Kinetic model for sorption of divalent heavy metal ions on low cost minerals

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Abstract−A mathematical model is proposed that could predict the kinetic parameters for adsorption of divalent heavy metal ions (lead, copper and zinc) onto low-cost adsorbents such as pyrophyllite and rock phosphate using experimental data. The experiments were conducted with the initial concentrations of metal ions ranging from 10 mg/L to 100 mg/L. The mathematical model is based on the application of the Redlich-Peterson isotherm to mass transfer across the film surrounding the adsorbent. The developed non-linear sorption kinetic (NSK) mathematical model was solved using numerical integration by the trapezoidal method in Microsoft Excel along with the SOLVER function to obtain the best simulated values of the Redlich-Peterson constants A, B, r, the order of reaction n, and the film transfer coefficient α. Dissolution followed by precipitation was found to be the most probable mechanism responsible for heavy metal ion uptake by rock phosphate, while for pyrophyllite physical adsorption was governing mechanism at low concentrations (<100 mg/L). The values of parameters A, B, r and α lie in the ranges of 0.015-23.2, 0.00003-3.09, 0.072-1, and 0.000057-52.8 $[(L/mg)^{(n-1)}/min]$, respectively, under different experimental conditions.

Keywords: Adsorption, Divalent Heavy Metal Ions, Rock Phosphate, Pyrophyllite, Sorption Kinetic Model, Redlich-Peterson Isotherm

INTRODUCTION

The presence of heavy metals in the environment is a major concern because of their toxicity and threat to human life and the environment. The release of large quantities of heavy metals into the natural environment has not only intensified environmental pollution problems, but also the deterioration of several aquatic ecosystems with the accumulation of metals in biota and flora. Thus, concern about environmental protection has increased over the years from a global view point.

Sorption processes are recognized as the most efficient, promising and widely used fundamental approach in wastewater treatment processes [1]. The most commonly used adsorbent is activated carbon, but activated carbon is not cost-effective for the removal of metal ions under consideration because of its high price and expensive regeneration. With this in view, a large number of experimental and theoretical studies have been reported on the adsorption of cations, particularly heavy metal ions, on various adsorbents. Various low-cost adsorbents being used include montmorillonite [2], slag [3], humic acid [4], kaoline [5], peat [6,7], fly ash [8], other carbonaceous substrates [9] and phosphatic minerals [10,11]. The use of bioadsorbents based on renewable resources as a low cost adsorbent for heavy metal ions has received increasing attention recently [12,13].

In the present study two cost effective industrial minerals, low-grade (<12% P_2O_5) rock phosphate found in Jhabua, Madhya Pradesh,

India and pyrophyllite, found in Jhansi, Uttar Pradesh, India, have been used as an adsorbent. Our earlier studies [10,14] on rock phosphate and by other investigators [15-18] on pyrophyllite in the recent past have highlighted the utility of these very low cost and environmental friendly minerals' use as an adsorbent for divalent cations from aqueous solutions. However, only a limited number of articles have addressed the mathematical modelling of the adsorption of heavy metal ions onto mineral adsorbents. Earlier reported mathematical models for the sorption of heavy metal ion include surface complexation [19,20], cation exchange [21], triple layer model [22] and finite difference Simpson's 1/3rd rule [23].

Several simplifying assumptions have been made by various authors because of the complex nature of the adsorption process. A mathematical model called SPNSM (static, physical, non-equilibrium sorption model) was suggested by [3] for phosphorous sorption onto slag. This model assumes first-order rate of reaction (n=1) and uses the Freundlich isotherm to develop the mathematical expression. It also assumes the Freundlich Isotherm Constant (N) as unity, which reduces the isotherm to S=KC. The mathematical expression obtained from SPNSM is as follows:

$$\frac{C}{C_o} = \frac{1 + \left(\frac{m}{V}\right) K \exp\left[-\alpha\left\{1 + \frac{V}{mK}\right\}t\right]}{1 + \left(\frac{m}{V}\right) K} \tag{1}$$

Other simplified approaches include empirical model based on cation exchange equation with scalable selectivity coefficients which was developed by [21]. Similarly, the homogeneous surface diffusion model (HSD model) proposed by [23] assumes only film trans-

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fer coefficient and diffusivity to be the dominant design variables for adsorption.

It appears that most of the models available are either empirical or based on greatly simplifying assumptions. The present investigation was undertaken to develop a more rigorous nonlinear sorption kinetic (NSK) model that could be used to predict the kinetic parameters A, B, r, n, and α. The proposed model was further tested to fit the experimentally observed data obtained for the removal of divalent cations (lead, copper, and zinc) using rock phosphate as well as pyrophyllite as the adsorbent.

