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Characterization and Application of Bentonite Clay for Lead Ion Adsorption from Wastewater: Equilibrium and Kinetic Study

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ABSTRACT

The main objective of this study was to characterize Bentonite natural clay from West of Saudi Arabia and evaluate its performance for lead ions adsorption from wastewater at different temperatures. It was found that the adsorption capacity of Bentonite clay increased by increasing the temperature of the system. The Langmuir model described the experimental data at different temperatures very well. The maximum adsorption capacity of Bentonite clay was 51.19 mg g⁻¹ at 20°C and 54.62 mg g⁻¹ at 80°C. The thermodynamic parameters such as enthalpy, entropy and Gibbs energy were also obtained. The results showed that the adsorption is endothermic and favorable at high temperatures. The kinetics of lead ions on Bentonite clay was determined. The mathematical models, to characterize experimental results for the batch systems, included the resistance models based on external mass transfer and internal mass diffusion. The kinetic model based on external mass transfer predicted the experimental adsorption behavior for only a short time. A novel diffusion model called as Saad Internal Diffusion Model (SIDM) was obtained to calculate the internal diffusion coefficient in a batch adsorber. It was observed that the internal mass diffusion is a major rate-controlling step during the lead ions removal process from wastewater. The economic study based on adsorption capacity showed potential feasibility of using Bentonite clay as an alternative to activated carbon for lead ions removal from wastewaters.

Key words: Lead ions, Bentonite clay, adsorption capacity, kinetic, internal diffusion, temperatures

INTRODUCTION

Lead ions in wastewater is an inorganic pollutant and harmful both to human being and water environments. Therefore, it is necessary to eliminate lead ions from the wastewater prior to its disposal to the environment. In general, adsorption of heavy metals from wastewater is carried by activated carbon (Quek *et al.*, 1998). On the other hand, use of activated carbon for lead ions removal is relatively costly. Many investigators have used different types of clays as an alternative adsorbent for the adsorption of lead ions on cost effective basis (Potgieter *et al.*, 2006; Unuabonah *et al.*, 2007a, b; Singh *et al.*, 2001; Diaz *et al.*, 2007). However, no research has been found on Bentonite natural clay (from Saudi Arabia) as an adsorbent to adsorb lead ions from wastewater.

Adsorption of lead ions on clay from South Africa was investigated using batch adsorber. The saturation capacity of lead ions on this clay was 62.1 mg g⁻¹. A study showed that the adsorption capacity increased with increasing pH in a batch adsorber (Potgieter *et al.*, 2006). The lead ions adsorption on kaolinite clay from Nigeria was studied at different initial concentrations and temperatures. The adsorption capacity increased from 3.94 to 8.85 mg g⁻¹ by increasing the solution

temperature. This indicated that the adsorption of lead ions on kaolinite clay is an endothermic (Unuabonah *et al.*, 2007a). Adsorption of lead ions on phosphatic clay from USA was investigated using a batch equilibrium technique. It was found that the adsorption capacity of lead ions was 32 mg g⁻¹ (Singh *et al.*, 2001). The adsorption of lead ions on tripolyphosphate-impregnated kaolinite clay (where kaolinite from Nigeria) was studied by changing the pH of the solution. It was found that the adsorption of the lead ions from solution depends on the pH of the solution. For example, at pH = 4 and concentration = 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 to adsorb lead ions from aqueous solution. The results showed that the maximum adsorption capacity of functionalized vermiculite clay to adsorb lead ions was 33 mg g⁻¹ and higher than the maximum adsorption capacity of the functionalized hectorite of 10 mg g⁻¹ (Diaz *et al.*, 2007). Some researchers used three types of Saudi natural clays (Tabuk, Baha and Khaiber) to adsorb lead ions from wastewater. They found that the maximum adsorption capacities of Tabuk, Baha and Khaiber clays were 30, 25 and 10 mg g⁻¹, respectively (Al-Jlil and Alsewailem, 2009).

The kinetic and equilibrium parameters are necessary to design a batch adsorber and fixed bed system. The external mass transfer coefficient characterizing the resistance of the hydrodynamic boundary layer can be obtained from the initial adsorption data. While, the internal mass transfer coefficient can be obtained from the experimental adsorption rate data after the initial period of adsorption. However, a review of literature showed that single resistance models based on external mass transfer can be used to calculate the external mass transfer coefficient. Accordingly the internal mass transfer coefficient can be calculated from single resistance models where these diffusion models are used to describe pore diffusion resistance or surface diffusion resistance. The diffusion of solute within the pellet through the liquid in the pores is called pore diffusion. While, the surface diffusion occurs when the solute diffuses within the pellet along the walls of the pores (McKay and Al-Duri, 1990).

The aim of this study is to examine the use of Bentonite natural clay as an adsorbent for the adsorption of lead ions from wastewater and calculate the kinetic and equilibrium parameters.

