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Kinetic of Adsorption of Chromium and Lead Ions on Bentonite Clay Using Novel Internal Parallel Model

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ABSTRACT

The main objective of this study was to characterize the Bentonite clay collected from West of Saudi Arabia and investigate its potential for the adsorption of chromium (Cr) and lead (Pb) ions from wastewater. Application of Saad models described the experimental data very well. The maximum adsorption capacity of Bentonite clay was 13.79 mg g⁻¹ for chromium and 51.19 mg g⁻¹ for lead ion. The results for the effect of different agitation speed and the initial concentrations on adsorption of Cr and Pb ions on Bentonite clay showed that increasing the agitation speed increased the adsorption rate of metal ions on Bentonite clay. The kinetics of chromium and lead ions on Bentonite clay were also determined. A novel diffusion model called as the Saad Two Resistances Internal Diffusion Model (STRIDM) was used to calculate the time constant in a batch adsorber. It was found that the internal mass diffusion is a major rate-controlling step for maximum removal of chromium and lead ions from wastewater.

Key words: Kinetics, Bentonite clay, adsorption, chromium, lead, agitation speed, batch adsorber

INTRODUCTION

Majority of the waste waters in the world are contaminated with varying degrees of organic and inorganic pollutants depending on its production source. Among these pollutants, presence of some heavy metals such as chromium (Cr) and lead (Pb) poses a serious threat to the water bodies and the environment. In general, activated carbon is used for the adsorption of heavy metals from wastewater (Quek *et al.*, 1998) but it is an expensive proposition. An alternative adsorbent such as clay can be used as a low cost adsorbent. Previously, many researchers used different types of clay and rocks for the adsorption of heavy metals such as copper, zinc, chromium, iron, hydrogen arsenate, cadmium, nickel ions from waste waters (Alkan and Dogan, 2001; Kwon *et al.*, 2005; Rahman *et al.*, 2005; Babel and Opiso, 2007; Steinhauser and Bichler, 2008; Alemayehu and Lennartz, 2009; Shah *et al.*, 2009; Potgieter *et al.*, 2006; Unuabonah *et al.*, 2007a, b; Singh *et al.*, 2001; Diaz *et al.*, 2007; Al-Jlil and Alsewailem, 2009). But, no research study was found on Bentonite clay (from Saudi Arabia) as an adsorbent to adsorb lead and chromium ions from waste water.

Adsorption of copper ions on perlite was investigated using batch adsorber (Alkan and Dogan, 2001). Studies on the effect of pH showed that the adsorption of heavy metal ions (Cr, Pb) increased with increasing pH while it decreased with increasing the temperature and acid treatment. Also, the experimental data correlated with Langmuir model well.

Adsorption of zinc (Zn) ion on scoria as a volcanic rock was investigated by Kwon *et al.* (2005) using a batch equilibrium technique. The results indicated that the Langmuir model fitted the

experimental data well. Also, the rate of adsorption increased with decreasing the initial concentration and the particle size of the metal.

Adsorption of different types of heavy metals such as lead, cadmium, chromium, mercury ions on indigenous rocks (andesite and limestone) were studied by Rahman *et al.* (2005). They reported that indigenous rocks proved efficient material for the adsorption of these heavy metals.

Adsorption of chromium ions from wastewater was studied using two volcanic ash soils from Mt. Isarog and Mandalagan (Babel and Opiso, 2007) to determine the effect of initial concentration, pH and the contact time. They reported that the maximum adsorption of chromium was 89% and 65% for volcanic ash soil from Isarog and Mandalagan, respectively.

Investigations for the adsorption of Cr^{3+} , Fe^{3+} , HAsO_4^{2-} (hydrogen arsenate) ions from wastewater was carried using pumice volcanic powder as an adsorbent (Steinhauser and Bichler, 2008). They found that minimum adsorption of hydrogen arsenate ions was 1.8 mg kg^{-1} and that of Fe^{3+} was 5.8 mg kg^{-1} on the pumice volcanic powder.

In another study, Alemayehu and Lennartz (2009) studied the adsorption of cadmium (Cd) ions from wastewater on Pumice and Scoria volcanic rocks depending on some factors such as contact time, pH and initial concentration. They observed that the maximum adsorption was at $\text{pH} = 6$ and the initial adsorption rate was very fast. On the other hand, equilibrium experiments showed that Langmuir and Freundlich isotherm models fitted well the experimental data.

Adsorption of nickel ions on weathered basaltic andesite products was evaluated by Shah *et al.* (2009) involving different factors such as contact time, initial nickel concentration and the temperature. Use of various isotherm models such as Freundlich, Langmuir, Temkin and Dubinin-Kaganer-Radushkevich isotherms showed that the kinetic data fitted well and the pseudo-second-order described the data well.

A study on the adsorption of lead (Pb) ions on clay from South Africa was done in a batch adsorber with pH as a determining factor. The saturation capacity of lead ions on clay was 62.1 mg g^{-1} which increased with increasing the pH of the system (Potgieter *et al.*, 2006). Also, lead ions adsorption on kaolinite clay from Nigeria at different initial concentrations and temperatures showed that the adsorption capacity increased from 3.94 to 8.85 mg g^{-1} by increasing the solution temperature. This suggested that the adsorption of lead ions on kaolinite clay is an endothermic (Unuabonah *et al.*, 2007a). The adsorption of lead ions on phosphatic clay from USA using batch equilibrium technique was 32 mg g^{-1} (Singh *et al.*, 2001). The effect of changing pH of solution on Pb ion adsorption by tripolyphosphate-impregnated kaolinite clay (where kaolinite from Nigeria) indicated that the adsorption depends on the pH of the solution. For example, at $\text{pH} = 4$ and the concentration as 500 ppm , the adsorption capacity was 24.7 mg g^{-1} (Unuabonah *et al.*, 2007b). Hectorite clay from USA and vermiculite clay from Spain were converted to functionalized hectorite and functionalized vermiculite using thiol groups and used to adsorb lead ions from aqueous solution. The maximum adsorption capacity of functionalized vermiculite clay for lead ions was 33 mg g^{-1} and higher than the functionalized hectorite of 10 mg g^{-1} (Diaz *et al.*, 2007). Three types of Saudi natural clays (namely Tabuk, Baha and Khaiber) were used to adsorb lead ions from wastewater. The maximum adsorption capacity of these clays was 30 , 25 and 10 mg g^{-1} for Tabuk, Baha and Khaiber clay, respectively (Al-Jlil and Alsewailem, 2009).

