Kinetic and equilibrium studies in removing lead ions from aqueous solutions by natural sepiolite

Nihal Bektaş*, Burcu Akman Ağım, Serdar Kara

Environmental Engineering Department, Gebze Institute of Technology, 41400 Gebze, Turkey

Abstract

The capacity of sepiolite for the removal of lead ions from aqueous solution was investigated under different experimental conditions. The Langmuir and Freundlich equations, which are in common use for describing sorption equilibrium for wastewater-treatment applications, were applied to data. The constants and correlation coefficients of these isotherm models for the present system at different conditions such as pH, temperature and particle size were calculated and compared. The equilibrium process was well described by the Langmuir isotherm model and the maximum sorption capacity was found to be 93.4 mg/g for the optimal experimental condition. The thermodynamic parameters (ΔG°, ΔH° and ΔS°) for lead sorption on the sepiolite were also determined from the temperature dependence. The influences of specific parameters such as the agitation speed, particle size and initial concentration for the kinetic studies were also examined. The sorption kinetics were tested for first order reversible, pseudo-first order and pseudo-second order reaction and the rate constants of kinetic models were calculated. The best correlation coefficients were obtained using the pseudo-second order kinetic model, indicating that lead uptake process followed the pseudo-second order rate expression.
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1. Introduction

Lead, one of the toxic priority pollutants, can reach the environment from vary anthropogenic sources as well as natural geochemical processes. It can accumulate along the food chain and are not amenable to biological degradation [1,2]. The EC and WHO limit for lead in drinking water is $50\,\mu g/dm^3$ [3,4]. The main industrial sources for lead include metal finishing, mining and mineral processes, and oil [5] refining industries as well as motor vehicles use leaded petrol. There are several methods to the treat metal contaminant effluent such as ion exchange, chemical precipitation, oxidation, reduction, and reverse osmosis [6]. However, many of these approaches can be cost effective or difficult to implement. Especially, the main disadvantages of the sorption methods are the high price of the adsorbents, which increases the price of wastewater treatment. Eco-friendly natural materials, which are less expensive and addressed local sources with high affinity toward toxic metals, are being investigated. Clay minerals are useful due to their chemical and mechanical stability, high surface area and structural properties.

Sepiolite ($Mg_4Si_6O_{15}(OH)_2\cdot6H_2O$) is a natural clay mineral with formula of magnesium hydro-silicate. The unique fibrous structure allows penetration of organic and inorganic ions into the structure of sepiolite. Naturally occurring low cost sepiolite as an ion exchanger offers great potential for removing lead from industrial wastewater. Several work related to wastewater treatment using sepiolite has been used studied [7,8]. The interaction between some heavy metals including lead and sepiolite has been studied in order to verify the heavy-metal cation sorption–desorption rates [9]. In the other work by the same group, the equilibrium properties of single and multi metal solutions have been widely investigated [10].

The sorption capacity of sepiolite is restricted to the external surface, which can be enhanced, by chemical [11] and heat treatment [12]. The enhanced surface area of sepiolite is given in the range of $263–350\,m^2/g$ in the literature [9,13,14].

* Corresponding author. Tel.: +90 262 7542360;
fax: +90 262 6538490.
E-mail address: nihal@gyte.edu.tr (N. Bektaş).

The aim of this paper is to investigate the ability of sepiolite to remove lead from aqueous solutions. The influences of specific parameters such as the agitation speed, particle size and initial concentration for the kinetic studies were examined. The equilibrium studies for the uptake process were also determined at the different experimental conditions namely pH, particle size and temperature. These parameters would be useful in understanding of sorption removal of lead by sepiolite from an aqueous environment.

2. Material and methods

2.1. Chemicals and characterization of sepiolite

All chemicals used were analytical grade and used without further treatment. Distilled water was used in all experiments. Perkin-Elmer model SIMAA 6000 atomic absorption spectrometry (AAS) was used to determinate the concentrations of lead in solutions. An extra care was taken when making necessary dilution for AAS lead measurements. The calibrations of these dilutions were often checked by measuring standard lead solution at high concentration. X-ray diffraction (XRD) measurements were taken by Rigaku D-max 1000 model diffractomer.

