically above pH 7.0. The observed decrease beyond pH 11 may be due to the formation of soluble hydroxyl complexes. The hydrolysis of cations occurs by the replacement of metal ligands in the inner coordination sphere with the hydroxyl groups. This replacement occurs after the removal of the outer hydration of metal cations [37].

Percent removal of Pb²⁺ ions from the aqueous solution (50 ml, pH 11) using 0.2 to 1.4 g of

Ikpoba clay is shown in Fig. 2. The effect of adsorbent dosage on the uptake of Pb(II) by Ikpoba clay was studied for initial concentration of Pb(II) = 20 mg/l. It is found that the removal of Pb(II) by Ikpoba clay increases with an increase in the adsorbent dose. Increase in percentage removal of Pb(II) with the adsorbent dosage could be attributed to increase in the adsorbent surface areas, augmenting the number of adsorption sites available for adsorption, as reported elsewhere [38].

It is also found that any further addition of the adsorbent beyond 1 g did not cause any significant change in the adsorption. This may be due to overlapping of adsorption sites as a result of over-crowding of adsorbent particles.

The highest percentage removal of 84 is rather low. This may however be due to the low specific surface area (8.6932 m²/g) of the clay sample used. This low specific surface area and hence poor adsorption efficiency is usually improved by activation or modification of kaolinitic clays as shown in other studies [39,40].

Table 5. Chemical composition (%) of Ikpoba clay

Sample	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	P ₂ O ₅	MnO	K ₂ O	Cr ₂ O ₃	CaO	TiO ₂	ZnO
Ikpoba clay	78.65	15.17	3.49	0.62	0.02	0.27	0.01	0.14	1.57	0.06

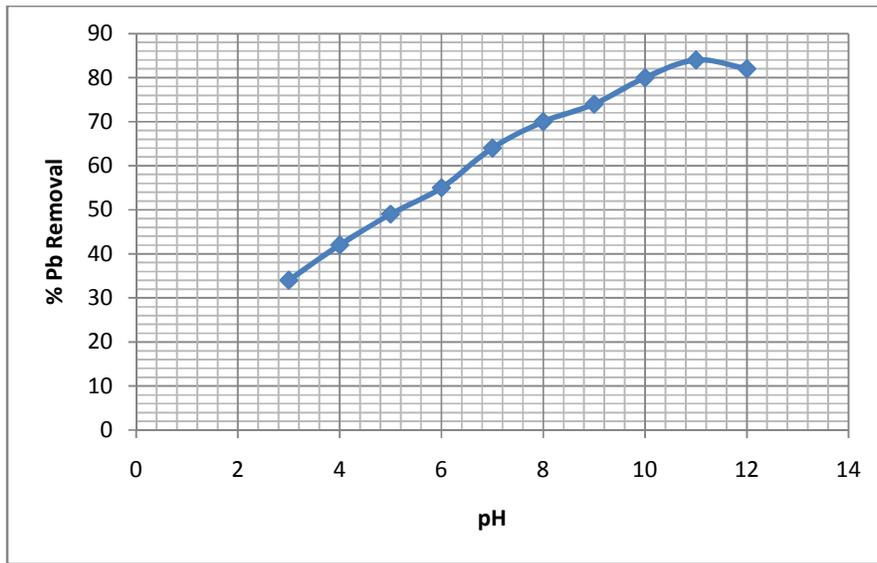


Fig. 1. Effect of pH of solution on adsorption of Pb(II) onto Ikpoba clay (adsorbent dosage= 0.80 g, initial Pb(II) concentration 20 mg/l, contact time of 2 hrs and temperature 25°C)