MATERIALS AND METHODS

Materials: The adsorbent used in this study was the Bentonite natural clay obtained from Bentonite city in the west of Saudi Arabia. The adsorbate was the lead ions solution prepared from lead nitrate purified LR [Pb(NO₃)₂] supplied by S.define-chem., Limited (Laboratory Rasayan).

Characterization of Bentonite natural clay (adsorbent): The chemical analysis of Bentonite natural clay was carried by X-Ray Diffraction (XRD) and presented in Table 1. The physical properties of Bentonite natural clay were done by the standard methods as shown in Table 2. The results from the XRD verify the presence of a minimum of 80% montmorillonite, 10% kaolinite and illite and quartz 10% as a maximum in Bentonite natural clay.

Equilibrium experiments: Equilibrium isotherms for the Bentonite clay were determined by placing a constant mass of clay (1 g) with 50 mL lead ions solution in glass bottles on an agitation shaker. In each isotherm run, the lead ions solution concentrations ranged from 50-1300 mg L⁻¹. The particle size of clay used to determine the isotherms was 0.25 mm. The solution temperatures ranges were 20-80°C. The adsorption process reached to a state of equilibrium after 30 min but the

Table 1: Chemical analysis of Bentonite natural clay by XRD

Elements	Content (wt%)
SiO ₂	55.00±3.00
Al ₂ O ₃	22.00±2.00
TiO ₂	1.50±0.25
Fe ₂ O ₃	5.67±0.50
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 natural 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 were carried for 3 h ensure that the adsorption process has attained the state of equilibrium. After that, the samples were filtered using filter papers, then diluted and absorbance measured using atomic absorption spectroscopy. Later on, the absorbance of samples was converted to concentrations using the established calibration curve for lead ions. The amount of lead 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 clay mass (g), V is volume of the solution (L), q_e is, the amount of adsorption (mg g⁻¹). C₀ is initial solution concentration of lead ions (mg L⁻¹) and C_e is concentration of the lead ions at equilibrium (mg L⁻¹). The amount of lead ions adsorbed on clay versus the lead ions concentration was plotted to obtain the equilibrium adsorption isotherm curves.

Kinetic experiments: The kinetic experiments were performed to obtain the experimental adsorption rates. In these experiments, the lead ions concentration in the bulk solution was decreased over time until it reached to a state of equilibrium. In the adsorption rate experiment for a period of 3 h and using a specific agitation speed, 1 g mass of clay was added to 50 mL of lead ions solution having a specific initial lead ions solution concentration in bottles placed on a thermostat-controlled shaker. After starting the shaking, a sample of one bottle was taken at

different period of times until completing the 3 h. The filtration of the mixture was done and the absorbance measured by atomic absorption spectroscopy. After that, the absorbance measurement was converted to concentration.

RESULTS AND DISCUSSION

Effect of pH on lead ions adsorption on the Bentonite clay: The effect of changing pH from 1.8 to 7.5 by NaOH (0.5 M) and HCl (0.5 M) on the adsorption of lead ions on Bentonite clay was studied. Because the precipitation of lead starts at pH of 7.48 as observed from the experimental preparations. At low pH, the positive charges increase (Elliott and Huang, 1981) and the adsorption decreases due to the increase of positive charge sites on the clay as shown in Fig. 1.

Equilibrium experiments: The amount of lead adsorbed on Bentonite clay versus the lead equilibrium concentration in the solution was plotted to obtain the equilibrium adsorption isotherm curves at different temperatures as shown in Fig. 2. The maximum adsorption capacity of lead ions on Bentonite clay was 51.19 mg g^{-1} at 20°C and 54.62 mg g^{-1} at 80°C . The lead ions adsorption on the negative sites of the clay is the result of the electrostatic attraction between these sites and the lead ions. The number of negative sites formed on the clay surface is mainly due to presence of silica (Elliott and Huang, 1981).

Kinetic experiments: The effect of two parameters namely agitation speed and initial lead ions concentrations was studied on the adsorption rate of lead ion on clay.

