

Heavy Metals Removal from Aqueous Solution by Modified Natural Zeolites Using Central Composite Design

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Received: 06 September 2018, Accepted: 27 February 2019, Published online: 27 May 2019

Abstract

Removal of heavy metals including Pb, Co, Cr and Zn from an aqueous solution was investigated using modified clinoptilolite zeolites as adsorbents. The adsorbents were characterized by X-ray, FTIR, SEM and BET. The central composite design defined under response surface methodology was applied for design of experiments. According to the results, clinoptilolite/MgO showed higher capacity for absorption of lead (98.38 %) in comparison to clinoptilolite/NaOH. The removal percentage of Co, Cr and Zn was obtained 89.51 %, 81.07 % and 78.24 %, respectively, using clinoptilolite/MgO. Moreover, the equilibrium experimental data well fitted the Freundlich isotherm model, as compared with the Langmuir isotherm. The results show that the complete regeneration of adsorbents can be achieved at room temperature using NaCl (0.35 M).

Keywords

heavy metal, clinoptilolite zeolite, NaOH, MgO, response surface methodology

1 Introduction

Recently, environmental pollution by hazardous materials including heavy metals has attracted the attention of scientists. With the development of various industries, significant amounts of heavy metals with industrial waste have been discharged into the environment, thus endangering the human health [1-2]. Because of their high degree of toxicity, arsenic, lead, mercury, cadmium and chromium are considered as toxic and extremely dangerous, even at trace levels [3-7]. There are several methods to remove heavy metals from water or wastewater such as chemical settling, flocculation, ion exchange, membrane processes, evaporation and adsorption [8]. Among them, adsorption is known today as an effective and economic method for wastewater treatment from heavy metals. In the adsorption process, the adsorbent plays an important role in the removal of heavy metals, clay mineral, bioadsorbent, industrial by-products, fly ash, coal, chitosan and zeolite are used as low-cost adsorbents. Since zeolites are the cheapest and most readily available adsorbents, they are most frequently used in comparing to the other mentioned low-cost adsorbents [9]. Zeolite is hydrated crystalline aluminosilicate made up of three-dimensional structure and tetrahedral alumina (AlO_4) and silica (SiO_4) [10-12].

Clinoptilolite is one of the useful natural zeolites due to its high absorption rate, cation exchange, catalysis and dehydration capacities. Some research has shown that clinoptilolite zeolite has a high selectivity relative to some heavy metal ions such as copper, lead and cadmium [13, 14]. In addition to adsorbents, other parameters such as heavy metal ion concentration, temperature, pH and time affect the removal of heavy metals from water and wastewater. To investigate the effects of various variables simultaneously, the use of an appropriate design of experiment (DOE) method is required. One of the useful methods for design of experiments, statistical modeling and process optimization is response surface methodology (RSM) [15, 16].

In this work, the removal of heavy metals from an aqueous solution was investigated by an adsorption process over clinoptilolite zeolite and clinoptilolite zeolite modified with NaOH and MgO. The influences of effective parameters including heavy metal ion concentration in aqueous solution, temperature, contact time and adsorbent dosage were simultaneously investigated for removal percentage of heavy metals including lead, cobalt, chromium and zinc over the modified clinoptilolite zeolite by designing an experiment using the RSM.

The optimum conditions for removal of heavy metals were obtained. Moreover, experimental data were analyzed by the Langmuir and Freundlich isotherm models to describe the adsorption process as a function of equilibrium concentration.

2 Experimental

2.1 Materials

Sodium hydroxide (NaOH), magnesium oxide (MgO) and acetic acid (CH₃COOH) were used for the modifying adsorbent. All these chemicals were obtained from Merck, Iran. Moreover, clinoptilolite zeolite was obtained from the Semnan area, Iran.

2.2 Preparation of the adsorbent

2.2.1 The modified zeolite with NaOH

The clinoptilolite zeolite was washed with deionized water and then dried at 120 °C for 24h. Afterwards, 10 g of the washed zeolite was mixed with 250 ml of sodium hydroxide (NaOH) 1M by reflux at 90 °C for 90 min with stirring speed of 300 rpm.

2.2.2 The modified zeolite with MgO

At this step, 2 g of the washed zeolite was mixed with 30 ml of acetic acid for 1 h with stirring speed of 250 rpm and then dried at 170 °C for 24 h. The weight ratio of 4:1 of acidified zeolite and magnesium oxide were mixed and then calcined at 400 °C for 4 h.

2.3 Characterization of the adsorbent

X-ray diffractometer (D8-Advance, Bruker AXS, Cu K α , $\lambda=1.54\text{\AA}$) was used to determine the structure of the synthesized adsorbents.