With the recent revival of mathematical modelling being used for adsorption studies, there has been a steadily growing interest using different isotherms (two/three parameters) to describe the adsorption phenomenon. Two-parameter Freundlich isotherm was used to describe the sorption process by earlier investigators [3] as well as in our earlier studies [24,25]. The two-parameter adsorption models habitually showed some limitations in their application. Therefore, models with more than two parameters were developed to mitigate these deficiencies.

In the present investigation, the Redlich-Peterson isotherm, a three-parameter adsorption isotherm, has been used instead of the conventional two-parameter Freundlich isotherm used in previous studies. It is a hybrid isotherm which contains three parameters and incorporates the features of the Langmuir and the Freundlich isotherms. The model has a linear dependence on concentration in the numerator and an exponential function in the denominator to represent adsorption equilibria over a wide concentration range, that can be applied either in homogeneous or heterogeneous systems due to its versatility [26,27]. Typically, a minimization procedure is adopted in solving the equations relating the experimental data points and theoretical model predictions with SOLVER add-in function of the Microsoft Excel [28]. It approaches the Freundlich isotherm model at high concentration (as the exponent tends to zero), and in turn it approaches the Langmuir isotherm model at low concentration limit of the ideal condition (as the exponent values tends to one) [29]. Redlich-Peterson isotherm has three isotherm constants, A, B, and r ($0<r<1$), and the equation is defined as:

$$S = \frac{AC}{1+BC^r} \tag{2}$$

2. Model Development

The model investigated in the present study is based on mass transfer phenomenon across the film surrounding the adsorbent coupled with the application of Redlich-Peterson isotherm. Previous investigators [3,30] have also considered similar approaches, but their models have been limited to first-order (n=1) reactions only. The model developed here is suitable even for orders of reaction other than unity. The adsorption kinetic behavior for the uptake of divalent heavy metal ions (Pb^{2+}, Cu^{2+}, Zn^{2+}) by an adsorbent as a function of time was studied and a model for n^{th} order sorption kinetics was developed. The proposed model assumes that an immobile water layer surrounds the particles of adsorbent and the liquid phase concentration of cations in this layer is in equilibrium with the solid phase concentration on the adsorbent surface.

If the initial solid phase concentration is S_o, then by mass bal-

ance the bulk liquid phase concentration as a function of solid phase concentration can be given by:

$$C_0 = C + \frac{m}{V}(S-S_0) \tag{3}$$

At any instant the rate of sorption (mg cation per second per unit volume of solution) can be given by the equation:

$$\frac{m}{V}\frac{dS}{dt} = -\alpha(C-C_e)^n \tag{4}$$

where α=film transfer constant [$(L/mg)^{(n-1)}$/min] and n =order of reaction

At equilibrium, concentration C in Eq. (2) becomes C_e. Substituting C_e at equilibrium ($C=C_e$) from Eq. (2) in Eq. (3) we get:

$$\frac{dS}{dt} = -\alpha\frac{V}{m}\left(C+\frac{m}{V}(S-S_o)-C_o\right)^n \tag{5}$$

Differentiating Eq. (1) with respect to t and substituting it in Eq. (4) with $S_o=0$, we get the following model equation in integral form:

$$t_{calc} = \int_{C_o}^{C} \frac{\frac{m}{V}(A+ABC^r(1-r))}{-\alpha\left(C-C_o+\frac{m}{V}\left(\frac{AC}{1+BC^r}\right)^n\right)(1+BC^r)^2} dC \tag{6}$$

The above equation was numerically integrated by trapezoidal method using Microsoft Excel. The SOLVER add-in function is used to determine the values of constants A, B, r, n, and α by minimizing the least square error,

$$D = \sum_{i=1}^{k}(t_i - t_{calc})^2 \tag{7}$$

where D is discrepancy and t_i is time corresponding to the concentration C_i, obtained from the experimental data.

While t_{calc} gives the time calculated using the model equation, corresponding to concentration C_i. Thus, discrepancy (D) indicates the sum of square of error between the observed and calculated time values.