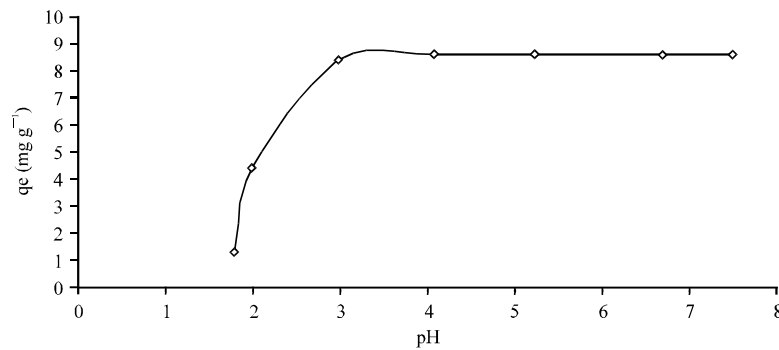


Fig. 1: pH effect on adsorption of leads ions on Jeddah clay

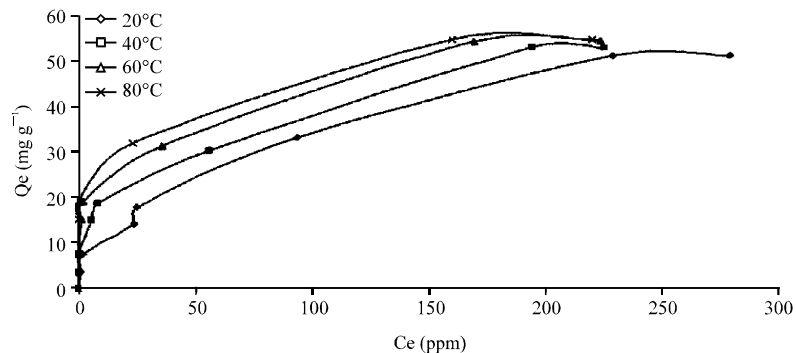


Fig. 2: Equilibrium isotherm for lead ions adsorption on Jeddah clay

In these experiments, various runs were carried at different agitation speeds (100, 200 and 270 RPM) to study the effect of agitation speed on the adsorption rate at 20°C with 1 g mass of clay having 0.25 mm particle diameter in 50 mL of lead ions solution at an initial concentration of 200 mg L⁻¹. In these experimental runs, the initial lead ions concentration was kept constant. The initial lead ions concentration was measured before adding the clay mass on the lead ions solution in the bottles. After starting the experiment over different time periods, the samples of lead ions solution were taken, filtrated and the absorbance was measured by atomic absorption spectroscopy. After that, these measurements were converted to concentration using the calibration curve. The data collected were plotted as concentration versus time as shown in Fig. 3.

Also, experimental runs were carried at different initial concentrations (200 to 700 mg L⁻¹) to investigate the effect of different initial concentrations on the adsorption rate at 20°C. For this purpose, 1 g of clay and an agitation speed of 200 RPM were used in 50 mL of lead ions solution with a particle diameter of 0.25 mm. The procedure used to determine the lead ions concentration in the bulk solution was the same as discussed above. The data collected were plotted as concentration versus time as shown in Fig. 4.

Equilibrium isotherm models: Two isotherm models namely Langmuir model and Freundlich model were applied in the linear forms to describe the experimental data for the Bentonite clay at different temperatures. These two models are described below.

Langmuir model: Langmuir model in the linear form is given as:

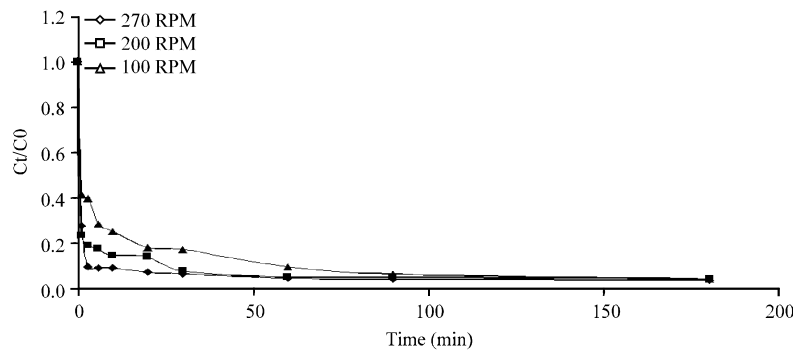


Fig. 3: Effect of agitation speed on adsorption rate of adsorption of lead ions on Jeddah clay

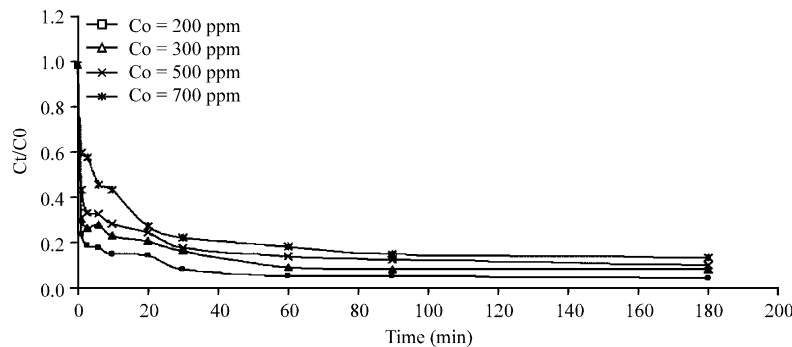


Fig. 4: Effect of initial concentration on adsorption rate of lead ions on Jeddah clay

