
ADSORPTION STUDIES FOR THE REMOVAL OF CU (II) AND PB (II) FROM AQUEOUS SOLUTION BY LOCAL ADSORBENT USING NONLINEAR REGRESSION METHODS

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Abstract: The sorption of two divalent metal ions - copper and lead - from aqueous solution onto Ikpoba clay in single component systems has been studied. Batch adsorption study for the clay fraction was conducted at ambient temperature, using <0.02mm particle sizes. The experimental data have been analysed using the Langmuir, Freundlich, Redlich-Peterson, Toth and Sips isotherm models. In order to determine the best fit isotherm for each system, five error analysis methods were used to evaluate the data: 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). However, the sum of normalized error (SNE) was further employed in order to have a better comparison between the error functions sets for the isotherm models. The error values indicated that the Sips isotherm was able to provide the best quality of fit for all the experimental data, over the concentration range (3-6 mg/L) studied for Cu(II) with error values of 13.9609, 0.3104, 0.0025, 2.9965, 0.1220 and 0.2111 for ARE, EABS, ERRSQ, HYBRID, MPSD and SNE respectively; while Toth isotherm gave the best quality of fit for all the experimental data, over the concentration range (20-40 mg/L) studied for Pb(II) with error values of 19.9202, 0.4070, 0.0469, 6.0984, 0.2316, 0.33072 for ARE, EABS, ERRSQ, HYBRID, MPSD and SNE respectively.

Keywords: Isotherms, Error-functions, Sorption, nonlinear regression, heavy metal

INTRODUCTION

The removal of heavy metals from water and wastewater is important in terms of protecting public health and environment ^[1]. A number of conventional treatment technologies have been considered for treatment of wastewater contaminated with organic substances. Precipitation, ion-exchange, phytoextraction, ultrafiltration, membrane separation and adsorption are the usual methods for the removal of heavy metal ions from aqueous solution ^[2]. Due to its simplicity and easy operational conditions, adsorption is a widely-used process ^[3]. Activated carbon has been the most employed adsorbent for heavy metal removal from aqueous solution, but it is however expensive ^[4]. The interest on cheaper and more efficient adsorbents is mounting, causing increased research to be conducted on adsorption ^[5]. 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 ^[6,7, 8, 9]. Sorption equilibria provide fundamental physicochemical data for evaluating the applicability of sorption processes as a unit operation. Sorption equilibrium is usually described by an isotherm equation whose parameters express the surface properties and affinity of the sorbent at a fixed temperature and pH. Thus an accurate mathematical description of the equilibrium isotherm, preferably based on a correct sorption mechanism is essential to the effective design of sorption systems ^[10]. Until relatively recently, the quality of the isotherm fit to the experimental data was assessed based on the magnitude of the correlation coefficient for the linear regression and the isotherm giving an

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R^2 value closest to unity was deemed to provide the best-fit. However, the linearization of adsorption isotherm equations using such data transformations would implicitly alter the error structure and could also violate the error variance and normality assumptions of standard least squares^[11]. As an alternative to the linear transformation, non-linear optimization has also been applied by various researchers^[10,11,12,13,14,15,16,17] to determine isotherm parameter values which require an error function assessment, in order to evaluate the fit of the isotherm to the experimental results for the removal of variety of components from the aqueous environment. For the present study, the Freundlich, Langmuir, Redlich-Peterson, Sips and Toth adsorption isotherms were examined for lead ion and copper ion sorption onto Ikpoba clay for their ability to model the equilibrium sorption data at a fixed temperature of 288 K and pH of 11. In this study, 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 [18]. The Freundlich, Langmuir, Redlich-Peterson, Sips and Toth isotherms were examined for their ability to model the equilibrium sorption data.

MATERIALS AND METHODS

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 4.0 kg of sample was collected and placed in small polythene bag and then dried at 80°C for 24h, pulverized and sieved to geometric mean size of <0.02 mm before analysis.

Preparation of Stock Solution

The salts used for the preparation of the aqueous solutions were: Lead (II) Nitrate and Copper (II) Sulphate. Stock solutions of 1000mg/L each of Cu(II) and Pb(II) were prepared by dissolving reagent grade CuSO_4 and $\text{Pb}(\text{NO}_3)_2$ in distilled water. Other chemicals used were: sodium hydroxide and trioxonitrate (V) acid. All reagents used were of analytical grade. Distilled water was used for preparing stock solutions and dilution.

