



## Studies on optimization of efficient parameters for removal of lead from aqueous solutions by natural zeolite as a low-cost adsorbent using response surface methodology

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### ARTICLE INFO

#### Article history:

Received 17 January 2017

Received in revised form

20 July 2017

Accepted 13 August 2017

#### Keywords:

Lead

Clinoptilolite

Zeolite

Adsorption isotherms

Response surface methodology

### ABSTRACT

In this research, the removal of lead from the aqueous solution was investigated using natural nontoxic zeolite (clinoptilolite) as a low-cost adsorbent in order to reduce human exposure to it. The clinoptilolite zeolite obtained from the Semnan area was characterized by X-ray diffraction pattern, FTIR spectroscopy and scanning electron microscopy (SEM). The central composite design (CCD) defined under the response surface methodology (RSM) was used for designing the experiments and analyzing the sorption of lead. Three parameters of contact time (43.07-101.93 min), initial concentration (508-3006 mg/L) and temperature (20-51°C) were applied to optimize the removal percentage of lead by zeolite. It was found that the initial concentration is the most important parameter affecting the removal percentage of lead, followed by the temperature of process. The optimum values of initial concentration, contact time and temperature were found to be 2750 ppm, 82.87 min and 65°C for 99.81% removal of lead, respectively, with a high desirability of 0.990. The adsorption data fitted the Freundlich adsorption model better than the Langmuir model, with the maximum sorption capacity of the clinoptilolite zeolite for Pb(II) equaling 136.99 (mg/g).

### 1. Introduction

According to the development of various industries including iron and steel, metallurgy, and aerospace and atomic energy, the waste of these industries containing heavy metals is discharged to the environment directly or indirectly, putting the human health and ecosystems at risk [1]. Heavy metals that exist in the environment may enter the food chain and their values may increase in human body because of their inseparability properties. Among these metals, lead, mercury, and cadmium are considered as toxic and extremely dangerous, even at trace levels [2]. Therefore, in order to protect the environment and human health, heavy metals should be removed from water and wastewater. Wastewater treatment needs a new, accurate and cost-effective method to remove heavy metals at high concentrations [3]. There are various methods for the

removal of heavy metals from wastewater, such as: chemical precipitation, ion exchange, flocculation, coagulation, membrane filtration, and adsorption [4,5]. Among them, the adsorption process is known as a good alternative for the above mentioned methods. The main advantages of this process are its cost-effectiveness, simplicity, being environmental-friendly, and easy separations of adsorbent from the liquid product without sludge formation at the end of the process [3,6,7]. In the adsorption process, adsorbent plays an important role in the removal of heavy metals. Many studies have investigated the removal of heavy metals from aqueous solutions in the presence of natural materials such as zeolites, clay, fly ash, coal, and oxides, due to their low cost and local availability as adsorbents [8]. The removal of heavy metals from aqueous solutions in the presence of zeolites has been reported in the literature, due to their

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DOI: 10.22104/AET.2017.1928.1092

ability of ion-exchange to remove unwanted heavy metals in addition to the advantages mentioned previously. For instance, the removal of heavy metals and other cations from wastewater using zeolites [9]; magnetic zeolites as a new adsorbent for the removal of metallic contaminants from water [10]; highly dealuminated Y zeolite as an efficient adsorbent for the hydrophobic fraction from wastewater- treatment plants' effluents [11]; and the adsorption characteristics of natural zeolites as solid adsorbents for phenol removal from aqueous solutions [12]. Moreover, the removal of lead ions from aqueous solutions on solid adsorbents has been reported in the literature; for instance, the removal of zinc, copper, and lead by natural zeolite, as well as a comparison of adsorption isotherms [13]; a comparative study of Cu (II) and Pb (II) adsorption by Iranian bentonite (Birjand area) in aqueous solutions [14]; kinetic study of Pb (II) and Ni (II) adsorption onto MCM-41 amine functionalized nano particles [15]; removal of lead and cadmium by hydrous iron and aluminium oxide from aqueous solutions and industrial waste [16]; removal of lead from solutions by a combination of natural zeolite-kaolin-bentonite as a new low-cost adsorbent [17]; and the removal of Pb<sup>2+</sup> from water using Na-Y zeolites prepared from Egyptian kaolins collected from different sources [18]. In addition to adsorbents, operating parameters such as temperature, concentration, pH, and time affect the removal of heavy metals such as lead. In order to study the effects of various variables, the use of an appropriate design- of- experiment (DOE) method that simultaneously investigates the interaction of several different variables is required. The response surface methodology (RSM) is one of the most useful methods utilized for the design of experiments, statistical modeling, and process optimization by many investigators [19,20]. In this work, the removal of lead from the aqueous solution was investigated by the adsorption process over clinoptilolite, a natural non-toxic zeolite, as a low-cost adsorbent. The influences of effective parameters including temperature, feed concentration, and time, on the removal percentage of lead were examined at various ranges of parameters by designing the experiment using RSM. The optimum conditions for the removal of lead from the aqueous solution over clinoptilolite were obtained. Experimental data were analyzed by the Langmuir and Freundlich isotherm models to describe the adsorption process as a function of equilibrium concentration.