In adsorption studies, some parameters such as kinetic and equilibrium are important in order to design a batch adsorber. To characterize the resistance of the hydrodynamic boundary layer, the external mass transfer coefficients can be obtained from the initial adsorption data. Whereas, the internal mass transfer coefficient can be obtained from the experimental adsorption rate data after

the initial period of adsorption. A review of literature indicated that single resistance models based on external mass transfer can be used to calculate the external mass transfer coefficient. The diffusion of solute within the pellet through the liquid in the pores is called pore diffusion. Normally, surface diffusion occurs when the solute diffuses within the pellet along the walls of the pores (McKay and Al-Duri, 1990).

The objective of this study was to test and evaluate Bentonite clay as an adsorbent for the adsorption of chromium and lead ions from wastewater using Saad two resistance internal diffusion model in order to calculate the time constant and equilibrium parameters required to design a batch adsorber.

MATERIALS AND METHODS

Materials: Bentonite clay from Jeddah city, Saudi Arabia was used as an adsorbent. The chromium (Cr) and lead (Pb) ions solution were prepared from chromium nitrate and lead nitrate purified LR supplied by S. define-chem. Limited (Laboratory Rasayan) and used as adsorbate.

Characterization of Bentonite clay (adsorbent): Bentonite clay was analyzed chemically by XRF (Table 1). The physical properties of Bentonite clay were determined by the standard methods (Table 2). The XRD analysis of Bentonite clay verified that it contained 80% montmorillonite, 10% kaolinite and illite and quartz as 10%.

Table 1: Chemical analysis of Bentonite clay by XRF

Elements	Content (wt%)
SiO ₂	55.00±3.0
Al ₂ O ₃	22.00±2.0
TiO ₂	1.50±0.25
Fe ₂ O ₃	5.67±0.5
MgO	2.30±0.45
CaO	<2.00
Na ₂ O	<2.00
K ₂ O	<1.00
P ₂ O ₅	0.20
S O ⁻³	0.002
Cl ⁻	0.20
Cr ₂ O ₃	0.02
Mn ₂ O ₃	0.03
Loss on ignition	9.80

Table 2: Characteristic properties of Bentonite clay

Characteristics	Values
BET surface area (m ² g ⁻¹)	62.5671
Pore volume (p/p ₀ = 0.97) (cm ³ g ⁻¹)	0.098005
Average pore width (Å)	62.656
Average pore diameter (Å)	95.650
Porosity (%)	16.7
Solid density (g cm ⁻³)	2.63

Equilibrium experiments: Equilibrium isotherms of Bentonite clay were determined by placing a constant mass of 1 g of clay with 50 mL lead ions solution in glass bottles on an agitation shaker. The concentration of lead ion solution ranged between 50 and 1300 ppm during each isotherm run. While, the concentration of chromium ions ranged between 50 and 800 ppm. The particle size of clay was 0.25 mm with temperature as 20°C for isotherm determination. Based on the preliminary observations, the adsorption process attained the state of equilibrium after 30 min, thus the equilibrium experiments were run for 3 h to ensure that the adsorption process is in equilibrium. After this process, the samples were filtered, diluted and the absorbance was measured by atomic absorption spectroscopy. The absorbance of samples was converted to concentrations using the standard calibration curves of lead and chromium ions. However, the amount of lead and chromium ions adsorption on the clay was calculated from the mass balance equation on the batch reactor as follows:

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

where, M is the clay mass (g), V is the volume of the solution (L), q_e is the amount of adsorption (mg g^{-1}), C_0 is the initial solution concentration of lead and chromium ions as (mg L^{-1}) and C_e is the concentration of the lead and chromium ions at equilibrium (mg L^{-1}). The equilibrium adsorption isotherm curves were obtained from the graph of amount of lead and chromium ions adsorbed on clay versus their concentration as shown in Fig. 1.

Kinetic experiments: Kinetic experiments were performed to determine the experimental adsorption rates. In these experiments, the lead and chromium ions concentration in the bulk solution was decreased over time until it reached the state of equilibrium. The experiments on the rate of adsorption were run for a total period of 3 h. A specific agitation speed was used with 1 g of clay sample added to 50 mL of lead and chromium ions solution separately having a specific initial metal ions solution concentration in bottles placed on a thermostat-controlled shaker. After starting the shaking, a sample of one bottle was taken at different time intervals till the end of

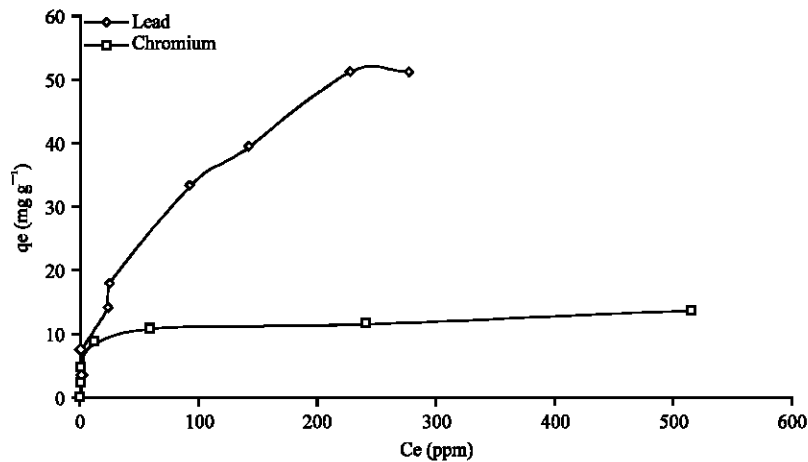


Fig. 1: Equilibrium isotherm for lead and chromium ions on Bentonite clay

3 h. Filtration of the mixture was done and the absorbance was measured by atomic absorption spectroscopy. Later on, the absorbance was converted to concentration.