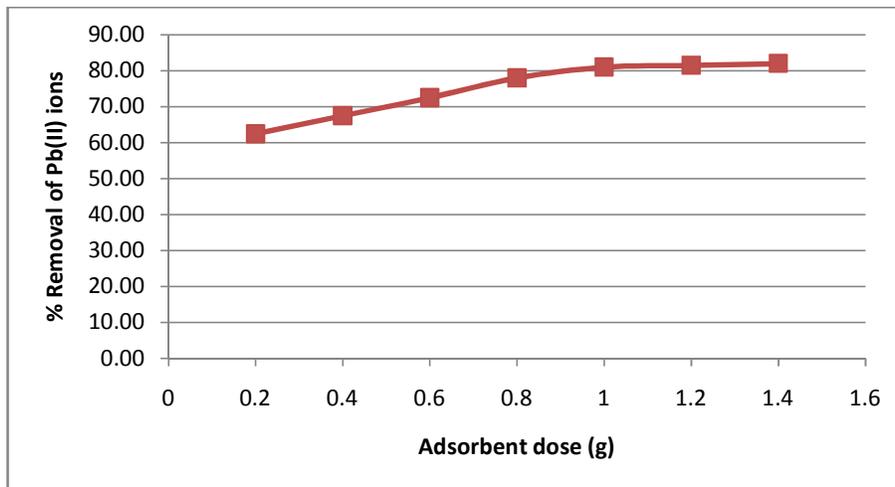


Fig. 2. Effect of adsorbent dosage on adsorption of Pb(II) onto Ikpoba clay: pH 11, initial Pb(II) concentration 20 mg/l, contact time 2 hrs and temperature 25°C

Percent removal of Pb(II) from the aqueous solutions (50 ml, pH 11) in the concentration range of 10 to 60 mg/l is shown in Fig. 3. The percentage removal is seen to be decreasing as concentration increases from 20 to 60 mg/l at constant adsorbent dosage level of 0.6 g. This effect can be explained as follows: with a high metal ion/adsorbent ratio increases, the higher energy sites are saturated and adsorption begins on lower energy sites, resulting in decreases in the adsorption efficiency [41].

Fig. 4 shows the percent removal of Pb^{2+} ions from the aqueous solution (50 ml, pH 11) using 0.8 g of Ikpoba clay as adsorbent with the contact time varied from 5 to 120 minutes at 300 rpm. It is seen that as the contact time increases from 5 to 120 minutes the percent removal of the Pb(II) increased from 5-60 mins and then it was constant. By increasing the agitation time, the boundary layer resistance will be reduced and there will be an increase in the mobility of ions in the solution [42].

Table 6 shows the error functions corresponding to the minimized deviations between the experimental equilibrium data and the predicted isotherms suggested. Non-linear optimization method was used to determine the isotherm model parameters as listed in Table 3. The parameters were determined by minimizing five non-linear statistics: HYBRID, MPSD, ERRSQ, ARE and EABS as described by Allen et al. [43]. Since the application of these five different error methods will produce different isotherm parameter sets, it is difficult to directly identify an

overall optimum parameter set. A standard procedure normalizing and combining various errors for better and meaningful comparison between the parameter sets (for single isotherm model) was adopted resulting in a so-called 'sum of normalized errors (SNE)' as used by researchers elsewhere [25]. This method allows a direct comparison of the scaled errors and hence identifies the isotherm parameters that would provide the closest fit to the measured data.