Characterization of Ikpoba Clay

The pore size distribution and specific surface area of the Ikpoba clay samples were carried by N_2 adsorption using Micromeritics instrument (Tristar 3000) and by using Brunauer-Emmett-Teller (BET) method, using the software of Micromeritics. The specific surface area of Ikpoba clay was determined from the Brunauer, Emmett and Teller (BET) multipoint method^[19] and the pore size distribution were obtained using Barret, Joyner, and Halenda (BJH) method^[20]. This was carried out by N_2 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 (cm^3/g). The cation exchange capacity (CEC) was determined by the procedure described by Mclean and Pratt^[21]. The mineralogical composition of the clay was obtained by XRD studies (PAN analytical X'Pert PRO MPD, PW 3040/60) using the K α radiation of Cu.

Batch Equilibrium Experiments and Analytical Method

The pH of solutions were adjusted to 11 by adding HNO₃ and NaOH aqueous solutions to Cu(II) and Pb(II) solution. This was monitored using pH meter (Suntex, model SP-701). Adsorption was performed in batch experiments where 50 mL of Pb(II) solutions in the concentration range of 20-40mg/L was added to 0.4 g of Ikpoba clay (size <0.02mm) in conical flasks and mixed with rotary shaker (optima model 08-752) at 300 rpm, 298K for 120 minutes. Solution and clay were separated by filtering through a filter paper (Whatmann no. 42). Adsorption was monitored at each selected concentration. Similar process was performed for Cu(II) in the concentration range of 3-6 mg/L The residual metallic ion concentrations were determined using an Atomic Absorption Spectrophotometer (Buck scientific, model 210 VGP). A duplicate was analyzed for every sample to track experimental error and show capability of reproducing results^[22]. The amount of the metal ion sorbed by the adsorbent was calculated by applying the Equation (1):

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

Where q_e is the specific uptake in mg/g at equilibrium, C_0 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.

Adsorption Isotherms Modeling

The isotherms models of Langmuir^[23], Freundlich^[24], Redlich-Peterson^[25], Sips^[26] and Toth^[27] were fitted to describe the equilibrium adsorption.

The equations of isotherms are given below:

$$\text{Langmuir isotherm: } q_e = \frac{Q_{max} K_L C_e}{1 + K_L C_e} \quad (2)$$

Where C_e is the supernatant concentration after the equilibrium of the system (mg L⁻¹), K_L the Langmuir affinity constant (L mg⁻¹), and Q_{max} is the maximum adsorption capacity of the material (mg g⁻¹) assuming a monolayer of adsorbate uptaken by the adsorbent:

$$\text{Freundlich isotherm: } q_e = K_F C_e^{1/n} \quad (3)$$

Where K_F is the Freundlich constant related with adsorption capacity [mg g⁻¹ (mg L⁻¹)^{-1/n}] and n is the Freundlich exponent (dimensionless)

$$\text{Sips isotherm: } q_e = \frac{Q_{max} K_s C_e^{1/n}}{1 + K_s C_e^{1/n}} \quad (4)$$

Where K_s is the Sips constant related with affinity constant (mg L⁻¹)^{-1/n}, Q_{max} is the Sips maximum adsorption capacity (mg g⁻¹), and n is the Sips exponent (dimensionless).

$$\text{Redlich-Peterson isotherm: } q_e = \frac{K_i C_e}{1 + \alpha_L C_e^\beta} \quad (5)$$

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where K_i (L/g), α_L (L/mg) and β are the isotherm parameters. It has two limiting cases: when $\beta=1$, the isotherm reduces to Langmuir type; and when $\beta=0$, the isotherm transform into a Henry's law equation.

$$\text{Toth isotherm: } q_e = \frac{aC_e}{[b+(C_e)^d]^{1/d}}, 0 < d \leq 1 \quad (6)$$

Where where a is the adsorbed amount (mg g^{-1}), b the adsorptive potential constant (mg L^{-1})^d and d characterizes the heterogeneity coefficient of the adsorbent. If surface is homogeneous, then $d = 1$, so the Toth equation reduces to the Langmuir equation.