Adsorption rate versus agitation speed and initial metal ions concentration: To determine the effect of agitation speed on the rate of metal ion adsorption, three agitation speeds (100, 200 and 270 RPM), at 20°C with 1 g of Bentonite clay having a particle diameter of 0.25 mm was placed in 50 mL of metal ions (chromium or lead ions) solution with an initial concentration of 200 ppm. In these experimental runs, the initial concentration of chromium and lead ions was kept constant before adding the Bentonite clay in the metal (chromium or lead) solution in the bottles. After starting the experiment, samples of metal (chromium or lead ions) solutions were collected at various time intervals during 3 h period, filtrated and the concentration was determined by atomic absorption spectroscopy. The data was plotted as the concentration versus the time as shown in Fig. 2 and 3.

The experiments were also carried at different initial concentrations of lead ion (154, 216, 307 ppm) to determine the effect of varying initial concentrations on adsorption rate at 20°C.

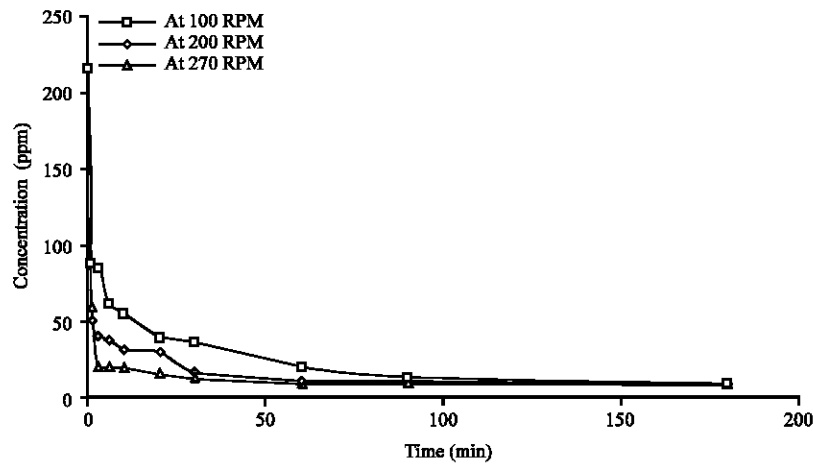


Fig. 2: Effect of different agitation speed on adsorption of lead on Bentonite clay

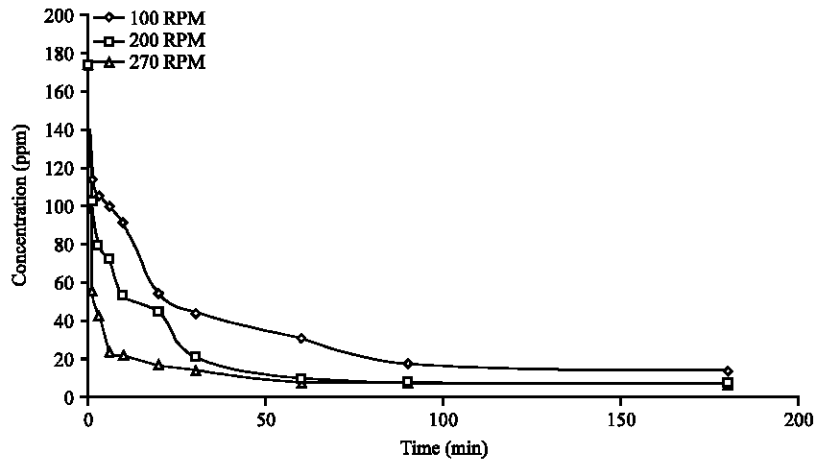


Fig. 3: Effect of different agitation speed on adsorption of chromium on Bentonite clay

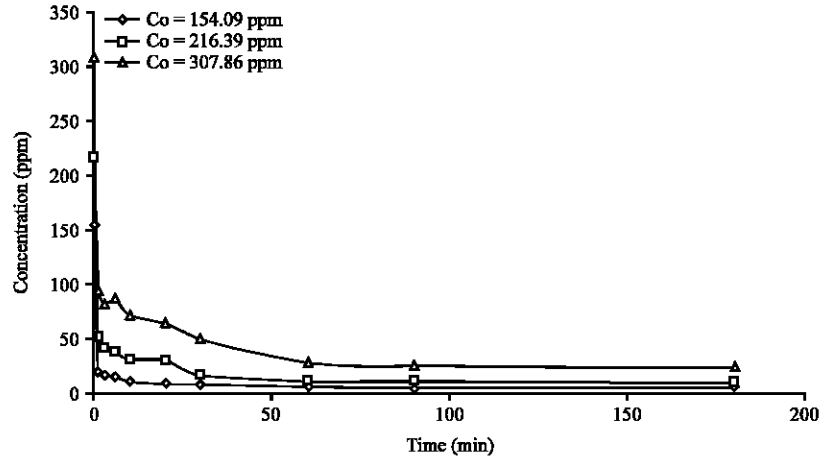


Fig. 4: Effect of different initial concentrations on adsorption of lead on Bentonite clay

