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Isotherm and Kinetic Studies on Adsorption of Pb, Zn and Cu by Kaolinite

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ABSTRACT

The feasibility of kaolinite used as a low-cost adsorbent for the removal of Pb(II), Zn(II) and Cu(II) from aqueous solutions was investigated. During the removal process, batch technique was used, and the effects of heavy metal concentration and contact time on adsorption efficiency at pH of 4.5, under a constant temperature of 20±1 °C were studied. The experimental results were analyzed using four adsorption isotherm models; Freundlich, Langmuir, Temkin and Redlich-Peterson. Evaluating the correlation coefficients showed that the Redlich-Peterson isotherm described the data appropriate than others. The adsorption capacities (q_m) from the Langmuir isotherm for Pb(II), Zn(II) and Cu(II) are found as 7.75 mg/g, 4.95 mg/g and 4.42 mg/g respectively. The effectiveness of kaolinite in the sorption of the three metals from aqueous system was Pb(II) > Zn(II) > Cu(II). Kinetic studies showed that a pseudo-second order model was more suitable than the pseudo first order model. It is concluded that kaolinite can be used as an effective adsorbent for removing Pb(II), Zn(II) and Cu(II) from aqueous solutions.

Keywords: Adsorption, Batch technique, Heavy metal ions, Kaolinite, Kinetic.

INTRODUCTION

Heavy metals in the environment are a source of some concern because of their potential reactivity, toxicity, and mobility in the soil. Some heavy metals (e.g., Cu and Zn) are essential for plant and animal health. However, at environmental concentrations above those necessary to sustain life, toxicity may occur. Other heavy metals (e.g., Cd and Pb) are not known to be essential to plants and animals. Toxicity may occur when these metals become concentrated in the environment above background levels (Selim and Amacher, 1997). According to World Health Organization (WHO), the metals of most immediate concern are chromium, copper, zinc, iron, cadmium and lead (WHO, 1984). In order to solve the problems of heavy metal pollution in the environmental, it is important to bring pragmatic solutions to the issue.

There are several methods for treatment of metal contaminated effluents such as chemical precipitation (Jüttner *et al.*, 2000; Bose *et al.*, 2002; Wingenfelder *et al.*, 2005),

coagulation-flocculation (Shammas *et al.*, 2004; Semerjian and Ayoub, 2003; Ayoub *et al.*, 2001), reverse osmosis (Metcalf and Eddy, 2003), ultra-filtration (Eckenfelder, 2000), electro-dialysis (Metcalf and Eddy, 2003), flotation (Jokela and Keskitalo, 1999; Matis *et al.*, 2003), ion exchange (Eckenfelder, 2000) and membrane processes (Yang *et al.*, 2001). They have their inherent advantages and limitations in application.

Among the physicochemical treatment processes for pollutant removal, adsorption is highly efficient, inexpensive and easy to adapt (Bhattacharya *et al.*, 2006). Clay minerals are copious in nature, cost less, have a high specific surface area and exchange capacity and hence are strong candidates as adsorbents for the removal of heavy metals from wastewaters. The removal of heavy metals using different types of clay has been the subject of several recent studies (see for example Singh *et al.*, 2001; Potgieter *et al.*, 2006; Al-Jlil and Alsewailem, 2009;

Bhattacharyya and Gupta, 2008; Chantawong *et al.*, 2003; Zhu *et al.*, 2008).

This study investigated the feasibility of kaolinite used as a low-cost adsorbent for the removal of Pb(II), Cu(II) and Zn(II) from aqueous solution. The sorption capacity of kaolinite was evaluated using four equilibrium isotherm models (Freundlich, Langmuir, Temkin and Redlich-Peterson isotherm models) and the sorption dynamics were analyzed using pseudo first order and pseudo second order kinetic models.

MATERIALS AND METHODS

Materials

The materials used in this study are kaolinite (from the Iran china clay industries Co.) and chemical materials such

as solutions and reagents. Kaolinite was used as the adsorbent. The chemical composition and some physical properties of kaolinite are presented in Table 1. The molecular structure of kaolinite is sketched in Figure 1 (Vimonses *et al.*, 2009). Its structural formula is $\text{Al}_2\text{Si}_2\text{O}_5\text{OH}_4$. The elements contained in pure kaolinite are arranged to form one silica sheet and one alumina sheet (Bohn *et al.*, 1985; Sposito, 1989; Yong *et al.*, 1992). Solutions of selected heavy metals (lead, copper and zinc) were used as the adsorbate for batch adsorption experiments. With reference to the soil profile and groundwater contamination, a low pH for solution was chosen. Accordingly, hydrochloric acid was used to adjust the pH of each solution to 4.5.

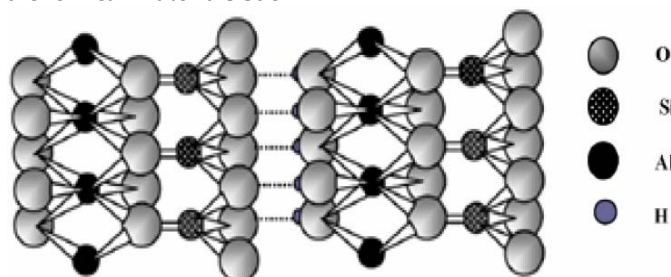


Fig 1. Molecular structure of kaolinite (Vimonses *et al.*, 2009).