Validity of Adsorption Isotherm- Error Functions

Due to the inherent bias resulting from linearization, isotherm parameters were determined by nonlinear regression. This provides a mathematically rigorous method for determining isotherm parameters using the original form of the isotherm equation^[10,12]. In this study, five non-linear error functions were employed for the determination of isotherm parameters. Similar error functions were used by Allen *et al*^[16]. A derivative of Marquardt's Percent Standard Deviation (MPSD)^[28], a composite fractional error function (HYBRID)^[29], average relative error (ARE)^[30], the Sum of the Squares of the Errors (ERRSQ)^[31] and the sum of the absolute errors (EABS)^[17] were also used to measure the goodness-of-fit to the isotherm models. MPSD, HYBRID, ARE, ERRSQ and EABS can be defined as:

$$MPSD = 100 \sum_{i=1}^n \left(\frac{q_{e,meas} - q_{e,calc}}{q_{e,meas}} \right)_i^2 \quad (7)$$

$$HYBRID = \frac{100}{n-p} \sum_{i=1}^n \left[\frac{(q_{e,meas} - q_{e,calc})^2}{q_{e,meas}} \right]_i \quad (8)$$

$$ARE = \frac{100}{n} \sum_{i=1}^n \left| \frac{q_{e,meas} - q_{e,calc}}{q_{e,meas}} \right| \quad (9)$$

$$ERRSQ = \sum_{i=1}^n (q_{e,meas} - q_{e,calc})_i^2 \quad (10)$$

$$EABS = \sum_{i=1}^n |q_{e,meas} - q_{e,calc}|_i \quad (11)$$

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 the single isotherm model) was adopted resulting in a so-called 'sum of the normalised errors (SNE)' as used by researchers elsewhere^[17, 31, 32, 33]. This method allows a direct comparison of the scaled errors and hence identifies the isotherm parameter that would provide the closest fit to the measured data. In the normalization process, each error function was selected and the results for each parameter set were determined. Secondly, the errors determined for a given error function were divided by the maximum error to obtain the normalized errors for each parameter set. Lastly, the normalized errors for each parameter

set were summed up. This method allows a direct comparison of the scaled errors and hence identifies the isotherm parameter that would provide the closest fit to the measured data.

RESULTS AND DISCUSSION

RESULTS

Table 1: Physico-chemical properties of Ikpoba clay

PARAMETERS	IKPOBA CLAY
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

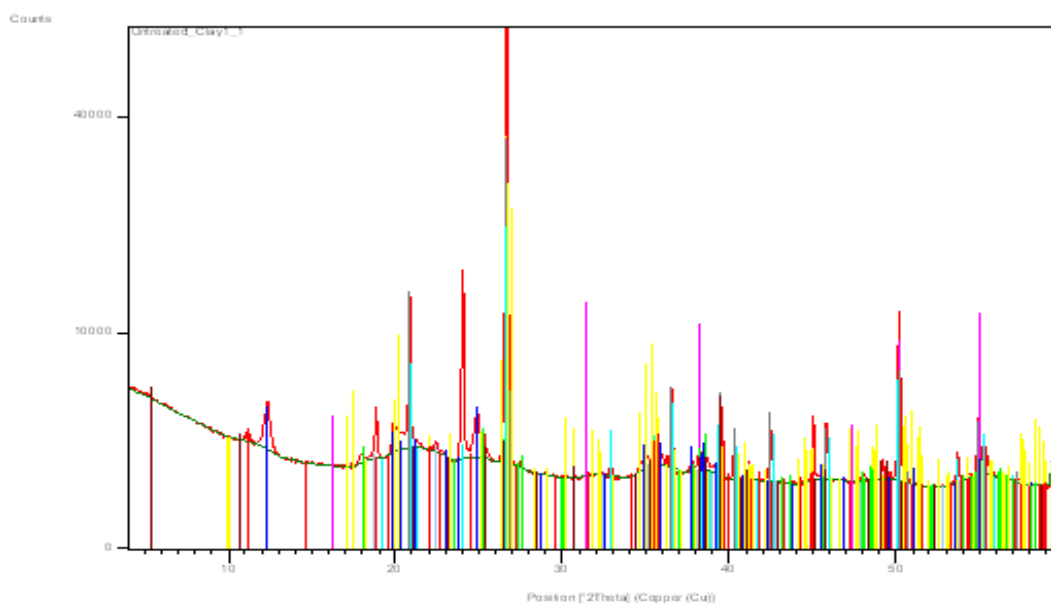


Figure 1: XRD Patterns for Ikpoba Clay

Table 2: Mineralogical composition of Ikpoba clay

Mineral	Ikpoba clay Composition (%)
Kaolinite (Al ₂ Si ₂ O ₅ (OH) ₄)	29.84
Quartz	27.42
Anatase (TiO ₂)	14.11
Mn ₂ O ₃	8.48
Fe(TiO ₃)	11.69
Violarite (FeNi ₂ SO ₄)	8.46