## 2. Materials and methods

### 2.1. Preparation of Clinoptilolite

Clinoptilolite sample was taken from Semnan, Iran. Zeolite was first washed with deionized water and then dried at 100°C for 24 h prior to use.

### 2.2. Adsorbent characterization

Clinoptilolite zeolite XRD (X-ray powder diffraction) patterns were recorded by an X-ray diffractometer (D8-Advance, Bruker AXS, Cu K $\alpha$ ,  $\lambda=1.54$  Å). The infrared spectrum of clinoptilolite zeolite was recorded in the range of 4000 to 400 cm<sup>-1</sup> using PERKIN ELMER Spectrum RXI FT-IR. The solid sample was mixed with KBr powder and compressed into pellet for analysis. The morphology of clinoptilolite was observed using scanning electron microscope (SEM) (JSM-6490 LV).

### 2.3. Experimental procedure in the adsorption process

For the adsorption of lead ions with clinoptilolite zeolite, a 10 mL vessel containing a determined concentration of Pb(II) was used. Aqueous solutions containing different concentrations of lead were prepared. First, 0.3 g of adsorbent was activated at 120°C in the oven for 2 h and then cooled to ambient temperature and added to the mixture. The mixture was shaken at a constant agitation speed (250 rpm) for a determined contact time to facilitate the adsorption of lead ions on clinoptilolite. The temperature of the process was controlled by a temperature controller, accurate to  $\pm 2^\circ\text{C}$ . These series of experiments were carried out at temperatures ranging from 20-52°C. After a determined contact time, the process was stopped and the products were withdrawn from the vessel. Suspensions were filtered for the separation of the adsorbent and were finally centrifuged at 3000 rpm for 30 min to separate the remaining adsorbent. The non-adsorbed concentrations of Pb<sup>+2</sup> in the final solution were determined by atomic absorption spectroscopy (Chemtech analytical CTA-2000). The analysis was repeated at least three times. The mean of analyses is reported for lead compositions. All the measurements were carried out in the peak- height mode.

### 2.4. Removal percentage and adsorption capacity calculations

Two important parameters, removal percentage and adsorption capacity, show the adsorbent activity for the removal of heavy metals from aqueous solutions. Removal percentage (R, %) and adsorption capacity (q<sub>e</sub>) were calculated using the following equation:

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

$$R(\%) = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (2)$$

q<sub>e</sub> (mg/g) is the mg of lead absorbed per g of zeolite at equilibrium; C<sub>0</sub> (mg/L) and C<sub>e</sub> (mg/L) are the initial and equilibrium concentrations of lead ion in the solution,

respectively;  $V$  (L) is the volume of solution; and  $m$  (g) is the amount of adsorbent [21,22].

### 2.5. Experimental design using RSM

In this research, the central composite design (CCD) defined under RSM was applied to investigate the combined influences of adsorption parameters consisting of initial concentrations of lead in the solution (508.77-3006.23 mg/L), contact time (43.07-101.93 min), and temperature (20.8639–51.1361°C). CCD was utilized to develop correlations between the adsorption's effective factors and response including the removal percentage of lead by zeolite. This CCD design involved examining the influences of 3 factors in 2 levels (high, +1 and low, -1 levels). The axial points were located at  $(\pm\alpha, 0, 0)$ ,  $(0, \pm\alpha, 0)$ , and  $(0, 0, \pm\alpha)$ , where  $\alpha$  equals with 1.682 in a single block and 17 sets of test conditions. In this research, the design of experiments was done via Design- Expert 7.0.0.

## 3. Results and discussion

### 3.1. Characterization of the adsorbent

The XRD pattern of the clinoptilolite zeolite is shown in Figure 1. The structure of zeolite is identified in the range of  $2\theta=4^\circ$  to  $2\theta=70^\circ$ . Clinoptilolite zeolite has several characteristic peaks at  $2\theta = 9.63^\circ$ ,  $22.40^\circ$ ,  $26.71^\circ$ ,  $30.19^\circ$  and  $32.74^\circ$  that are assigned to biotite ( $(K(Mg,Fe)_3AlSi_3O_{10}(F,OH)_2)$ ), clinoptilolite ( $((Na,K,Ca)_2-3Al_3(Al,Si)_2Si_{13}O_{36}\cdot 12(H_2O))$ ), quartz ( $SiO_2$ ), feldspar ( $KAlSi_3O_8$ - $NaAlSi_3O_8$ - $CaAl_2Si_2O_8$ ) and dolomite ( $CaMg(CO_3)_2$ ), respectively. Similar results were reported in various studies for the phase composition of zeolite based on XRD results [21,23].