Table 1. The chemical composition and some physical properties of kaolinite used in the present study

Constituents	Quantity(%)
Al_2O_3	38.60
SiO_2	45.71
Fe_2O_3	0.38
TiO_2	1.15
CaO	0.10
MgO	0.34
Na_2O	0.31
K_2O	0.10
Loss on ignition	13.31
Cation exchange capacity	8 meq/100g
Mean particle size	59×10^{-4} cm
Surface area	$12.76 \text{ m}^2/\text{g}$
Porosity	0.42
Density	$1.49 \text{ g}/\text{cm}^3$

Batch Adsorption Experiments

Suspensions were prepared on dry solid basis into a uniform powdery texture and mixed with various concentrations of metal solutions. The initial concentration of Pb, Cu and Zn solutions were selected as 50, 200, 500, 1000, and 2000 mgL^{-1} . These metal concentrations were selected to cover a wide range most commonly found in sewage

sludge, some industrial wastes, and municipal solid wastes. The solutions of heavy metals were applied to the kaolinite at 1:10 (solid: solution ratio); i.e., 40 g of dry kaolinite and 400 mL of solutions. The mixed solutions are mounted on the stirrer plate during experimental period, to prevent any possible sedimentation, and to provide proper agitation. Following agitation, 15 mL

aliquots were removed to determine metal concentrations. Aliquots were then centrifuged at 6000 rpm for 10 minutes. The final metal concentration in the supernatant (or liquid phase) was measured on an AAS. The total initial metal concentration minus the metal concentration in the supernatant was taken as the metal adsorbed by kaolinite. Experiments were conducted at room temperature (20 ± 1 °C), over a range of metal concentrations, keeping the initial pH constant (without replication).

Data Evaluation

The amount of Pb(II), Zn(II) and Cu(II) adsorbed by kaolinite was determined using a mass balance equation expressed in equation 1.

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

where q_e is metal concentration on the kaolinite (mg/g) at equilibrium, C_e is metal concentration in solution (mg/L) at equilibrium, C_0 is initial metal concentration in solution (mg/L), v is volume of initial metal solution used (L), and m is mass of kaolinite used (g).

RESULTS AND DISCUSSION

Effect of Contact Time and Initial Metal Ion Concentration

Contact time is an important parameter because this factor determines the adsorption kinetics of an adsorbate at a given initial concentration of the adsorbate. The effect of contact time on the heavy metal ions adsorption by kaolinite was investigated for 120 hours (Figs. 2, 3 and 4).

The kinetic studies were carried out for different initial concentrations 50, 500 and 2000 mg/L for Pb(II), Zn(II) and Cu(II) ions on kaolinite at 20 ± 1 °C and pH of 4.5. Figures (2-4) show the amount of metal ions adsorbed on kaolinite as a function of time and concentration. A similar trend is observed for three metal ions adsorbed from the aforementioned figures. Also, it can be seen that the adsorbed concentrations are zero at the beginning. Within a short time period they vary considerably and then they end up with a very gradual and quite narrow variation range. The initial rapid phase is due to the presence of large number of vacant sites, leading to increase in concentration gradient between adsorbate in solution and the adsorbent surface. As time proceeds, this concentration is reduced due to the accumulation of metal concentrations on the vacant sites, leading to decrease in gradient the adsorption rate. The time of reaching equilibrium depends on the initial concentration of the metal; i.e. the lower the initial concentration, the shorter the equilibrium time interval. If the initial concentration is about 50 mg/L, the time of reaching equilibrium is about 12 hours. In the case of concentrations of about 500 and 2000 mg/L, the time of reaching equilibrium is about 24 and 48 hours, respectively. Thus, to be conservative in obtaining the equilibrium concentration of adsorbed Pb(II), Zn(II) and Cu(II) ions, a minimum of 48 hours is recommended to keep the test running. It also shows that increases in initial metals ion concentration increased the amount of metal ions uptake per unit weight of kaolinite (mg/g), as was expected.

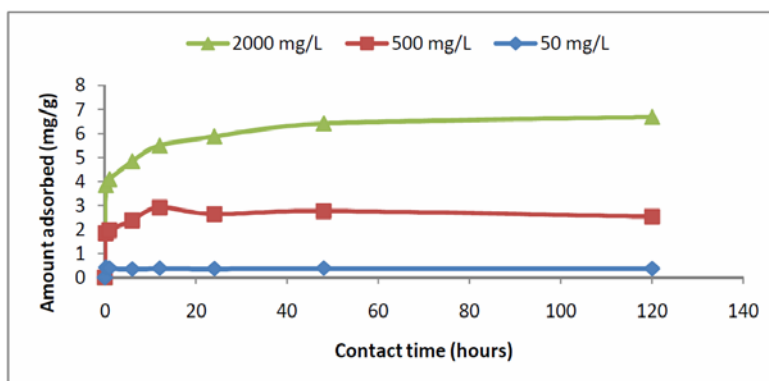


Fig 2. Effect of contact time and initial Pb(II) concentration on the adsorption of Pb(II).