The infrared spectra of the adsorbents were recorded using Perkin Elmer Spectrum RXI FT-IR in the range of 4000 to 400 cm⁻¹. The solid samples were mixed with KBr powder and compressed into pellet for analysis.

Scanning electron microscopy (SEM) (JEOL, JSM 6490 LV) was used for determining the morphology of the non-modified and modified clinoptilolite zeolite with electron acceleration voltage of 20 kV.

Surface area and pore size of the adsorbents were measured using the nitrogen adsorption-desorption method (by ASAP 2010 instrument) at liquid nitrogen temperature (-196 °C). Prior to the measurements, the sample was degassed at 300 °C under vacuum for 6 h.

2.4 Heavy metal adsorption

For the adsorption of metals, Pb(NO₃)₂, Co(NO₃)₂, Cr(NO₃)₂ and ZnSO₄ hydrated salts were used for preparation of aqueous solutions containing different concentrations of metal ions. The experiment conditions are shown in Table 1. First, the determined amount of the adsorbent was activated at 120 °C in oven for 2 h and then cooled to ambient temperature. Subsequently, the adsorbent was mixed with 10 mL of an aqueous solution of metal ions with determined concentration and temperature. The mixture was shaken at a constant agitation speed (250 rpm) for a determined contact time. After the contact time, the process was stopped and the products were withdrawn from the vessel and centrifuged at 3600 rpm for 30 min to separate the remaining adsorbent. In these experiments, pH of initial solutions before addition of adsorbent were determined 4.7-4.3 for solutions at concentration of 300-1500 mg/L respectively. The concentrations of metal ions in the solutions before and after adsorption were determined using atomic absorption spectroscopy (Chemtech analytical CTA-2000). All the results were expressed as averaged values of duplicate tests. The adsorption capacity (q_e) and removal percentage (R , %) were calculated using the Eq. (1) and Eq. (2), respectively [14, 17]:

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

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

where q_e (mg/g) is the adsorption capacity for metal ions at equilibrium, C_0 (mg/L) is the initial concentrations of heavy metal ions in the solution, C_e (mg/L) is the equilibrium concentration of heavy metal ions remained in the solution, V (L) is the volume of the solution and m (g) is the amount of the adsorbent. In this research, first, the optimum condition of the adsorption of lead from the aqueous solution using clinoptilolite zeolite modified with NaOH was obtained by designing an experiment using the RSM. Then, at the obtained optimum condition, the adsorption of lead from the aqueous solution using MgO/clinoptilolite zeolite was performed. Finally, the adsorption of other metal ions such as chromium, cobalt and zinc was performed by MgO/clinoptilolite zeolite. Table 1 shows the experimental conditions for adsorption of lead from the aqueous solution over NaOH/clinoptilolite zeolite.

Table 1 Lead concentrations, temperature, contact time and adsorbent dosage in adsorption experiment using NaOH/Clinoptilolite zeolite.

Pb ²⁺ concentration (mg/L)	300	600	900	1200	1500
Temperature (°C)	17.50	25	32.50	40	47.50
Contact time (min)	5	20	35	50	65
Dosage of adsorbent (gr/L)	2	8	14	20	26

2.5 Regeneration of adsorbents

1 gr of adsorbent was mixed with 100 ml of an aqueous solution of metal ion at a concentration of 300 mg/L. The mixture was shaken at a constant agitation speed for 6 h. then the process was stopped and the solution was filtered to separate the adsorbent from solution and the filtrate was analyzed in AAS for its metal ion content.

Also the solid matters with adsorbed heavy metal were washed with deionized water and dried at 100 °C for 20 h. Then the adsorbent was placed into the 100 ml of NaCl at the concentration of 0.35 M and desorption experiment were performed for 6 hours under suitable stirring. Then the solution was filtered and the adsorbent was separated; the filtrate was analyzed for its metal ion content.

2.6 Experimental design using the response surface methodology (RSM)

In this research, the central composite design (CCD) was selected to study the combined influences of the parameters and process optimization. The studied parameters consisted of Pb²⁺ concentration (in range of 300-1500 mg/L), temperature (in range of 17.50-47.50 °C), contact time (in range of 5-65 min) and dosage of adsorbent (in range of 2-26 g/L). This design examined the influences of 4 factors in 2 levels (high +1 and low -1). The axial points were located at ($\pm\alpha$, 0, 0), (0, $\pm\alpha$, 0) and (0, 0, $\pm\alpha$), where α equaled 2. The software provided 27 experiments at different conditions with three border points. In this research, the design of the experiments was done by Design Expert version 7.0.0.

