

# Lead removal from aqueous solution by natural and pretreated clinoptilolite: Adsorption equilibrium and kinetics

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## Abstract

Adsorption of Pb(II) ions from aqueous solution onto clinoptilolite has been investigated to evaluate the effects of contact time, initial concentration and pretreatment of clinoptilolite on the removal of Pb(II). Experimental data obtained from batch equilibrium tests have been analyzed by four two-parameter (Freundlich, Langmuir, Temkin and Dubinin–Radushkevich), four three-parameter (Redlich–Peterson, Sips, Toth and Khan) isotherm models, and kinetic models including the pseudo-first order, the pseudo-second order and Elovich equations using nonlinear regression technique. Of the two-parameter isotherms, Temkin isotherm was the best to describe the experimental data. Three-parameter isotherms have higher regression coefficients (>0.99) and lower relative errors (<5%) than two-parameter isotherms. The best fitting isotherm was the Sips followed by Toth and Redlich–Peterson isotherm equations. Maximum experimental adsorption capacity was found to be 80.933 and 122.400 mg/g for raw and pretreated clinoptilolite, respectively, for the initial concentration of 400 mg/L. Kinetic parameters; rate constants, equilibrium adsorption capacities and related coefficients for each kinetic model were evaluated according to relative errors and correlation coefficients. Results of the kinetic studies show that best fitted kinetic models are obtained to be in the order: the pseudo-first order, the pseudo-second order and Elovich equations. Using the thermodynamic equilibrium coefficients, Gibbs free energy of the Pb(II)–clinoptilolite system was evaluated. The negative value of change in Gibbs free energy ( $\Delta G^\circ$ ) indicates that adsorption of Pb(II) on clinoptilolite is spontaneous.

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## 1. Introduction

Lead is one of the common contaminants of industrial wastewaters. Lead pollution exists in aqueous waste streams of many industries such as manufacture of storage batteries, printing, painting, pigments, dying, leaded glass [1,2]. Lead poisoning causes various health hazards, such as damage to liver, kidney and reduction in hemoglobin formation, mental retardation, infertility and abnormalities in pregnant women [3].

Unlike organic compounds, lead is nonbiodegradable and accumulates in living organism, therefore, must be removed from water and wastewater. Various methods of lead removal from wastewater have been applied including chemical precipitation, membrane processes, ion-exchange and adsorption. One

of the most effective methods for the treatment of heavy metals from aqueous solution has been based on adsorption using low-cost adsorbents [4,5].

Cost-effective materials that have been investigated for their potential use as adsorbents for heavy metal uptake include biomass [6–8] moss [9], fly ash [10,11], natural materials like clay and zeolite; chabazite and clinoptilolite [12–21] and synthetic resins [22]. Among the most frequently studied natural zeolite, clinoptilolite is shown to have selectivity for many cations mainly ammonium and heavy metals such as Pb, Cu, Zn, Cd [13,23].

Adsorption capacity of clinoptilolite is influenced significantly by physical and chemical pretreatment and loading or regeneration of clinoptilolite. Pretreatment of natural zeolites by acids, bases and surfactants, etc. is an important method to improve their ion-exchange capacity [4,24–27]. Practically, any pretreatment operation increases the content in a single cation, what is called homoionic form. Therefore, prior to any

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ion-exchange application, certain ions from the structure of the material are removed by pretreatment and located more easily removable ones [28].

Although the large number of different studies on the removal of Pb(II) ion from aqueous solutions using zeolite, every special zeolite material requires individual research. The present work describes the batch adsorption characteristic of Pb(II) on clinoptilolite concentrating on various operational parameters; such as contact time, initial Pb(II) concentration and the effect of pretreatment of clinoptilolite on adsorption capacity. Experimental data have been analyzed by adsorption isotherms, kinetics and thermodynamic parameters.

## 2. Materials and methods

### 2.1. Chemical and physical properties of the clinoptilolite

The adsorbent (clinoptilolite) used in the experiments was obtained from Balıkesir, in the northwestern part of Turkey. The chemical properties of the clinoptilolite used in this study were given in Table 1 [29,30].

### 2.2. Pretreatment procedure of the clinoptilolite

Clinoptilolite was ground and sieved into a diameter of 0.30–0.60 mm. Prior to the batch adsorption experiments, the samples were washed with distilled water to remove the surface dust, and then dried in an oven at 70 °C.

Lead removal studies were carried out using two different clinoptilolite forms, raw and treated samples. Clinoptilolite was treated with 2 M NaCl solution at 22 °C by shaking for a period of 24 h, and was separated from the supernatant by filtration using Whatman 42 paper. This was then followed by a through distilled water wash to remove any excess of NaCl present on the surface.

### 2.3. Test chemicals and analysis

Synthetic samples were prepared to give Pb(II) concentrations of 15, 30, 60 and 100 mg/L by adding appropriate amounts of Pb(NO<sub>3</sub>)<sub>2</sub> stock solution to distilled water for kinetic studies.

Table 1  
Characterization of clinoptilolite

Constituents (%)	This study	Yücel and Çulfaz [29]	Sirkecioğlu and Şenatar [30]
SiO <sub>2</sub>	75.283	67.6	64.99
Al <sub>2</sub> O <sub>3</sub>	12.047	11.3	9.99
K <sub>2</sub> O	4.497	2.17	1.95
CaO	4.431	3.26	3.51
Na <sub>2</sub> O	0.344	–	0.18
MgO	1.219	1.18	1.01
Si	–	–	–
Fe <sub>2</sub> O <sub>3</sub>	1.113	0.77	3.99
MnO	–	0.02	–
TiO <sub>2</sub>	0.065	0.07	–
NaO <sub>2</sub>	–	0.3	–
H <sub>2</sub> O	–	13.4	14.47

Adsorption isotherms were performed for initial Pb(II) concentrations of 50, 100, 150, 200, 250, 300 and 400 mg/L.