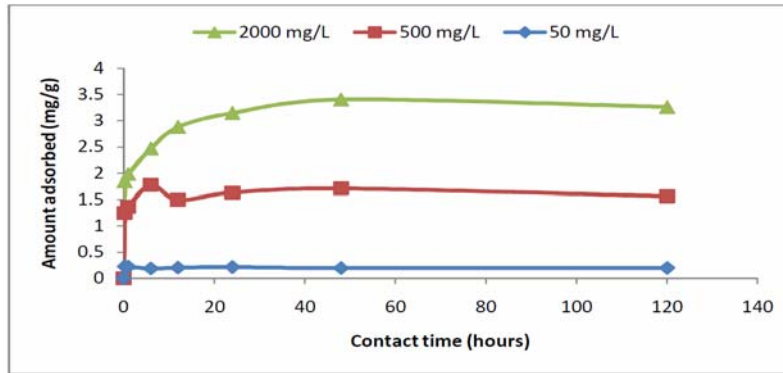


Fig 3. Effect of contact time and initial Zn(II) concentration on the adsorption of Zn(II).

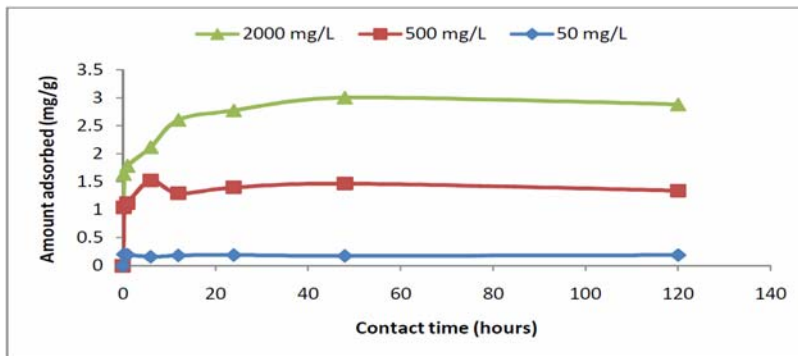


Fig 4. Effect of contact time and initial Cu(II) concentration on the adsorption of Cu(II).

Adsorption Isotherms

Adsorption isotherms are mathematical models that describe the distribution of the adsorbate specie among liquid and solid phases, based on a set of assumptions that are related to the heterogeneity/homogeneity of the solid surface, the type of coverage, and the possibility of interaction between the adsorbate specie. In this study, equilibrium data were analyzed using the Freundlich, Langmuir, Temkin and Redlich-Peterson isotherms expression.

Freundlich Equation

The Freundlich (1906) equation is an empirical equation based on adsorption on a heterogeneous surface. The equation is commonly represented as:

$$q_e = K_F C_e^{1/n} \quad (2)$$

Eq. (2) can be expressed in its linear form as:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (3)$$

Where C_e (mg/L) is the equilibrium concentration and q_e (mg/g) is the amount adsorbed metal ion per unit mass of the adsorbent. The constant n is the Freundlich equation exponent that represents the parameter characterizing quasi-Gaussian energetic heterogeneity of the adsorption surface (Bansal and Goyal, 2005). K_F (L/g) is the Freundlich constant indicative of the relative adsorption capacity of the adsorbent. The Freundlich exponent, n , should have values lying in the range of 1 to 10 for classification as favorable adsorption (citing from Chantawong *et al.*, 2003). The Freundlich model was chosen to estimate the adsorption intensity of the sorbate on the sorbent surface. The experimental data from the batch sorption study of the three metal ions on kaolinite were plotted logarithmically (Figure 5) using the linear Freundlich isotherm equation.

Table 2. Freundlich isotherm parameters.

Metal ions	1/n	K_F (L/g)	r^2
Pb(II)	0.593	0.101	0.983
Zn(II)	0.735	0.019	0.971
Cu(II)	0.730	0.016	0.979

The linear Freundlich isotherm constants for Pb(II), Zn(II) and Cu(II) on kaolinite are presented in Table 2. The Freundlich isotherm parameter $1/n$ measures the adsorption intensity of metal ions on the kaolinite. The high $1/n$ value of Zn(II) (0.735) in relation to Cu(II) (0.730) and Pb(II) (0.593), first indicate the preferential sorption of Zn(II) than Cu(II) and Pb(II) probably due to its smaller ionic radius and secondly shows the ability of the kaolinite to remove these three metal ions from solution even at high concentrations. The ultimate adsorption

capacity K_F , of the adsorbent was calculated from the isothermal linear regression equation. The K_F value of Pb(II) (0.101 L/g) is greater than that of Zn(II) (0.019 L/g) and Cu(II) (0.016 L/g), suggesting and confirming that Pb(II) has greater adsorption tendency towards the kaolinite than the other two metals. This remarkable difference is due to the considerable difference among the hydrated radii of these metals (hydrated radii of Pb(II), Zn(II), and Cu(II) are about 4.5, 6.0, and 6.0 Å, respectively). The smaller the hydrated radius, the higher affinity for adsorption onto the kaolinite.