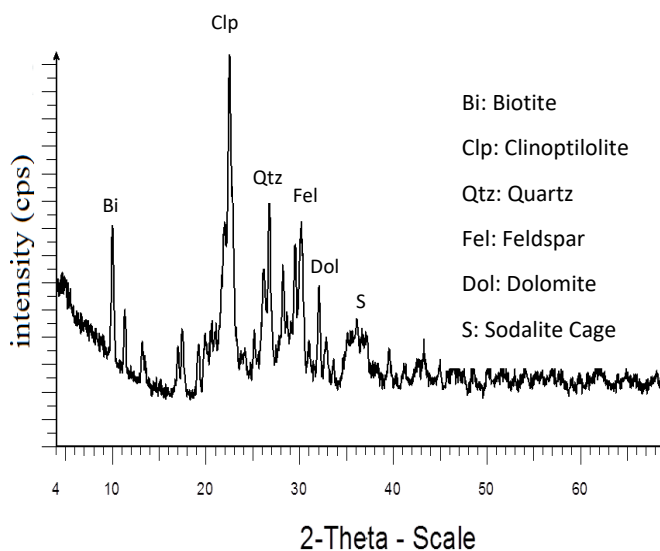


Fig. 1. XRD pattern of clinoptilolite zeolite.

Figure 2 demonstrates the FTIR spectrum of the natural zeolite (clinoptilolite) sample. Based on Figure 2, the IR absorption band in the range of  $460$ – $800\text{ cm}^{-1}$  represents the

symmetric stretching bands. In addition, the peak around  $1300\text{ cm}^{-1}$  can be assigned to the asymmetric stretching band related to the vibrations of Al-O or Si-O, indicating the presence of aluminum and silicon on the surface of zeolite [24]. The strong band observed at  $1047\text{ cm}^{-1}$  is assigned to the stretching vibration band of Si-(Al)-O in tetrahedral  $Si(Al)O_4$  [25]. The spectrum of the bending mode of water molecules appears at  $1635\text{ cm}^{-1}$ . Moreover, based on Figure 2, a broad peak is located around  $3400$ – $3600\text{ cm}^{-1}$  which is assigned to the hydroxyl groups.

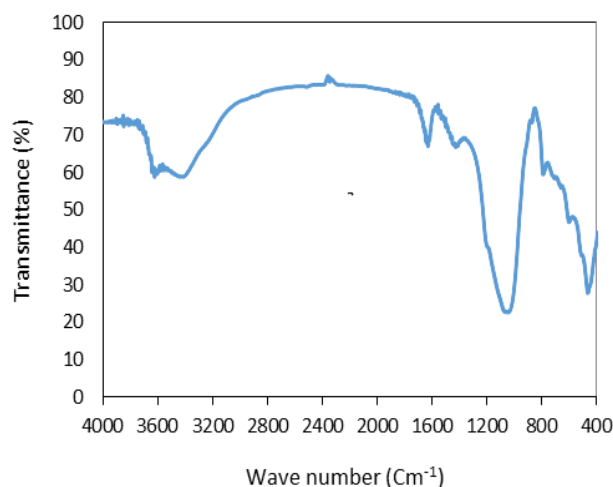


Fig. 2. FTIR spectra of clinoptilolite zeolite.

The band at  $3400\text{ cm}^{-1}$  is attributed to Si-O (H)-Al and Si-OH. The FTIR spectrum at  $3600\text{ cm}^{-1}$  is typically for Brønsted acidity [21,26]. The SEM micrograph of the clinoptilolite zeolite is depicted in Figure 3. Based on this Figure, the clinoptilolite zeolite has an unruly surface. Furthermore, the porosity of the sample is low because of its impurities such as quartz ( $SiO_2$ ) and feldspar.