3 Results and discussion

3.1 Characterization of the adsorbent

Fig. 1 shows FTIR spectra of clinoptilolite zeolite and the modified clinoptilolite zeolite with NaOH and MgO, respectively. The spectra in the range of 400-800 cm⁻¹ represented the symmetric stretching vibration [18] that decreased in the modified zeolites due to decationization from of clinoptilolite zeolite [19, 20]. The strong spectrum around 1047 cm⁻¹ was stretching vibration Si-(Al)-O in

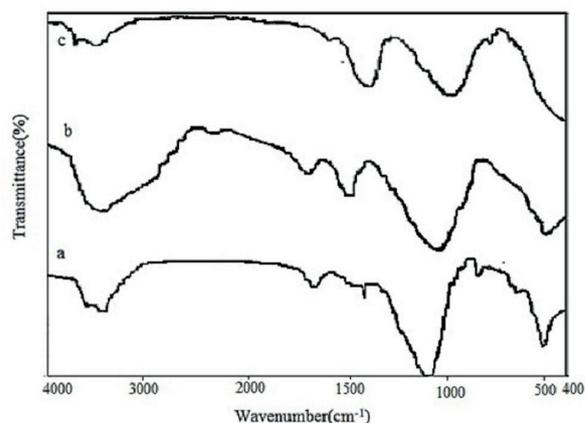


Fig. 1 FTIR spectra: (a) clinoptilolite zeolite, (b) NaOH/clinoptilolite zeolite and (c) MgO/clinoptilolite zeolite.

tetrahedral Si(Al)O₄ [21]. The band appeared at 1300 cm⁻¹ was related to the asymmetric stretching vibration Al-O or Si-O in clinoptilolite zeolite [19]. The spectrum at 1300 cm⁻¹ that increased in the modified NaOH/clinoptilolite zeolite comparing with clinoptilolite zeolite, indicated the presence of aluminum on the surface and desilication in the NaOH/clinoptilolite zeolite [22]. As seen in Fig. 1 (c), the displacement of the band can confirm the MgO influence on the clinoptilolite zeolite. Moreover, the bands observed at 1429 and 1640 cm⁻¹ were assigned to MgO and COO⁻, respectively. The broad spectrum in the range of 3400-3600 cm⁻¹ was assigned to hydroxyl groups. In Fig. 1 (b), this band increased due to increasing the ratio of Al to Si and increasing OH in the modified zeolite with NaOH [20, 21].

The structure of the various synthesized samples was identified with XRD in from 2 θ = 4° to 2 θ = 70° (Fig. 2). Clinoptilolite zeolite had several characteristic peaks at 2 θ = 9.63°, 22.40°, 26.71°, 30.19° and 32.74°, which were assigned to biotite, clinoptilolite, quartz, feldspar and dolomite, respectively [20, 21]. For the NaOH/clinoptilolite zeolite sample, the intensity of the characteristic peaks of clinoptilolite zeolite had an overall decrease. Moreover, the intensity of the peak at 2 θ = 35° increased due to the entering of the hydroxyl group of NaOH into the sodalite cavity of clinoptilolite zeolite [20, 22]. Moreover, it was observed in Fig. 2 (c) that the peak intensity of MgO/clinoptilolite zeolite decreased, as compared with that of clinoptilolite zeolite. The characteristic peaks of MgO appeared in 2 θ = 42.91° and 62.32°, indicating the presence of MgO in the pores of the zeolite [23].

The SEM micrographs of the synthesized samples are shown in Fig. 3. The results showed that the surface of clinoptilolite zeolite was unruly and its porosity was low [24].

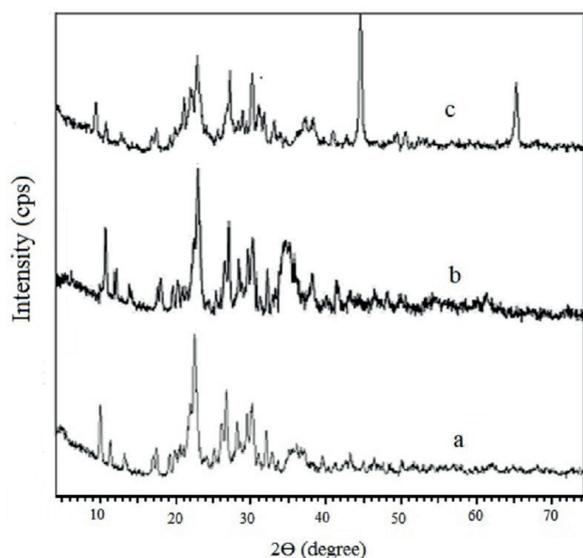


Fig. 2 XRD patterns: (a) clinoptilolite zeolite, (b) NaOH/clinoptilolite zeolite and (c) MgO/clinoptilolite zeolite

In the NaOH/clinoptilolite zeolite sample, the particles were accumulated, causing to increase the porosity of this sample. As can be seen in Fig. 3 (c), the formation of clinoptilolite zeolite/MgO sheet structure was confirmed by SEM. The porosity of this sample was higher than that of the other samples [14].