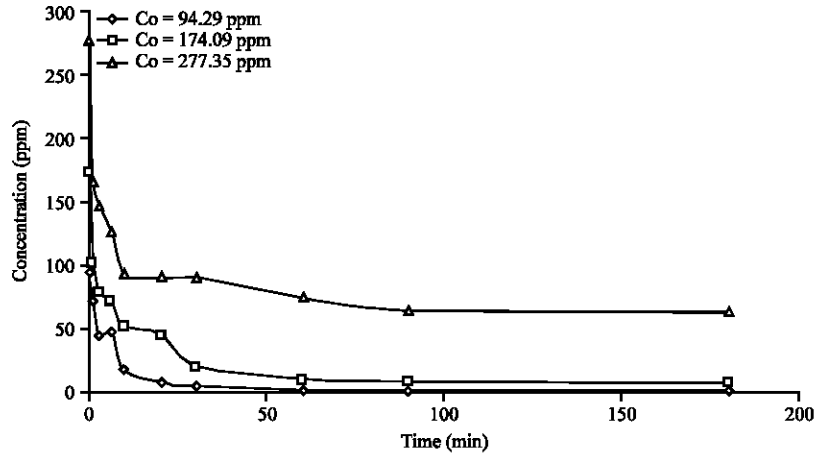


Fig. 5: Effect of different initial concentrations on adsorption of chromium on Bentonite clay

One gram of Bentonite clay having a particle diameter of 0.25 mm was added to 50 mL of lead solution. The agitation speed was 200 RPM. The experimental procedure was the same as followed for chromium ion. The data were plotted as concentration versus time as shown in Fig. 4.

Further experiments were carried at different initial concentration of chromium ion (94, 174, 277 ppm) to determine the effect of varying initial concentrations on the adsorption rate at 20°C. In this case, 1 g of Bentonite clay having a particle diameter of 0.25 mm with an agitation speed of 200 RPM was added to 50 mL of chromium solution. The experimental procedure to determine the chromium ions concentration in the bulk solution was the same as described earlier. The data collected were plotted as concentration versus time as shown in Fig. 5.

Analysis of equilibrium isothermal model: One form of equilibrium isotherm model namely Saad isotherm model was employed in this study. The equilibrium parameters were estimated by correlating the equilibrium equations with the data from equilibrium experiments using nonlinear regression technique (i.e., `fminsearch` function from MATLAB). Hence, the equilibrium parameters were utilized to describe the chromium and lead ions removal by Bentonite clay as an adsorbent in a batch adsorber.

Saad isotherm model: The study presented a novel isotherm model, a modification of Langmuir model and used instead of Langmuir model. Because, the Langmuir model can not fit the experimental data very well on a heterogeneous surface. This model was called as Saad isotherm model. This model has three parameters and was used to fit the experimental data on heterogeneous surface. The Saad isotherm model can be written as follows:

$$q_e = \frac{K_s C_e}{[1 + b_s C_e]^{bb}} \quad (2)$$

Where:

$$bb = 1 - S^2 b_s C_e$$

The main advantage of this model is its applicability to equilibrium experiments on homogeneous and heterogeneous surfaces. Where, S is the heterogeneity parameter and when $S = 0$, this model is converted to Langmuir model. It is well known that, Langmuir model fits the experimental data on homogenous surface very well. At $S < 0$, the model fits the experimental data on heterogeneous surface as shown from the results in Table 3.

The Saad isotherm model parameters K_s , b_s and S were obtained using the non-linear regression technique given in Eq. 2.

Data in Fig. 6 and 7 show the non-linear relationship between C_e and q_e for the Bentonite clay. The equilibrium parameters K_s , b_s and S were calculated by non-linear regression technique and presented in Table 3. The results in Fig. 6 and 7 illustrate that Saad equation fitted the experimental data well.

Table 3: Saad equilibrium parameters for the chromium and lead ions adsorption on Bentonite clay

Metal type	K_s (L g ⁻¹)	b_s (L mg ⁻¹)	S	R ²
Chromium	12.4558	1.2378	0.0088	0.9695
Lead	1.0075	0.0204	0.1464	0.9755

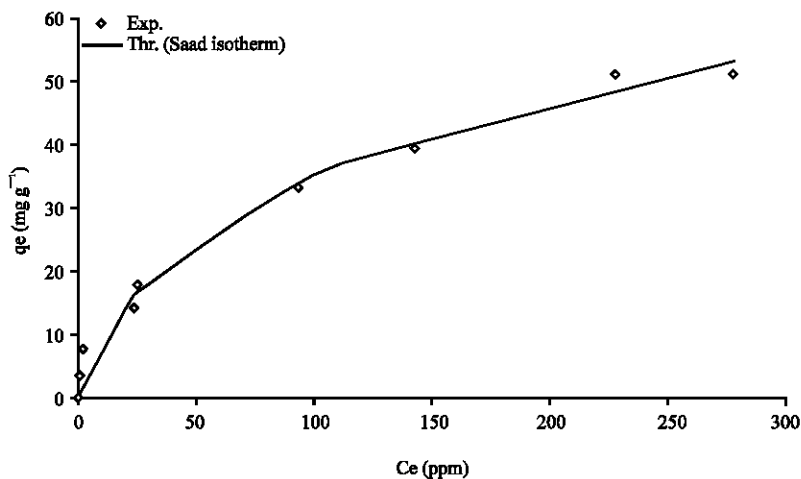


Fig. 6: Equilibrium isotherm data fitting with Saad isotherm model between lead ions and Bentonite clay