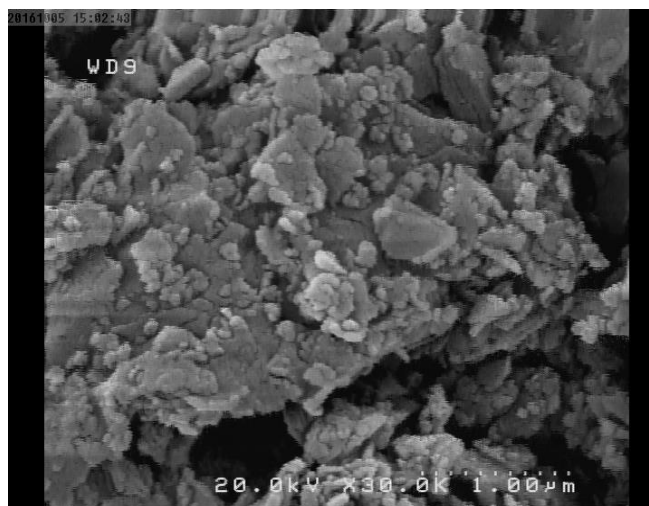
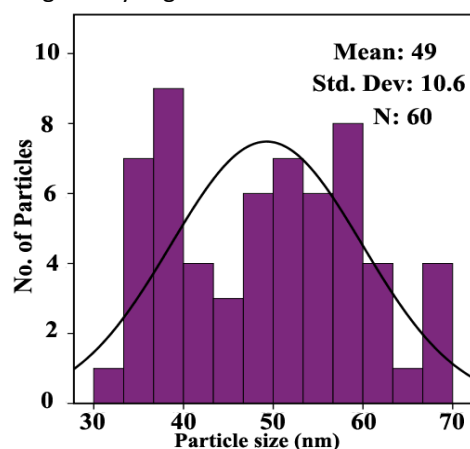


Fig. 3. SEM image of natural clinoptilolite.

**Table 1.** Experimental conditions and results of CCD for removal of lead over clinoptilolite zeolite.

Run	Levels			Adsorption operating parameters			Response
				Initial concentration (ppm)	Temperature (°C)	Time (min)	Removal percentage (%)
1	-1	-1	-1	1015.00	27.00	55.00	79.25
2	+1	-1	-1	2500.00	27.00	55.00	78.45
3	-1	+1	-1	1015.00	45.00	55.00	83.12
4	+1	+1	-1	2500.00	45.00	55.00	84.33
5	-1	-1	+1	1015.00	27.00	90.00	81.27
6	+1	-1	+1	2500.00	27.00	90.00	79.60
7	-1	+1	+1	1015.00	45.00	90.00	84.76
8	+1	+1	+1	2500.00	45.00	90.00	85.42
9	-1.682	0	0	508.77	36.00	72.50	84.23
10	+1.682	0	0	3006.23	36.00	72.50	75.19
11	0	-1.682	0	1757.50	20.86	72.50	80.00
12	0	+1.682	0	1757.50	51.14	72.50	85.90
13	0	0	-1.682	1757.50	36.00	43.07	83.37
14	0	0	+1.682	1757.50	36.00	101.93	82.11
15	0	0	0	1757.50	36.00	72.50	86.17
16	0	0	0	1757.50	36.00	72.50	85.95
17	0	0	0	1757.50	36.00	72.50	85.76

These impurities cover the pores of zeolite [4]. Mean particle size of the clinoptilolite zeolite is 49 nm, obtained by image analyzing. Results are illustrated in Figure. 4.

**Fig. 4.** The particle size distribution of natural zeolite.

### 3.2. Adsorption of lead from the aqueous solution

The experimental conditions and results of adsorption of lead from the aqueous solution over clinoptilolite zeolite are presented in Table 1

The relationship between effective variables, i.e. temperature, contact time, and initial concentrations of lead in the solution, and the removal percentage of lead from the aqueous solution were analyzed. Table 2 shows the analysis of variance (ANOVA) for the response surface reduced cubic model removal percentage of lead. The Model F-value of 71.37 implies that the model is significant. Based on the mentioned table, values of "Prob > F" less than 0.0500 indicate that model terms are significant, and values greater than 0.1000 indicate that model terms are not significant. Among various parameters (initial concentration (A), temperature (B), and contact time (C)) for the removal percentage of lead, A, B, AB, A<sup>2</sup>, B<sup>2</sup>, C<sup>2</sup>, A<sup>2</sup>C, AB<sup>2</sup> are significant model terms. Based on the F-value, effective variables can be ranked as A<sup>2</sup> > A > B > AB<sup>2</sup> > C<sup>2</sup> > B<sup>2</sup> > A<sup>2</sup>C > AB > B<sup>3</sup>. The R<sup>2</sup> value is 0.9892 (very close to 1), indicating that there is a good agreement between the experimental and the predicted removal percentages of lead. In addition, the predicted R<sup>2</sup> value of 0.8292 is reasonably in agreement with the adjusted R<sup>2</sup> of 0.9754 reasonably. Moreover, adequate precision is equal to 27.068 which implies that the model can be applied to navigate the design space. The final

empirical equation in terms of coded factors for the removal percentage of lead is presented in Eq. (3).

$$R^3 = 6.346E+5 - 51283.55A + 54541.47B + 10889.84AB - 41924.56A^2 - 20151.96B^2 - 22411.51C^2 + 14850.96A^2C + 50339.25AB^2 - 6476.49B^3 \quad (3)$$

The predicted values versus experimental values for the removal percentage of lead at different conditions are demonstrated in Figure 5. This figure shows the close proximity of the predicted values with the actual data, signifying the validity of the regression model. The  $R^2$  of this model is 0.9892 which is very close to unity. Figure 6

illustrates normal probability versus internally studentized residuals. The residual points are near the straight line, confirming the normal distribution of errors and the normality of data. Studentized residuals versus the ascending predicted removal percentage of lead are shown in Figure 7. The plot should be a random scatter, representing the spectrum which is remained stable across the plot. Equal scattering around the x-axis proves that the proposed model is sufficient and there is a constant variance. In fact the adsorption sites of zeolite decrease at high concentration of lead in the solution similar to the trend reported by Deshpande et al. [24].