Sepiolite samples used in this work were obtained from Eskişehir, Turkey. All samples were ground in a laboratory type ball-mill and washed with 1N HCl then distilled water in order to remove the surface dust and impurities. X-ray diffraction (XRD) analysis was performed on the both pure and acid washed sepiolite samples to confirm the crystal structure and identity. The results showed that the structure was not changed by acid treatment (Fig. 1). All samples were then ground and sieved to obtain with sizes ranging from 0.3 to 1.6 mm. The BET single point surface area of sepiolite used was determined as 167.7 m^2/g using Micrometrics FlowSorbII-2300.

2.2. Batch experiments

Sorption studies of lead were investigated by batch experiments. All batch-technique experiments were carried out in 100 mL glass flasks. A known amount of adsorbent was weighed and placed in flask containing solution at desired concentration. If necessary, pH was adjusted using 0.1N HCl or 0.1N NaOH. Then the suspensions were placed in a shaker. Final metal concentrations were measured in the equilibrium solution after separating the sepiolite through the filtration paper. If necessary, the solutions were stored in plastic tubes with a few drops of HNO$_3$.

Kinetic experiments were obtained by mixing 0.25 g of sepiolite with 25 mL of lead solution in the conical flasks at different experimental conditions such as initial lead concentrations (30–135 mg/L), agitation speed (125–200 rpm) and particle size (0.5–1.6 mm). In order to evaluate kinetic data, separate flasks were prepared for each time interval and only one flask was taken for desired time. The solution and sorbent were separated through the standard filter designed for a wide range of laboratory applications (MF-Millipore membrane filter, mixed cellulose ester, 0.45 μm).
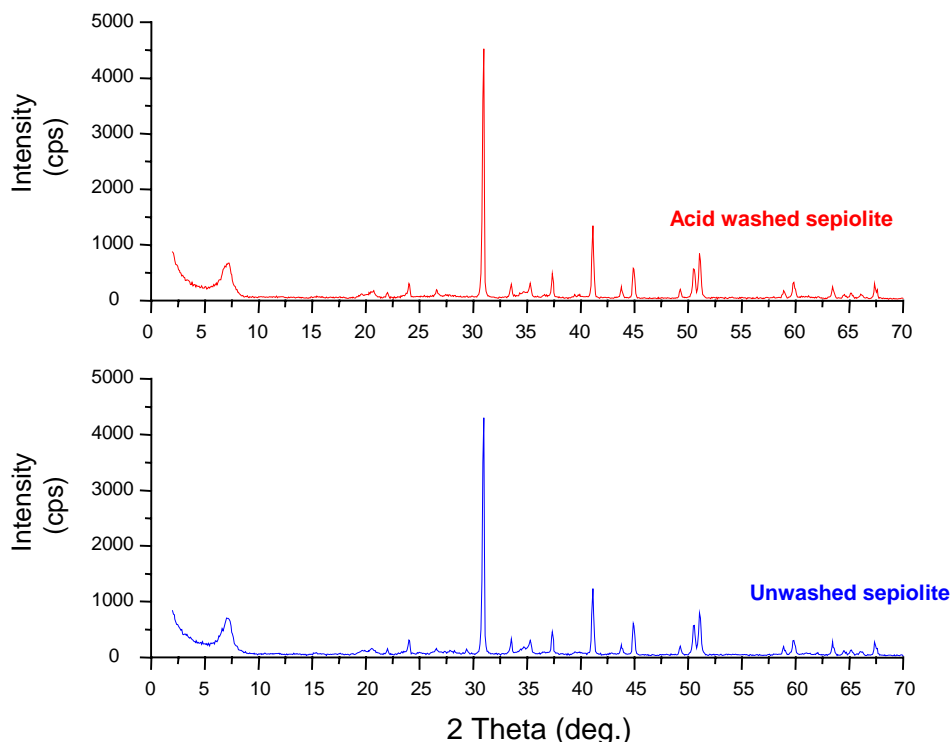

Fig. 1. XRD spectrum of sepiolite sample used.

The equilibrium behaviours, described in terms of equilibrium isotherms, were also determined by mixing 0.25 g of sepiolite (0.5–0.8 mm) with 25 mL of lead solution in the conical flasks. Three sets of isotherm plot were obtained using three different initial pH values (4–6), three different temperature values (20–50 °C) and particle size ranging from 0.3 to 1.6 mm. Each isotherm consisted of eight lead concentrations varied from 100 to 2100 mg/L, except for those obtained using different pH values whereas the concentrations varied between 100 and 1400 mg/L.