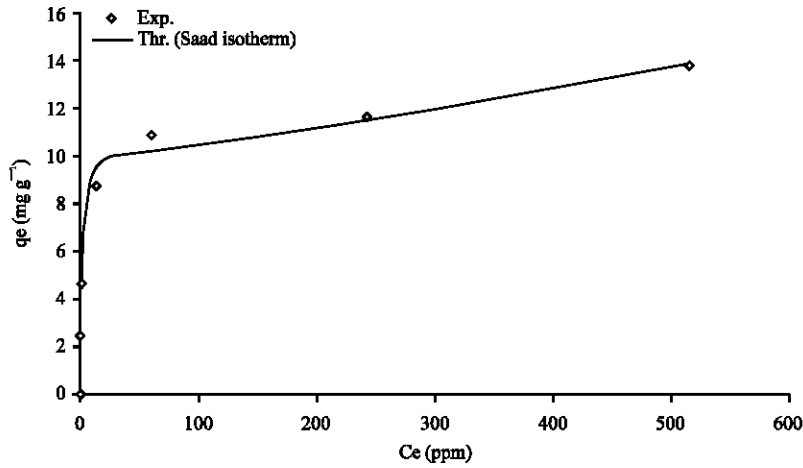


Fig. 7: Equilibrium isotherm data fitting with Saad isotherm model between chromium ions and Bentonite clay

Saad two internal parallel resistances model: The study presented a novel mass transfer model based on two internal resistances in parallel with nonlinear isotherm equation (Saad isotherm equation). This model was named as Saad Two Internal Parallel Resistances Model (STIPRM) and was used to calculate the adsorption rate constants, k_1 and k_2 (1 sec^{-1}) and the adsorption fraction f . It is helpful to use internal mass transfer model as the only rate controlling step for explaining the experimental adsorption rate data after the initial period of adsorption and to calculate preliminary kinetic parameters. The kinetic parameters can be used to predict the concentration-time curves in the batch adsorber.

Presentation of saad two internal parallel model mechanism: The internal layers of the clay particles expand during adsorption causing variations in pore sizes during the process. In examining this mechanism, the influence of the external mass transfer resistance seems insignificant as compared to the internal diffusion resistance. Therefore, mass transfer control shifts to the internal pores. For example, there is a diffusion into the pores of the clay. The presentation of parallel model mechanism is shown in Fig. 8, where the shape of the clay particle can be represented as a sphere.

Mass transfer model based on two internal resistances in parallel with Saad isotherm equation: The basic equations describing this model are as follows:

The two adsorption rates occurring in parallel inside the clay particle were represented as follows:

$$f(dq_1/dt) = k_1 (q_s - q_1) \quad (3)$$

$$(1-f) (dq_2/dt) = k_2 (q_s - q_2) \quad (4)$$

The mass balance equation on the batch adsorber is given by:

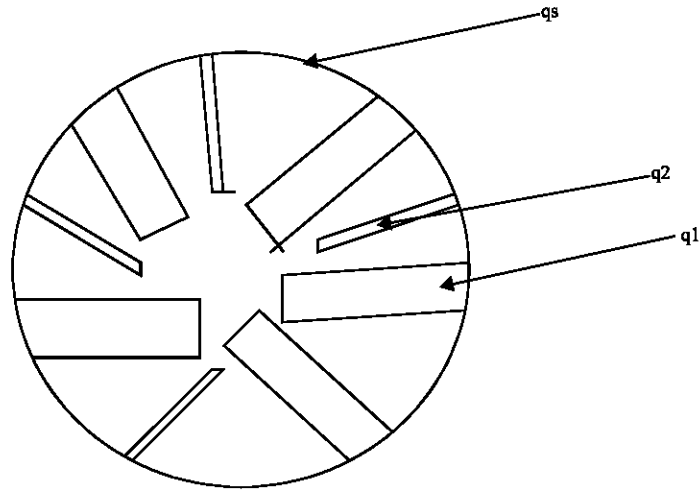


Fig. 8: Presentation of parallel model mechanism

$$C_o - C_t = M_s (q_1 + q_2) \quad (5)$$

As there is no external mass transfer resistance, q_s is in equilibrium with C_t . Therefore, the Saad model can be written as follows:

$$q_e = \frac{K_s C_t}{[1 + b_s C_t]^{bb}} \quad (6)$$

Where:

$$bb = 1 - S^2 b_s C_t$$

where, q_s is the adsorbed metal ions concentration on the outer surface (mg g^{-1}), q_1, q_2 is the adsorbed metal ions concentration within the different pores of the clay (mg g^{-1}), C_o is the initial concentration of metal ions (mg L^{-1}) and C_t is the metal ions concentration in bulk solution at equilibrium (mg L^{-1}). k_1 and k_2 is the adsorption rate constants expressed as sec^{-1} and f is the adsorption fraction. Where $f = q_1 / (q_1 + q_2)$.

By substituting Eq. 6 in Eq. 3, we get:

$$f (dq_1/dt) = k_1 \left(\frac{K_s C_t}{[1 + b_s C_t]^{bb}} - q_1 \right) \quad (7)$$

By rearranging Eq. 7, we get:

$$dq_1/dt = \frac{k_1}{f} \left(\frac{K_s C_t}{[1 + b_s C_t]^{bb}} - q_1 \right) \quad (8)$$

By rearranging Eq. 5, we get:

$$q_2 = (C_o - C_t - q_1 Ms) / Ms \quad (9)$$

By substituting Eq. 6 and 9 into Eq. 4, we get:

$$(1-f) \{d[(C_o - C_t - q_1 Ms) / Ms] / dt\} = k_2 \left\{ \frac{K_s C_t}{[1 + b_s C_t]^{bb}} - [(C_o - C_t - q_1 Ms) / Ms] \right\} \quad (10)$$