The Pb(II) concentration of the samples was determined by atomic absorption spectrometric method using UNICAM 929A [31].

### 2.4. General procedures

Batch mode adsorption isotherm and kinetic studies were carried out at 22 °C. An amount of 0.5 g clinoptilolite was introduced into conical flasks with 200 ml of lead solution. The flasks were placed in a thermostatic shaker and agitated for 4 h at a fixed agitation speed of 200 rpm. Preliminary tests confirmed that 3–4 h contact time were enough to reach a steady-state Pb(II) concentration. Samples were taken periodically for measurement of aqueous phase of lead concentrations. All the experiments were carried out at initial pH 4.5. Since, above pH 7 precipitation may occur [32], initial pH was adjusted by adding 0.1 M HNO<sub>3</sub>.

The amount of Pb(II) in the solid phase,  $q$  (mg/g), was calculated by using the equation

$$q = (C_0 - C_t) V/m \quad (1)$$

where  $C_0$  and  $C_t$  are the amount of initial and retained Pb(II) ion in the solution at time  $t$  (mg/L), respectively,  $V$  is the solution volume (ml) and  $m$  is the weight of adsorbent (g).

The adsorption isotherms or adsorption kinetic models having two parameters can be transformed into linear forms to obtain adjustable parameters just by graphical means or by linear regression analysis. But, the models having more than two adjustable parameters are not fitted to experimental data by linear regression or graphical means. In this case it is necessary to apply nonlinear least squares analysis. Kumar and Sivanesan [33] have stated that nonlinear regression analysis method is a better way of obtaining the parameters involved in the pseudo-second order kinetic expressions. For that reasons, a minimization procedure has been adopted to solve isotherms and kinetic equations by minimizing the sum of error squared (SSE) between the predicted values and the experimental data using the solver add-in function of the Microsoft Excel [34].

$$SSE = \sqrt{\sum (q_{\text{exp}} - q_{\text{cal}})^2 / N} \quad (2)$$

where the subscripts “exp” and “cal” are the experimental and calculated values of  $q$ , respectively and  $N$  is the number of measurements.

In order to quantitatively compare the applicability of isotherm equations and adsorption kinetic models in fitting to data, nonlinear correlation coefficient and relative error,  $\Delta q$ , were calculated.

$$\Delta q (\%) = \frac{1}{N} \sum_{i=1}^N | [q_{\text{calc}} - q_{\text{exp}}] / q_{\text{exp}} | \times 100 \quad (3)$$

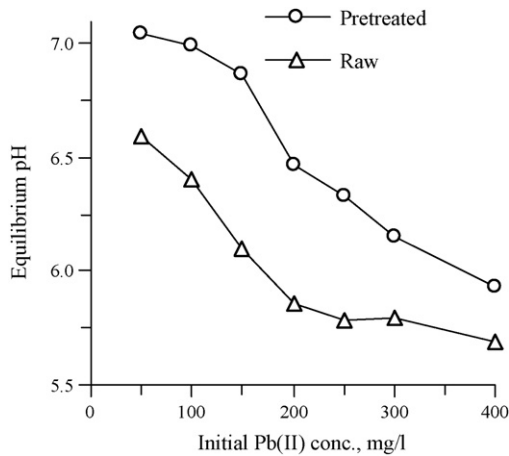


Fig. 1. Equilibrium pH of batch Pb(II) adsorption by clinoptilolite (initial pH 4.5, clinoptilolite conc. 2.5 g/L, Pb(II) conc. 50–400 mg/L, 22 °C, and adsorption period 4 h).

### 3. Results and discussion

#### 3.1. Effect of initial Pb(II) concentration on equilibrium pH

Fig. 1 shows the effect of initial Pb(II) concentration on equilibrium pH. The pH value during the experiments was increased from 4.5, which is the initial pH value, to between 5.75 and 7.05 depending on initial concentration. This significant increase in the pH value was due to the simultaneous uptake of hydrogen ions by zeolite samples and hydrolysis of zeolites [4,35].

#### 3.2. Influence of initial Pb(II) concentration on removal efficiency

It was observed that the uptake capacity of pretreated clinoptilolite was higher than raw one. The amount of Pb(II) adsorbed increased from 19.321 to 80.933 and 19.602 to 122.400 mg/g with an increase in the initial adsorbate concentration from 50 to 400 mg/L for raw and pretreated clinoptilolite, respectively. However, the efficiency of Pb(II) removal is affected by the initial concentration, with decreasing removal percentages as the concentration increases from 50 to 400 mg/L (figure is not shown). These effects can be explained as follows: there are number of exchangeable sites in clinoptilolite structure at low Pb(II)/clinoptilolite ratios. As Pb(II)/clinoptilolite ratio increases, exchangeable sites are saturated, resulting in a decrease in the adsorption efficiency.

#### 3.3. Adsorption isotherms

In this study, the relationship between the adsorbed and the aqueous concentrations at equilibrium has been described by four two-parameter isotherm models; Freundlich, Langmuir, Temkin and Dubinin–Radushkevich, and four three-parameter adsorption isotherm models; Redlich–Peterson, Sips, Toth and Khan.