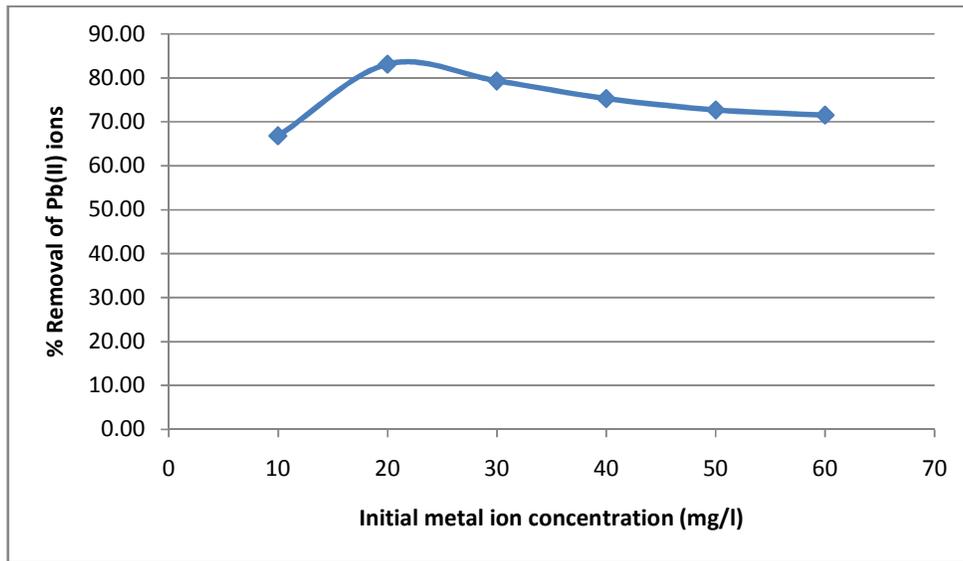


Fig. 3. Effect of initial concentration on the adsorption of Pb(II) by Ikpoba clay: pH 11, adsorbent dose 0.8g, contact time 2 hrs and temperature 25°C.

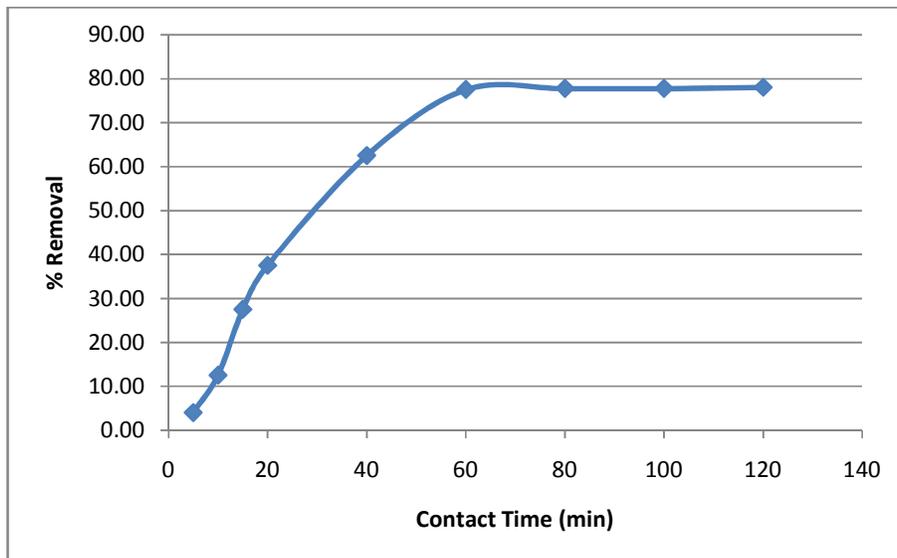


Fig. 4. Time dependent study of the sorption of Pb(II) on Ikpoba clay using 0.8 g adsorbent dose.; pH 11, initial Pb(II) concentration 20 mg/l and temperature 25°C

Table 6. Predicted isotherms by minimizing the error distributions using sorption onto Ikpoba clay four different error functions for lead (II)

Isotherm	Constants	Error function					
		ARE	EABS	ERRSQ	HYBRID	MPSD	SNE
Langmuir	Q _{max} (mg/g)	45.81361	41.12635	183.889	125.7845	108.4185	0.0139
	K _L (l/mg)	0.01241	0.014629	0.003023	0.004447	0.005164	
OF		0.1135	0.3926	0.00473	0.1154	0.1055	
Freundlich	K _F (mg ¹⁻ⁿ g ⁻¹ l ⁿ)	0.54536	0.545386	0.559137	0.5538	0.550387	0.3098
	n	1.004924	1.004865	1.014699	1.009384	1.00555	
OF		0.0418	0.1056	0.00538	0.0938	0.0652	
Sips	Q _{max} (mg/g)	19.66814	21.49124	23.42727	33.38511	33.58852	0.0108
	K _s (mg/l) ^{-1/n}	0.024468	0.022695	0.021284	0.015527	0.015522	
	n	0.844002	0.857787	0.873847	0.915867	0.919485	
OF		0.0529	0.0896	0.00295	0.0631	0.0634	
Redlich-Peterson	K _j (l/mg)	0.544047	0.543918	0.556	0.552091	0.549986	0.5524
	α _L (mg/l) ^{-1/n}	0.001151	0.001022	0.003645	0.002301	0.00191	
	β	0.887	0.924	0.900664	0.933738	0.875082	
OF		0.0419	0.1054	0.00479	0.0872	0.0633	