2.3. Sorption isotherms

The concentration of sorbed species on the sorbent the batch contact test was calculated using the following mass-balance equation;

$$q_e m = V(C_0 - C_e) \tag{1}$$

where q_e is the equilibrium capacity of lead on sorbent (mg/g of sorbent), C_0 the initial concentration of lead (mg/L), C_e the equilibrium lead concentration in solution (mg/L), m the mass of sorbent used (g) and V is the volume of solution (L).

All these parameters, expect, q_e which calculated from mass-balance equation, were measured experimentally. The data then can be correlated with a suitable isotherm. The Langmuir and the Freundlich equations are in common use for describing adsorption equilibrium for wastewater-treatment applications. The linear forms of the Langmuir and the Freundlich isotherms [15] are represented by the following equations, respectively:

$$\frac{C_e}{q_e} = \left(\frac{1}{Q^0 b}\right) + \left(\frac{1}{Q^0}\right) C_e \tag{2}$$

$$\log q_e = \log K_F + n \log C_e \tag{3}$$

where Q^0 (mg/g) and b (L/mg) are Langmuir isotherm constants. K_F and n are Freundlich isotherm constants. The value of Q^0 gives the maximum sorption capacity of sorbent.

2.3.1. Thermodynamic evaluation of the process

Thermodynamic parameters such as free energy of sorption (ΔG°), the heat of sorption and standard entropy changes (ΔH° and ΔS°) can be evaluated following equations [16–18];

$$K_d = \frac{q_e}{C_e} \tag{4}$$

where K_d is sorption distribution coefficient.

The K_d values are used in following equation to determine the Gibbs free energy of sorption process at different temperatures.

$$\Delta G^\circ = -RT \ln K_d \tag{5}$$

where ΔG° is the free energy of sorption (kJ/mol), T the temperature in Kelvin and R is the universal gas constant (8.314 J/(mol K)).

The sorption distribution coefficient may be expressed in terms of enthalpy change (ΔH°) and entropy change (ΔS°) as a function of temperature:

$$\ln K_d = \frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \tag{6}$$

where ΔH° is the heat of sorption (kJ/mol) and ΔS° is standard entropy changes (kJ/mol).

The values of ΔH° and ΔS° can be obtained from the slop and intercept of a plot of $\ln K_d$ against $1/T$.

2.4. Sorption kinetics

The chemical kinetic describes reaction pathways, along times to reach the equilibrium whereas chemical equilibrium gives no information about pathways and reaction rates. Sorption kinetics show large dependence on the physical and/or chemical characteristics of the sorbent material which also influence the sorption mechanism. In order to investigate the mechanism of sorption, three different models have been used at different experimental conditions for sorption processes.

2.4.1. First order reversible model

This kinetic model is based on a reversible reaction with equilibrium state being established between two phases and can be expressed as [19,20],

$$\frac{dC_B}{dt} = -\frac{dC_A}{dt} = C_A \frac{dX_A}{dt} = k_1 C_A - k_2 C_B$$
$$= k_1(C_{A_0} - C_{A_0} X_A) - k_2(C_{B_0} - C_A X_A) \tag{7}$$

where C_B (mg/g) is the concentration of solute on the sorbent, C_A (mg/L) the concentration of solute in solution at any time, C_{B_0} and C_{A_0} the initial concentrations of solute on sorbent and solution, respectively, X_A the fractional conversion of solute, k_1 and k_2 are the first-order rate constants. At equilibrium conditions,

$$\frac{dC_B}{dt} = -\frac{dC_A}{dt} = 0 \tag{8}$$

and

$$X_{A_e} = \frac{K_C - (C_{B_0}/C_{A_0})}{K_e + 1} \tag{9}$$

where X_{A_e} is the fractional conversion of solute at equilibrium and K_C is the equilibrium constant defined as follows:

$$K_C = \frac{C_{B_e}}{C_{A_e}} = \frac{C_{B_0} - C_{A_0} X_{A_e}}{C_{A_0} - C_{A_0} X_{A_e}} = \frac{k_1}{k_2} \tag{10}$$

where C_{B_e} and C_{A_e} are the equilibrium concentrations for solute on the sorbent and solution, respectively. The rate equation in terms of equilibrium conversion can be obtained from Eqs. (7), (9) and (10);

$$\frac{dX_A}{dt} = (k_1 + k_2)(X_{A_e} - X_A) \tag{11}$$

Integration of Eq. (11) and substituting for k_2 from Eq. (10), gives

$$-\ln\left(1 - \frac{X_A}{X_{A_e}}\right) = k_1\left(1 + \frac{1}{K_C}\right)t \tag{12}$$