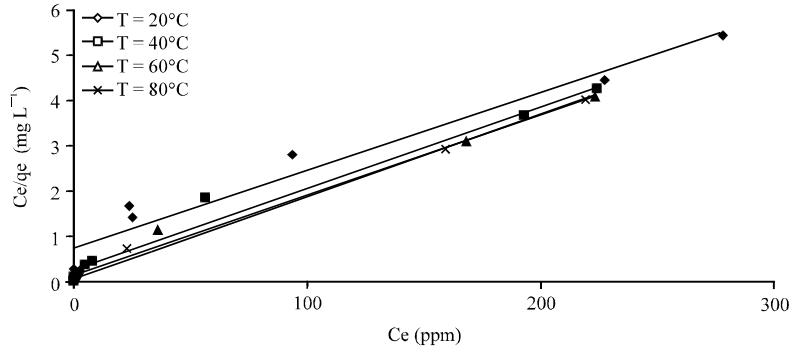


Fig. 5: Langmuir isotherm fits experimental data for lead ions adsorption

Table 3: Langmuir constants for the lead ions adsorption on Bentonite clay at different temperatures

Temperature (°C)	K_L ($L g^{-1}$)	b ($L g^{-1}$)	\hat{R}	R^2
20	1.336	0.023	0.135	0.948
40	3.241	0.060	0.069	0.963
60	6.627	0.122	0.035	0.981
80	9.588	0.175	0.025	0.986

$$\frac{C_e}{q_e} = \frac{1}{K_L} + \left(\frac{b}{K_L} \right) C_e \quad (2)$$

A plot of C_e/q_e versus C_e in Fig. 5 provides the constants K_L and b , for the system. The constants, K_L and b for lead ions are presented in Table 3.

The dimensionless equilibrium parameter, \hat{R} , is calculated to determine the favorability of the adsorption process of lead ions on Bentonite clay by using the following equation (El-Geundi *et al.*, 2005):

$$R' = \frac{1}{1 + bC_0} \quad (3)$$

where, b is the Langmuir constant and C_0 is the lead ions initial concentration. The dimensionless equilibrium parameter values for lead ions adsorbed on Bentonite clay were determined as given in Table 3. The values of the dimensionless equilibrium parameter are between $0 < \hat{R} < 1$. This range indicated that the adsorption process is favorable (El-Geundi *et al.*, 2005). Therefore, the adsorption process of lead ions on Bentonite clay is favorable.

Freundlich model: The Freundlich model in the linear form is described below:

$$\log q_e = \log K_F + \left(\frac{1}{n} \right) \log C_e \quad (4)$$

A plot of $\log (q_e)$ versus $\log (C_e)$ shown in Fig. 6 provides the constants, K_F and n for the system. The constants, K_F and n , for lead ions are presented in Table 4.

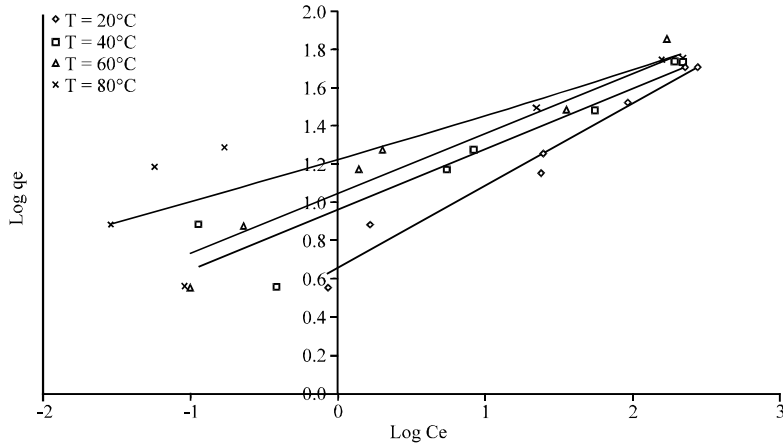


Fig. 6: Freundlich isotherm fits experimental data for lead ions on Jeddah clay

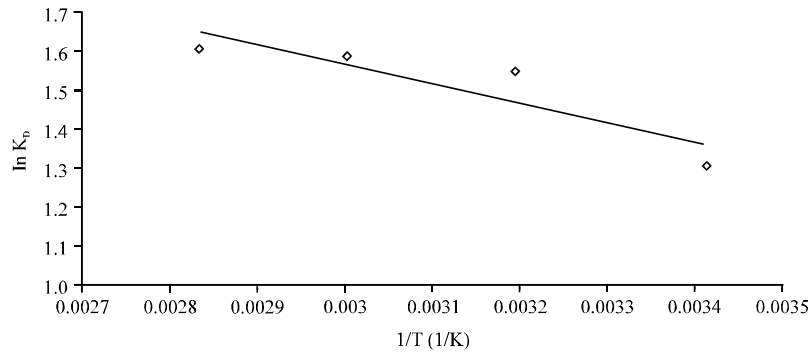


Fig. 7: Relationship between $\ln K_D$ vs. $1/T$

Table 4: Freundlich constants for the lead ions adsorption on Bentonite clay at different temperatures

Temperature (°C)	K_F ($L g^{-1}$)	n (-)	R^2
20	1.935	2.323	0.972
40	2.606	3.191	0.895
60	2.843	3.252	0.948
80	3.408	4.599	0.764

As shown from the values of R^2 in Table 3 and 4, Langmuir model fits the experimental data very well for lead ions adsorption on Bentonite clay and is slightly better than Freundlich model.

