

ORIGINAL RESEARCH PAPER

## Cd(II) Sorption on Iranian Nano Zeolites: Kinetic and Thermodynamic Studies

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### ABSTRACT

An uptake of Cd(II) from aqueous solutions by ion exchange on Iranian natural zeolitic (TOSKA) has been studied. Experiments were carried out using batch method as a function of the initial concentration of metal ions, contact time, and temperature. The adsorbent is characterized using XRF, FTIR, TEM, and XRD. The TEM images showed that the zeolite particle sizes are reduced into the size range of less than 90 nm by means of ball milling. The characterization of sample indicates that the natural zeolite used in this study was classified into clinoptilolite. Equilibrium modelling data were fitted to linear Langmuir and Freundlich models. Thermodynamics parameters such as change in free energy ( $\Delta G^\circ$ ), enthalpy ( $\Delta H^\circ$ ) and entropy ( $\Delta S^\circ$ ) were also calculated. The negative values obtained for  $\Delta G^\circ$  indicated that the sorption of Cd(II) on natural zeolite was spontaneous at all studied concentrations. These results show that natural zeolites hold great potential to remove Cd(II) from industrial wastewater.

**KEYWORDS:** Cd(II); Clinoptilolite; Ion exchange; Kinetic; Sorption; Nano zeolite

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## INTRODUCTION

The heavy metals are not biodegradable and their presence in streams and lakes leads to bioaccumulation in living organisms, causing health problems in animals, plants, and human beings[1]. Cadmium in particular, is a very toxic element that can be present in aqueous wastes from many industries, such as oil refineries, metal plating, mining operations, pigments and batteries. Excessive human intake of Cadmium leads to damage of kidney and renal system, skeletal deformation, cardiovascular diseases and hypertension. Therefore, the removal of excess heavy metal ions from wastewater is essential to protect human and environmental health. As a result, the removal of toxic heavy metal ions from sewage and from industrial and mining effluents

has been widely studied in recent years[2].

Numerous processes such as precipitation, phytoextraction, ultrafiltration, reverse osmosis, and electrodialysis exist for removing dissolved Cd(II) ions [2-5]. A major problem with this type of treatment is the disposal of the precipitated wastes. Ion exchange treatment which is the second most widely used method for metal ion removal does not present a sludge disposal problem and has the advantage of recovery of Cd (II). This method can reduce heavy metals to very low levels. However, usage of synthesized ion exchanger materials does not appear to be economical. The use of alternative low-cost materials as potential sorbents for the removal of heavy metals has been emphasized recently. Cost comparisons are difficult to make due to the scarcity of consistent

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cost information. Although many experiments have been accomplished in the area of low-cost sorbents, a great deal of work is necessary to understand better low-cost adsorption processes and to demonstrate the technology.

Inorganic ion exchange materials have emerged as an increasingly important replacement or complement for conventional organic ion exchange resins, particularly in liquid waste treatment due to their chemical stability and greater selectivity for certain important species, such as heavy metal ions [6]. Among of inorganic ion exchange materials, natural zeolites, have been received great attention, as potential adsorbents especially for application in liquid waste treatment due to their high cation exchange capacities and low cost[7].

Natural zeolite is porous material with high cation exchange capacity, cation selectivity, higher void volume and great affinity for metal ions [8]. Zeolites posses a negative net charge compensated by the presence of exchangeable cations. A variety of cations can be adsorbed on zeolites by the cation exchange mechanism.

Therefore, natural zeolites are known as efficient adsorbents for cation water pollutants[9].

The aim of this work was to determine the capacity of Iranian natural zeolite to remove cadmium ions from aqueous solutions and to predict and compare their performances from the adjustment of experimental data to models.

## EXPERIMENTAL

### *Materils and Characterization*

The Iranian natural zeolite used as an adsorbent in this study was a commercial sample, supplied from Toska Mining Company, Miyaneh, Iran. Ball milling of zeolite was performed by mean of a planetary ball mill (PM100; Retsch Corporation). It was characterized by X-ray diffraction (XRD, Phillips PW-1800), Fourier transform infrared (FT-IR, Bruker Vector 22 FT-IR spectrometer) and X-ray fluorescence (XRF, STIDY-MP-Germany). The morphology of natural zeolite after ball milling was characterized by Transmission electron microscopy (TEM, Phillips EM 2085). Inorganic chemicals were supplied by Merck as analytical-grade reagents and deionized water was used. The stock solution of Cd(II) was prepared using Cd(NO<sub>3</sub>)<sub>2</sub>.H<sub>2</sub>O salts. The Cd(II) ion concentrations were determined using an inductively coupled plasma atomic emission spectroscopy machine (ICP-AES, Optima 7300 DV, Perkin Elmer Co. USA).