Thus, Eq. (12) can be re-written in a different form:

$$\ln[1 - U_{(t)}] = -k'_r t \tag{13}$$

where k'_r is the overall rate constant. Furthermore,

$$k'_r = k_1\left(1 + \frac{1}{K_C}\right) = k_1 + k_2 \tag{14}$$

$$U_{(t)} = \frac{C_{A_0} - C_A}{C_{A_0} - C_{A_0}} = \frac{X_A}{X_{A_e}} \tag{15}$$

where $U_{(t)}$ is called the fractional attainment of equilibrium. Therefore, a plot of $-\ln(1 - U_{(t)})$ versus time will give a straight line and from the slope of this plot k_1 can be obtained.

2.4.2. Pseudo-first order model

This was the first equation for the sorption of liquid/solid system based on solid capacity [21,22]. In most cases, the pseudo-first order equation does not fit well for the whole range of contact time. This model may be represented;

$$\frac{dq_t}{dt} = k_s(q_e - q_t) \tag{16}$$

Eq. (16) can be integrated for the following boundary conditions to obtain Eq. (17).

$$t = 0, \ q_t = 0;$$
$$t = t, \ q_t = q_t \tag{17}$$
$$\log(q_e - q_t) = \log(q_e) - \frac{k_s}{2.303}t$$

where q_t is amount of solute on the surface of the sorbent at time t (mg/g) and k_s is the equilibrium rate constant of pseudo-first sorption (1/min).

In order to obtain the rate constants, the straight line plots of $\log(q_1 - q_t)$ against t for different experimental conditions have been analysed.

2.4.3. Pseudo-second order model

Pseudo-second order reaction model is based on sorption equilibrium capacity may be expressed as [23],

$$\frac{dq}{dt} = k(q_e - q_t)^2 \tag{18}$$

After integrating Eq. (18) for following boundary condition and rearranging it to obtain the linearised form is shown below.

$$t = 0, \ q_t = 0;$$
$$t = t, \ q_t = q_t$$
$$\frac{t}{q_t} = \frac{1}{k'_2 q_e^2} + \frac{1}{q_e}t \tag{19}$$
$$h = k'_2 q_e^2$$

where k'_2 is the equilibrium rate constant of pseudo-second order (g/(mg min)) h is the initial sorption rate (mg/(g min)).

The equations constants can be determined by plotting t/q_t against t.

3. Results and discussion

3.1. Influence of process variables

3.1.1. Effect of the initial concentration

Fig. 2 shows the effect of the initial concentration on the retention of lead, at concentration levels ranging from 30 to 135 mg/L. Series of experiments have been carried out with a constant agitation speed of 175 rpm and particle size of 0.3–0.5 mm. Fig. 2 clearly indicates that the sorption of the lead at different concentrations is increased instantly at initial stages and then keep increase gradually until the equilibrium is reached and remain constant. The equilibrium time was selected as 60 min for all the concentrations studied.

3.1.2. Effect of the particle size

Fig. 3 shows that the sorption of lead slightly increased with decreasing particle size as excepted that is increasing surface area of sepiolite. As the sorption being a surface
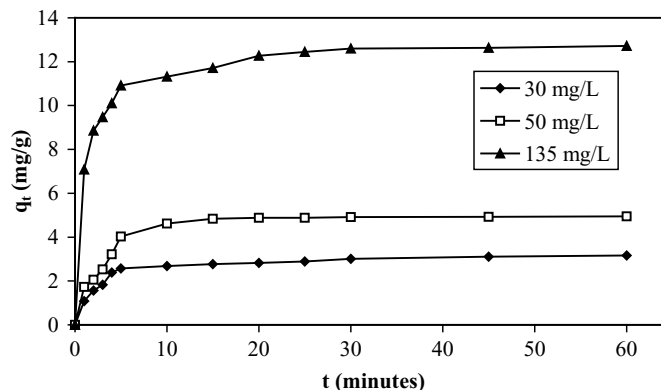