The rearrangement of Eq. 10 yields:

$$\frac{dC_t}{dt} = - \frac{M_s K_2 C_t K_s}{(1-f)(1 + b_s C_t)^{bb}} + \frac{k_2}{(1-f)} [(C_o - C_t - M_s q_1) - \frac{K_1 M_s}{f} \left[\frac{C_t K_s}{(1 + b_s C_t)^{bb}} - q_1 \right]] \quad (11)$$

By solving Eq. 8 with Eq. 11 we get the adsorption rate constants k_1 and k_2 (1 sec^{-1}) and the adsorption fraction f . In addition, we get the concentration-time curve for the batch adsorber. In this model, the values of M_s (mass of clay per metal ions solution volume) and K_s (the Saad isotherm constant) and b_s is the Saad isotherm constant and the initial concentration of metal ions in solution (C_o) was known.

Numerical solution of the non-linear adsorption systems: This system of ordinary differential equations was solved simultaneously using ODE15s solver from MATLAB with nonlinear regression method (i.e., fminsearch function) to find the optimum values of the adsorption rate constants such (k_1 , k_2), adsorption fraction (f) and to yield the bulk concentration-time curves for the batch adsorber. The average Absolute Relative Percentage Deviations (AARD%) between the experimental values and the theoretical values were calculated along with R^2 .

RESULTS AND DISCUSSION

The optimum values of k_1 , k_2 and f , the Average Absolute Relative Percentage Deviation (AARD%) and R^2 for the various experiments are presented in Table 4-8. Figure 9-18 show the

Table 4: Parallel model parameters for lead ions with Bentonite clay at $C_o = 216.39$ and 174.09 ppm, agitation speed = 100 RPM

Parallel model with	Saad isotherm
$C_o = 216.39$ (ppm)	
K_1	0.0218
K_2	0.0001
F	0.2694
AARD (%)	0.466
R^2	0.714
$C_o = 174.09$ (ppm)	
K_1	0.0193
K_2	0.0001
F	0.3787
AARD (%)	0.414
R^2	0.740

Table 5: Parallel model parameters for lead ions with Bentonite clay at $C_o = 216.39$ and $C_o = 174.09$ ppm, agitation speed = 200 RPM

Parallel model with	Saad isotherm
$C_o = 216.39$ (ppm)	
K_1	0.1619
K_2	0.0001
F	0.6260
AARD (%)	0.3549
R^2	0.938
$C_o = 174.09$ (ppm)	
K_1	0.0555
K_2	0.0001
f	0.4273
AARD (%)	0.474
R^2	0.776

Table 6: Parallel model parameters for lead ions with Bentonite clay at $C_o = 216.39$ and 174.09 ppm, agitation speed = 270 RPM

Parallel model with	Saad isotherm
$C_o = 216.39$ (ppm)	
K_1	0.2024
K_2	0.0001
f	0.8571
AARD (%)	0.2592
R^2	0.994
$C_o = 174.09$ (ppm)	
K_1	0.5202
K_2	0.0001
f	0.6955
AARD (%)	0.517
R^2	0.896

Table 7: Parallel model parameters for lead ions with Bentonite clay at $C_o = 154.09$ and 94.29 ppm, agitation speed = 200 RPM

Parallel model with	Saad isotherm
$C_o = 154.09$ (ppm)	
K_1	0.2863
K_2	0.0000
f	1.0000
AARD (%)	0.523
R^2	0.992
$C_o = 94.29$ (ppm)	
K_1	0.0257
K_2	0.0001
f	0.4910
AARD (%)	0.3688
R^2	0.933

comparison between the experimental data and the predicted bulk concentrations from Saad diffusion model with Saad isotherm equations. The results clearly showed that Saad diffusion model fits the experimental data well.

It is further clear that the adsorption time constant values increased with an increase in the agitation speed. This may be due to the fact that the adsorption process is a two step mechanism involving external mass transfer in addition to the internal mass transfer. Because, the enhanced

Table 8: Parallel model parameters for lead ions with Bentonite clay at $C_o = 307.86$ and 277.35 ppm, agitation speed = 200 RPM

Parallel model with	Saad isotherm
$C_o = 307.86$ (ppm)	
K_1	0.2349
K_2	0.0000
f	0.8940
AARD (%)	0.4126
R^2	0.784
$C_o = 277.35$ (ppm)	
K_1	0.1068
K_2	0.0001
f	0.3210
AARD (%)	0.1433
R^2	0.886

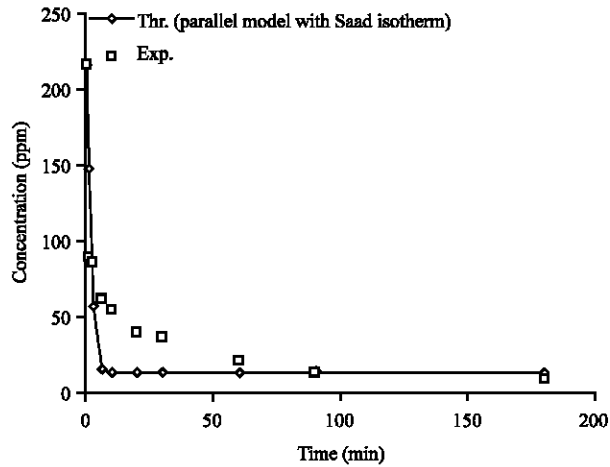


Fig. 9: Parallel model with Saad isotherm model fit of the kinetic data of lead with Bentonite clay, Conditions: $C_o = 216.39$ ppm, agitation speed = 100 RPM