Specific surface areas of the samples were determined using the BET equation and pore size were estimated by Barrett-Joyner-Halenda (BJH) method. The specific surface area and pore size of the studied adsorbents are presented in Table 2. Based on Table 2 the surface area of the adsorbents modified by NaOH and MgO were decreased which attributed to desilication and dealumination of Clinoptilolite zeolite. Furthermore, the pore diameters of modified samples were increased in compared to the Clinoptilolite zeolite. The pore diameter is very important parameters affected the amount of adsorbate molecules that transported into the surface inside of particles. The observed results were in good agreement with the reported values [20].

Table 2 Surface area and pore size of the clinoptilolite zeolite and modified adsorbents

Adsorbent	BET-surface area (m ² /g)	Pore diameter (Å)
Clinoptilolite zeolite	95.7	145.8
NaOH/Clinoptilolite	61.9	209.1
MgO/Clinoptilolite	78.4	263.5

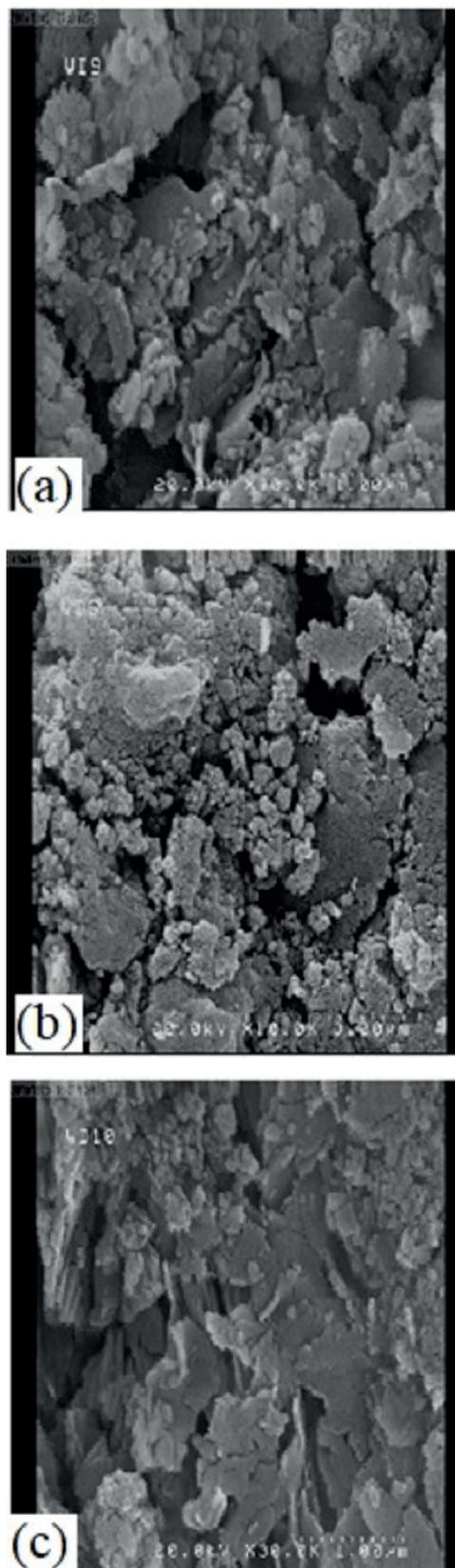


Fig. 3 SEM images: (a) clinoptilolite zeolite, (b) NaOH/clinoptilolite zeolite and (c) MgO/clinoptilolite zeolite.

3.2 Adsorption of lead from the aqueous solution

Table 3 shows experimental conditions and results of removal of lead from the aqueous solution by NaOH/clinoptilolite zeolite. The relationship between effective variables, i.e. temperature, contact time, initial concentrations of lead in the solution and zeolite dosage, and the removal percentage of lead from the aqueous solution was analyzed.

The analysis of variance (ANOVA) for response surface reduced quadratic model is presented in Table 4. The model F-value was obtained 6.58, showing that the model was significant. Values of “Prob > F” less than 0.0500 indicated that the model terms were significant whereas values greater than 0.1000 indicated that the model terms were not significant. According to F-values and the importance of parameters (initial concentration (A), temperature (B), contact time (C) and dosage adsorbent (D)), the following was observed: $D^2 > C^2 > B^2 > A^2$ that were

significant model terms.