Estimation of thermodynamic parameters: The thermodynamic parameters are enthalpy change (ΔH), Gibbs free energy change (ΔG) and entropy change (ΔS).

The enthalpy change (ΔH) was calculated using the following equation (Ruixia *et al.*, 2004):

$$\ln K_D = \ln k_o + \left(\frac{-\Delta H}{R T} \right) \quad (5)$$

Hence, a plot of $\ln K_D$ versus $[1/T]$ provided the enthalpy change (ΔH) for the adsorption process as shown in Fig. 7. The enthalpy change (ΔH) was determined from the slope of the linear form as shown in Fig. 7 and Table 5.

Table 5: Thermodynamic parameters for lead ions adsorption on Bentonite clay

T (K)	K_D	1/T (1/k)	$\ln K_D$	ΔH (kJ mol ⁻¹)	ΔS [KJ/(mol. K)]	ΔG (kJ mol ⁻¹)
293	3.6867	0.003413	1.304732	4.155	0.025028	-3.17833
313	4.7049	0.003195	1.548605	4.155	0.02615	-4.02991
333	4.8824	0.003003	1.585637	4.155	0.02566	-4.38993
353	4.982	0.002833	1.605831	4.155	0.025121	-4.71286

The standard Gibbs free energy change (ΔG) was calculated using Gibbs equation as follows (Ruixia *et al.*, 2004):

$$\Delta G = -RT \ln K_D \quad (6)$$

where, R is the gas constant, K_D is the dimensionless equilibrium constant, T is the absolute temperature and K_D is a constant. The K_D was calculated as follows according to Namasivayam and Ranganathan (1994).

$$K_D = \left(\frac{C_{s_m}}{C_{e_m}} \right) \quad (7)$$

where, C_{s_m} is the amount of lead ions adsorbed by the clay per liter of lead ions solution at equilibrium (mg L⁻¹) and C_{e_m} is the lead ions concentration in the solution at equilibrium (mg L⁻¹). The reference states were defined based on the amount of lead ions adsorption on clay as mg g⁻¹ and the lead ions concentration in the solution by mg L⁻¹.

The entropy change (ΔS) was calculated using Gibbs-Helmholtz equation (Ruixia *et al.*, 2004) as follows:

$$\Delta S = \left(\frac{\Delta H - \Delta G}{T} \right) \quad (8)$$

The values of these constants are given in Table 5. As shown from data in Table 5, the value of the enthalpy is positive, that means, the adsorption is endothermic. Also, it is clear from Table 5 that with increasing the temperature, the values of standard Gibbs free energy decreases which mean that the adsorption system is favorable at high temperatures. The positive value of entropy means that the system becomes more random at the interface of the clay-lead ions solution during the adsorption of lead ions on Bentonite clay (Qadeer and Khalid, 2005).

Kinetic models: The study of the kinetic of lead ions on Bentonite clay in a batch adsorber is significant in order to find the kinetic parameters such as diffusion coefficient by correlating the proposed model with the experimental data. Also, the adsorption rate controlling steps can be determined by correlating the batch kinetic results with the proposed kinetic model.

The four steps for lead ions adsorption on Bentonite clay were as below according to McKay *et al.* (1980):

Step 1: Mass transfer of lead ions from the solution to the outer surface of the particle

Step 2: Lead ions adsorption on the external adsorption sites after a crossing the film boundary layer

Step 3: Internal lead ions diffusion by pore diffusion mechanism or surface diffusion mechanism

Step 4: Lead ions adsorption on the internal adsorption sites

Generally, the adsorption process consists of the external mass transfer coefficient and internal mass transfer coefficient as described by the kinetic models. Because it is assumed that the adsorption rate is fast as compared to the diffusion rate. Consequently, external mass transfer and internal mass transfer resistances control the rate of the adsorption system. Therefore, only steps 1 and 3 are considered in the adsorption process modeling.

The objective of studying external and internal mass transfer models is to determine the adsorption rate-controlling steps as described in subsequent sections.

External mass transfer model: It is important to calculate the external mass transfer coefficients for the adsorption process in order to calculate the relationship between the concentration and time curves in the batch adsorber. Moreover, the calculation is useful for specifying the effect of the external boundary layer as it characterizes the external mass transfer rate.