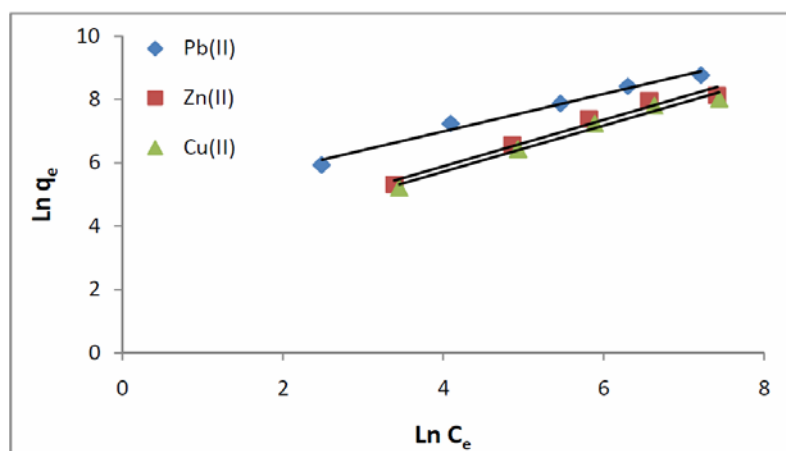


Fig 5. Freundlich equilibrium isotherm model for the sorption of the three metal ions onto kaolinite.

Langmuir Model

The Langmuir (Langmuir, 1918) model assumes that uptake of metal ions occurs on a homogenous surface by monolayer adsorption without any interaction between adsorbed ions. The Langmuir equation may be written as:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (4)$$

Eq. (4) can be expressed in its linear form as:

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \quad (5)$$

where q_e is the amount adsorbed (mg/g), C_e is the equilibrium concentration of the metal ion (mg/L), q_m (mg/g) is the maximum amount of adsorbed metal ion per unit mass of sorbent corresponding to complete coverage of the adsorptive sites, K_L (L/mg) is the Langmuir constant related to the energy of adsorption.

The Langmuir isotherm model was chosen for the estimation of maximum adsorption capacity corresponding to complete monolayer coverage on the kaolinite surface. The plots of specific sorption (C_e/q_e) against the equilibrium concentration (C_e) for Pb(II), Zn(II) and Cu(II) are shown in Figure 6 and the linear isotherm parameters, q_m , K_L and the coefficient of determinations are presented in Table 3. The sorption capacity, q_m , which is a measure of the maximum sorption capacity corresponding to complete monolayer coverage showed that the kaolinite had a mass capacity for Pb²⁺ (7.75 mg/g) than Zn²⁺ (4.95 mg/g) and Cu²⁺ (4.42 mg/g). The adsorption coefficient, K_L that is related to the apparent energy of sorption for Pb²⁺ (3.07×10^{-3} L/g) was greater than that of Zn²⁺ (1.46×10^{-3} L/g) and Cu²⁺ (1.32×10^{-3} L/g). The data in Table 3 further indicated that, the effectiveness of kaolinite in the sorption of the three metals

from an aqueous system was $\text{Pb(II)} > \text{Zn(II)} > \text{Cu(II)}$. This preferential sorption behavior could be explained in terms of ionic radii of the metal ions ($\text{Pb(II)} = 1.19$

Å ; $\text{Zn(II)} = 0.70 \text{ Å}$; $\text{Cu(II)} = 0.57 \text{ Å}$). The element with smaller ionic radius will compete faster for exchange sites than those of larger ionic radius.

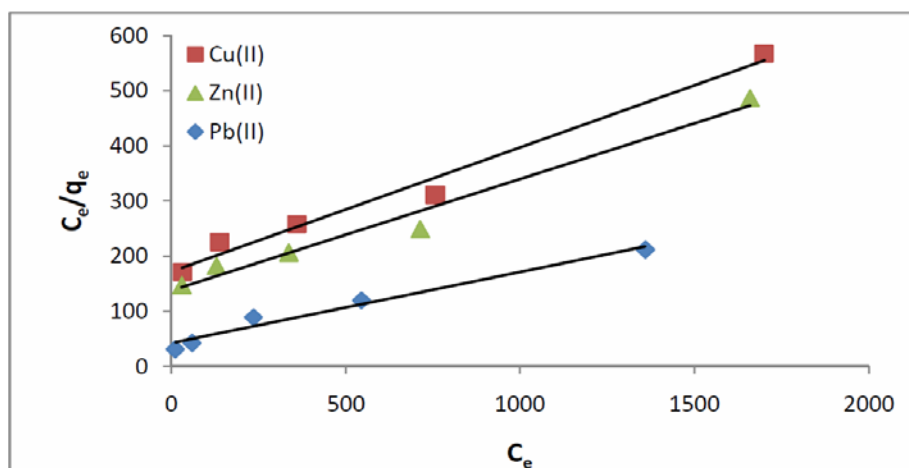


Fig 6. Langmuir equilibrium isotherm model for the sorption of the three metal ions onto kaolinite.

Table 3. Linear Langmuir isotherm parameters.