The isotherm constants, SSE, average relative errors ( $\Delta q_e$ , %) and correlation coefficients ( $r^2$ ) based on the actual deviation

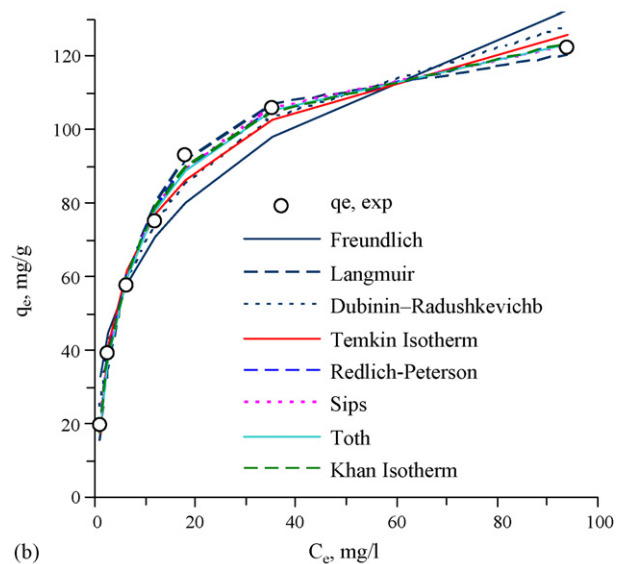
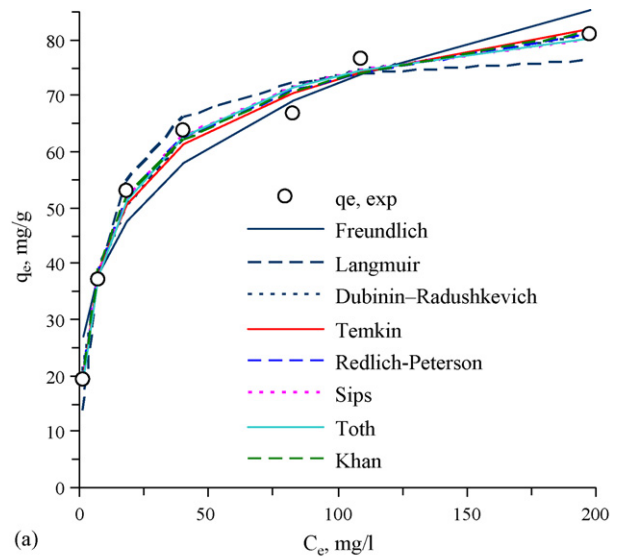


Fig. 2. Comparison of the various adsorption isotherms for Pb(II) ion removal (initial pH 4.5, clinoptilolite conc. 2.5 g/L, Pb(II) conc. 50–400 mg/L, and adsorption period 4 h); (a) raw, (b) pretreated.

between the experimental points and predicted values were given in Fig. 2 and Table 2.

##### 3.3.1. Two-parameter isotherms

3.3.1.1. Freundlich isotherm. Freundlich isotherm assumes heterogeneous surface with a nonuniform distribution of heat of adsorption. Freundlich isotherm is given as [36]:

$$q_e = K_f C_e^{1/n} \quad (4)$$

where  $q_e$  is equilibrium solid phase concentration (mg/g),  $K_f$  and  $n$  are indicative isotherm parameters of adsorption capacity and intensity, respectively,  $C_e$  is equilibrium liquid phase concentration (mg/L).

The  $n$  values in Freundlich equation were calculated as 4.115 and 3.279 for raw and pretreated clinoptilolite, respectively.

Table 2  
Adsorption isotherm constants and statistical comparison values

	Two-parameter isotherms	
	Raw	Pretreated
<b>Freundlich</b>		
$K_f$	23.615	33.139
$1/n$	0.243	0.305
$r^2$ (nonlinear)	0.951	0.934
SSE	4.600	8.979
$\Delta q$ (%)	10.385	17.247
<b>Langmuir</b>		
$K_L$	9.732	17.345
$a_L$	0.123	0.134
$q_m = K_L/a_L$	79.323	129.716
$r^2$ (nonlinear)	0.971	0.993
SSE	3.747	3.204
$\Delta q$ (%)	7.668	6.721
<b>Temkin</b>		
$K_{Te}$	2.655	2.091
$b$	187.938	107.402
$r^2$ (nonlinear)	0.988	0.989
SSE	2.195	3.627
$\Delta q$ (%)	3.460	5.486
<b>Dubinin–Radushkevich</b>		
$q_m$	90.776	162.162
$E$	9.157	9.118
$r^2$ (nonlinear)	0.988	0.986
SSE	2.259	4.209
$\Delta q$ (%)	3.693	6.903
	Three-parameter isotherms	
	Raw	Pretreated
<b>Redlich–Peterson</b>		
$K_R$	18.422	22.139
$a_R$	0.431	0.242
$\beta$	0.875	0.921
$r^2$ (nonlinear)	0.990	0.995
SSE	2.002	2.339
$\Delta q$ (%)	3.096	3.983
<b>Sips</b>		
$q_m$	94.481	141.575
$a_s$	0.188	0.159
$1/n$	0.638	0.821
$r^2$ (nonlinear)	0.989	0.997
SSE	2.110	1.916
$\Delta q$ (%)	2.651	2.290
<b>Toth</b>		
$q_m$	102.162	146.331
$K_{To}$	1.588	3.314
$n$	0.483	0.712
$r^2$ (nonlinear)	0.990	0.996
SSE	2.051	2.056
$\Delta q$ (%)	2.502	2.905
<b>Khan</b>		
$q_m$	45.239	96.612
$b_K$	0.358	0.215
$a_K$	0.860	0.905
$r^2$ (nonlinear)	0.990	0.995
SSE	2.032	2.461
$\Delta q$ (%)	3.401	4.420

Table 3  
Types of isotherms for different values of  $R_L$

$R_L$ value	Type of isotherm
$R_L > 1$	Unfavorable
$R_L = 1$	Linear
$0 < R_L < 1$	Favorable
$R_L = 0$	Irreversible

Since they lie between one and ten, this indicate favorable adsorption of Pb(II) onto clinoptilolite.