The external mass transfer coefficients were calculated as follows:

When the external mass transfer is the rate-controlling step in the adsorption process, the adsorption rate $\left(\frac{dq_s}{dt}\right)$, can be written as:

$$m_s \bullet \left(\frac{dq_s}{dt}\right) = k_f \bullet S_s (C_t - C_s) \quad (9)$$

The mass balance on the batch system can be expressed as follows:

$$\left(\frac{dC_t}{dt}\right) = -k_f \bullet S_s (C_t - C_s) \quad (10)$$

From the initial conditions:

$$q = 0, C_t = C_0 \text{ at } t = 0 \quad (11)$$

When the adsorbent particle is assumed to be spherical, the external surface area, S_s , is evaluated as follows:

$$S_s = \left(\frac{6m_s}{dp \rho_s (1 - \epsilon_p)}\right) \quad (12)$$

External mass transfer resistance is the controlling step in the adsorption system since a negligible lead ions diffused into the pores of the adsorbent. If the equilibrium isotherm is linear then q_s is given as below:

$$q_s = K C_s \quad (13)$$

These equations can be solved analytically by the substituting Eq. 13 and joining the two differential Eq. 9 and 10 yield:

$$\left(\frac{d^2 C_t}{dt^2}\right) + k_f \bullet S_s \left(\frac{1+m_s K}{m_s K}\right) \left(\frac{dC_t}{dt}\right) = 0 \quad (14)$$

Equation 14 is linear ordinary differential equation and has an analytical solution (Mckay, 1983; McKay *et al.*, 1981) as follows:

$$\left(\frac{C_t}{C_0} - \frac{1}{1+m_s K}\right) = \left(\frac{m_s K}{1+m_s K}\right) \exp \left[-\left(\frac{1+m_s K}{m_s K}\right) K_f S_s t \right] \quad (15)$$

In logarithmic shape:

$$\ln \left(\frac{C_t}{C_0} - \frac{1}{1+m_s K}\right) = \ln \left(\frac{m_s K}{1+m_s K}\right) - \left[\left(\frac{1+m_s K}{m_s K}\right) K_f S_s t\right] \quad (16)$$

A straight line near $t = 0$ yields by plotting $\ln[C_t/C_0 - (1/1+m_s K)]$ versus time. Therefore, the external mass transfer coefficient can be calculated from the slope by recognizing the values of m_s and K .

Where:

- m_s is the mass of clay per lead ions solution volume (g cm^{-3})
- dp is the average particle diameter (cm)
- ϵ_p is the particle porosity
- ρ_s is solid density (g cm^{-3})
- K is the equilibrium constant for the linear segment of the equilibrium curve ($\text{cm}^3 \text{g}^{-1}$)

Calculating the K_f for the agitation speed and the initial lead ions concentration were done and the results are presented in Table 6 and 7.

As shown in Table 6, increasing the agitation speed caused a reduction in the external film mass transfer resistance and increased the external mass transfer coefficient thus increasing the adsorption rate. Consequently, the external mass transfer resistance is important in controlling the external adsorption rate (Marshall *et al.*, 1993; Asfour *et al.*, 1985).

Table 6: Effect of agitation speeds on external and internal mass transfer coefficients

Agitation speed (RPM)	External mass transfer coefficient, K_f (cm min^{-1})	Internal mass transfer coefficient, D_e ($\text{cm}^2 \text{min}^{-1}$)
100	0.1222	1.424e-9
200	0.2286	1.0737e-9
270	0.3564	7.233e-10

Table 7: Effect of initial lead ions concentrations on external and internal mass transfer coefficients

Initial lead ions concentration (ppm)	External mass transfer coefficient, K_f (cm min^{-1})	Internal mass transfer coefficient, D_e ($\text{cm}^2 \text{min}^{-1}$)
200	0.2286	1.0737e-9
300	0.1802	1.2433e-10
500	0.1527	8.0246e-10
700	0.0709	8.0246e-10

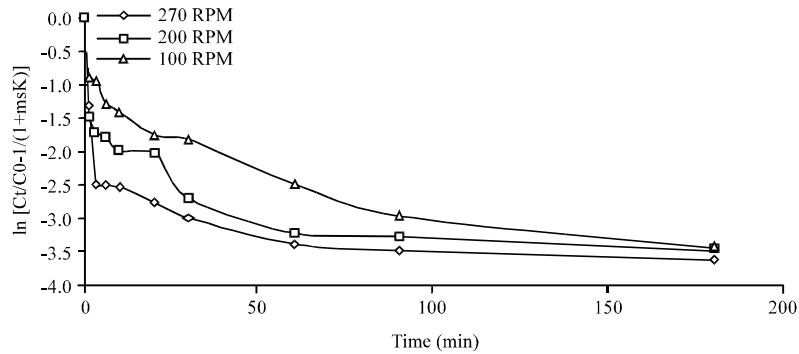


Fig. 8: Effect of different agitation speed on adsorption rate for adsorption lead ions Jeddah clay