The R^2 value equal to 0.8763 showed that there was good agreement between the experimental data and predicted data. The predicted R^2 value of 0.8735 agreed with the adjusted R^2 of 0.7430 reasonably. Also the effect estimates of all terms are presented in Table 5. Based on Table 5, coefficient estimate specified the size and the positive or negative effect of the each parameters on the response. The equation of response comes from coefficient estimate. Equation (3) is a modified equation to predict the removal of lead.

$$R = 1.53 \times A - 0.12 \times B - 0.32 \times C + 0.46 \times D - 1.04 \times A \times B + 0.24 \times A \times C - 0.46 \times A \times D + 0.34 \times B \times C + 0.2 \times B \times D + 0.043 \times C \times D + 19.13 \times A^2 + 19.65 \times B^2 + 20.21 \times C^2 + 20.22 \times D^2. \quad (3)$$

Table 3 Experimental conditions and results of CCD for removal of lead over NaOH/clinoptilolite zeolite

Run	Levels				Adsorption operating parameters				Response
					Initial concentration (ppm)	Temperature (°C)	Time (min)	Zeolite dosage (g/L)	Removal percentage (%)
1	-1	-1	-1	-1	600.00	25.00	20.00	8.00	75.57
2	+1	-1	-1	-1	1200.00	25.00	20.00	8.00	83.14
3	-1	+1	+1	-1	600.00	40.00	20.00	8.00	78.34
4	+1	+1	-1	-1	1200.00	40.00	20.00	8.00	75.08
5	-1	-1	+1	-1	600.00	25.00	50.00	8.00	73.24
6	+1	-1	+1	-1	1200.00	25.00	50.00	8.00	78.16
7	-1	+1	+1	-1	600.00	40.00	50.00	8.00	74.40
8	+1	+1	+1	-1	1200.00	40.00	50.00	8.00	80.72
9	-1	-1	-1	+1	600.00	25.00	20.00	20.00	76.12
10	+1	-1	-1	+1	1200.00	25.00	20.00	20.00	81.99
11	-1	+1	-1	+1	600.00	40.00	20.00	20.00	80.50
12	+1	+1	-1	+1	1200.00	40.00	20.00	20.00	80.21
13	-1	-1	+1	+1	600.00	25.00	50.00	20.00	77.83
14	+1	-1	+1	+1	1200.00	25.00	50.00	20.00	79.61
15	-1	+1	+1	+1	600.00	40.00	50.00	20.00	77.84
16	+1	+1	+1	+1	1200.00	40.00	50.00	20.00	78.62
17	-2	0	0	0	300.00	32.50	35.00	14.00	75.19
18	+2	0	0	0	1500.00	32.50	35.00	14.00	81.76
19	0	-2	0	0	900.00	17.50	35.00	14.00	81.33
20	0	+2	0	0	900.00	47.50	35.00	14.00	79.81
21	0	0	-2	0	900.00	32.50	5.00	14.00	82.07
22	0	0	+2	0	900.00	32.50	65.00	14.00	83.54
23	0	0	0	-2	900.00	32.50	35.00	2.00	83.62
24	0	0	0	+2	900.00	32.50	35.00	26.00	82.06
25	0	0	0	0	900.00	32.50	35.00	14.00	84.04
26	0	0	0	0	900.00	32.50	35.00	14.00	84.73
27	0	0	0	0	900.00	32.50	35.00	14.00	83.23

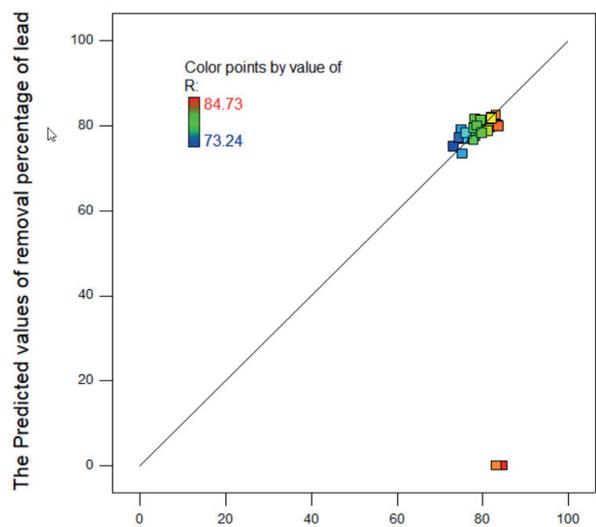
Table 4 ANOVA table for response surface reduced quadratic model for Removal percentage of lead