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Table 3a: Isotherm Constants for Cu (II) Adsorption

Isotherm	Constants	ERROR FUNCTION				
		ARE	EABS	ERRSQ	HYBRID	MPSD
Langmuir	Q _{max}	1.4726	1.5603	1.2276	1.3000	1.2000
	K _L	1.2078	1.1200	1.8466	2.0300	2.5000
Freundlich	N	3.06014	2.0938	2.3178	2.793706	3.4534
	K _F	0.6499	0.8161	0.7716	0.723241	0.6499
Redlich-Peterson	K _j	51.5180	51.1634	55.4000	57.5000	53.4000
	α _L	63.2439	63.5368	64.5000	77.4200	65.7000
	β	0.60175	0.4228	0.5686	0.6426	0.7185
Sips	K _s	0.0081	0.0104	0.0094	0.0086	0.0074
	Q _{max}	81.9796	80.0010	83.0000	85.0000	87.9988
	N	2.8278	2.3042	2.3046	2.7814	3.4411
Toth	a	101.2300	98.4502	100.0002	100.0022	100.0090
	b	0.7327	0.6222	0.8374	0.4752	0.3502
	d	0.1144	0.1002	0.1260	0.0786	0.0593

Table 3b: Isotherm Constants for Pb(II) Adsorption

Isotherm	Constants	ERROR FUNCTION				
		ARE	EABS	ERRSQ	HYBRID	MPSD
Langmuir	Q _{max}	1.5223	2.1373	1.8588	1.3394	1.4500
	K _L	1.7820	1.1667	1.4524	2.6811	2.4000
Freundlich	N	2.7168	1.4693	1.8689	2.4130	3.4326
	K _F	0.8246	1.1961	1.0968	0.9516	0.7510
Redlich-Peterson	K _j	27.7249	59.6851	53.5600	51.2100	49.7600
	α _L	32.2315	49.8273	61.2400	53.4500	51.2400
	β	0.6465	0.4209	0.4642	0.5835	0.5430
Sips	K _s	0.0770	0.0104	0.0094	0.0086	0.0074
	Q _{max}	78.0000	80.0010	83.0001	85.0001	87.9988
	N	0.1144	2.3042	2.3046	2.7814	3.4412
Toth	a	80.9697	80.0940	80.0944	80.0969	80.1114
	b	0.6763	0.9548	0.9557	0.5519	0.3305
	d	0.1138	0.1580	0.1557	0.0980	0.0604

Table 4a: Error values for Various Isotherms for Cu(II) Adsorption onto Ikpoba Clay

Heavy Metal	Error Function	Langmuir	Freundlich	Redlich-Peterson	Sips	Toth
Cu(II)	ARE	29.895	12.5447	17.4956	13.9609	19.8974
	EABS	0.4417	0.3145	0.3120	0.3104	0.3497
	ERRSQ	0.0699	0.0247	0.0392	0.0025	0.0337
	HYBRID	8.5804	1.9851	3.4933	2.9965	3.5212
	MPSD	0.8341	0.1215	0.3500	0.1220	0.1372
SNE		25.183	5.0059	0.3326	0.2111	0.2370

Table 4b: Error values for Various Isotherms for Pb(II) Adsorption onto Ikpoba Clay

Heavy Metal	Error Function	Langmuir	Freundlich	Redlich- Peterson	Sips	Toth
Pb(II)	ARE	29.4980	17.1620	19.3758	79.9557	19.9202
	EABS	0.4333	0.3322	0.3620	0.4977	0.4070
	ERRSQ	0.0712	0.03822	0.1235	0.1413	0.0469
	HYBRID	8.1260	3.4088	6.1760	9.4699	6.0984
	MPSD	0.8803	0.2088	0.4293	0.2922	0.2316
	SNE	20.192	8.0371	0.7333	1.1477	0.33072