### *Adsorption Studies*

The ion exchange behavior of the zeolite materials for Cd(II) ions was carried out using batch equilibrium method. The influence of parameters such as shaking time, intial concentration and temperature were tested to evaluate the zeolite material characteristics. Batch adsorption experiments were conducted using 0.1 g of adsorbent with 20 ml of solutions containing Cd(II) ions of desired concentrations at different temperatures in 50 ml plastic bottles with continuous stirring at 600 rpm. After shaking (in order to determine the amount of Cd(II) ions sorbet) the solid phase was separated from the solution by filtration and the concentration of Cd(II) was determined in the liquid phase using ICP-AES.

In order to obtain the sorption capacity, the amount of ions adsorbed per unit mass of adsorbent ( $q_e$  in milligrams of metal ions per gram of adsorbent) was evaluated using the following expression[10]:

$$q_e = \frac{(C_0 - C_e)V}{M}$$

where  $C_0$  is the initial metal ion concentration (mg l<sup>-1</sup>),  $C_e$  the equilibrium metal ion concentration (mg l<sup>-1</sup>), V the volume of the aqueous phase (l), and M the amount of the adsorbent used (g). Distribution ratio (Kd) were calculated using the equation[11];

$$K_d = \frac{C_0 - C_e}{C_e} \times \frac{V}{M}$$

where V is the volume of the solution (ml) and M is the weight of the adsorbent (g).

## RESULTS AND DISCUSSION

### *Characterization*

The XRD pattern of natural zeolites is shown in Fig. 1. The XRD pattern showed that the sample exhibited high crystallinity, with the characteristic reflection peaks at Bragg angle (2θ)=10°, 11.3°, 13.2°, 22.5°, 27°, 30.02° and 32°, respectively. The pattern indicates that the Iranian natural zeolite used in this study was classified into clinoptilolite[12]. Clinoptilolite with the ideal formula of (Na,K)<sub>6</sub>Si<sub>30</sub>A<sub>16</sub>O<sub>72</sub>.nH<sub>2</sub>O is the most common natural zeolite found mainly in sedimentary rocks of volcanic origin[13].

The FT-IR spectra of the natural zeolite was investigated in the 4000–400 cm<sup>-1</sup> region (Fig. 2), Peaks at 1060 cm<sup>-1</sup>, 794 cm<sup>-1</sup> and 609 cm<sup>-1</sup> were characteristic of clinoptilolite [13-15].

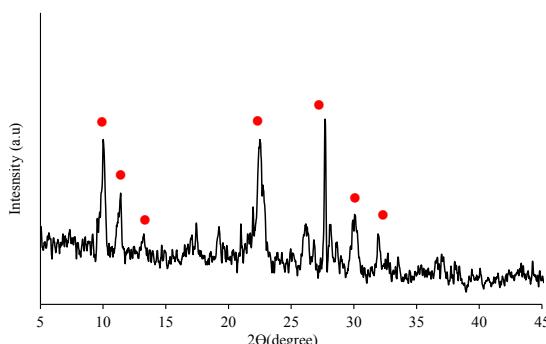


Fig. 1. XRD analysis of natural zeolite.

The strongest band observed at  $1060\text{ cm}^{-1}$  was assigned to asymmetric stretching of the external tetrahedral linkages[13-14]. The second strongest band at  $465\text{ cm}^{-1}$  corresponded to internal tetrahedral bending. The band observed at  $609\text{ cm}^{-1}$  was related to the presence of double rings in the framework structure. Other bands at ca.  $1208\text{ cm}^{-1}$ ,  $790\text{ cm}^{-1}$  and  $711\text{ cm}^{-1}$  were assigned to the asymmetric stretching modes of internal tetrahedra, symmetric stretching of external tetrahedra and symmetric stretching of internal tetrahedra, respectively[13-15]. The  $670\text{ cm}^{-1}$  band arises from symmetric tetrahedral stretching. In addition, the FT-IR spectra exhibited several bands at  $1690\text{ cm}^{-1}$ ,  $3450\text{ cm}^{-1}$  and  $3630\text{ cm}^{-1}$  arising from the deformation of water molecules, the bending vibrations of sorbed water, hydrogen-bonded -OH groups and isolated -OH groups, respectively[12-15].

The chemical composition characterization of the natural zeolite was carried out by XRF technique and is presented in Table 1. This table shows that silica and alumina are the major components of the adsorbent. Oxides of other metals are present in trace amounts [16].