**3.3.1.2. Langmuir isotherm.** Basic assumption of Langmuir isotherm is that adsorption takes place at specific homogeneous sites within the adsorbent. Langmuir isotherm can be represented as [37]:

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

where  $K_L$  and  $a_L$  are the Langmuir constants related to the adsorption capacity and energy of adsorption, respectively. The theoretical maximum monolayer adsorption capacity,  $q_m$  (mg/g), is given by  $K_L/a_L$ .

The essential characteristics of Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor,  $R_L$ , which is defined as:

$$R_L = 1 / (1 + a_L C_0) \quad (6)$$

The  $R_L$  values were found to vary within a range, 0.140–0.020 and 0.130–0.018 for raw and pretreated clinoptilolite, respectively, for the initial Pb(II) concentration values of 50–400 mg/L. They are in the range of 0–1 which indicates favorable adsorption [38] (Table 3).

Maximum monolayer adsorption capacities were obtained to be 79.323 and 129.716 mg/g for raw and pretreated clinoptilolite, respectively (Table 2).

**3.3.1.3. Temkin isotherm.** Temkin isotherm assumes that decrease in the heat of adsorption is linear and the adsorption is characterized by a uniform distribution of binding energies. Temkin isotherm is expressed by the following equation [39]:

$$q_e = \frac{RT}{b} \ln(K_{Te} C_e) \quad (7)$$

where  $K_{Te}$  is equilibrium binding constant (L/g),  $b$  is related to heat of adsorption (J/mol),  $R$  is the gas constant ( $8.314 \times 10^{-3}$  kJ/K mol) and  $T$  is the absolute temperature (K).

The Temkin constants,  $K_{Te}$  and  $b$ , were found to be 2.655, 2.091 L/g and 187.938, 107.402 J/mol for raw and pretreated clinoptilolite, respectively.

The isotherm was the best to describe the experimental data, compared to other two-parameter models, as low relative errors ( $\Delta q_e$ , %), high regression coefficients ( $r^2$ ) and low SSE values were observed (Table 2).

**3.3.1.4. Dubinin–Radushkevich isotherm.** Dubinin–Radushkevich isotherm is applied to find out the adsorption mechanism

based on the potential theory assuming heterogeneous surface [40]. Dubinin–Radushkevich is expressed as follows [41,42]:

$$q_e = q_m \exp\left(\frac{(RT \ln(1 + 1/C_e))^2}{-2E^2}\right) \quad (8)$$

where  $q_m$  is the maximum adsorption capacity (mg/g) and  $E$  is energy of adsorption (kJ/mol).

Dubinin–Radushkevich isotherm constants,  $q_m$ , for raw and pretreated clinoptilolite were found to be 90.776 and 162.162 mg/g, respectively (Table 2).

Energy of adsorption is the free energy of transfer of 1 mol of solute from infinity (in solution) to the surface of clinoptilolite. The magnitude of  $E$  is used for estimating the type of adsorption mechanism. If this value is between 8 and 16 kJ/mol, the adsorption type can be explained by ion-exchange [43]. The calculated values of  $E$  are 9.157 and 9.118 kJ/mol for raw and pretreated clinoptilolite, respectively, and they are in the range of values for ion-exchange reactions. Ahmad et al. [44] also calculated that the adsorption mean free energy from Dubinin–Radushkevich isotherm for uptake of lead on lateritic minerals was  $13.96 \pm 0.74$  kJ/mol. Kurtoğlu and Atun [45] have concluded that Pb(II) ions are removed by ion-exchange mechanism from the solutions below  $5 \times 10^{-4}$  M (103.6 mg/L) while formation of surface complexes between Pb(II) species and surface hydroxyl groups increases Pb adsorption at higher concentrations.

### 3.3.2. Three-parameter isotherms

**3.3.2.1. Redlich–Peterson isotherm.** Redlich–Peterson isotherm approximates to Henry's law at low sorbate concentrations, and at high concentrations it behaves like the Freundlich isotherm. It is given as [46]:

$$q_e = \frac{K_R C_e}{1 + a_R C_e^\beta} \quad (9)$$

where  $K_R$  (L/g) and  $a_R$  (L/mg) are Redlich–Peterson isotherm constants and  $\beta$  is the exponent which lies between 0 and 1.

Redlich–Peterson isotherm constants for adsorption of Pb(II) onto raw and pretreated clinoptilolite are shown in Table 2. The isotherm constants,  $K_R$  and  $a_R$ , were calculated to be 18.422, 22.139 L/g, 0.431, 0.242 L/mg for raw and pretreated clinoptilolite, respectively. Exponent  $\beta$  values were 0.875 and 0.921 for raw and pretreated clinoptilolite, respectively.