**Table 2.** ANOVA table for response surface reduced cubic model for Removal percentage of lead.

Source	Sum of Squares	Degree of freedom (df)	Mean Squarer	F Value	p-value Prob > F	
Model	6.495E+010	9	7.217E+009	71.37	< 0.0001	Significant
A	1.488E+010	1	1.488E+010	147.14	< 0.0001	
B	8.451E+009	1	8.451E+009	83.58	0.0182	
AB	9.487E+008	1	9.487E+008	9.38	< 0.0001	
A <sup>2</sup>	1.981E+010	1	1.981E+010	195.97	0.0003	
B <sup>2</sup>	4.578E+009	1	4.578E+009	45.28	0.0001	
C <sup>2</sup>	5.662E+009	1	5.662E+009	56.00	0.0042	
A <sup>2</sup> C	1.764E+009	1	1.764E+009	17.45	< 0.0001	
AB <sup>2</sup>	8.397E+009	1	8.397E+009	83.05	0.0692	
B <sup>3</sup>	4.647E+008	1	4.647E+008	4.60	< 0.0001	
Residual	7.078E+008	7	1.011E+008			
Lack of Fit	6.664E+008	5	1.333E+008	6.44	0.1398	not significant
Pure Error	4.139E+007	2	2.069E+007			
Cor Total	6.566E+010	16		71.37		

$R^2 = 0.9892$ ,  $R^2$  (adjusted) = 0.9754,  $R^2$  (predicted) = 0.8292, adequate precision = 27.068.

Design-Expert® Software  
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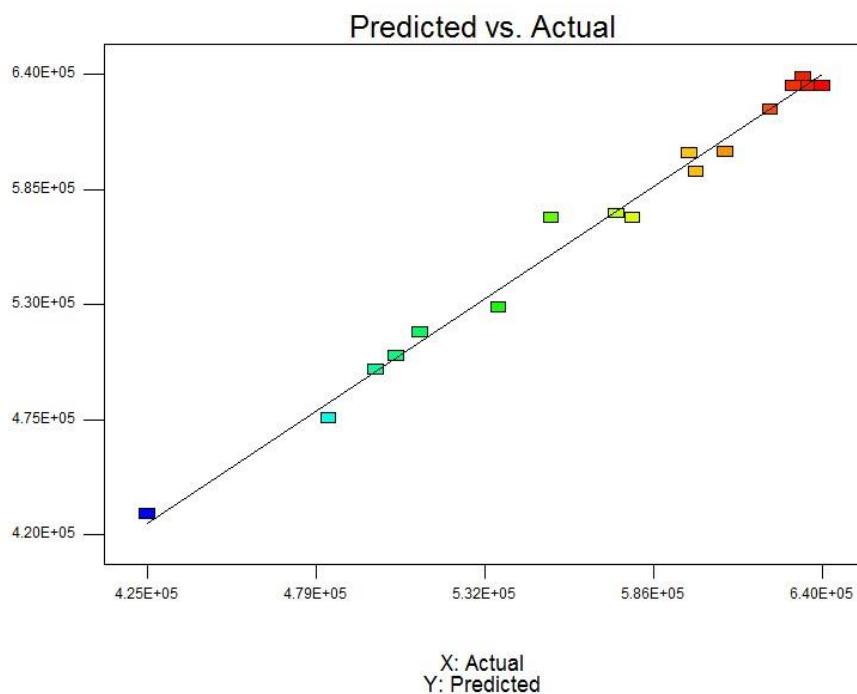


Fig. 5: Predicted versus experimental values for removal percentage of lead.