Freundlich had the best fit to experimental data based on ARE error function with a value of 0.0416. Also, on the basis of MPSD error function, Redlich-Peterson had the best fit to experimental data with a value of 0.00633; and on the basis of EABS, ERRSQ and HYBRID error functions, Sips isotherm had the best fit to experimental data for Pb(II) adsorption onto Ikpoba clay with respective values of 0.0896, 0.00295 and 0.0631. Sum of normalized errors (SNE) was obtained and used as an indicator of which isotherm had the overall best fit to the experimental equilibrium data. Sips isotherm gave the overall best fit to experimental data for Pb(II) adsorption onto Ikpoba as it was observed to have the least SNE value of 0.0108. This implies that at low sorbate concentrations it effectively reduces to a Freundlich isotherm and thus does not obey Henry's law. At high sorbate concentrations, it predicts a monolayer sorption capacity which is characteristic of the Langmuir isotherm.

The R^2 values obtained were 0.7845 for pseudo-first order; 0.9887 for pseudo-second order; 0.6340 Elovich; 0.7043 for intraparticle diffusion for varying initial concentrations of Pb(II) as seen in Table 7. Their respective SEE values were 0.195 for Pseudo-first order; 3.22×10^{-6} for Pseudo-second order; 0.2475 for Elovich and 0.0574 for Intraparticle diffusion for varying initial concentrations of Pb(II). The pseudo-second order kinetic model best fits the data as it had the lowest error value (SEE) of 3.22×10^{-6} . This implies that the rate limiting step is chemical adsorption (chemisorption) and not mass transport.

The differences of the R^2 and the SEE values could be clearly shown for pseudo-first-order kinetic model and intraparticle diffusion. At R^2 value of 0.8614, the SEE was 0.0271, meanwhile at R^2 value of 0.7845 the SEE value was 0.1995; while at R^2 value of 0.7043, the SEE value was 0.0574 for intraparticle diffusion. These results further underscore the need to consider error function values in establishing a model.

Table 7. Kinetic model parameters obtained using the nonlinear methods

Kinetic models	Parameters	
Pseudo first order	K ₁ (min ⁻¹)	0.2054
	q _e (mg g ⁻¹)	4.7968
	R ²	0.7845
Pseudo second order	SEE	0.1995
	K ₂ (g mg ⁻¹ min ⁻¹)	0.089
	q _e (mg g ⁻¹)	5.0000
	R ²	0.9887
Elovich	SEE	3.22E-06
	β (gmg ⁻¹)	2.5
	α(mgg ⁻¹ min)	45783.2
	R ²	0.6340
Intraparticle diffusion:	SEE	0.2475
	K _p (mgg ⁻¹ min ^{-1/2})	0.0765
	C(mgg ⁻¹)	5.54
	R ²	0.7043
	SEE	0.0574

4. CONCLUSION

The equilibrium adsorption and kinetics of Pb(II) ions by Ikpoba clay has been reported. The adsorption of Pb(II) ions onto the Ikpoba clay is

found to be dependent on the initial metal ion concentration, solution pH, adsorbent dose and contact time.

The equilibrium results have been modelled and evaluated using four different isotherms, Langmuir, Freundlich, Sips and Redlich-Peterson. Non-linear optimization method was used to determine the isotherm model that best describes the data by minimizing six different error functions, ARE, EABS, ERRSQ, HYBRID, MPSD and SNE. Sips isotherm was found to best-fit the equilibrium data for adsorption of Pb(II) ions onto Ikpoba clay within the experimental range.

Four kinetic models fitted were pseudo-first order, pseudo-second-order, Elovich and intraparticle diffusion. The pseudo-second order model gave the best fit to the kinetic data.

The adsorption efficiency of adsorbent was rather low, hence there is need to subject it to activation (chemical or thermal) to increase its adsorption efficiency.

COMPETING INTERESTS

Author has declared that no competing interests exist.

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