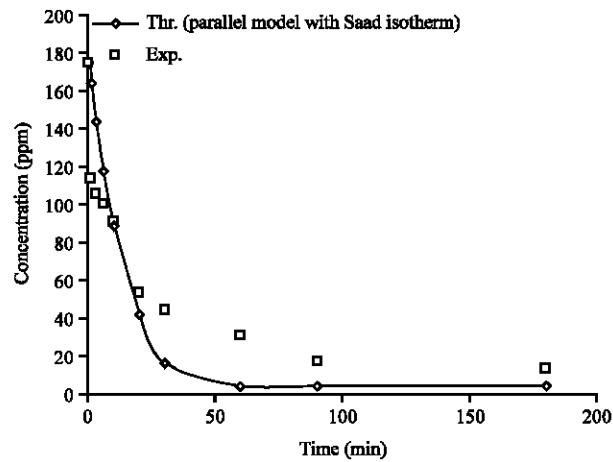


Fig. 10: Parallel model with Saad isotherm model fit of the kinetic data of chromium with Bentonite clay, conditions: $C_o = 174.09$ ppm, agitation speed = 100 RPM

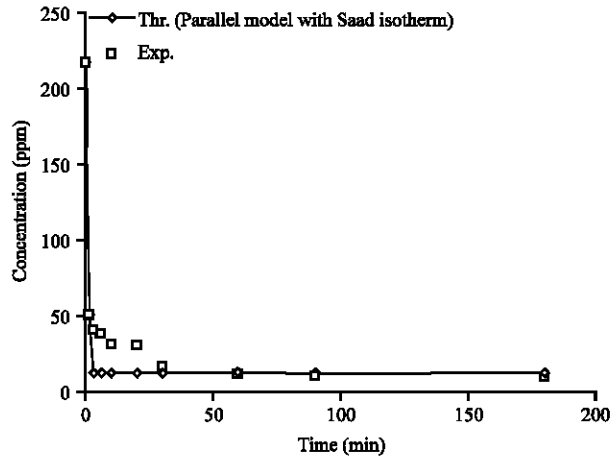


Fig. 11: Parallel model with Saad isotherm model fit of the kinetic data of lead with Bentonite clay, Conditions: $C_o = 216.39$ ppm, agitation speed = 200 RPM

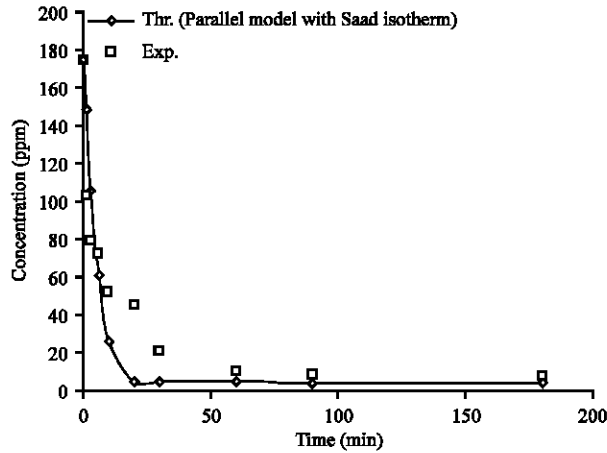


Fig. 12: Parallel model with Saad isotherm model fit of the kinetic data of chromium with Bentonite clay, Conditions: $C_o = 174.09$ ppm, agitation speed = 200 RPM

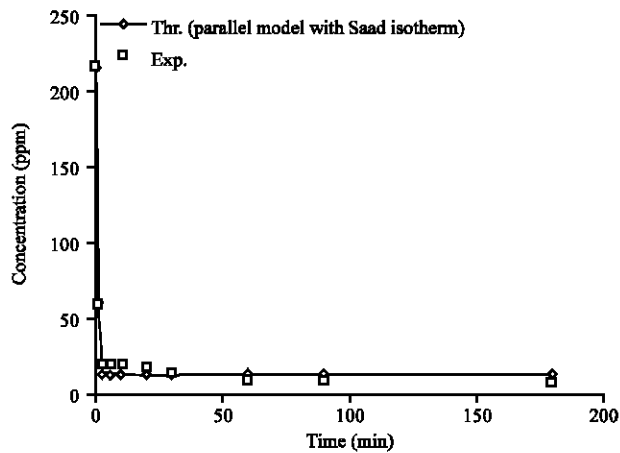


Fig. 13: Parallel model with Saad isotherm model fit of the kinetic data of lead with Bentonite clay, Conditions: $C_o = 216.39$ ppm, agitation speed = 270 RPM

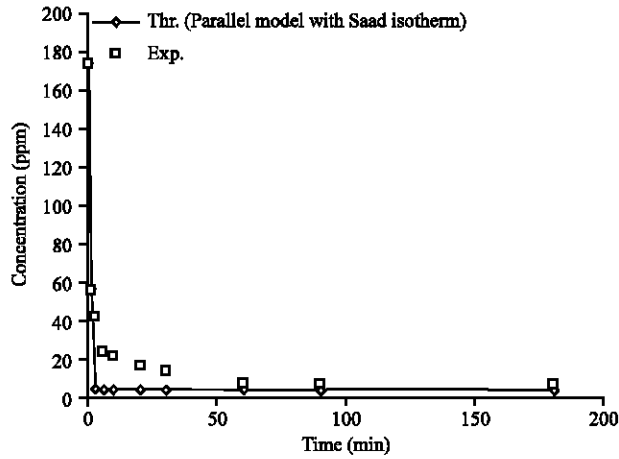


Fig. 14: Parallel model with Saad isotherm model fit of the kinetic data of chromium with Bentonite clay, Conditions: $C_0 = 174.09$ ppm, agitation speed = 270 RPM