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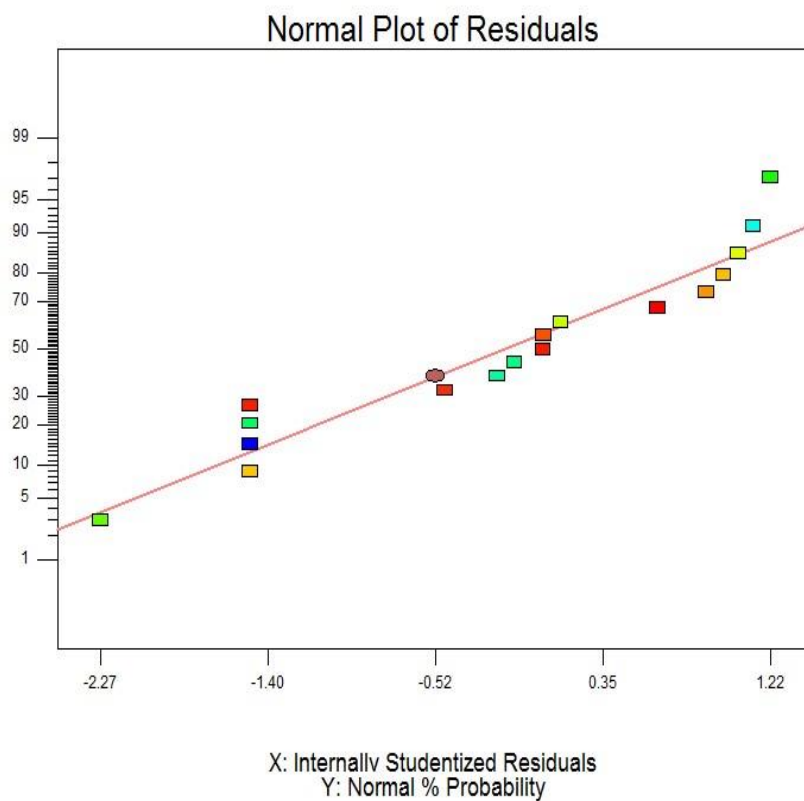
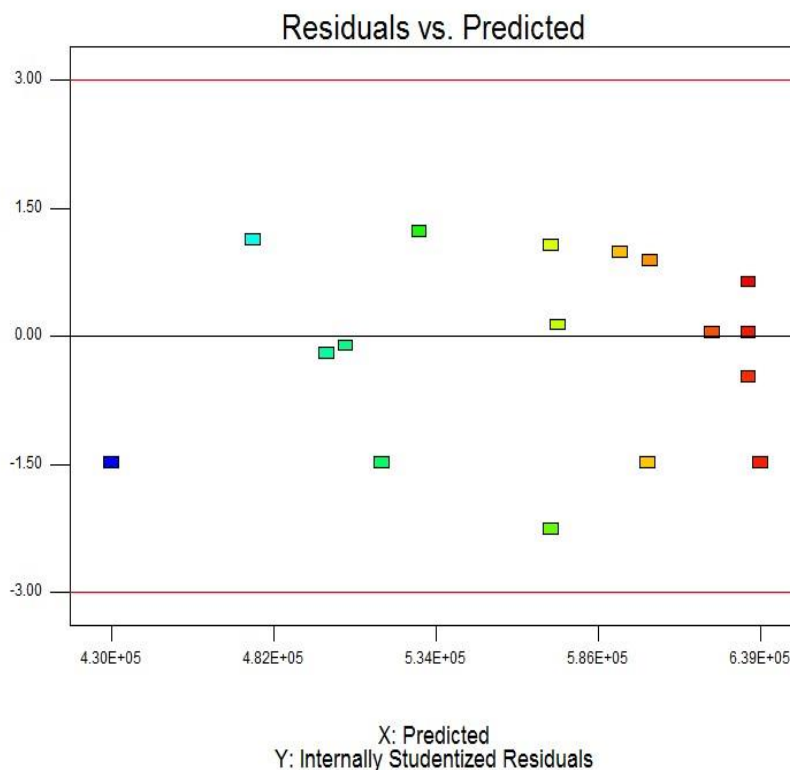


Fig. 6: Normal probability plot of studentized residuals for removal percentage of lead.



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**Fig. 7.** Residual versus predicted of removal percentage of lead on removal percentage of lead at the contact time = 72.5 min.

Also, Figure 8 depicts that the removal percentage of lead is increased by increasing the temperature, except in low concentrations of lead. In the latter condition, at higher temperatures, the removal percentage of lead decreases. Figure 9 illustrates the influences of contact time and initial concentration on the removal percentage of lead. As shown in the Figure, increasing contact time has a positive effect on the removal percentage of lead. The removal percentage of lead is increased by increasing contact time at low initial concentrations of lead. There is also small change in the high initial concentration of lead. As previously mentioned, the effect of initial concentration is higher than the effect of contact time on the removal percentage of lead. Therefore, the curvature of Figure 9 is due to the initial concentration. As a result, due to opposite influences of different parameters on the response, the optimization of operating variables is required to maximize the removal percentage of lead. Several optimized solutions are suggested by the Design-Expert software. The best condition was obtained to

be the initial concentration of 2750 ppm, process temperature of 65°C, and contact time of 82.87 min, in which the removal percentage of lead equaled 99.81% with the high desirability of 0.990.