The root mean square (RMS) values of discrepancy D were calculated as follows:

$$RMS = \sqrt{\frac{D}{number\ of\ data\ points}} \tag{8}$$

MATERIALS AND METHODS

1. Adsorbent Materials

Pyrophyllite is an abundant aluminosilicate mineral whose adsorbent properties result from its large surface area and negative layer charge when in contact with water [16]. Representative samples of pyrophyllite were obtained from M/S Eastern Mineral, Jhansi (U.P.), India. The samples (1 kg) were sized and ground separately for the experimental work. Representative ground samples, taken after coning and quartering, were subjected to wet chemical analysis. An electric rotary shaking machine and Systronic digital pH meter were, respectively, used for equilibration and pH measurement of the solutions. For all three heavy metals, a 0.5 g sample of

Table 1(a). Physical properties and chemical composition of adsorbent of pyrophyllite

Physical properties	Chemical composition	
	Constituents	Weight percent
Surface area: 1.45 m^{2}g^{-1}	SiO$_2$	53.00
	Al$_2$O$_3$	28.14
C.E.C.: 1.238 meq g^{-1}	Fe$_2$O$_3$	0.61
	TiO$_2$	0.10
Porosity: 45.2%	MgO	1.09
	CaO	1.63
Specific gravity: 2.6489	K$_2$O	9.21
	Na$_2$O	0.32
Hardness: 1.35	L.O.I.*	5.55

*L.O.I., loss on ignition

Table 1(b). Physical properties and chemical composition of rock phosphate

Physical properties	Chemical composition	
	Constituents	Weight percent
Surface area: 0.152 m^{2}g^{-1}	P$_2$O$_5$	12.50
	SiO$_2$	26.50
C.E.C.: 3.74 meq g^{-1}	Al$_2$O$_3$	6.08
	Fe$_2$O$_3$	1.59
Porosity: 49.0%	CaO	32.60
Specific gravity: 2.7		
Hardness: 4.5		

*L.O.I., loss on ignition

the adsorbent was used. Characterization studies of sericitic pyrophyllite carried out by X-ray diffraction, I.R. and S.E.M., reported mainly pyrophyllite, α-quartz, kaolinite and muscovite [31]. Due to the presence of the muscovite phase, the pyrophyllite sample used in the present studies is termed as 'sericitic pyrophyllite' (SP). Physical and chemical properties of pyrophyllite are as shown in Table 1(a).

Rock phosphate is basically a low-grade (<12% P$_2$O$_5$) carbonate substituted rock phosphate (CRP) containing fluorine with its apatite lattice being partially substituted by carbonate. Mineralogical analysis for CRP samples reported mainly calcite, apatite, and quartz. Dolomite and iron oxide are the other associated gangue minerals present in phosphate samples in minor amounts. The detailed characterization studies of CRP by XRD, DTA, IR, etc. are discussed elsewhere [32,33]. The representative samples of rock phosphate mineral (one kg) were ground and sized separately for experimental work. Rock phosphate mineral samples of −100+75 μm size ranges were used in the present study for removal of lead, copper and zinc ions from aqueous solutions. For all the three heavy metals batch adsorption studies, 0.5 g sample was used as adsorbent. Physical and chemical properties of rock phosphate are as shown in Table 1(b).

2. Methods

Stock lead, copper, and zinc ion solutions (1,000 mg/L each) were prepared from analytical-grade lead nitrate, copper nitrate, and zinc nitrate using doubly distilled water and were serially diluted to prepare solutions of varying initial concentration for the experimental work. Rock phosphate and pyrophyllite mineral samples were equilibrated separately with 100 mL of solutions of different concentrations of lead, copper, and zinc ions. The suspensions were shaken on a mechanical shaker at 25 °C for 40 minutes. Samples from the suspensions were collected after 5 minute intervals and then filtered through Whatman filter paper (No. 42). The filtrates were analyzed for Pb^{2+}, Cu^{2+} and Zn^{2+} concentrations by using an atomic absorption spectrophotometer (GBC model 902). To determine the required quiescent time needed to attain adsorption equilibrium, the quiescent time was varied between 10 and 40 minutes in intervals of five minutes for different initial lead, copper, and zinc concentrations. Equilibrium was observed to be reached within 30 minutes in each case. Random tests were done for different concentrations to check the reproducibility of the results. For each set of experiments the pH values of the solution just before addition of the adsorbent and after shaking with the adsorbent were recorded.