DISCUSSION

Adsorbent characterization

Table 2 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 $8.6932\text{m}^2/\text{g}$, the average pore diameter was 26.22612nm and pore volume was $0.101267\text{cm}^3/\text{g}$. As observed, the surface area for the clay is relatively low; below the range of 10 to $20\text{m}^2/\text{g}$ established for kaolinite^[34, 35,36]. This may be due to the high quartz content of the clay. The CEC was also observed to be low ($4.8\text{meq}/100\text{g}$). This is however within the range of values of 3 and $15\text{meq}/100\text{g}$ for Kaolinite given elsewhere^[37]. With a pore diameter of 26.22612nm , the clay sample is mesoporous based on IUPAC classification^[38]; thus its rather low pore volume of $0.101267\text{cm}^3/\text{g}$ is understandable. From XRD analysis presented in Table 1 and Figure 1, the results show that kaolinite has the highest percentage of 29.84 while the lowest mineral in the clay was Violarite with 8.47% . The kaolinite mineral content (29.84%) obtained is much less than the percentage reported for Kaolinitic clay from elsewhere^[39, 40]; in the same context, the high percentage (27.42%) of free quartz is comparable to the value recorded in the literature for free quartz of Kalabsha^[41].

Adsorption Isotherms

The analysis of the equilibrium data by fitting them onto different isotherm models is an important step to find the suitable model that can be used for design process. The used isotherm equations used are: Langmuir; Freundlich, Redlich-Peterson, Sips and Toth. Non-linear optimization method was used to determine the isotherm model parameters as listed in Tables 3a and 4b. The parameters were determined by minimizing five non-linear statistics: HYBRID, MPSD, ERRSQ, ARE and EABS as described by Allen *et al.*^[16]. Sum of normalized errors (SNE) was obtained and used as an indicator as to which isotherm had the best fit to experimental equilibrium data. Tables 4a and 4b show a summary of the errors associated with the five isotherm models studied. Tables 3a and 3b show the Langmuir, Freundlich, Redlich-Peterson, Toth and Sips parameters for Cu(II) and Pb(II) adsorption. Langmuir isotherm has the worst fit to experimental data for both Cu(II) and Pb(II) adsorption as it can be observed to have the largest SNE values as shown in Table 4a and 4b. Freundlich had the best fit to experimental data for both Cu(II) and Pb(II) adsorption based on ARE, ERRSQ, HYBRID and MPSD, and also best fit for Pb(II) adsorption based on EABS. It was however noticed that Freundlich isotherm generally gave a relatively poor fit to experimental data for both Cu(II) and Pb(II) adsorption as can be observed from the relatively large SNE values in Table 4a and 4b. Sips isotherm gave the best fit to experimental data for Cu(II) adsorption based on EABS; it was also observed that Sips isotherm generally gave the best fit to experimental data for Cu(II) adsorption as it was observed to have the least SNE value in Table 4a. Toth isotherm generally gave the best fit to experimental data for Pb(II) adsorption as it was observed to have

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the least SNE value in Table 4b. The Redlich-Peterson isotherm was found to provide the second best fit to the experimental data for both Cu(II) and Pb(II). Minimization of ERRSQ error resulted in better determination of all parameters for all five isotherms for both Cu(II) and Pb(II) as can be observed from Tables 4a and 4b. In the present study, based on the sum of normalized errors (SNE), the quality of the isotherm fit can be arranged in order of increasing weightage of the errors as: Sips<Toth<Redlich-Peterson<Freundlich<Langmuir for Cu(II) adsorption, and for Pb(II), Toth< Redlich-Peterson<Sips< Freundlich<Langmuir for Pb(II)

CONCLUSIONS

A detailed error analysis was carried out to determine the best isotherm models for sets of equilibrium sorption data for Pb(II) and Cu(II) onto Ikpoba clay. The optimum isotherm-error function combination was identified using the sum of normalised errors. Regarding the results presented for the both the two parameter and three parameter isotherms examined, several comments can be made:

- The ERRSQ error function generally produced the best fit isotherm parameter values for the two parameter isotherms examined.
- The Redlich-Peterson isotherm was found to provide the second best fit to the experimental data for both Cu(II) and Pb(II).
- Three-parameter isotherm models (Toth and Sips) respectively fitted the Cu(II) and Pb(II) adsorption equilibrium data better than the two-parameter isotherm models.
- The Freundlich isotherm model fitted the equilibrium data better than Langmuir isotherm model, revealing that the adsorption of Cu(II) and Pb(II) onto the Ikpoba clay was multilayer adsorption.

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