**3.3.2.2. Sips isotherm.** Sips isotherms is a combination of the Langmuir and Freundlich isotherm type models and expected to describe heterogeneous surfaces much better. At low sorbate concentrations it reduces to a Freundlich isotherm, while at high sorbate concentrations it predicts a monolayer adsorption capacity characteristic of the Langmuir isotherm [47]. The model can be written as [48]:

$$q_e = \frac{q_m a_s C_e^{1/n}}{1 + a_s C_e^{1/n}} \quad (10)$$

where  $q_m$  is monolayer adsorption capacity (mg/g) and  $a_s$  is Sips constant related to energy of adsorption.

According to Sips model, the monolayer adsorption capacity values were 94.481 and 141.575 mg/g for raw and pretreated clinoptilolite, respectively (Table 2). The exponent  $1/n$  value for pretreated clinoptilolite was closer to unity than raw clinoptilolite. It means that Pb(II) adsorption data for pretreated clinoptilolite is more of Langmuir form rather than that of Freundlich, considering relative errors for Freundlich and Langmuir isotherms for pretreated clinoptilolite.

**3.3.2.3. Toth isotherm.** Toth isotherm is Langmuir-based isotherm and considers a continuous distribution of site affinities. It is expressed as [49]:

$$q_e = \frac{q_m C_e}{(K_{T0} + C_e^n)^{1/n}} \quad (11)$$

where  $K_{T0}$  is the Toth model constant and  $n$  the Toth model exponent ( $0 < n \leq 1$ ). It is obvious that for  $n = 1$  this isotherm reduces to the Langmuir equation.

Toth model constant  $K_{T0}$  and exponent  $n$  values for raw and pretreated clinoptilolite were found to be 1.588, 3.314 and 0.483, 0.712, respectively (Table 2).

**3.3.2.4. Khan isotherm.** Khan et al. [50] have suggested a generalized isotherm for pure solutions. Khan isotherm is given as:

$$q_e = \frac{q_m b_K C_e}{(1 + b_K C_e)^{a_K}} \quad (12)$$

$q_m$  and  $b_K$  is the Khan model constant and  $a_K$  is the Khan model exponent.

For the results given in Table 2,  $q_m$  and  $b_K$  values were observed to be 45.239, 96.612 and 0.358, 0.215, and  $a_K$  values were 0.860, 0.905 for raw and pretreated clinoptilolite, respectively.

### 3.3.3. Comparison of isotherms

It was determined that best fitted adsorption isotherm models considering the relative errors were obtained for two-parameter isotherms to be in the order of prediction precision: Temkin, Dubinin–Radushkevich, Langmuir and Freundlich isotherms. Three-parameter isotherms have higher regression coefficients ( $>0.99$ ) and lower relative errors ( $<5\%$ ) than two-parameter isotherms. Comparing the values of SSE,  $\Delta q$ , and  $r^2$  obtained from the adsorption models shows that the fitness between the experimental values and the predicted values using the models were generally very good for all three-parameter isotherm models. However, the Sips and Toth isotherms provided the best correlation for raw and pretreated clinoptilolite, respectively.

The experimental and predicted isotherm data are shown graphically in Fig. 2. The applicability of all isotherm models to the Pb(II)–clinoptilolite system implies that both monolayer adsorption and heterogeneous surface conditions exist under the experimental conditions studied. The adsorption of Pb(II) ions on the clinoptilolite is thus complex, involving more than one mechanism [51].

Calculated monolayer adsorption capacities,  $q_m$ , from Langmuir isotherm were consistent with the experimental  $q_m$  values



Table 4  
Values of maximum adsorption capacities of some adsorbents for Pb(II)

Adsorbent	Size (mm)	$Q_e$ (mg/g)	Source
Zeolite (Phillipsite)-raw	0.18–0.71	104.0	Ali and El-Bishtawi [52]
Zeolite (Clinoptilolite)-raw	0.10–2.00	78.7	Curkovic et al. [4]
Zeolite (Clinoptilolite)-pretreated	0.10–2.00	85.0	Curkovic et al. [4]
Zeolite (Clinoptilolite)	0.50–0.10	64.0	Peric et al. [53]
Zeolite (Clinoptilolite)	0.32–0.50		Bektaş and Kara [54]
Zeolite (Clinoptilolite)-raw	0.30–0.60	80.9	This study
Zeolite (Clinoptilolite)-pretreated	0.30–0.60	122.4	This study

(Table 2). Maximum experimental adsorption capacity of Pb(II) for the pretreated clinoptilolite was approximately 1.5 times higher than that of the natural one. Similar trend was also observed for Sips and Toth isotherm constants related to the adsorption capacity. From these observations, it is appeared that the surface properties of zeolite could be improved upon application of NaCl as previously reported by other researchers [25,26,28]. Comparison of maximum experimental adsorption capacities of Pb(II) for some minerals were also given in Table 4 [4,52–54]. It can be seen from the table, clinoptilolite used in this study has high adsorption capacity.

### 3.4. Adsorption kinetics

The removal of Pb(II) ions by adsorption onto clinoptilolite increased with time, attaining a maximum value at about 60–120 min, and thereafter it remained constant, as presented in Fig. 3a and b. It is very clear from the figure that the agitation time required for maximum uptake (or to reach equilibrium) of Pb(II) by clinoptilolite was depended on the initial Pb(II) concentration. The adsorption rate of Pb(II) by the clinoptilolite initially was fast up to 20–25 min, and then gradually decreased with increase in contact time.

The results obtained from the experiments were used to study the rate-limiting step in the adsorption process, such as mass transport and chemical reaction processes. Moreover, information on the kinetics of metal uptake is required for selecting optimum operational conditions for full-scale metal removal processes. Determination of the kinetic parameters and explanation of the mechanism in heterogeneous systems is often a complex procedure, as surface effects can be superimposed on chemical effects [55].