RESULTS AND DISCUSSION

1. Effect of Initial pH on Pyrophyllite

The influence of pH on the adsorption of divalent metal ions on sericitic pyrophyllite was examined in the pH region between 1.0 and 7.0. The pH was limited to 7.0 because of precipitation of metal hydroxide at higher pH as described elsewhere [34]. Fig. 1 shows that the adsorption of Pb^{2+}, Cu^{2+} and Zn^{2+} increases with pH and reaches a maximum at pH 3.0 for all the three metal ions. At pH>3.0, percent adsorption decreases slightly till pH=6.0 and thereafter it appears to remain constant. As the pH changes, surface charge also changes and the sorption of charged species is affected (attraction between the positively charged metal ions and the negatively charged clay surface). It is conceivable that at low pH, where there is an excess of H$_3$O$^+$ ions in solution, a competition exists between the positively charged hydrogen ions and metal ions for the available adsorption sites on the negatively charged pyrophyllite
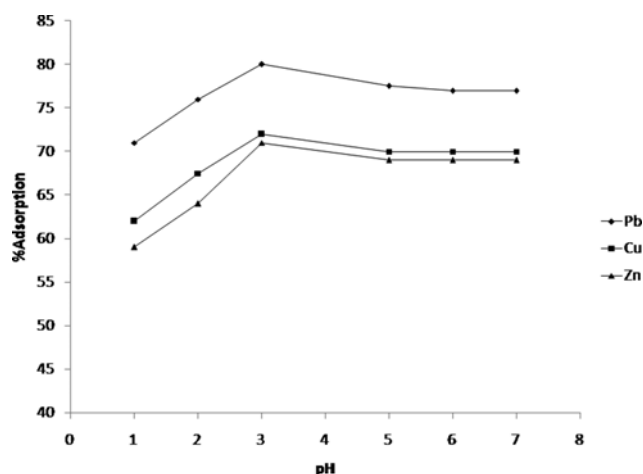

Fig. 1. Effect of pH on adsorption of divalent metal ions (adsorbate mass=0.5 g, volume=100 ml, equilibration time=30 min, metal concentration=20 mg/L.

Table 2. pH's of Lead Ions Solutions using rock phosphate mineral

Pb^{2+} concentration (μmol/L)	$pH_1{}^a$	$pH_2{}^b$	Ca^{2+} concentration (μmol/L)
24.1	6.45	7.17	199.44
48.3	5.82	6.63	274.23
241.5	5.20	5.89	750.39
483.0	4.10	5.34	1495.80

Table 3. pH's of copper ions solutions using rock phosphate mineral

Cu^{2+} concentration (μmol/L)	$pH_1{}^a$	$pH_2{}^b$	Ca^{2+} concentration (μmol/L)
78.65	7.70	7.58	336.55
157.30	6.73	7.35	387.66
786.50	6.47	6.96	1530.70
1573.00	5.91	6.45	3265.83

Table 4. pH's of zinc ions solutions using rock phosphate mineral

Zn^{2+} concentration (μmol/L)	$pH_1{}^a$	$pH_2{}^b$	Ca^{2+} concentration (μmol/L)
76.4	7.60	7.42	398.88
152.8	6.60	7.29	498.66
764.0	6.17	6.42	2096.61
1528.0	5.66	6.20	3739.50

surface. As the pH increases and the balance between H_3O^+ and OH^- is more equal, more of the positively charged metal ions in solutions are adsorbed on the negative clay surface and thus the percentage removal of metal ions increases [34].

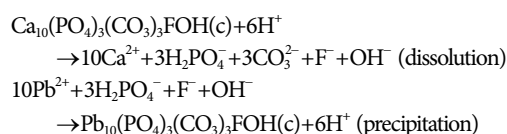**2. Effect of Initial pH on Rock Phosphate**

The present study was carried out under natural conditions, i.e., no effort was made to control the solution pH during the experiments and no ionic strength was imposed. The initial pH (pH_1) of the metal solutions and final pH (pH_2) of the filtrate at adsorption equilibrium were measured for each metal concentration. The pH values for all test solutions, as reported in the Tables 2-4 decreased with increasing metal concentration and increased gradually after equilibration with the adsorbent. The decrease of the pH as the initial metal concentration increases might be due to the release of H^+ ions and might indicate an adsorption mechanism by ion exchange. If cation substitution were responsible for heavy-metal removal, then the decrease in pH with increasing metal concentration would result in less heavy-metal adsorption because more rock phosphate would dissolve and less rock phosphate would be available for cation substitution at lower pH [35].

3. Mechanism of Removal of Divalent Cations

(i) Pyrophyllite: A number of governing mechanisms such as surface adsorption, dissolution and subsequent precipitation (complexation), ion exchange, and absorption, have been reported for the separation of aqueous heavy metals, namely, Pb, Cu, Zn, Cd, etc., by many investigators. The values of mean sorption energy obtained in our previous study [34] suggest removal of divalent cations by physical adsorption. At low concentration (<100 mg/L)

essentially physical adsorption without excluding ion exchange becomes preponderant and a remarkable deviation occurs at higher concentration (>100 mg/L). This could probably be due to the formation of a complex phenomenon such as mass transfer by means of chemical reactions. The assumptions of the Langmuir and Redlich-Peterson isotherms do not take into account these aspects [36]. One possible explanation of physical adsorption at lower concentration may be the release of weakly bonded potassium ions at higher temperature into the solution which makes it easy for metal ion removal by ion exchange. The dominance of muscovite $[KAl_2(AlSi_3O_{10})(FOH)_2]$, which has a layered structure of aluminum silicate sheets weakly bonded together by layers of potassium ions, is observed in chemical analysis of sericitic pyrophyllite as reported in our previous study [34]. The weakly bonded potassium ions may get released into the solution at higher temperature and cation exchange may occur in the interlayers resulting from the interactions between cations and negative permanent charge [34].