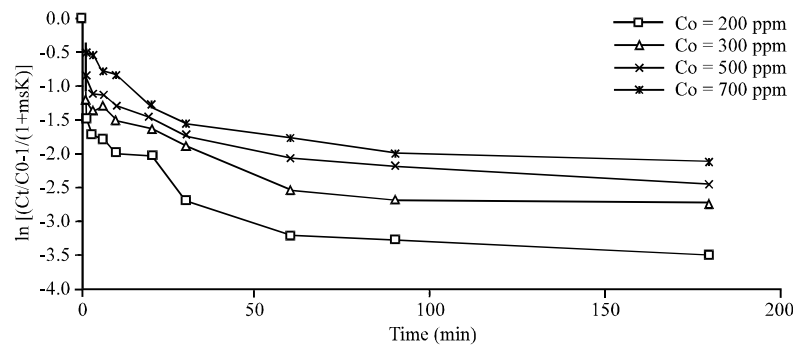


Fig. 9: Effect of different initial concentrations on adsorption rate of adsorption lead ions Jeddah clay

As shown in Table 7, increasing the initial lead ions concentration decreased the external mass transfer coefficients which may be attributed to the increase of driving force between the bulk solution concentration and the concentration of lead ions solution on the surface of the clay particle (Sekaran *et al.*, 1995; Marshall *et al.*, 1993).

From Fig. 8 and 9, it is clear that under the different experimental conditions, the external mass transfer controlled the adsorption rate for a short time say approximately for 3 min.

Internal mass transfer model: This study presented a novel diffusion model called as “Saad Internal Diffusion Model” (SIDM) and used to calculate the internal diffusion coefficients if the internal mass transfer controls the rate of the adsorption process. 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 (i.e., diffusion coefficient). The kinetic parameters can be used to predict the concentration-time curves in the batch adsorber as well as to predict the breakthrough curve in the fixed bed adsorber.

Saad Internal Diffusion Model (SIDM): The SIDM was used to calculate the internal diffusion coefficient. This model is derived subsequently.

The adsorption rate is represented by the linear driving force model. This model is a lumped parameter model in which the adsorption rate of the lead ions on a spherical clay particle changes linearly with the driving force $(q_s - q_{avg})$. This model can be written as follows (Seader and Henley, 1998):

$$\left(\frac{dq_{avg}}{dt}\right) = \left(\frac{15D_e}{R_p^2}\right)(q_s - q_{avg}) \quad (17)$$

$$\text{at } t = 0, q = 0 \quad (18)$$

Where:

- q_s is the concentration of lead ions adsorbed on the outer surface of the clay particle
- q_{avg} is the average adsorbed lead ions
- D_e is the internal diffusion coefficient
- R_p is the radius of the adsorbent

Since there is no external mass transfer resistance, q_s is in equilibrium with C_t . Therefore:

$$q_s = K C_t \quad (19)$$

The mass balance equation on the batch adsorber as follows:

$$C_t = C_0 - \left(\frac{M q_{avg}}{V}\right) \quad (20)$$

where, M indicates clay mass in gram, V is the solution volume in liter, q_{avg} is the adsorbed lead ions concentration in milligram per gram, C_0 is initial concentration of lead ions (mg L^{-1}) and C_t is the lead ions concentration in bulk solution at equilibrium (mg L^{-1}).

Combining Eq. 17, 19 and 20 yields the following equation:

$$\left(\frac{dq_{avg}}{dt}\right) = \left(\frac{15D_e}{R_p^2}\right) \left(K \left(C_0 - \frac{Mq_{avg}}{V}\right) - q_{avg}\right) \quad (21)$$

Rearrangement Eq. 21 and integration yields an analytical solution as follows:

$$-\ln\left(\frac{KC_0/(1+K m_s)-q_{avg}}{K C_0/(1+K m_s)}\right) = \left(\frac{15D_e}{R_p^2}\right) (1+m_s K) t \quad (22)$$

The final form for Eq. 22 is:

$$\ln\left(\frac{C_t}{C_0} - \frac{1}{1+m_s K}\right) = \ln\left(\frac{m_s K}{1+m_s K}\right) - \left(\frac{15D_e}{R_p^2}\right) (1+m_s K) t \quad (23)$$

Plotting $\ln[C_t/C_0 - (1/1+m_s K)]$ versus time yields a straight line, hence, it can be used to obtain the value of the internal mass transfer coefficient (D_e) from the slope of the plot with a known value of m_s (mass of clay per lead ions solution volume) and K (the isotherm constant for the actual

Table 8: Price of lead ions removal by Bentonite natural clay in comparison with activated carbon