The morphology of zeolite was analyzed by TEM (Fig. 3a, b and c). The TEM images show the zeolite is composed of an irregular particles with the different size range about 60–1000 nm. A irregular surface with particles size less than 100 nm as a separated particle or in the form of larger agglomerates shown in Fig.3 a and c. Moreover, it can be seen that the rods with a diameter about 60–65 nm without agglomeration are revealed by TEM analysis (Fig. 3 b). The nanostructure formation is result of zeolite's ball milling. The pervious study showed that larger than 1 mm particle size of clinoptilolite powder may mechanically be reduced into the size range of less than 100 nm by means of planetary ball milling[17].

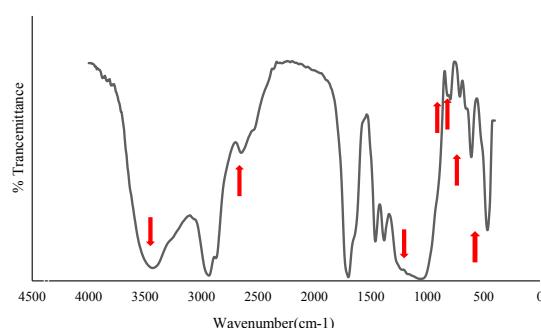


Fig. 2. FTIR spectra of natural zeolite

#### Effect of Initial Concentration and Temperature

The effect of the initial ion concentration was performed at initial concentrations of 50, 250, 500, 750 and 1000 mg/L at different sorption temperatures of 298, 313 and 333 K for the sorption of Cd(II) ions onto the natural zeolite the results were shown in Fig. 4. It is clear that the sorption amount of Cd(II) ions increase with increasing the initial ion concentration. These results reflect the efficiency of the zeolite materials towards Cd(II) ions. Also the Fig. 4 shows the variation of the amounts of Cd(II) ions sorbed at fixed initial concentration, at different sorption temperatures of 298, 313 and 333 K. The data showed that the amount of the sorbed Cd(II) ions increases with the increase in temperature indicating an endothermic nature of the sorption processes.

#### Effect of Contact Time and Initial Concentration

Fig. 5 shows the effect of shaking time on the removal of Cd(II) ion using the natural zeolite. The amount of Cd(II) ions sorbed sharply increases for

Table 1. XRF pattern of natural zeolite

Analyte	Concentration
LOI	13.15 (Wt %)
Na <sub>2</sub> O	0.55 (Wt %)
MgO	0.78 (Wt %)
Al <sub>2</sub> O <sub>3</sub>	8.58 (Wt %)
SiO <sub>2</sub>	72.59 (Wt %)
P <sub>2</sub> O <sub>5</sub>	0.37 (Wt %)
SO <sub>3</sub>	0.18 (Wt %)
K <sub>2</sub> O	1.08 (Wt %)
CaO	1.22 (Wt %)
TiO <sub>2</sub>	0.19 (Wt %)
Fe <sub>2</sub> O <sub>3</sub>	1.13 (Wt %)
Sr	600 ppm
ZrO <sub>2</sub>	300 ppm