(ii) Rock phosphate: Sorption involving surface adsorption, dissolution, subsequent precipitation (complexation), ion exchange and absorption has been reported as the governing process of aqueous divalent metals ions attachment from a solution to a coexisting solid surface. Processes such as adsorbent dissolution, cation exchange, and metal complexation on an adsorbent (apatite/rock phosphate) surface, followed by precipitation of a new metal phase, had been proposed earlier [37-40] to describe the uptake of different metal ions from aqueous solutions by synthetic hydroxyapatite (HA) and rock phosphate. Here, it is proposed that the dissolution of rock phosphate and precipitation of a carbonated fluoropyromorphite-like mineral is the primary mechanism for divalent metal ions removal by rock phosphate. Assuming the presence of equal amounts of PO_4^{3-}, CO_3^{2-}, F^-, and OH^- as an example, this mechanism can be expressed by the following.

$$Ca_{10}(PO_4)_3(CO_3)_3FOH(c)+6H^+$$
$$\rightarrow 10Ca^{2+}+3H_2PO_4^-+3CO_3^{2-}+F^-+OH^- \text{ (dissolution)}$$
$$10Pb^{2+}+3H_2PO_4^-+F^-+OH^-$$
$$\rightarrow Pb_{10}(PO_4)_3(CO_3)_3FOH(c)+6H^+ \text{ (precipitation)}$$

The above mechanism can be justified by the analysis of the solution for Ca^{2+} and observation of pH changes occurring during Pb^{2+} uptake. The decrease in pH as the initial metal concentration increases might be due to the release of H^+ ions, and might indicate an adsorption mechanism by ion exchange. If cation substitution were responsible for heavy-metal removal, then the decrease in pH with increasing metal concentration would result in less heavy-metal adsorption. This is because more rock phosphate would dissolve and less rock phosphate would be available for cation substitution at lower pH. In the presence of this evidence, it appears that cation substitution (ion exchange) is taking place, but it is more predominant at lower concentration, i.e., at a considerably higher pH of the metal solution when greater amounts of the adsorbent (rock phosphate) are available [35].

4. Mathematical Model

The proposed model minimizes the discrepancy (D) by optimizing the values of the five constants A, B, n, α, and r. Table 5 gives the residual RMS values of different data sets of three metal ions with varying initial concentration. It can be interpreted from

Table 5. RMS values for different metals adsorbed for different initial concentrations

Initial metal concentration	Rock phosphate			Pyrophyllite		
	Lead	Copper	Zinc	Lead	Copper	Zinc
10 mg/L	0.746	1.611	0.280	3.613	4.837	0.306
50 mg/L	0.344	1.533	1.616	2.144	1.634	1.919
100 mg/L	0.342	1.590	1.121	1.565	1.890	1.175

Eqs. (7) and (8) that the lower the RMS value, the lower the value of D, i.e., the lesser the difference between experimental data and calculated data. Thus the model would better explain uptake of that particular ion which has lower RMS value. It is evident from Table 5 that for both rock phosphate and pyrophyllite lower RMS values are obtained for lead at a concentration of 100 mg/L in comparison to copper and zinc. So the developed model better explains for uptake of lead ion. This is coincident with our earlier findings [35] for evaluating film-transfer constant at different initial concentrations. While comparing RMS values for three cations, lower RMS values are obtained for lead and zinc at lower concentration (10 mg/L) for both rock phosphate and pyrophyllite. It appears this model would better explain in the lower concentration range for lead and zinc. Similar observation of model explanation was made in earlier studies [25].