Metal ions	q_m (mg/g)	K_L (L/g)	r^2
Pb(II)	7.75	3.07 E-03	0.973
Zn(II)	4.95	1.46 E-03	0.977
Cu(II)	4.42	1.32 E-03	0.982

Furthermore favorability of adsorption of the three metal ions on the kaolinite was tested using the essential features of the Langmuir isotherm model, expressed in terms of a dimensionless constant called separation factor S_F , which is defined by the following relationship:

$$S_F = 1/(1 + K_L C_0) \quad (6)$$

Where K_L (L/mg) is Langmuir isotherm constant and C_0 (mg/L) is initial metal ion concentration. The S_F value for the adsorption of Pb(II), Zn(II) and Cu(II) on

kaolinite at initial concentration of 50 mg/L (lowest concentration studied) and 2000 mg/L (highest concentration studied) are listed in Table 4. The separation parameters for the three metals are less than unity indicating that kaolinite is an appropriate adsorbent for the three metal ions. The smaller S_F value indicates a highly favorable adsorption. However, S_F value of $\text{Cu(II)} > \text{Zn(II)} > \text{Pb(II)}$, indicates that in a mixed metal ion system, Pb(II) will compete for binding sites faster than Zn(II) and Cu(II).

Table 4. Separation factor S_F for adsorption of Pb(II), Zn(II) and Cu(II) on kaolinite.

Metal ions	Initial concentration	
	$C_0 = 50 \text{ mg/L}$	$C_0 = 2000 \text{ mg/L}$
Pb(II)	0.867	0.140
Zn(II)	0.932	0.255
Cu(II)	0.938	0.275

Temkin Isotherm Equation

The Temkin isotherm equation assumes that the heat of adsorption of all the molecules in layer decreases linearly with coverage due to adsorbent-adsorbate

interactions, and that the adsorption is characterized by a uniform distribution of the bonding energies, up to some maximum binding energy (Temkin, 1940). The Temkin isotherm is represented by the following equation:

$$q_e = \frac{RT}{b} \ln(K_T C_e) \tag{7}$$

Equation (9) can be expressed in its linear form as:

$$q_e = B_T \ln K_T + B_T \ln C_e \tag{8}$$

Where, T is the absolute temperature (K), R is the universal gas constant (8.314 J/mol.K), K_T is the equilibrium binding constant (L/mg), and b_T is the variation of

adsorption energy (kJ/mol). B_T is Temkin constant related to the heat of adsorption (kJ/mol).

The Temkin adsorption isotherm model was chosen to evaluate the adsorption potentials of the adsorbent for adsorbates. The Temkin isotherm plot for the three metal ions are presented in Figure 7 and the isotherm parameters is given in Table 5.

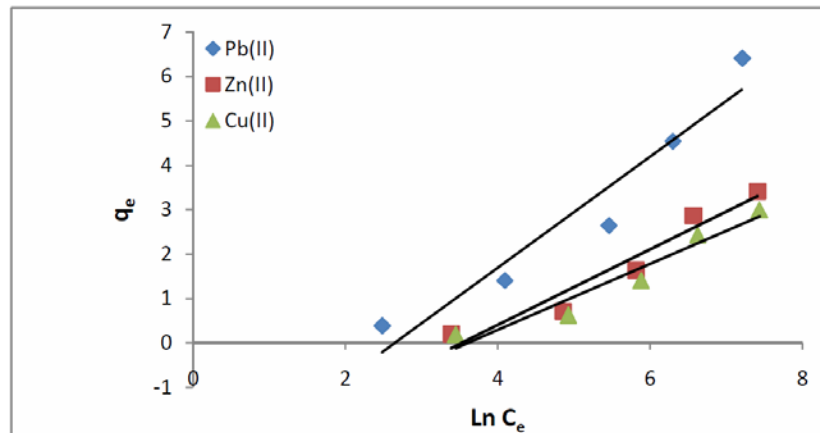


Fig 7. Temkin equilibrium isotherm model for the sorption of the three metal ions onto kaolinite.

The Temkin adsorption potential, K_T , of kaolinite for Pb(II), Zn(II) and Cu(II) are 0.070, 0.029 and 0.027 respectively, indicating a lower kaolinite-metal ion potential for Cu(II) probably due to its small ionic radius. The Temkin constant, b_T , related to heat of sorption for the three metal ions were 1.961 kJ/mol, 2.882

kJ/mol and 3.305 kJ/mol for Pb(II), Zn(II) and Cu(II) respectively. It has been reported (Ho *et al.*, 1996) that the typical range of bonding energy for ion-exchange mechanism is 8-16 kJ/mol. The low values in this study indicates a weak interaction between sorbate and sorbent, supporting an ion-exchange mechanism for the present study.

Table 5. Temkin isotherm parameters.

Metal ions	K_T (L/mg)	b_T (kJ/mol)	r^2
Pb(II)	0.070	1.961	0.924
Zn(II)	0.029	2.882	0.937
Cu(II)	0.027	3.305	0.934

Redlich-Peterson Model

Redlich-Peterson model is used as a compromise between Langmuir and Freundlich models, which can be written as (Redlich and Peterson, 1959):

$$q_e = \frac{K_{RP} C_e}{1 + \alpha_{RP} C_e^\beta} \tag{9}$$

Eq. (9) can be expressed in its linear form as:

$$\frac{C_e}{q_e} = \frac{1}{K_{RP}} + \frac{\alpha_{RP}}{K_{RP}} C_e^\beta \tag{10}$$

where K_{RP} (L/g), α_{RP} (L/mmol) and β are Redlich-Peterson constants. The value of β

lies between 0 and 1. The Redlich-Peterson isotherm constants can be predicted from the plot between C_e/q_e versus C_e^β . However, this is not possible as the linearized form of Redlich-Peterson isotherm equation contains three unknown parameters α_{RP} , K_{RP} and β . Therefore, a minimization procedure is adopted to maximize the coefficient of determination r^2 , between the theoretical data for q_e predicted from the linearized form of Redlich-Peterson isotherm equation and the experimental data. The Redlich-Peterson isotherm plot

for the three metal ions are presented in Figure 8 and the isotherm parameters is

given in Table 6.