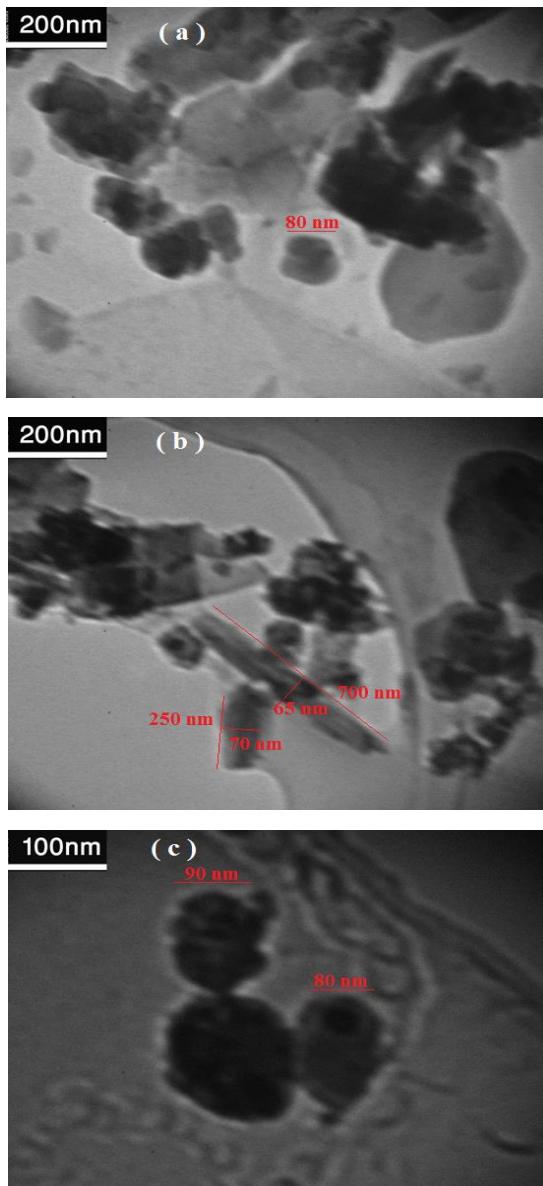


Fig. 3. TEM images of zeolite.

each adsorbent with time in the initial stage (0–100 min range). It reached up 90% within 100 min and became very slow with increasing of shaking time. This may be ascribed to the utilization of the most readily available adsorbing sites of the zeolite that leads fast diffusion and rapid equilibrium attain [18].

#### Kinetics Analysis

The Cd(II) sorption dependence on time was investigated at 298 K for solutions with  $C_0=50$ , 250, 500, 750 and 1000 ppm. The time dependence was followed until the sorption equilibrium has

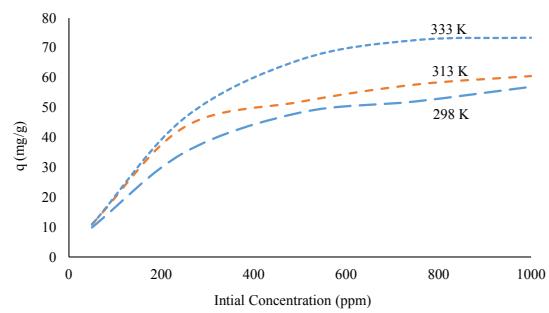
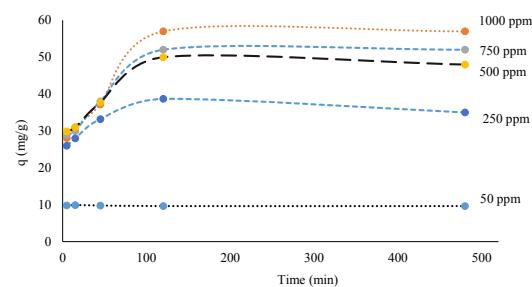
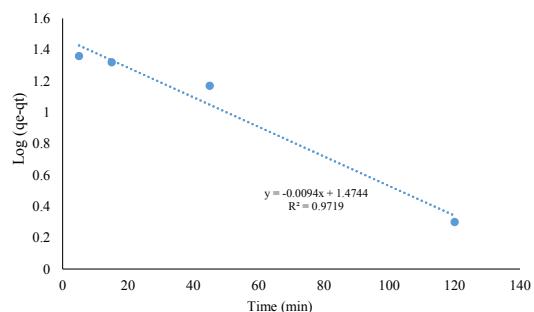


Fig. 4. Effect of initial concentration on the amount sorbed of Cd(II) ions onto natural zeolite at different temperatures

Fig. 5. Effect of initial ion concentration and contact time on the amount sorbed of Cd<sup>2+</sup> ions onto natural zeolite.Fig. 6. Pseudo first-order kinetic model fit for Cd<sup>2+</sup> sorption onto natural zeolite.

essentially been reached. Fig. 5 shows the variation of the amounts uptake values of Cd(II) from solution at different time intervals.

It is well recognized that the characteristic of the sorbent surface is a critical factor that affect the sorption rate parameters and that diffusion resistance plays an important role in the overall transport of the ions. To describe the changes in the sorption of metal ions with time, two simple kinetic models were tested.

The data of the kinetics such as rate constants of Cd(II) ions removal from aqueous solutions by natural zeolite at different intial concentration,

Table 2. Adsorption kinetic model rate constants for Cd(II) adsorption on natural zeolite.