Three kinetic models; pseudo-first order, pseudo-second order and Elovich equations were used to test experimental data to examine the adsorption kinetics.

#### 3.4.1. Pseudo-first order model

Pseudo-first order model is one of the most widely used procedures for the adsorption of a solute from aqueous solution [56]. The pseudo-first order equation can be expressed as follows:

$$q_t = q_e(1 - \exp(-k_1 t)) \quad (13)$$

where  $q_t$  is the amount of Pb(II) adsorbed at time  $t$  (mg/g);  $q_e$  is equilibrium solid phase concentration and  $k_1$  is first order rate constant for adsorption (L/min).

The rate constants  $k_1$  were found to be in the range of 0.047–0.025 L/min for raw and pretreated clinoptilolite for the initial Pb(II) concentration values of 15–100 mg/L (Table 5). These were comparable with recently reported values for lead biosorption onto *Rhizopus nigricans* 0.0619, 0.0654 and 0.0560 L/min for the initial concentrations of 250, 400 and 500 mg/L, respectively [57].

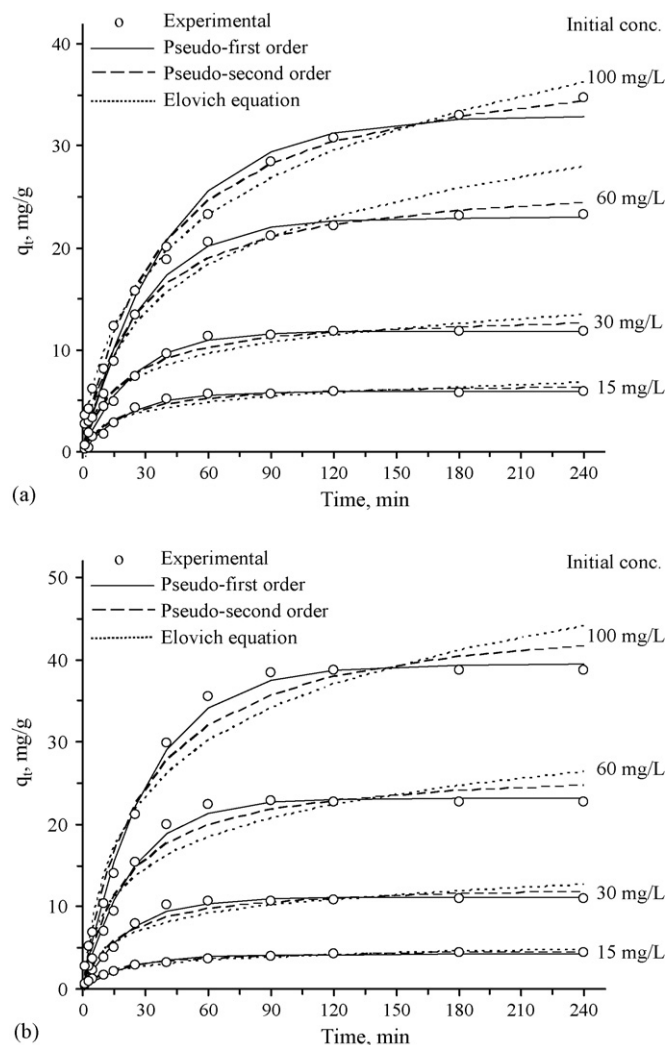


Fig. 3. Effect of agitation time and initial Pb(II) concentration on the adsorption of Pb(II); (a) raw, (b) pretreated. (initial pH 4.5, clinoptilolite conc. 2.5 g/L, and adsorption period 4 h).

Table 5  
Comparison of adsorption kinetics constants

	Raw clinoptilolite				Pretreated clinoptilolite			
	15 <sup>a</sup>	30 <sup>a</sup>	60 <sup>a</sup>	100 <sup>a</sup>	15 <sup>a</sup>	30 <sup>a</sup>	60 <sup>a</sup>	100 <sup>a</sup>
$q_e$ , exp. (mg/g)	5.90	11.88	23.24	34.78	4.48	11.03	22.80	38.69
Pseudo-first order								
$q_e$ , (mg/g)	5.91	11.86	22.98	33.01	4.19	11.11	23.24	39.45
$k_1$ (min <sup>-1</sup> )	0.047	0.043	0.035	0.025	0.047	0.047	0.042	0.025
SSE	0.77	1.57	3.00	5.71	0.82	1.28	3.07	3.64
$\Delta q$ (%)	1.93	1.03	1.48	2.15	1.64	1.79	1.30	1.27
$R^2$	0.990	0.990	0.989	0.989	0.980	0.993	0.989	0.995
Pseudo-second order								
$q_e$ , (mg/g)	6.76	13.52	26.99	39.56	4.76	12.71	26.99	46.30
$k_2$ (min <sup>-1</sup> )	0.00814	0.00388	0.00146	0.00070	0.01227	0.00431	0.00181	0.00081
$h_0$ (mg/g min)	0.372	0.708	1.064	1.091	0.279	0.697	1.300	1.739
SSE	1.32	1.93	4.31	3.64	0.34	2.52	5.44	7.13
$\Delta q$ (%)	3.06	0.97	1.72	1.47	0.82	2.10	2.12	1.39
$R^2$	0.972	0.982	0.977	0.994	0.996	0.971	0.965	0.979
Elovich equation								
$a$ (mg/g min)	0.835	1.332	1.482	1.520	0.563	1.516	2.244	3.122
$b$ (g/mg)	0.746	0.353	0.140	0.100	1.034	0.393	0.172	0.098
$t_0$ (1/ab), min	0.454	2.125	2.959	7.451	1.717	0.599	2.591	2.543
SSE	1.98	3.18	8.19	3.17	0.52	3.88	8.41	11.17
$\Delta q$ (%)	4.54	2.16	3.08	0.82	0.71	4.45	2.95	2.19
$R^2$	0.931	0.951	0.946	0.993	0.989	0.925	0.916	0.948

<sup>a</sup>  $C_0$  (initial concentration) (mg/L).