While obtaining the values of these constants using the model, we observed that the model is sensitive towards B, r, n and α, but one Redlich-Peterson constant A has less influence on the curve fitting parameter, D. It (D) is a strong function of B, r, n and α, but a weak function of A. Figs. 2(a) and 2(b) show different curves for lead adsorption onto pyrophyllite and rock phosphate at an initial lead concentration of 100 mg/L for different values of A, ranging from 5 to 500 $((L/mg)^r)$. It can be observed that the curves almost overlap each other despite large variation.
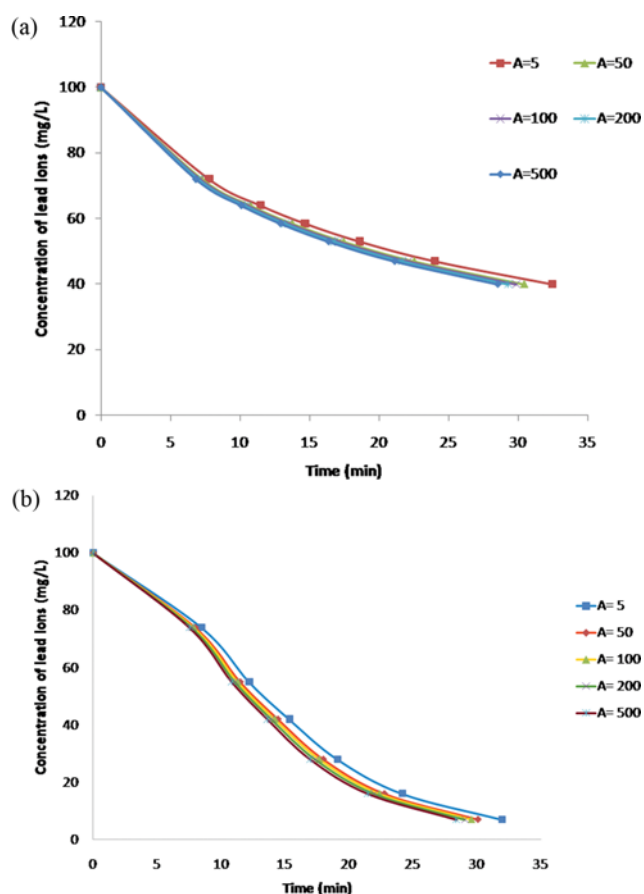

Fig. 2. (a) Concentration versus time plots for lead adsorption onto pyrophyllite at an initial lead concentration of 100 mg/L for different values of A, ranging from 5 to 500 $((L/mg)^r)$. (b) Concentration versus time plots for lead adsorption onto rock phosphate at an initial lead concentration of 100 mg/L for different values of A, ranging from 5 to 500 $((L/mg)^r)$.

Table 6. Values of constants A, B, r, n and α for sorption of lead, copper and zinc onto pyrophyllite and rock phosphate at different initial concentrations (10, 50, 100 mg/L) obtained from the proposed model

Initial concentration	Constants	Rock phosphate			Pyrophyllite		
		Lead	Copper	Zinc	Lead	Copper	Zinc
10 mg/L	A	12.61	5.04	0.0381	23.20	2.71	0.0391
	B	0.155	0.101	0.0688	3.05	0.000234	0.0436
	r	0.553	0.211	0.974	0.918	0.200	0.996
	n	1.088	0.816	0.110	0.738	0.799	0.205
	α	0.029	0.562	18.47	0.634	0.848	11.96
50 mg/L	A	0.309	1.19	4.31	9.793	1.044	5.169
	B	0.093	0.0860	0.500	3.09E-05	0.0844	0.102
	r	0.100	0.0850	0.148	0.999	0.0719	0.213
	n	0.645	0.711	0.748	1.37	0.704	0.807
	α	3.60	1.97	0.933	0.000214	2.067	0.516
100 mg/L	A	0.015	5.58	5.56	1.43	5.122	14.50
	B	0.0087	0.0878	0.160	0.480	0.0997	0.042
	r	0.952	0.912	0.897	0.999	0.856	0.98
	n	0.118	0.727	0.688	0.366	0.709	1.27
	α	52.79	0.337	0.328	0.658	0.304	5.70E-05

Table 6 lists the values of constants A, B, r, n and α for sorption of lead, copper and zinc onto pyrophyllite and rock phosphate at different initial concentrations (10, 50, 100 mg/L) obtained from the proposed model. For lead sorption on rock phosphate at different initial concentrations (10, 50, 100 mg/L), the values of Redlich-Peterson constants A and B and order of reaction (n) decrease from lower to higher concentrations, while the film transfer coefficient (alpha) increases. However, for lead sorption onto pyrophyllite, the value of the Redlich-Peterson constant A decreases from lower to higher initial concentrations, while the value of r remains almost constant. Again, as far as zinc sorption onto pyrophyllite is considered, the values of Redlich-Peterson constant A and order of reaction increase from lower to higher concentrations, while the value of film transfer coefficient (α) decreases from lower to higher initial concentrations. The apparent dependency of r and α on initial concentration is perhaps due to the presence of both r and α in the denominator of Eq. (5) in such a way that the effect of change in initial concentration is counterbalanced by mutual adjustment in the value of the parameters. Therefore, these values may or may not show any correlation with initial metal ion concentration. This indicates
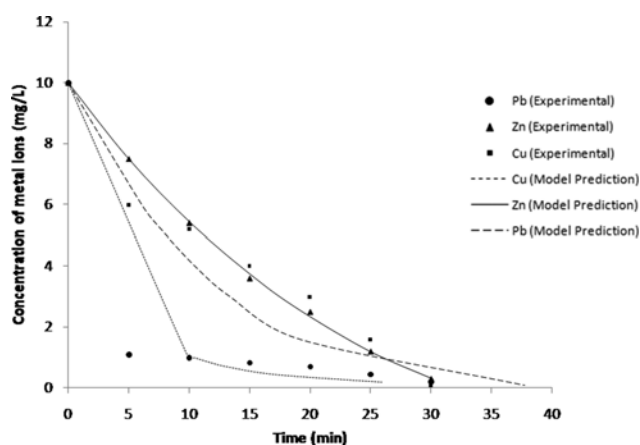