	Time (min)					
q(mg/g)	5	15	45	120	20	480
q <sub>t</sub>	29	31	37	50	52	52
q <sub>e</sub> -q <sub>t</sub>	23	21	15	2	0	0
Log(q <sub>e</sub> -q <sub>t</sub> )	1.36	1.32	1.17	0.30	-	-
Metal ion	First-order kinetic parameters			Second-order kinetic parameters		q <sub>e</sub> , exp. (mg/g)
	k <sub>1</sub> (cm <sup>-1</sup> )	q <sub>e</sub> , calc.(mg/g)	R <sup>2</sup>	k <sub>2</sub> (cm <sup>-1</sup> )	q <sub>e</sub> , calc.(mg/g)	R <sup>2</sup>
Cd <sup>2+</sup>	0.0046	29.81	0.9713	0.0016	54.34	0.9983
					h(mg/g min)	60.5
						4.72

as illustrated in Fig. 6 and 7, were analyzed using pseudo first-order and pseudo second-order. The conformity between experimental data and each model predicted values was expressed by the correlation coefficient (R<sup>2</sup>). A relatively high R<sup>2</sup> values indicates that the model successfully describes the kinetics of metal ion sorption removal.

The sorption kinetics of Cd(II) ions from liquid phase to solid is considered as a reversible reaction with an equilibrium state being established between two phases. A simple pseudo first order model was, therefore, used to correlate the rate of reaction and expressed as follows:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (1)$$

where q<sub>e</sub> and q<sub>t</sub> are the concentrations of ion in the adsorbent at equilibrium and at time t, respectively, (mg/g) and k<sub>1</sub> is the pseudo first-order rate constant (min<sup>-1</sup>). After integration and applying boundary conditions t=0 to t=t and q<sub>t</sub> = 0 to q<sub>t</sub> = q<sub>e</sub>, the integrated form of Eq. (1) becomes:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.033}t \quad (2)$$

The slopes and intercept of the plots of log(q<sub>e</sub> - q<sub>t</sub>) versus t, as shown in Fig. 6, were used to determine the first order rate constant (k<sub>1</sub>) and the theoretical equilibrium sorption capacities (q<sub>e</sub>), respectively. The calculated values of k<sub>1</sub> and q<sub>e</sub> with the values of the linear correlation coefficients (R<sup>2</sup>) of plot are presented in Table 2. Approximately linear fits were observed for the adsorbent, over the entire range of shaking time explored and at all temperatures with low correlation coefficients, indicating that the pseudo first-order kinetic model is not so valid for the present systems. Another important issue that in the study of a kinetic model must be considered is the agreement of the theoretically calculated equilibrium sorption capacities, q<sub>e</sub>,

and the experimental sorption capacity value q<sub>ex</sub>. As can be seen from Table 2, although the linear correlation coefficient of the plot is acceptable, the q<sub>e</sub> (calculated) value is not in agreement with q<sub>ex</sub> (experimental) for studied sorption processes. So, it could suggest that the sorption of Cd(II) ions onto zeolite is not a first-order reaction.

A pseudo second-order rate model is also used to describe the kinetics of the sorption of Cd(II) ions onto adsorbent materials. The pseudo second-order rate model is expressed as[19, 20]:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (3)$$

For the boundary conditions t=0 to t=t and q<sub>t</sub>=0 to q<sub>t</sub>=q<sub>e</sub>, the integrated form of Eq. (3) becomes:

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + k_2 t \quad (4)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (5)$$

where k<sub>2</sub> is the rate constant of pseudo second-order equation (g/mg min).

If the initial sorption rate h (mg/L h) is:

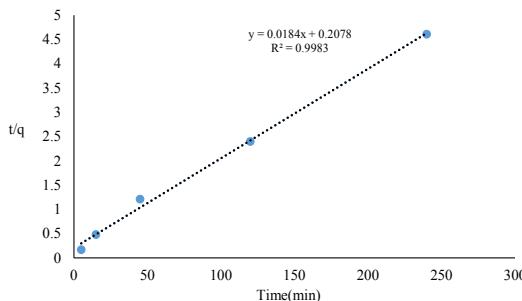
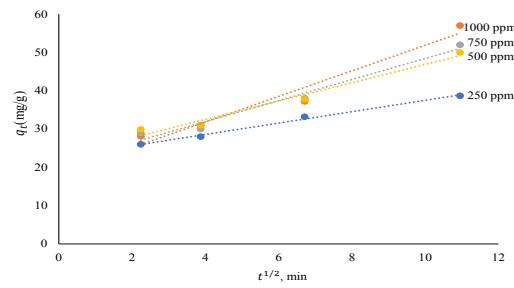
$$h = k_2 q_e \quad (6)$$

Then Eqs. (10) and (11) become:

$$\frac{t}{q} = \frac{1}{h} + \frac{1}{q_e} t \quad (7)$$

The kinetic plots of t/q<sub>t</sub> versus t for Cd(II) ions sorption is presented in Fig. 7. The relation is linear, and the correlation coefficient (R<sup>2</sup>), suggests a strong correlation between the parameters and also explains that the sorption process follows pseudo second-order kinetics.