Fig. 2. Effect of initial lead concentrations for removal capacity of sepiolite (175 rpm, 20 °C, 0.3–0.5 mm).
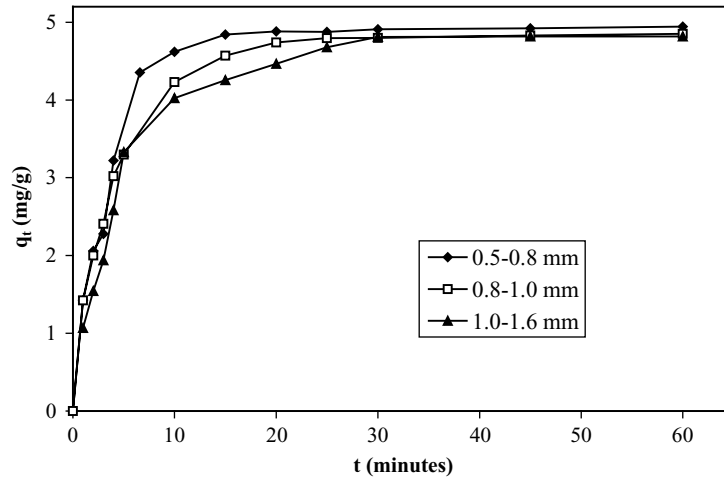
Fig. 3. Effect of particle size for lead removal capacity of sepiolite (50 mg/L, 175 rpm and 20 °C).

phenomenon, the smaller sorbent sizes offered comparatively larger surface areas and hence higher lead removal at equilibrium.

3.1.3. Effect of the agitation speed

Fig. 4 shows the experimental results obtained from series of experiments performed, using different agitation speeds using the range from 125 to 200 rpm. The uptake of lead increased with increasing agitation speed. Increasing agitation rate reduced the film boundary layer surrounding sepiolite particles thus increasing the external film transfer coefficient and hence the rate of uptake. Similar trend has been reported by Wong et al., in the removal Cu and Pb by modified rice [24].

3.2. Sorption isotherms

Fig. 5 shows the relationship between the amount of lead adsorbed per unit mass of sepiolite (q_e, mg/g) and its equilibrium concentration in the solution (C_e, mg/L) for four series of experiments using different initial pH values, tem-

peratures, particle sizes and agitation speeds. The effect of additional ions coming from the solutions that used for pH adjustment was negligible from the point of sorption process. Since sepiolite has more affinity to lead compared to those ions, sorption capacity will not be affected especially for high concentrations of lead. No isotherm studies were included at pH value greater than 6. This is due to precipitation of lead ions may also take place in the lead removal process since the precipitation of Pb^{2+} ions in the form of $Pb(OH)_2$ increases after pH 6.0 [25].

Sorption equations were obtained by experimental data with Eqs. (2) and (3). The isotherm constants were calculated and presented in Table 1. The Langmuir equation represent the sorption process very well, the r^2 value is higher for Langmuir-isotherm than the Freundlich-isotherm. This may be due to homogenous distribution of active sites on sepiolite surface. Brigatti et al. [10] also suggested that the sorption of lead ions onto sepiolite was described by the Langmuir equation. In the literature, lead removal using different minerals has been also described by Langmuir-isotherm model [26,27].
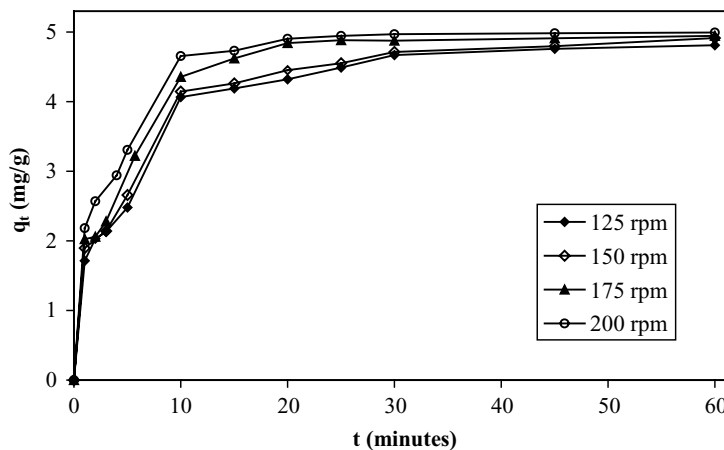