Fig. 5. Concentration versus time graph for metal ion adsorption onto pyrophyllite at an initial concentration of 100 mg/L.
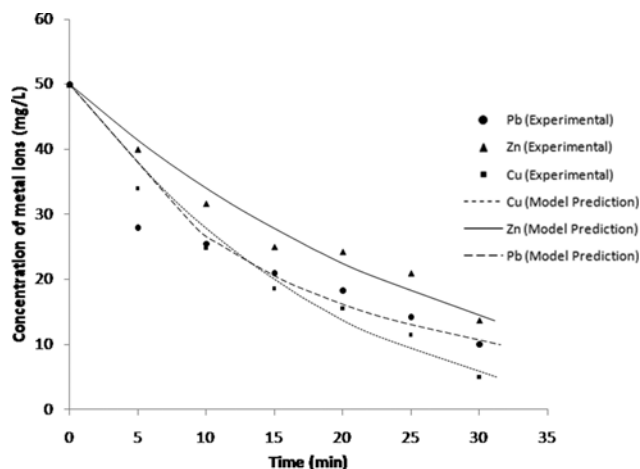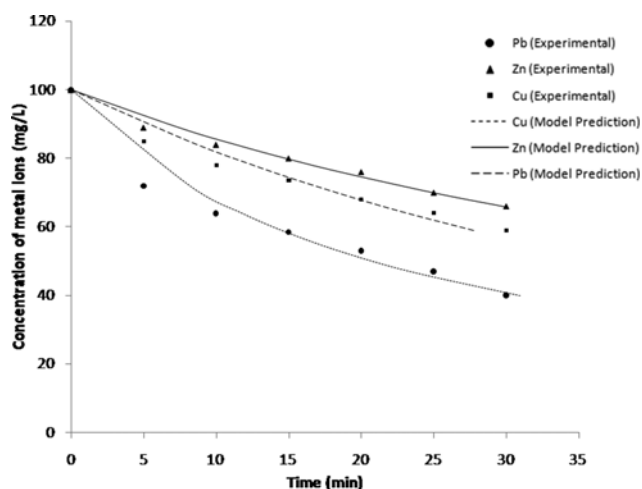

Fig. 3. Concentration versus time graph for metal ion adsorption onto pyrophyllite at an initial concentration of 10 mg/L.
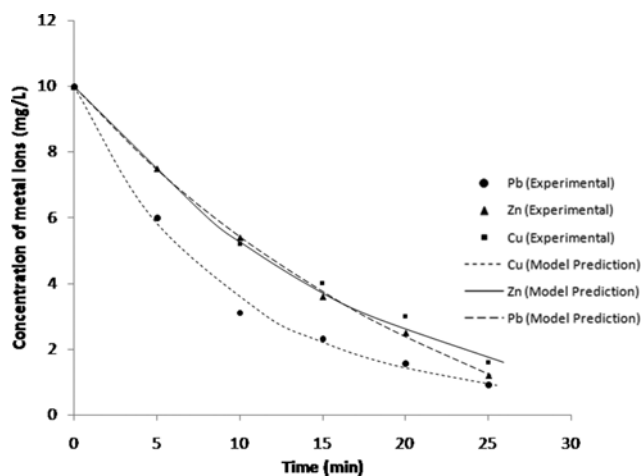