From Table 2 it is also can be seen that theoretically calculated equilibrium sorption capacities, q<sub>e</sub>, is very close to the experimentally

Fig. 7. Pseudo second-order kinetics of Cd<sup>2+</sup> sorption onto natural zeolite.Fig. 8. Morris-Weber kinetic plots for the sorption of the sorption of Cd<sup>2+</sup> ions from aqueous solutions.Table 3. Internal diffusion rate constant for the sorption Cd<sup>2+</sup> ions onto natural zeolite at different initial concentration.

Initial concentration(ppm)	k <sub>ad</sub> (mg/g min <sup>1/2</sup> )	Intercept (b)	R <sup>2</sup>
1000	3.33	18.5	0.956
750	2.74	20.92	0.973
500	2.39	22.96	0.975
250	1.48	22.64	0.994

measured values,  $q_{ex}$  for pseudo second-order kinetic model indicating that the pseudo-second-order model gives a better description of the Cd(II) ions sorption kinetics as judged by the  $R^2$  values (Table 2). This agrees with general observations in heavy metal sorption studies.

#### Diffusion Model

Though the Cd(II) ions removal by clinoptilolite occurs via ion exchange, but the ion-exchange reaction might not alone be adequate in explaining the sorption kinetics of Cd(II); diffusional processes have also to be taken into account. In order to examine the role of diffusion in the sorption process, the data were also analyzed by the Weber-Morris mass transfer model [21]. This model is defined by the rate equation (5):

$$q_t = k_{ad} t^{1/2} + b$$

Where the  $q_t$  (mg g<sup>-1</sup>) is the adsorption capacity at time  $t$  (min),  $k_{ad}$  (mg g<sup>-1</sup> min<sup>-1/2</sup>) is the diffusion rate constant and, and  $b$  (mg g<sup>-1</sup>) is the boundary layer diffusion. According to this model, plotting a graphic of  $q_t$  vs.  $t^{1/2}$  for various initial Cd (II) concentrations, if a straight line with intercept  $b$  is obtained, it can be assumed that the involved mechanism is a diffusion of the species as shown in Fig. 8.

As can be seen in all case a liner relationship

between  $q_t$  and  $t^{1/2}$  are found suggesting that the diffusion mechanism is involved. In this case the slope of the linear plot is the rate constant of intraparticle transport. The values of  $K_{ad}$  were calculated, from the slope of the linear plots obtained, and the values of  $b$  were calculated from the intercept that presented in Table 3.

#### Thermodynamic Study

The data obtained by sorption experiments at 298, 313 and 333K, and the initial Cd(II) concentrations of 50, 250, 500, 750 and 1000 ppm, were used for the estimation of some thermodynamic parameters. The standard free energy of sorption ( $\Delta G^\circ$ ) was calculated by Eq. 8

$$\Delta G^\circ = -RT \ln K \quad (8)$$

$R$  is the universal gas constant and  $K$  is the equilibrium constant at the temperature  $T$ . The constant  $K$  was calculated by using Eq. (9) [20]:

$$K = \frac{q_e}{C_e} \quad (9)$$

$C_e$  is the equilibrium concentration of the Cd(II) ions (mg l<sup>-1</sup>). The enthalpy and entropy of sorption were calculated from Eq. (10):

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (10)$$

$$\ln K = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (11)$$

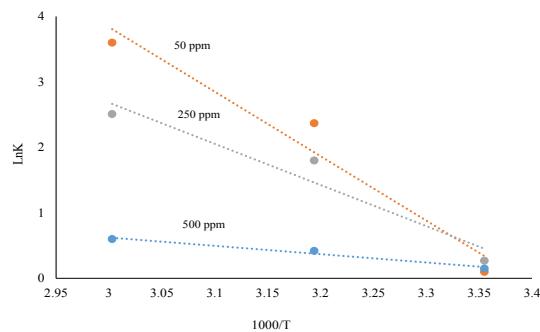


Fig. 9. Variation of the distribution coefficient ( $K_d$ ) in Cd(II) ion removal using the natural zeolite as a function of temperature

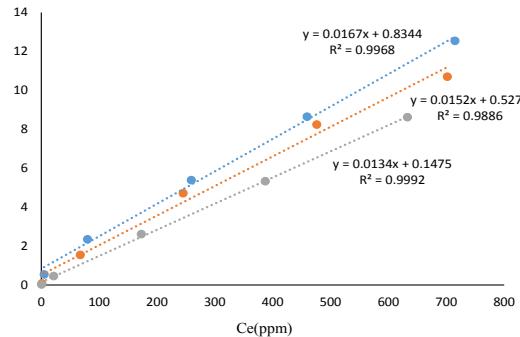


Fig. 10. The linearized Langmuir isotherm for adsorption of Cd(II) by natural zeolite

Table 4. Thermodynamic parameters for zeolite adsorption of cadmium ions.