Fig. 4. Effect of agitation speed for lead removal capacity of sepiolite (50 mg/L, 20 °C and 0.3–0.5 mm).
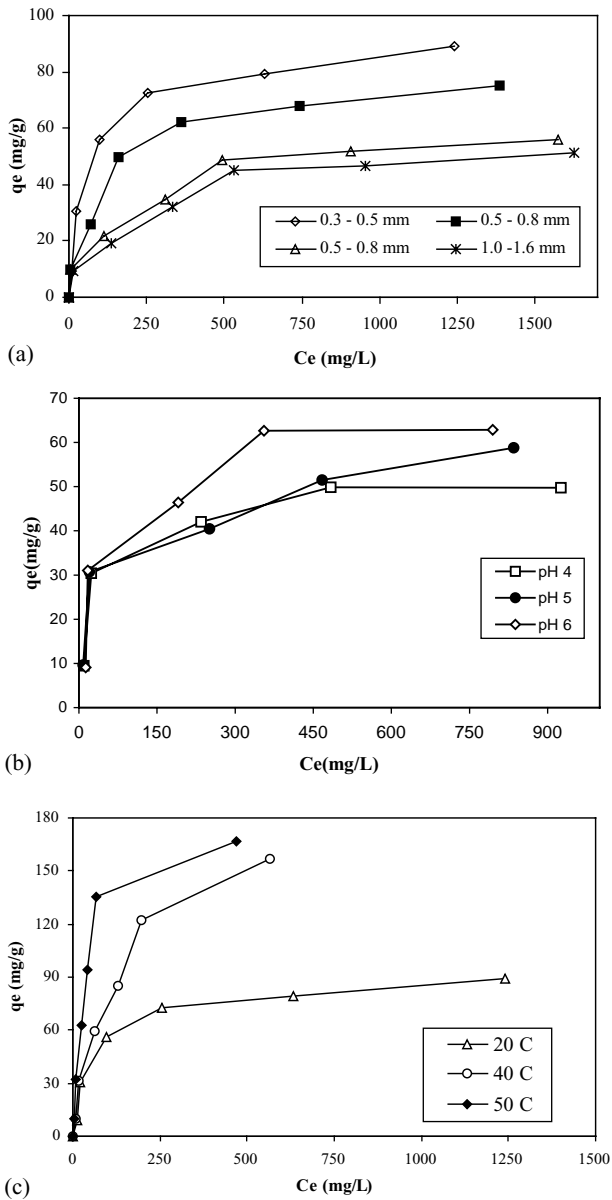
Fig. 5. Equilibrium isotherms for lead removal using sepiolite (a) effect of particle size; (b) effect of pH; (c) effect of temperature.
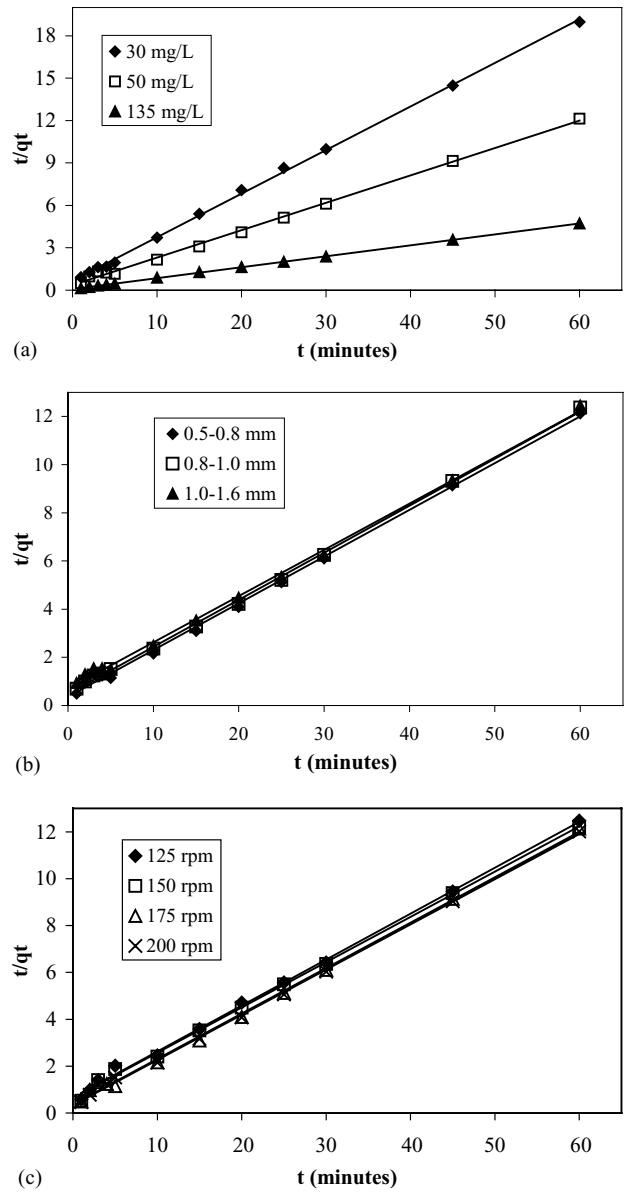