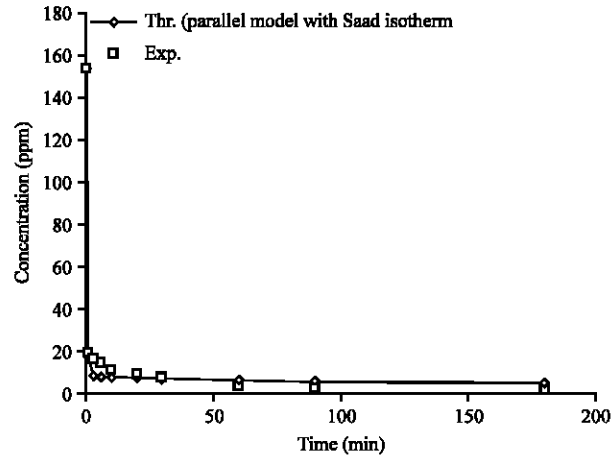


Fig. 15: Parallel model with Saad isotherm model fit of the kinetic data of lead with Bentonite clay, Conditions: $C_0 = 154.09$ ppm, agitation speed = 200 RPM

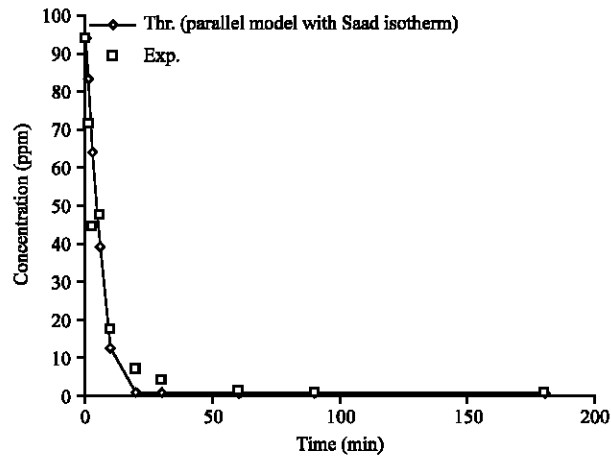


Fig. 16: Parallel model with Saad isotherm model fit of the kinetic data of chromium with Bentonite clay, Conditions: $C_0 = 94.29$ ppm, agitation speed = 200 RPM

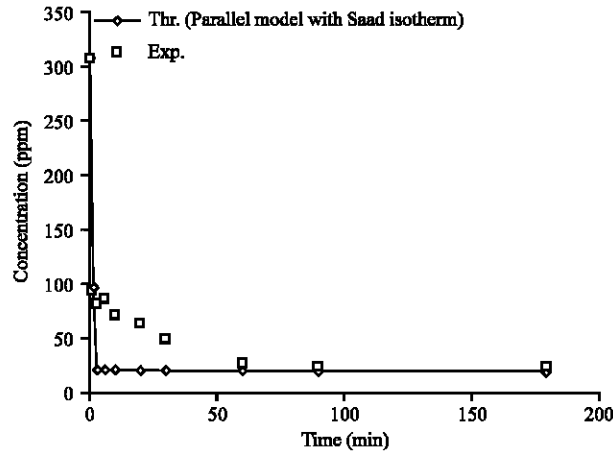


Fig. 17: Parallel model with Saad isotherm model fit of the kinetic data of lead with Bentonite clay, Conditions: $C_o = 307.86$ ppm, agitation speed = 200 RPM

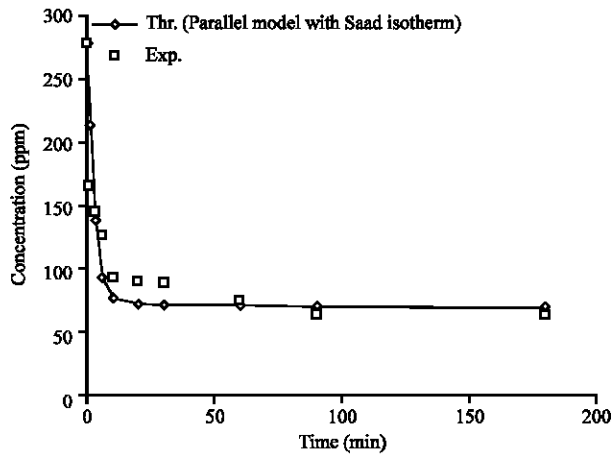


Fig. 18: Parallel model with Saad isotherm model fit of the kinetic data of chromium with Bentonite clay, Conditions: $C_o = 277.35$ ppm, agitation speed = 200 RPM

agitation speed decreases the external mass transfer resistance thus enabling the metal ions to concentrate on clay surface. Consequently there will be greater driving force for internal diffusion resulting in higher adsorption time constant values. Similar views were reported by McKay (1983) and Potgieter *et al.* (2006) who stated that increasing the agitation speed increases the adsorption rate constant in the adsorption process between the metal ions and the adsorbent.

Furthermore, there was an increase in the values of adsorption time constant with increasing the initial metal solution concentrations. This indicated that increasing the bulk solution concentration increases the driving force of metal ions from the bulk onto the clay surface and then into the pores of clay particle. These research findings are agreement with those of McKay (1983) who observed the same pattern in the metal ions adsorption process with increasing the concentration of the bulk solution.

From data in Fig. 9-18, it is clear that under different experimental conditions, the external mass transfer controlled the adsorption rate for a short time and then the main resistance to adsorption was internal diffusion.

CONCLUSION

This study for the adsorption of lead and chromium ions on Bentonite clay showed that Saad isotherm model agreed most favorably with the experimental data. Calculations of the internal diffusion time constants to characterize the slow rate of adsorption indicated that most of the adsorption occurred during the initial period. This phenomena of adsorption occurrence at the initial period suggested that internal diffusion is the major rate-controlling step for quantifying the rate of lead and chromium ions removal from wastewater.

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