$C_e$ (ppm)	T (K)	$\Delta G^\circ$ (kJ mol <sup>-1</sup> )	$\Delta H^\circ$ (kJ mol <sup>-1</sup> )	$\Delta S^\circ$ (j K <sup>-1</sup> )	$R^2$
50	298	-0.28	81.72	277.10	0.952
	313	-6.167			
	333	-10			
250	298	-0.67	52.21	178	0.9352
	313	-4.88			
	333	-7			
500	298	-0.36	10.6	36.8	0.9733
	313	-1.10			
	333	-1.7			

The plot of  $\ln K$  vs.  $1/T$  gives a straight line (Fig. 9), and the values of  $\Delta S^\circ$  and  $\Delta H^\circ$  are evaluated from its intercept and slope, respectively. The calculated thermodynamic parameters are listed in Table 4.

As can be seen from Fig. 9 and from the  $R^2$  values in Table 4, the linearity of the  $\ln K$  vs.  $1/T$  plot is satisfactory for the initial concentrations of 500, and 250 ppm, and less so for 50 ppm. The  $\Delta G^\circ$  values given in Table 4 show that the sorption of Cd(II) on zeolite occurs spontaneously in the 298–333 K range. The spontaneity slightly increases with temperature for all initial Cd(II) concentrations of 500 ppm. The Cd(II) sorption is endothermic ( $\Delta H^\circ > 0$ ) and proceeds with an increase in entropy. The positive  $\Delta S^\circ$  values reflect the fact that the sorption involves the liberation of more ions when one Cd(II) ion is bound to the sorbent. It is also evident from Table 4 that the spontaneity (at a given temperature), as well as the  $\Delta H^\circ$  and  $\Delta S^\circ$  values all decrease as the initial Cd(II) concentration increases.

#### Isotherms Equations

Several sorption isotherm models have been applied to describe experimental data of sorption isotherms. For the sake of convenience, explicit and

simple models are preferred and commonly used; these include several two- and three-parameter isotherm models. The Langmuir and Freundlich models are the most frequently employed models.

The data obtained were applied to the Langmuir adsorption isotherm and linear expression of this model has been demonstrated as below (eq. 11):

$$C_e/q_e = 1/bK + C_e/b \quad (11)$$

where  $q_e$  is the amount of metal ion sorbed per unit weight of zeolite (mg/g),  $C_e$  the equilibrium concentration of the metal ion in the equilibrium solution (mg/L), and  $K$  (L mg<sup>-1</sup>) and  $b$  are the Langmuir constants related to the sorption capacity and energy of adsorption ( $b \propto e^{-\Delta G/RT}$ ), respectively.

Langmuir, the simplest type of isotherm, is based on the view that every adsorption site is equivalent and independent; the ability of a molecule to bind is independent of whether or not neighboring sites are occupied.

Another adsorption isotherm, the Freundlich isotherm, was calculated from the adsorption data. This isotherm is more general than the Langmuir isotherm since it does not assume a homogenous surface or constant sorption potential and this

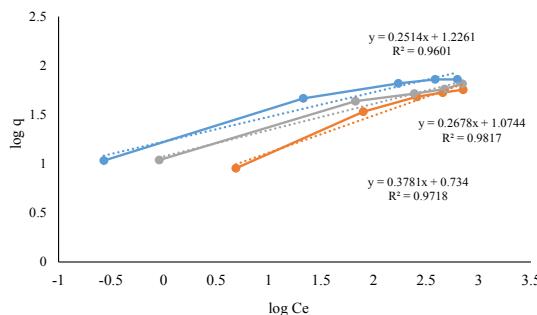


Fig. 11. The linearized Freundlich isotherm for adsorption of Cd(II) by natural zeolite

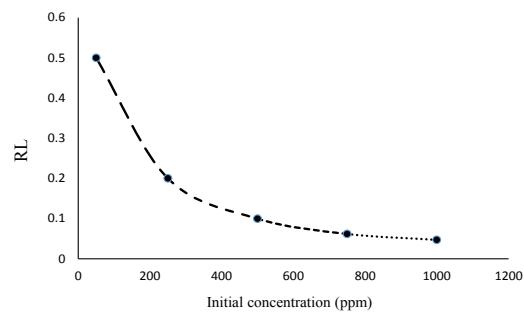


Fig. 12. Variation of separation factor (RL) as a function of initial Cd<sup>2+</sup> ion concentration at 298 °K.