Fig. 7. Pseudo-second order plots for lead removal using sepiolite (a) different initial concentrations; (b) different particle sizes; (c) different agitation speeds.
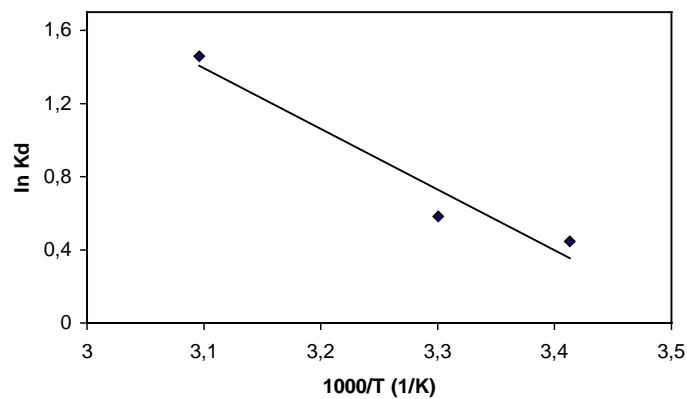

Fig. 6. A plot of $\ln K_d$ against $1/T$ for lead sorption by sepiolite.

Table 1
A comparison of the Langmuir and Freundlich sorption constants obtained at different experimental conditions

Parameters	Langmuir constants			Freundlich constants		
	Q°	b	r^2	n	K_f	r^2
pH[a]						
4	51.82	0.0298	0.998	0.31	7.063	0.779
5	60.60	0.0167	0.984	0.32	7.178	0.815
6	67.56	0.0177	0.991	0.38	6.095	0.735
Particle size (mm)						
0.3–0.5	93.46	0.0133	0997	0.42	5.943	0.824
0.5–0.8	79.36	0.0100	0.995	0.40	5.058	0.953
0.8–1.0	60.24	0.0070	0.987	0.34	5.016	0.975
1.0–1.6	56.18	0.0056	0.985	0.38	3.358	0.968
Temperature (°C)						
20	93.46	0.0133	0.997	0.42	5.93	0.824
30	151.52	0.0078	0.985	0.54	4.47	0.911
50	185.19	0.2090	0.985	0.57	9.66	0.793

[a] Each isotherm consisted of eight lead concentrations varied from 100 to 2100 mg/L except for those obtained using different pH values whereas the concentrations varied between 100 and 1400 mg/L.

Table 2
Thermodynamic parameters for the lead sorption by sepiolite

ΔH° (kJ/mol)	ΔS° (kJ/mol(K))	ΔG° (kJ/mol)		
		20 °C	30 °C	50 °C
6.606	0.205	−0.205	−0.438	−0.903

Values of Q^0, which is defined as the maximum capacity of sorbent, at different pH values, temperatures and particle sizes have calculated from the Langmuir plots. The maximum capacities of sepiolite for lead have been calculated in range of 51.8–185.2 mg/g at different experimental conditions. These values compare favourably with some of those reported in the literature. The maximum sorption capacities of other minerals for lead ions removal were given in range of 60–35 mg/g [28,29].