Source	Sum of Squares	Degree of freedom (df)	Mean Square	F Value	p-value Prob >F
Model	1.506E+005	14	10760.71	6.58	0.0008
A	56.52	1	56.52	0.035	0.8554
B	0.37	1	0.37	2.277E-0004	0.9882
C	2.40	1	2.40	1.467E-003	0.9700
D	5.00	1	5	3.054E-003	0.9568
AB	17.20	1	17.20	0.011	0.9199
AC	0.96	1	0.96	5.840E-004	0.9811
AD	3.43	1	3.43	2.098E-003	0.9642
BC	1.84	1	1.84	1.126E-003	0.9737
BD	0.64	1	0.64	3.887E-004	0.9846
CD	0.030	1	0.030	1.819E-005	0.9967
A ²	14045.55	1	14045.55	8.58	0.0117
B ²	14825.37	1	14825.37	9.06	0.0100
C ²	15680.54	1	15680.54	9.06	0.0100
D ²	15694.12	1	15694.12	9.58	0.0085
Residual	21269.48	13	1636.11	9.59	0.0085
Lack of Fit	21268.36	11	1933.49		
Pure Error	1.13	2	0.56	3429.99	0.0003
Cor Total	1.719E+005	27			

R² = 0.8763, R² (adjusted) = 0.7430, R² (predicted) = 0.8735.

Table 5 Effect estimates of parameters for response surface reduced quadratic model for Removal percentage of lead

Factor	Coefficient estimate	Degree of freedom (df)	Standard error
A	1.53	1	8.26
B	-0.12	1	8.26
C	-0.32	1	8.26
D	0.46	1	8.26
AB	-1.04	1	10.11
AC	0.24	1	10.11
AD	-0.46	1	10.11
BC	0.34	1	10.11
BD	0.20	1	10.11
CD	0.043	1	10.11
A ²	19.13	1	6.53
B ²	19.65	1	6.53
C ²	20.21	1	6.53
D ²	20.22	1	6.53



The experimental values of removal percentage of lead

Fig. 4 Predicted versus experimental values for removal percentage of lead.

The predicted values versus experimental values for the removal percentage of lead at different conditions are demonstrated in Fig. 4. This figure showed the close proximity of the predicted values with the actual data, signifying the validity of the regression model. Fig. 5 illustrates the

influences of temperature and initial concentration on the removal percentage of lead. As shown in the figure, increasing temperature had a negative effect on the removal percentage of lead initially and then had positive effect. For increasing of initial concentration the same trend was observed.

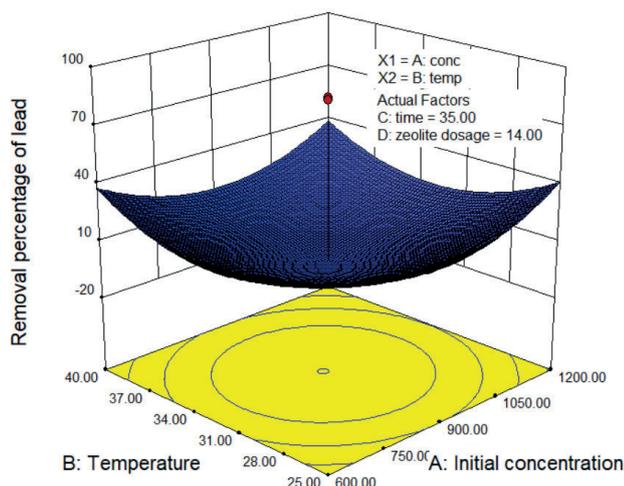


Fig. 5 Effects of temperature and initial concentration on removal percentage of lead.

The effect of the pH on the lead adsorption by prepared adsorbents was studied for pH 3, 5, 7 and 9. These experiments were carried out at the same condition for each adsorbent (initial concentration of 900 ppm, process temperature of 32.50°C, contact time of 35 min and adsorption dosage of 14 g/L). The results were shown in Fig. 6. As can be seen in Fig. 6, the adsorption efficiency of MgO/clinoptilolite zeolite for all pH was higher than that of other adsorbents. Also for all adsorbents the removal percentage of lead increased with an increase in pH from 3 to 9. The low lead adsorption at acidic media has been attributed to the competition between the positively charged of H_3O^+ ions and lead ions for the available active sites on the negatively charged adsorbent surface. By increasing of pH and decreasing in the concentration of H_3O^+ ions, the competition between two mentioned ions for surface sites would decrease and then the adsorption of lead was increased.

3.3 Adsorption isotherm models

The experimental data were analyzed by the Langmuir and Freundlich isotherm models [10, 25]. The Langmuir isotherm is to the monolayer adsorption and homogeneous surfaces (Eq. (4)).

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

where q_m (mg/g) is the maximum amounts of adsorbate onto the adsorbent and K (L/mg) is the Langmuir constant which represents energy of adsorption [10, 22]. In Fig. 7, q_m and K were calculated by plotting C_e/q_e versus C_e .