Fig. 6. Concentration versus time graph for metal ion adsorption onto rock phosphate at an initial concentration of 10 mg/L.
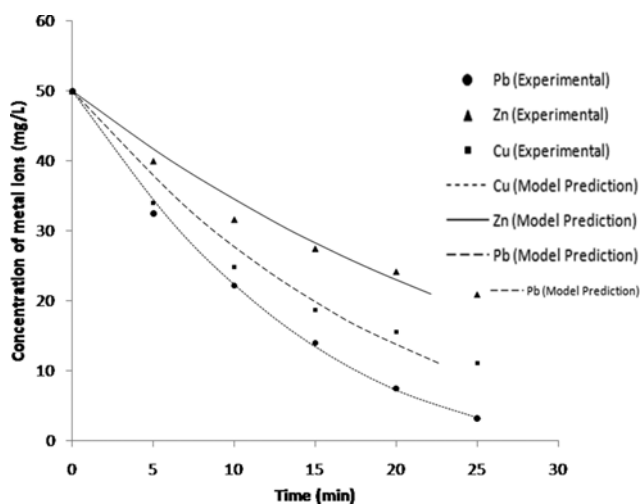

Fig. 4. Concentration versus time graph for metal ion adsorption onto pyrophyllite at an initial concentration of 50 mg/L.

Fig. 7. Concentration versus time graph for metal ion adsorption onto rock phosphate at an initial concentration of 50 mg/L.
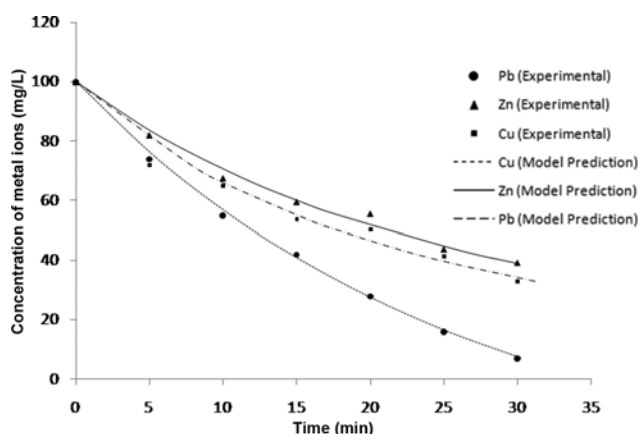
Fig. 8. Concentration versus time graph for metal ion adsorption onto rock phosphate at an initial concentration of 100 mg/L.

that the present approach for estimating parameters is applicable only when data are available at various initial concentrations of metal ions. The present studies reveal that pyrophyllite and rock phosphate are possible adsorbents for the removal of metal ions. However, due to their low cost, and availability in abundance, this can prove to be a viable alternative. The plots of concentration v/s time of various metal ions adsorption onto low-grade rock phosphate and low cost mineral pyrophyllite at different initial concentrations, namely, 10, 50 and 100 mg/L, are shown in Figs. 3-8, respectively. These graphs show the experimental data points and the model curve (calculated values), which corresponds to the simulated values of kinetic parameters (A, B, r, n and α) as listed in Table 6. These figures show that the model results are in fairly good agreement with the experimental data used for validation. Thus, the developed model accurately estimates the kinetic parameters for adsorbate removal.

CONCLUSIONS

We have developed a mathematical model to predict kinetic parameters for the adsorption of divalent heavy metal ions onto low cost industrial minerals. Dissolution followed by precipitation was found to be the most probable mechanism responsible for metal uptake by rock phosphate, while for pyrophyllite physical adsorption was the governing mechanism at low concentrations (<100 mg/L). The proposed model fits the data satisfactorily and it is suitable for order of reactions other than unity. The model is sensitive to order of reaction (n), film transfer coefficient (α), and the Redlich-Peterson constants B, and r except for a few initial concentrations, while it is almost insensitive for A. It was found that the model explained lead and zinc adsorption onto both rock phosphate and pyrophyllite better than copper adsorption at low concentration. The values of parameters A, B, r and α lie in the ranges of 0.015-23.2, 0.00003-3.09, 0.072-1, and 0.000057-52.8 [(L/mg)$^{(n-1)}$/min], respectively, under different experimental conditions.

LIST OF ABBREVIATIONS

C   : bulk liquid phase concentration [mg/L]
C_0 : initial cation concentration [mg/L]
C_e : liquid phase concentration in equilibrium with the solid phase concentration
D   : discrepancy, sum of square of the difference between calculated and observed values of time [min^2]
r   : Redlich-Peterson isotherm constant
B   : Redlich-Peterson isotherm constant [(L/mg)^r]
m   : mass of adsorbent [g]
A   : Redlich-Peterson isotherm constant [L/mg]
n   : order of reaction
S   : solid phase concentration [mg cation/mg adsorbent]
S_0 : initial solid phase concentration [mg cation/mg solid]
V   : volume of the solution [L]
α : film transfer constant [(L/mg) (n−1)/min]
SP   : sericitic pyrophyllite
CRP   : carbonate substituted rock phosphate

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