### 3.3. Adsorption isotherm models

Experimental data were analyzed via Langmuir and Freundlich isotherm models. The Langmuir isotherm is suitable for homogeneous surfaces and monolayer adsorption. The Langmuir isotherm model is given in Eq. (4).

$$q_e = \frac{q_m K C_e}{1 + K C_e} \quad (4)$$

$q_m$  (mg/g) is the maximum amounts of adsorbate onto the adsorbent, and  $K$  (L/mg) is the Langmuir constant which represents the energy of adsorption [22,27].  $q_m$  and  $K$  are calculated by plotting  $C_e/q_e$  against  $C_e$ , as can be seen in Figure 10.

Design-Expert® Software

Original Scale

 $(R)^3$ 

86.17

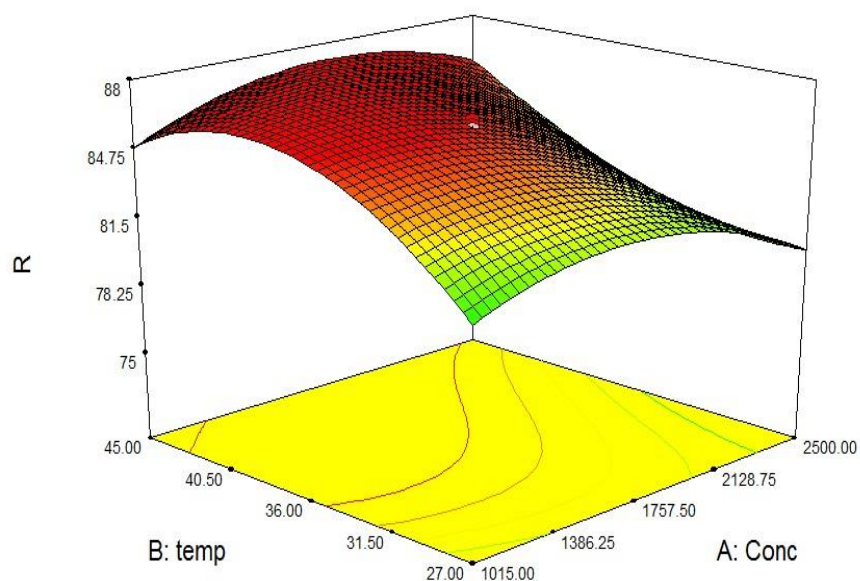
75.19

X1 = A: Conc

X2 = B: temp

Actual Factor

C: time = 72.50



**Fig. 8.** Effects of initial concentration and temperature on removal percentage of lead at the contact time = 72.5 min.