Fig. 3a and b show good compliance with the pseudo-first order equation. The experimental points are shown together with the theoretically generated lines. The agreement between the sets of data is reflected by the extremely high correlation coefficients and low relative errors and these values are shown in Table 5. The correlation coefficients for the first-order kinetic model were greater than 0.98. The calculated  $q_e$  values also agree very well with the experimental data in the case of pseudo-first order kinetics.

### 3.4.2. Pseudo-second order model

The pseudo-second order equation is based on the adsorption capacity of the solid phase [58,59]. Contrary to other models, it predicts the behavior over the whole range of adsorption [60].

Pseudo-second order based on adsorption equilibrium capacity may be expressed in the form [56]:

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

where  $k_2$  (g/mg min) is the rate constant of pseudo-second order adsorption.

The initial adsorption rate,  $h$  (mg/g min), as  $t \rightarrow 0$  can be defined

$$h_0 = k_2 q_e^2 \quad (15)$$

The pseudo-second order reaction constants  $k_2$  and correlation coefficients are presented in Table 5 for all initial Pb(II) concentrations. The values of  $k_2$  were found to be in the ranges of  $8.14 \times 10^{-3}$ – $0.70 \times 10^{-3}$  and  $12.27 \times 10^{-3}$ – $0.81 \times 10^{-3}$  g/mg min for raw and pretreated clinoptilolite, respectively. The values of the overall second-order adsorption

rate constants,  $k_2$ , decreased with increase in initial Pb(II) concentrations from 15 to 100 mg/L. El-Bishtawi and Al-Haj Ali [61] observed similar phenomena in adsorption of Pb(II) on zeolite tuff.

For any  $C_0$  value in the range investigated, the initial adsorption rate increased with increase in initial concentrations. Predicted initial adsorption rates ( $h_0$ ) for raw clinoptilolite are 0.372, 0.708, 1.064, 1.091 mg/g min for 15, 30, 60 and 100 mg/L, respectively. This indicates that  $h_0$  increased rapidly with  $C_0$  up to 60 mg/L, after which no significant effect on initial rate was observed due to fact that the adsorption process is limited by the active sites in the solid phase for raw clinoptilolite. For pretreated clinoptilolite, initial adsorption rates ( $h_0$ ) also increased but not levelled out with increase in initial concentrations up to 100 mg/L.

### 3.4.3. Elovich equation

In reactions involving chemisorption of adsorbate on a solid surface without desorption of products, adsorption rate decreases with time due to an increased surface coverage. One of the most useful models for describing such 'activated' chemisorption is the Elovich equation [62]. The Elovich equation can be written as [63,64]:

$$\frac{dq_t}{dt} = a \exp(-bq_t) \quad (16)$$

where  $a$  is the initial adsorption rate (mg/g min) because  $(dq_t/dt) \rightarrow a$  as  $q_t \rightarrow 0$ .

Given that  $q_t = 0$  at  $t = 0$ , the integrated form of Eq. (16)

$$q_t = (1/b) \ln(t + t_0) - (1/b) \ln t_0 \quad (17)$$

where  $t_0 = 1/(ab)$ . If  $t$  is much larger than  $t_0$  ( $t \gg t_0$ ), Eq. (17) can be simplified as:

$$q_t = (1/b) \ln ab + (1/b) \ln t \quad (18)$$

Elovich equation parameters,  $a$ ,  $b$ ,  $t_0$ , and correlation coefficients and relative errors are presented in Table 5 for all initial Pb(II) concentrations. The values of the initial adsorption rate constants,  $a$ , were found to increase with increase in initial Pb(II) concentration. But constant  $b$  decreased with increase in initial Pb(II) concentration.

Teng and Hsieh [65] commented on that the constant  $a$  is related to the rate of chemisorption and the constant  $b$  is related to the surface coverage. Therefore, increasing the concentration of solution and the mass of adsorbent will increase the rate of chemisorption. If the constant  $b$  is related to the extent of surface coverage, then the increasing of the concentration of solution will decrease the available adsorption surface for the sorbates. An increase in the mass of adsorbent will increase the available surface for the sorbates.

Values of  $t_0$  under the conditions studied are in the range of 0.454–7.451 and 1.717–2.543 min for raw and pretreated clinoptilolite, respectively.

#### 3.4.4. Comparison of adsorption kinetics

The parameter values obtained from the application of kinetic models were used to predict the variation of adsorbed Pb(II) ion with time. The resulting curves and kinetic parameters are compared to the experimental data in Fig. 3a, b and Table 5, respectively. As seen, relative errors of the first-order model are less than in all other models, and the correlation coefficients of the first-order model were high, indicating that the first-order model best describe the adsorption of Pb(II) on clinoptilolite. For the range of process variables investigated, results indicated that the adsorption kinetic coefficients were dependent on initial Pb(II) concentration.

Table 5 shows that the least values of  $\Delta q$  are given by the first-order rate equation. The pseudo-second order equation follows the first-order rate equation and also provides a good fitting to the experimental data points. Considering all the above results, the kinetics of Pb(II) adsorption on clinoptilolite can be described in the order of fitting; the pseudo-first order, the pseudo-second order and Elovich equations.