3.2.1. Thermodynamic evaluation of the process

Thermodynamic parameters such as free energy of sorption (ΔG°), the heat of sorption (ΔH°) and standard entropy changes (ΔS°) were evaluated using Eqs. (4), (5) and (6). The temperature range used was from 20 to 50 °C. The Gibbs free energy indicates the degree of spontaneity of sorption process and the higher negative value reflects a more energetically favourable sorption. ΔH° and ΔS° were obtained from the slop and intercept of a plot of $\ln K_d$ against $1/T$ (Fig. 6). The calculated parameters are given in Table 2. The negative value of ΔG° indicates the spontaneous nature of sorption of lead by sepiolite. The value of ΔG° becomes more negative with increasing temperature. This shows that the removal process is favoured by an increased in temperature. The positive value of ΔH° showed that the sorption process was endothermic in nature and positive value of ΔS° shows

Table 3
A comparison of first order reversible, pseudo-first order and pseudo-second order kinetic models rate constants obtained at different experimental conditions

Parameters	First order reversible					Pseudo-first order			Pseudo-second order		
	K_c	k'	$k_1 \times 10^3$	$k_2 \times 10^3$	r^2	k_s	r^2	$k'_2 \times 10^3$	h	q_e, cal	r^2
Agitation speed (rpm)											
125	7.911	0.0189	16.78	2.121	0.585	0.068	0.943	57.82	1.504	5.099	0.9978
150	13.744	0.0156	14.54	1.058	0.549	0.060	0.930	59.04	1.580	5.173	0.9981
175	35.160	0.0137	13.32	0.378	0.653	0.054	0.656	102.9	2.739	5.157	0.9959
200	81.852	0.0044	4.350	0.053	0.495	0.050	0.705	111.5	2.998	5.184	0.9990
C_0 (mg/L)											
30	35.599	0.0606	58.94	1.656	0.942	0.060	0.942	144.32	1.517	3.242	0.9991
50	35.160	0.0137	13.32	0.378	0.653	0.054	0.656	102.98	2.739	5.157	0.9977
135	16.352	0.0487	45.89	2.806	0.836	0.048	0.836	70.950	11.90	12.95	0.9999
Particle size (mm)											
0.5–0.8	35.160	0.0137	13.32	0.378	0.653	0.054	0.656	102.97	2.739	5.157	0.9977
0.8–1.0	17.576	0.0648	61.31	3.488	0.786	0.064	0.786	78.418	2.056	5.120	0.9989
1.0–1.6	22.514	0.0560	53.62	2.381	0.815	0.056	0.815	52.289	1.418	5.208	0.9979

the increasing randomness at solid/liquid interface during the.

3.3. Sorption kinetics

In order to predict of sorption kinetic models of lead ions, first order reversible, pseudo-first order and pseudo-second order kinetic models were applied to data. The effect of the initial lead concentrations, agitation speeds and particle sizes were investigated to find the best kinetic model. The straight-line plots of $-\ln(1 - U_{(t)})$ against time were tested to obtain the first order rate constant at the different experimental conditions. For the pseudo-first sorption rate constant, the straight line plots of $\log(q_1 - q_t)$ against time for different experimental conditions were analysed. The equilibrium rate constants of pseudo-second order were determined by plotting t/q_t against t. Only the pseudo-second order plots are presented in Fig. 7. The kinetic constants and correlation coefficients of these models were given in Table 3. Good correlation coefficients were obtained for the pseudo-second order kinetic model, which shows that lead uptake process follows the pseudo-second order rate expression.

4. Conclusion

Equilibrium and kinetic data for lead removal using sepiolite were presented. The parameters, which have the influence on the removal processes, were investigated. The uptake rates of lead for all concentrations were rapid at initial stages and then keep increase gradually until the progress until equilibrium is reached. The sorption of lead was slightly increased with decreasing particle that is increasing surface area of sepiolite. The batch sorption kinetics were tested for first order reversible reaction, pseudo-first order and pseudo-second order reaction for different experimental conditions. The pseudo-second order kinetic reaction model found to be the best correlation of the data for lead removal from aqueous solution using sepiolite. The experimental data were correlated better by the Langmuir isotherm model. The maximum sorption capacities at different experimental conditions, calculated from Langmuir plots, were in range of 51.8–185.2 mg/g. Thermodynamic parameters of the removal process were also investigated. The reaction for lead uptake by sepiolite was found to be endothermic nature.

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