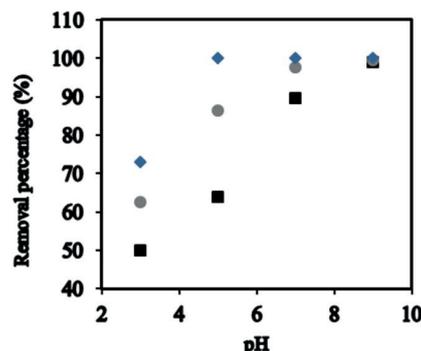


Fig. 6 Effect of pH on removal percentage of Pb^{2+} ; Clinoptilolite zeolite: ■; NaOH/Clinoptilolite zeolite: ●; MgO/Clinoptilolite zeolite: ◆

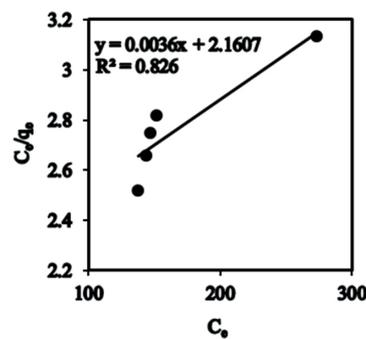


Fig. 7 Langmuir adsorption isotherm for NaOH/Clinoptilolite zeolite.

The Freundlich isotherm is to the multilayer adsorption and heterogeneous surfaces (Eq. (5)).

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

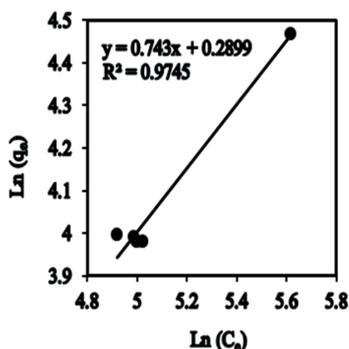
The Freundlich constants are K_f ((mg/g)/(mg/L) $^{1/n}$) and $1/n$ related to the adsorption capacity and adsorption intensity, respectively [10, 25].

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 Fig. 8. The parameters of these isotherm models along with their results are given in Table 6. According to the results in this table, the Freundlich model fitted the adsorption data better than the Langmuir model. Based on Table 6, $1/n$ less than 1 indicated that the adsorption was desirable.

Maximum sorption capacity of NaOH/clinoptilolite zeolite for Pb(II) was obtained to be 258.714 (mg/g). By comparing the adsorption capacity of NaOH/clinoptilolite zeolite with that of Iranian bentonite (57.803 mg/g) [26], natural zeolite–kaolin–bentonite (140.9 mg/g) [27], and Na-Y zeolites prepared from Egyptian kaolins (260.6 meq/100 g) [28], it can be concluded that the NaOH/clinoptilolite

Table 6 The Langmuir and Freundlich model

	Langmuir Parameters	Freundlich Parameters
q_m (mg/g)	258.71	-
K_L (L/mg)	0.0016	-
K_F ((mg/g)	-	1.299
1/n	-	0.749
R^2	0.826	0.974

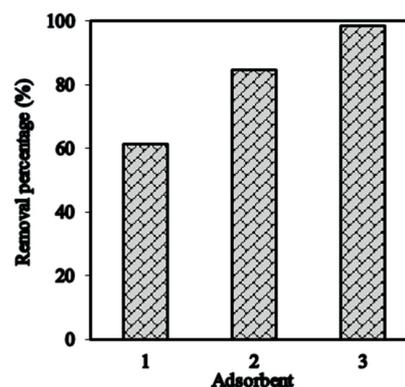
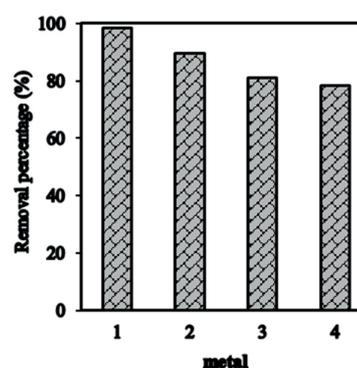

Fig. 8 Freundlich adsorption isotherm for NaOH/Clinoptilolite zeolite.

zeolite efficiency in Pb (II) adsorption was comparable to the mentioned adsorbents.