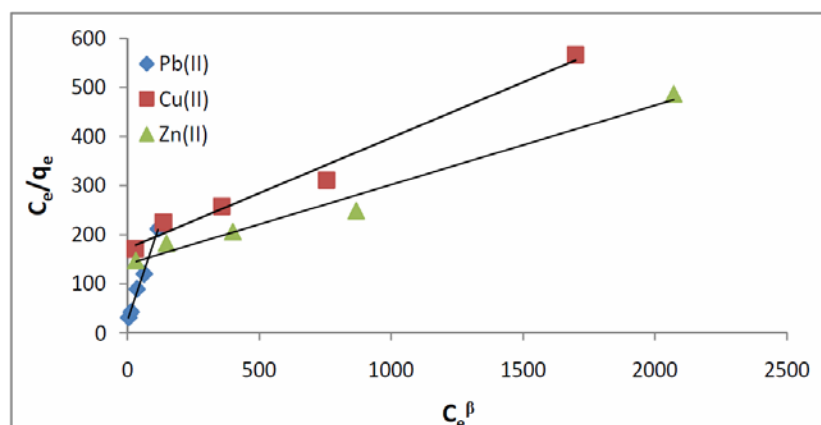


Fig 8. Redlich-Peterson equilibrium isotherm model for the sorption of the three metal ions onto kaolinite.

The higher r^2 values for Redlich-Peterson shows that the experimental equilibrium data was found to follow Redlich-Peterson isotherm equation. This was expected, because a degree of heterogeneity (β) is

included and this equation can be used successfully at high solute concentrations (Guibal *et al.*, 1998). Langmuir is a special case of Redlich-Peterson isotherm when constant β is unity.

Table 6. Redlich-Peterson isotherm parameters.

Metal ions	K_{RP} (L/g)	a_{RP} (L/mmol) $^\beta$	β	r^2
Pb(II)	0.043	0.064	0.67	0.995
Zn(II)	0.007	0.001	1.03	0.980
Cu(II)	0.006	0.001	1.00	0.982

Coefficients of Determination

It has been suggested that linearization plots may not be a significant basis to reject or accept a model (Horsfall and Vicente, 2007). To further analyze the suitability of the four models (Freundlich, Langmuir, Temkin and Redlich-Peterson), their fitness to the experimental data was assessed. The

fitness of the data was established using a single statistical parameter (r^2) which is called the coefficient of determination. The coefficient of determination values for the four models as shown in Table 7 shows that the four models are applicable in describing the data (as all $r^2 > 0.90$) with the Redlich-Peterson model being more appropriate.

Table 7. Adsorption isotherm coefficients of determination (r^2).

Adsorption isotherms	Heavy metals		
	Pb(II)	Cu(II)	Zn(II)
Freundlich	0.983	0.979	0.971
Langmuir	0.973	0.982	0.977
Temkin	0.924	0.934	0.937
Redlich-Peterson	0.995	0.982	0.977

Due to the bias resulting from linearization, the internal structure not accessible at first glance of the r^2 values in Table 7 were determined by two-way analysis of variance (ANOVA) without replication ($P < 0.05$). The summary of the statistical analysis is presented in Table 8A and B. Consideration of the comparative

magnitudes of the r^2 values (Table 8A) suggest that the Redlich-Peterson isotherm model does provide a better model for the sorption systems and that Cu(II) experimental data exhibits a better fitting to the four isotherm models. However, the two-way ANOVA results (Table 8B) indicate significant difference between the

four isotherm models in describing the sorption process of the three metal ions on

kaolinite.

Table 8. Two-way analysis of variance (ANOVA) without replication at $\alpha = 0.05$.

A. Summary					
	Count	Sum	Average	Variance	
Freundlich	3	2.933	0.978	3.75×10 ⁻⁵	
Langmuir	3	2.932	0.977	2.05×10 ⁻⁵	
Temkin	3	2.795	0.932	4.65×10 ⁻⁵	
Redlich-Peterson	3	2.954	0.985	8.65×10 ⁻⁵	
Pb(II)	4	3.875	0.968	9.71×10 ⁻⁴	
Cu(II)	4	3.877	0.969	5.54×10 ⁻⁴	
Zn(II)	4	3.862	0.965	3.69×10 ⁻⁴	

B. ANOVA					
Source of variation	SS	df	MS	F	Fcrit
Models	52.98×10 ⁻⁴	3	17.66×10 ⁻⁴	28.12*	4.76
Metals	0.330×10 ⁻⁴	2	0.165×10 ⁻⁴	0.263	5.14
Error	3.770×10 ⁻⁴	6	0.628×10 ⁻⁴		
Total	57.08×10 ⁻⁴	11			

* Indicates a significant difference at the 95% confidence level.