Parameters	Adsorbent	
	Activated carbon ¹	Bentonite clay ²
Maximum capacity (mg g ⁻¹)	25.00	51.1900
Cost of 1 kg of adsorbent compared to activated carbon cost to activated carbon cost	1.00	0.0270
Cost to remove 1 kg of lead ions compared to activated carbon cost	1.00	0.0132
Mass of adsorbent by kg required to remove 1 kg lead ions	40.00	19.5400

¹Price of activated carbon is between \$2 to \$2.54 per lb (average is \$2.25 per lb or \$4.962 per kg) (Cooper and Alley 1994), Saudi clay costs around \$0.134 per kg (price as sold by Dirah drilling and heavy equipment company in Saudi Arabia)

equilibrium linear portion is obtained from the equilibrium isotherm curve). The C_0 in this case, however, is the concentration of lead ions in solution at the beginning of the period when the mass transfer is controlled by the internal resistance.

D_e can be calculated from the slope of $\ln[Ct/C_0 - 1/(1+ms K)]$ versus time from Fig. 8 and 9 after the initial rapid period of adsorption has taken place.

Using the above equations, D_e for the agitation speed and the initial lead ions were calculated and the results were listed in Table 6 and 7. The Internal diffusion coefficients characterizing the internal resistance for agitation speed are given in Table 6 which shows a decreasing trend with increasing the stirring speed. While, the internal diffusion coefficients for the initial lead ions concentration are shown in Table 7. However, increasing the initial lead ions concentration caused a reduction in the internal diffusion coefficient value. Similar findings were reported by other researchers (Mckay, 1996; Hui *et al.*, 2003).

From Fig. 8 and 9, it is clear that under the different experimental conditions external mass transfer controlled the adsorption rate for a short time say approximately for 3 min and after that the major resistance to adsorption was internal diffusion.

Rough economic study: Evaluation of the price of employing Bentonite natural clay for adsorption of lead ions from wastewater was prepared using the maximum capacity of the adsorbent only, exclusive of considering other factors in the adsorption process such as regeneration. Bentonite clay and activated carbon were evaluated using the maximum capacity obtained from equilibrium results. The maximum capacity of the commercial activated carbon was taken from Minceva *et al.* (2007). The adsorption process price was evaluated as the relative cost to remove 1 kg of lead ions as shown in Table 8.

As shown in Table 8, Bentonite natural clay is an efficient adsorbent relative to activated carbon because it is cheap and has a reasonable high maximum adsorption capacity. Also, Bentonite natural clay is cheap, therefore, regeneration is not necessary after the adsorption process.

CONCLUSION

The adsorption capacity of Bentonite natural clay increased with increasing the temperature of lead ions solution thus suggesting that the adsorption process is endothermic process.

Among the various isotherm models tested, the Langmuir isotherm agreed most favorably with the experimental data. The thermodynamic parameters indicated that the adsorption is endothermic and favorable at high temperatures.

The external mass transfer coefficients (for mass transfer to the outer surface) were determined for the initial rapid part of the adsorption but the external mass transfer model achieved only limited success. Internal diffusion coefficients were calculated to characterize the slower adsorption

occurring after the initial period. Although most of the adsorption occurs during the initial period, internal diffusion is the rate-controlling step for the removal of the remaining lead ions from solution.

A rough economic study based on the adsorbent capacity showed that Bentonite natural clay is economically attractive proposition for the adsorption of lead ions from wastewater.

NOMENCLATURE

- a_L = Langmuir isotherm parameter ($L\ mg^{-1}$)
 S_s = External surface area (cm^{-1})
 C_o = Initial lead ions solution concentration ($mg\ L^{-1}$)
 C_e = Equilibrium lead ions solution concentration ($mg\ L^{-1}$)
 C_s = Lead ions solution concentration on the outer clay surface ($mg\ L^{-1}$)
 C_t = Lead ions solution concentration at any time t ($mg\ L^{-1}$)
 d_p = Average particle diameter (cm)
 D_e = Internal diffusion coefficient ($cm^2\ sec^{-1}$)
 K = Equilibrium constant for the linear portion of the equilibrium isotherm ($L\ g^{-1}$)
 K_f = External mass transfer coefficient ($cm\ sec^{-1}$)
 K_F = Freundlich isotherm parameter ($L\ g^{-1}$)
 K_L = Langmuir isotherm parameter ($L\ g^{-1}$)
 M = Mass of adsorbent (g)
 M_s = Mass of clay per lead ions solution volume ($g\ cm^{-3}$)
 n = Freundlich isotherm parameter
 q = Adsorbed lead ions concentration ($mg\ g^{-1}$)
 q_e = Equilibrium lead ions adsorbed concentration ($mg\ g^{-1}$)
 t = Time (min)
 V = Lead ions solution volume (L)

GREEK SYMBOLS

- ρ_s = Solid density ($g\ cm^{-3}$)
 ϵ_p = Particle porosity

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