Table 5. The Langmuir and Freundlich constants and correlation coefficients of isotherm models at different temperature

Temperature (°K)	Langmuir isotherm			Freundlich isotherm		
	b	K	R <sup>2</sup>	1/n	K <sub>f</sub>	R <sup>2</sup>
298	59.88	0.020	0.9968	0.3781	5.42	0.9718
313	65.78	0.028	0.9886	0.2678	11.75	0.9817
333	74.62	0.090	0.9992	0.2514	16.83	0.9601

model has a linear expression, which has been demonstrated as below (eq.12):

$$q_e = K_F C_e^{1/n} \text{ or } \log q_e = \log K_F + 1/n \log C_e \quad (12)$$

where  $K_F$  ( $\text{mg g}^{-1}$ ) is the Freundlich constant related to the sorption capacity of the sorbent, and  $1/n$  is the Freundlich constant related to the energy heterogeneity of the system and the size of the adsorbed molecule. Other parameters ( $C_e$ ,  $q_e$ ) have been mentioned above.

The resulting adsorption isotherms for the Zeolite used in this study are shown in Fig. 10 and 11. The regression values and correlation coefficients ( $R^2$ ) presented in Table 5 indicate that the adsorption data for Cd(II) removal best fitted the Langmuir adsorption isotherm. However, the Freundlich isotherms are important because they do not assume a homogeneous surface. The maximum adsorption capacity based on the Langmuir isotherm is 74.6 ( $\text{mg g}^{-1}$ ).

The Freundlich isotherm constants  $K_F$  and  $n$  are determined from the intercept and slope of a plot of  $\log q_e$  versus  $\log C_e$  (Fig. 11). In this study  $n$  values are greater than unity indicating chemisorption (Table 3) [23]. Isotherms with  $n > 1$  are classified as L-type isotherms reflecting a high affinity between adsorbate and adsorbent and is indicative of chemisorption [24]. The Freundlich constant,  $K_F$  which is related to the adsorption capacity, increased with temperature, indicating that the

adsorption process is endothermic.

On the other hand, the dimensionless equilibrium parameter or separation factor,  $R_L$ , based on the further analysis of Langmuir equation can be given by (eq.13);

$$R_L = \frac{1}{1 + K_C C_0} \quad (13)$$

where  $C_0$  ( $\text{mg L}^{-1}$ ) is the initial amounts of adsorbate and  $k$  is Langmuir constant. The  $R_L$  parameter is considered as more reliable indicator of the adsorption. There are four probabilities for the  $R_L$  value; (A) for favorable adsorption,  $0 < R_L < 1$ , (B) for unfavorable adsorption,  $R_L > 1$ , (C) for linear adsorption,  $R_L = 1$ , (D) for irreversible adsorption,  $R_L = 0$  [25]. Fig. 12 shows the variation of  $R_L$  with initial concentration of the Cd(II) ions. As could be seen from the curve, the  $R_L$  parameters lied between 0 and 1 represent that the removal of Cd(II) ions by natural zeolite is propitious. Fig. 12 also indicates that the  $R_L$  value approaches zero as the  $C_0$  value is increased, and it means that the adsorption of Cd(II) ions onto natural zeolite is less favorable at high concentration of the solution.

## CONCLUSIONS

Zeolites have exchange sites with different positions in the lattice and thus different bond energies. Steric hindrance and unfavorable charge distributions can affect extent and kinetics of

cation exchange in zeolites. This study showed the possibility of the selected sorbents (Iranian natural zeolite, Toska) utilization for Cd(II) ions removal from aqueous solutions. The influence of parameters such as shaking time, initial concentration and temperature were tested to evaluate the zeolite material characteristics. The characterization of sample indicates that the natural zeolite used in this study was classified into clinoptilolite. The Langmuir isotherm showed a better fit than the Freundlich isotherm, thus, indicating the applicability of monolayer coverage of cadmium on zeolite surface. Thermodynamic analysis showed that the adsorption process was endothermic and spontaneous in nature and increasing temperature improved adsorption performance for the zeolites. Results from this study suggest that Iranian natural zeolite (Toska) is a very effective adsorbent for cadmium(II) ions, as anticipated.

### CONFLICT OF INTEREST

The authors declare that there are no conflicts of interest regarding the publication of this manuscript.

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