Adsorption Kinetics

Most of the sorption/desorption transformation processes of various solid phases are time-dependent. To understand the dynamic interactions of pollutants with solid phases and to predict their fate with time, knowledge of the kinetics of these processes is important (Sparks and Suarez, 1991; Sparks, 1989). Various kinetic models have been used by various researchers, whereas in this study the pseudo-first-order and pseudo-second-order models were studied.

Pseudo-First Order Model

Pseudo-first order equation or Lagergren's kinetics equation (Lagergren, 1898) is widely used for the adsorption of an adsorbate from an aqueous solution.

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (11)$$

After integration and applying boundary conditions $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_t$, the integrated form of equation (11) becomes:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (12)$$

where q_t is the amount of metal adsorbed per unit of adsorbent (mg/g) at time t , k_1 is the pseudo-first order rate constant (L/min), and t is the contact time (min). The adsorption rate constant (k_1) were calculated from the plot of $\ln(q_e - q_t)$ against t .

Pseudo- Second Order Model

Ho and McKay, (1999) presented the pseudo-second order kinetic as:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (13)$$

For the boundary conditions $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_t$, the integrated form of Eq. (13) becomes:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \left(\frac{1}{q_e}\right)t \quad (14.a)$$

where k_2 is the pseudo-second order rate constant (g/mg.min). The initial adsorption rate, h (mg/g.min) at $t \rightarrow 0$ is defined as:

$$h = k_2 q_e^2 \quad (14.b)$$

The h , q_e and k_2 can be obtained by linear plot of t/q_t versus t .

Kinetic studies for the adsorption of Pb(II), Zn(II) and Cu(II) on kaolinite were conducted using pseudo-first order and pseudo second order kinetic models which are shown in Figs. 9a and b. Pseudo second order kinetic plot of (t/q_t) versus (t) gave the perfect straight line for the adsorption of all metal ions onto kaolinite indicating that adsorption reaction can be approximated with pseudo-second order kinetic model. The values of model parameters k_1 , k_2 , h , q_e and correlation coefficients (r^2) are obtained from the plots and presented in Table 9. As shown in this table, the correlation coefficients for the second order rate equation, for all the

metals, are greater than 0.99 and substantially higher than that for the first-order rate equation. And also, the q_e values calculated from the second order kinetic

model agree well with the experimental values. This show that the adsorption of lead, zinc and copper can be represented by the pseudo second-order model.

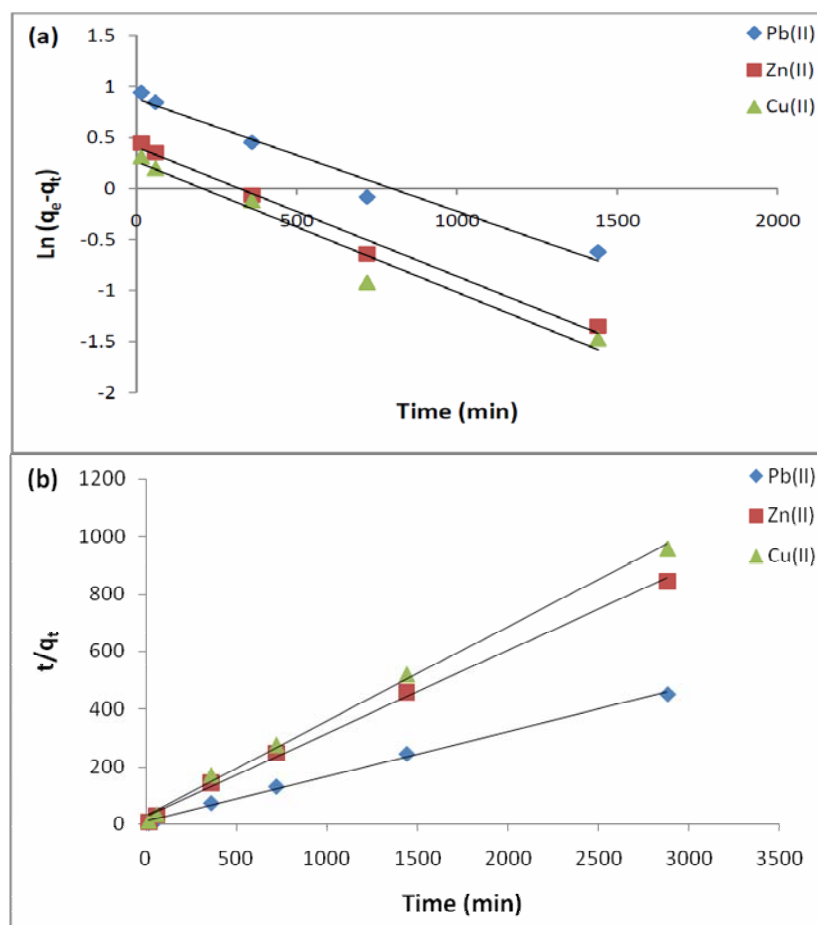


Fig 9. Kinetic models for the adsorption of lead, zinc and copper on kaolinite ($C_0=2000$ mg/L, pH=4.5, Temperature = $20\pm 1^\circ\text{C}$) (a) Pseudo-first order and (b) Pseudo-second order model.