Design-Expert® Software

Original Scale

 $(R)^3$ 

86.17

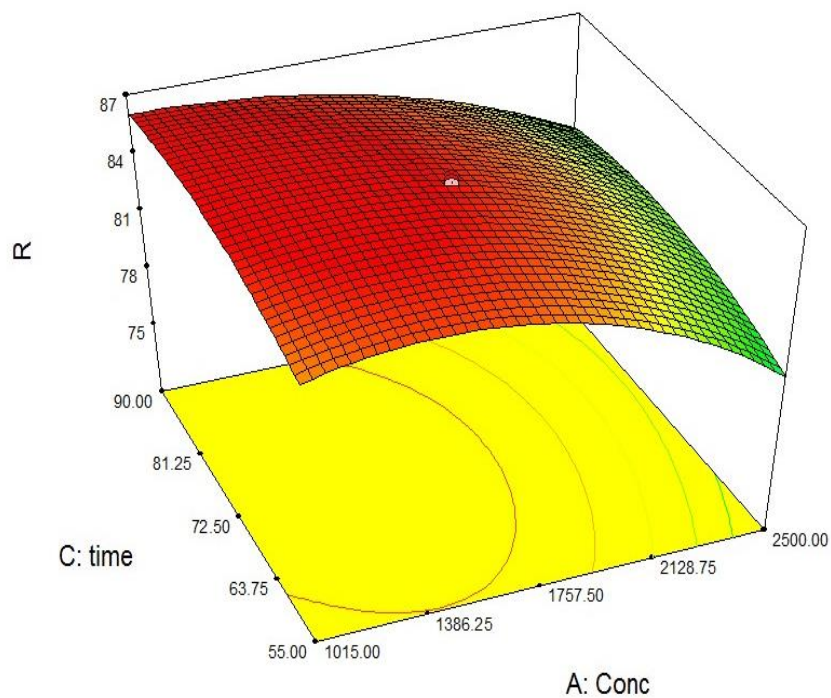
75.19

X1 = A: Conc

X2 = C: time

Actual Factor

B: temp = 36.00



**Fig. 9.** Effects of contact time and initial concentration on removal percentage of lead at the temperature = 36°C.



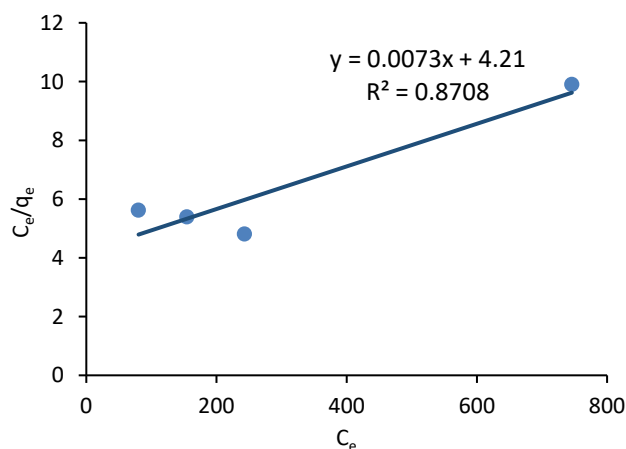


Fig. 10. Langmuir adsorption isotherm for clinoptilolite zeolite.

The Freundlich isotherm is applicable to heterogeneous surfaces and multilayer adsorption. The Freundlich isotherm model is given in Eq. (5).

$$q_e = K_f C_e^{1/n} \quad (5)$$

$K_f$  ((mg/g)/(mg/L)<sup>1/n</sup>) and  $1/n$  are Freundlich constants related to adsorption capacity and adsorption intensity, respectively [22]. Values of  $n$  greater than 1 imply the favorable nature of adsorption.  $K_f$  and  $n$  are obtained from plotting  $\log(q_e)$  versus  $\log(C_e)$ , as illustrated in Figure 11.

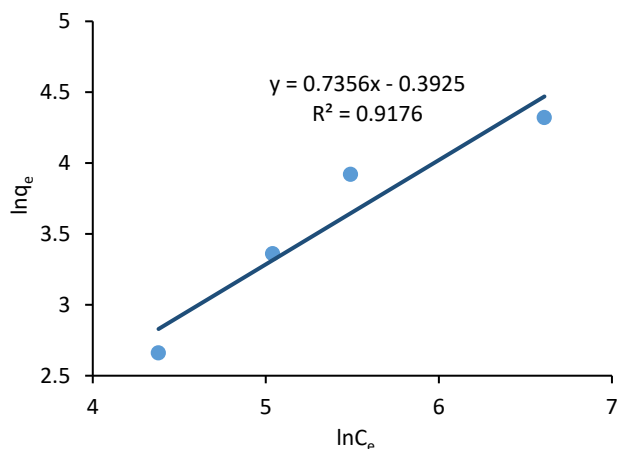


Fig. 11. Freundlich adsorption isotherm for clinoptilolite zeolite.

The parameters of these isotherm models and the results are presented in Table 3. According to the data in Table 3, the  $R^2$  of the Freundlich model is higher than the correlation coefficients of Langmuir model, indicating that the Freundlich model fits the adsorption data better than the Langmuir model. The agreement between the Freundlich model and the experimental data describes the multilayer coverage of lead on the surface of zeolite. The value of  $n$  is greater than 1, showing that adsorption is favorable. Maximum sorption capacity of clinoptilolite zeolite for Pb(II) was obtained to be 136.99 (mg/g). When comparing the adsorption capacity of clinoptilolite zeolite with that of Iranian bentonite (57.803 mg/g) [14], natural zeolite–

kaolin–bentonite (140.9 mg/g) [17], and Na-Y zeolites prepared from Egyptian kaolins (260.6 meq/100 g) [18], the clinoptilolite zeolite efficiency in Pb (II) adsorption was comparable to the mentioned adsorbents.

Table 3. The Langmuir and Freundlich model parameter of Pb<sup>+2</sup>.

Langmuir model		
$q_m(\text{mg/g})$	$K(\text{L/mg})$	$R^2$
136.99	0.00173	0.8708
Freundlich Model		
$K_f((\text{mg/g})/(\text{mg/L})^{1/n})$	$n$	$R^2$
0.675	1.36	0.9186

#### 4. Conclusions

In this work, the removal of Pb<sup>+2</sup> ions from the aqueous solution over natural zeolite as a low-cost adsorbent was researched. RSM was employed for the design of experiments and the analysis of removal results. A CCD was conducted to study the effects of process parameters on the removal percentage of lead from the aqueous solution. It was found that the effect of initial concentration is the most important parameter on the removal percentage of lead, followed by the temperature of process. Also, the results revealed that contact time at the range of experiments has little effect on the response. The optimum conditions obtained were 2750 ppm initial concentration, 65°C process temperature, and 82.87 min contact time, resulting in 99.81% removal percentage of lead with the high desirability of 0.990. The Langmuir and Freundlich models were investigated for adsorption isotherms that the Freundlich isotherm fitted with equilibrium data better than the Langmuir isotherm.

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