3.4 Adsorption of various metal ions with MgO/clinoptilolite zeolite

According to the results of the experiments for the adsorption of lead using clinoptilolite zeolite modified with NaOH, the same condition, i.e. initial concentration of 900 ppm, process temperature of 32.50 °C, contact time of 35 min and adsorption dosage of 14 g/L, was used to analyze the performance of the modified zeolite with MgO as adsorbent for adsorption of lead. The results are shown in Fig. 9. The Fig. 9 clearly shows that there was a significance difference in the amount of the adsorbed lead on each adsorbent at the same condition. In general, it can be concluded that the ability of MgO/clinoptilolite zeolite in adsorbing lead was higher than that of NaOH/clinoptilolite zeolite. The high ability of adsorption of MgO/clinoptilolite zeolite is probably due to the additional active groups from the Mg source on the surface of zeolite, which provide more active groups that are ready to interact with metal ions, e.g. lead.

To study the performance of MgO/clinoptilolite zeolite for removal of other metal ions such as chromium, cobalt and zinc, the experiments were performed at the same condition for lead removal. The results are shown in Fig. 10. According to these results, the reduction of heavy metals from the aqueous solution had the order of $Pb^{2+} > Co^{2+} > Cr^{2+} > Zn^{2+}$.


Fig. 9 Effect of adsorbent on removal percentage of Pb^{2+} : Clinoptilolite zeolite: 1; NaOH/Clinoptilolite zeolite: 2; MgO/Clinoptilolite zeolite: 3.

Fig. 10 The removal percentage of different heavy metal ions by MgO/Clinoptilolite zeolite, Pb^{2+} : 1, Co^{2+} : 2, Cr^{2+} : 3, Zn^{2+} : 4.

3.5 Regeneration studies

In this study the regeneration of adsorbents were checked using NaCl (0.35 M) for four adsorption/desorption cycles for heavy metal ions. The change in removal percentage for each adsorbent was also studied by contacting regenerated adsorbent with an aqueous solution of heavy metal ions. The results are presented in Table 7. According to these results, the removal percentages of all heavy metal ions were retained with a very slight decrease during the four adsorption/desorption cycles. This finding was in agreement with the research carried out by Katsou et al. [29].

This phenomenon could be occurred due to the replacement of the heavy metal ions and ions originally present in the mineral structure by sodium ions present in the desorbing solution that could regenerated the adsorbent and there is not significant loss in the performance of adsorbents on the regeneration cycles experiments. Moreover, the formation of complexes between chlorides and each heavy metal ions in the desorbing solution could be caused the removal of heavy metal ions from adsorbent.

Table 7 Removal of heavy metal ions over regenerated adsorbents in four adsorption/desorption cycles.

Removal at cycle	Metal ion	Adsorbent	
		NaOH/clinoptilolite	MgO/clinoptilolite
1	Pb ²⁺	78.14 %	90.37 %
2		76.42 %	88.97 %
3		75.68 %	90.02 %
4		77.08 %	89.19 %
1	Co ²⁺	71.09 %	82.22 %
2		67.73 %	82.56 %
3		69.12 %	79.49 %
4		68.46 %	81.09 %
1	Cr ²⁺	64.39 %	74.46 %
2		65.01 %	73.07 %
3		62.76 %	72.38 %
4		62.09 %	71.66 %
1	Zn ²⁺	62.14 %	71.86 %
2		61.68 %	70.54 %
3		57.19 %	71.05 %
4		60.53 %	69.18 %

metal ion concentration=300 (mg/L), pH=4.7, T=25°C and t=6 h.

4 Conclusion

The present study showed that clinoptilolite zeolite modified with NaOH and MgO had much potential as adsorbents for the removal of heavy metal ions from the

aqueous solution. The properties of natural and modified zeolites were studied by various techniques such as XRD, FTIR, SEM and BET. The influences of the initial concentration, contact time, temperature and amount of adsorbent on adsorption of the metal ions and their interactions were investigated by a response surface methodology and ANOVA. The results showed that the importance of parameters (initial concentration (A), temperature (B), contact time (C) and dosage adsorbent (D)), the following was observed: $D^2 > C^2 > B^2 > A^2$. The equilibrium data were fitted using the Freundlich and Langmuir isotherm models. The Freundlich isotherm model was more appropriate for the results obtained on NaOH/clinoptilolite zeolite. By comparison between NaOH/clinoptilolite and MgO/clinoptilolite, it can be concluded that the ability of MgO/clinoptilolite zeolite in adsorbing lead was higher than that of NaOH/clinoptilolite zeolite at the same conditions. The obtained results also showed that MgO/clinoptilolite zeolite exhibited effective adsorption for Pb²⁺, Co²⁺, Cr²⁺ and Zn²⁺ ions in the aqueous solution with removal percentage in the order Pb²⁺ > Co²⁺ > Cr²⁺ > Zn²⁺.

The regenerated adsorbents were used for four adsorption experiment and the obtained results indicated that the removal percentage of all heavy metal ions is the same or changed slightly.

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