#### 3.5. Gibbs free energy of Pb(II)–clinoptilolite system

Gibbs free energy can be calculated from the thermodynamic equilibrium constant,  $K_0$ , which is defined as follows:

$$K_0 = \frac{a_s}{a_e} = \frac{v_s q_e}{v_e C_e} \quad (19)$$

where  $a_s$  is the activity of adsorbed Pb(II),  $a_e$  is the activity of Pb(II) in solution at equilibrium,  $v_s$  is the activity coefficient of the adsorbed Pb(II) and  $v_e$  is the activity coefficient of the Pb(II) in solution at equilibrium. As the Pb(II) concentration in the solution decreases and approaches zero, the activity coefficient

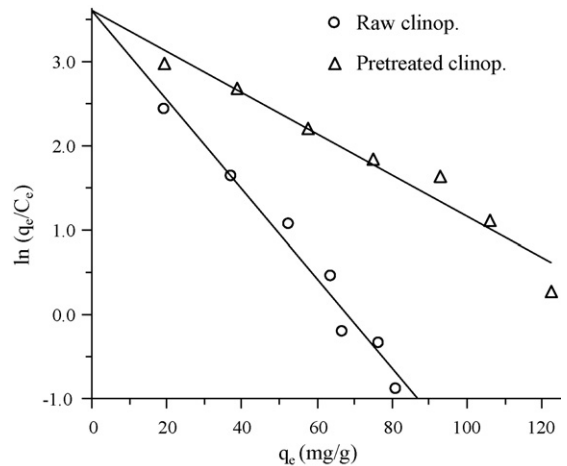


Fig. 4. Plots of  $\ln(q_e/C_e)$  vs.  $q_e$  for adsorption of Pb(II) on clinoptilolite.

$v$  approaches to unity. Eq. (19) may be written as:

$$\lim_{q_e \rightarrow 0} \frac{a_s}{a_e} = \frac{q_e}{C_e} = K_0 \quad (20)$$

$K_0$  can be obtained by plotting a straight line of  $\ln(q_e/C_e)$  versus  $q_e$  (Fig. 4) and extrapolating  $q_e$  to zero [66]. Its intercept gives the values of  $K_0$ .

The adsorption standard free energy changes ( $\Delta G^\circ$ ) can be calculated according to

$$\Delta G^0 = -RT \ln K_0 \quad (21)$$

where  $R$  is the universal gas constant ( $8.314 \times 10^{-3}$  kJ/K mol) and  $T$  is the temperature in Kelvin.

The values obtained are shown in Table 6. The negative free energy changes in Pb(II)–clinoptilolite system are  $-8.86$  and  $-8.89$  kJ/mol for raw and pretreated clinoptilolite, respectively, indicating the adsorption process is spontaneous at room temperature. These results are consistent with Gibbs free energy for adsorption of Pb(II) on lateritic minerals, which are between  $-10.87$  and  $-14.82$  kJ/mol at temperature range of 278–323 K [50]. Çulfaz and Yağız [67] calculated the values of the thermodynamic quantities  $K_0$  and  $\Delta G^\circ$  as 16.6 and  $-6.96$  kJ/mol (3.48 kJ/eq) for lead–sodium system; and 0.16 and  $+4.54$  kJ/mol ( $+2.27$  kJ/eq) for cadmium–sodium system, respectively. Yadava et al. [68] also calculated that Gibbs free energy of Pb(II) adsorption on China clay as  $-8.08$ ,  $-4.53$  and  $-3.07$  kJ/mol for the temperature of 20, 30 and  $40^\circ\text{C}$ , respectively.

Table 6

Equilibrium constant and Gibbs free energy of adsorption of Pb(II) on clinoptilolite

	Raw clinoptilolite	Pretreated clinoptilolite
Intercept, $\ln K_0$	3.60	3.61
$\Delta G^\circ$ (kJ/mol)	$-8.86$	$-8.89$
$r^2$ (linear)	0.968	0.952



#### 4. Conclusions

The following conclusions can be drawn from this study.

- Clinoptilolite is an effective adsorbent for the removal of Pb(II) from aqueous solution. The batch studies indicated that the lead adsorption on clinoptilolite increased with increase in initial Pb(II) concentration. The experimental maximum adsorption capacities of Pb(II) onto clinoptilolite were 80.933 and 122.400 mg/g for raw and pretreated clinoptilolite, respectively, for the initial concentration of 400 mg/L.
- Of the two-parameter isotherm models, Temkin isotherm best describe the adsorption of Pb(II) on clinoptilolite. Considering all isotherm models, Sips and Toth isotherms provided the best correlation for raw and pretreated clinoptilolite, respectively.
- Adsorption of Pb(II) appears to take place by an ion-exchange mechanism. According to Dubinin–Radushkevich isotherm, the calculated values of  $E$  are 9.157 and 9.118 kJ/mol for raw and pretreated clinoptilolite, respectively. These are in the range of values for ion-exchange reactions.
- Pseudo-first order kinetic model best described the kinetic data. The pseudo-second order equation follows the first-order rate equation and also provides a good fitting to the experimental data points.
- The negative value of change in Gibbs free energy ( $\Delta G^\circ$ ) indicates that adsorption of Pb(II) on clinoptilolite is spontaneous.
- It may be concluded that clinoptilolite may be used, as a low-cost and abundant source, for the removal of Pb(II) and it may be an alternative to more costly materials such as synthetic resins.

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