The rate constant of pseudo-second order adsorption (k_2) obtained for Pb(II) was found to be lower than that computed for Zn(II) and Cu(II) (Table 9). This indicates that the uptake of Pb(II) onto kaolinite from aqueous solution was more rapid and favorable. It can be observed

that the initial adsorption rate, h (mg/g.min), is higher for Pb(II) than Zn(II) and Cu(II). This is an indication that initial adsorption of Pb(II) by kaolinite was faster and in a mixture of metals of this group, Pb(II) may be quantitatively removed before others.

Table 9. Parameters of the kinetic models for the adsorption of Pb(II), Zn(II) and Cu(II) onto kaolinite ($C_0=2000$ mg/L, pH=4.5, Temperature = $20\pm 1^\circ\text{C}$).

Heavy metals	$q_{e,exp}$	Pseudo-first order			Pseudo-second order			
		k_1	$q_{e,cal}$	r^2	k_2	$q_{e,cal}$	h	r^2
Pb(II)	6.41	1.1×10^{-3}	2.41	0.9743	1.97×10^{-3}	6.47	0.082	0.9970
Zn(II)	3.41	1.3×10^{-3}	1.51	0.9879	3.26×10^{-3}	3.46	0.039	0.9969
Cu(II)	3.00	1.3×10^{-3}	1.30	0.9616	3.77×10^{-3}	3.04	0.035	0.9969

CONCLUSION

This study investigated the feasibility of kaolinite used as a low-cost adsorbent for the removal of Pb(II), Zn(II) and Cu(II) from aqueous solution. The experimental results were analyzed using four adsorption isotherm models, the Freundlich, Langmuir, Temkin and Redlich-Peterson, isotherm models. Evaluating the correlation coefficients from the four isotherm equations using two-way ANOVA at $p < 0.05$ for fitting the analytical data showed that the Redlich-Peterson isotherm described the data appropriate than others. This was expected, because a degree of heterogeneity (β) is included and this equation can be used successfully at high solute concentrations. By using the Langmuir isotherm, the adsorption capacities for Pb(II), Zn(II) and Cu(II) are found as 7.75 mg/g, 4.95 mg/g and 4.42 mg/g respectively. The effectiveness of kaolinite in the sorption of the three metals from aqueous system was Pb(II) > Zn(II) > Cu(II). This preferential sorption behavior could be explained in terms of ionic radii of the metal ions. The separation parameters, S_F , for the three metals are less than unity indicating that kaolinite is an appropriate adsorbent for the three metal ions. However, S_F value of Cu(II) > Zn(II) > Pb(II), indicate that in a mixed metal ion system, Pb(II) will compete for binding sites faster than Zn(II) and Cu(II). The adsorption data of Pb(II), Zn(II) and Cu(II) ions on kaolinite showed that the pseudo-second order model was more suitable than the pseudo-first order model. The calculated rate constants of the adsorption showed that the uptake of Pb(II) onto kaolinite from aqueous solution was more rapid and favorable. In batch mode adsorption studies, the amount of Pb(II), Zn(II) and Cu(II) ions uptake (mg/g) was found to increase in concentration and contact time. As a result of this study, it may be concluded that kaolinite may be used for removal of heavy metal pollution from wastewater since it is of low-cost, abundant and a locally available adsorbent.

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مطالعه ایزوترم و سینتیک جذب سرب، روی و مس توسط کائولینیت

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چکیده

در مطالعه حاضر قابلیت کائولینیت به عنوان یک جاذب کم هزینه و ارزان برای حذف فلزات سنگین سرب، روی و مس از محلول های آبی مورد ارزیابی قرار گرفت. برای این منظور آزمایش batch انجام شد و تاثیر غلظت فلز سنگین و زمان تماس بر راندمان جذب در $\text{pH}=4/5$ و تحت دمای ثابت 20 ± 1 درجه سانتی گراد بررسی شد. داده های ایزوترم تجربی با استفاده از چهار مدل همدمای جذب؛ فروندلیچ (Freundlich)، لانگمویر (Langmuir)، تمکین (Temkin) و ردلیچ-پترسون (Redlich-Peterson) آنالیز گردید. بررسی های ضرایب همبستگی نشان داد همدمای جذب ردلیچ-پترسون بهتر از بقیه مدل ها داده ها را برازش می کند. ظرفیت جذب (q_m) همدمای لانگمویر برای سرب، روی و مس بترتیب ۷/۷۵، ۴/۹۵ و ۴/۴۲ میلی گرم بر گرم بدست آمد. به عبارت دیگر، اثربخشی کائولینیت در جذب سه فلز از سیستم آبی بصورت زیر می باشد: سرب < روی < مس. مطالعات سینتیکی نشان داد واکنش جذب سطحی این ترکیبات از محیط آبی بر روی کائولینیت از معادله مجازی مرتبه دوم تبعیت نمود. نتایج نشان دادند کائولینیت می تواند به عنوان یک جاذب موثر برای حذف یون های Pb(II) ، Zn(II) و Cu(II) از محلول های آبی استفاده شود.