

Adsorption of Cr(VI) by Natural Clinoptilolite Zeolite from Aqueous Solutions: Isotherms and Kinetics

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The main aim of this study was to evaluate the efficiency of natural zeolite for Cr(VI) removal from aqueous solutions. Following simple modification of adsorbent, the effect of operational parameters including pH (2–10), adsorbent dosage (2–20 g/L), contact time (5–150 min) and Cr(VI) concentration (10–50 mg/L) were studied according to one-factor-at-a-time procedure. The maximum Cr(VI) removal of 99.53% was obtained at initial pH of 2, contact time of 30 min, adsorbent dosage of 8 g/L and initial chromium concentration of 10 mg/L. The Freundlich isotherm was best fitted with experimental data ($R^2 = 0.951$). Also, type 1 pseudo second order kinetic model showed the most correlation ($R^2 = 1$) with the experimental data. According to obtained results, it can be concluded that the application of clay-like adsorbents such as natural clinoptilolite zeolite can be considered as an efficient alternative for final treatment of effluents containing Cr(VI).

Keywords: Adsorption, Clinoptilolite Zeolite, Cr(VI), Isotherm, Reaction Kinetics.

INTRODUCTION

The water contamination to heavy metals has been considered as an environmental concern due to their toxicity, health effects, long persistence and bioaccumulation in the food chain. Heavy metals even at low concentrations are toxic to humans, flora and fauna¹. Chromium is one of the most hazardous toxic metals and is released through effluents of photography, leather, ceramics and glass industries, pigments, dyes, fungicides and Cr(VI) alloy production. The uptake of Cr(VI) at concentration more than 0.1 mg/L by humans can cause poisoning, vomiting, bleeding, nose irritation, skin ulcers, lung cancer and respiratory diseases such as asthma².

Cr(VI) with high mobility can rapidly penetrate into surface and ground water and cause to hazardous effects on any living life. In addition, Cr(VI) can easily diffuse and cross in cell membranes³. Therefore, International Agency for Research on Cancer (IARC) and the United States Environmental Protection Agency (EPA), classify Cr(VI) as a carcinogenic substance for humans. The maximum allowable concentration (MAC) of Cr(VI) in soil and drinking water are 0.1 and 0.05 mg/L, respectively. Different removal methods including chemical precipitation, ion exchange, electrochemical precipitation⁴, filtration, evaporation and membrane technologies are applied for treating industrial effluents Cr(VI)-containing effluents⁵. These processes may be inefficient or not cost effective due to initial high Cr(VI) concentrations. Another problem with conventional treatment technologies is production of considerable amounts of toxic sludge which makes the overall treatment and disposal incompatible with the environmental friendly processes⁶. Considering the above-mentioned statements⁷, the removal of toxic heavy metals in an environmentally friendly and cost-effective manner is very important². The use of adsorbents such as activated carbon, inorganic materials such as zeolite

and clay, biological adsorbents and industrial wastes for removal of metal ions has been increasingly studied^{8,9}. In recent years, researchers have paid considerable attention on the use of natural wastes as an effective alternative for adsorption of heavy metals². Among the various removal technologies of heavy metals from water and wastewater, sorption by zeolites has been deeply studied due to their efficiency, economical aspects and ease of access. Special characteristics of natural zeolites such as clinoptilolite include ion exchange capability, molecular sieve, abundance, low cost, capability to be used as a support for photocatalysts and compatibility with the environment^{10,11}. The internal crystalline and complex structure has led to high specific surface area of these natural compounds up to 300 m²/g^{12–14}. Due to presence of a net permanent negative charge of zeolites they count as good cation exchangers^{15–17}. Owing ion exchange and adsorption characteristics, these structures are able to remove majority of the water soluble compounds. Chromium form oxyanions in aqueous solution, consequently the resulting negative ions reduce the cationic exchange capacity and adsorption ability increases¹⁸.

According to absorptive characteristics of natural zeolites, the main purpose of the present study was to determine the removal efficiency of Cr(VI) from aqueous solutions using natural Clinoptilolite and describing the isotherm model.

EXPERIMENTAL

Material

Removal experiments in this study were carried out using synthetic wastewater prepared by Merck chemicals. The Clinoptilolite zeolite was purchased from Afrazand Mining Corporation. The Cr(VI) stock solution was produced using potassium dichromate (K₂Cr₂O₇). The range

of chromium concentrations were selected according to usual Cr(VI) concentrations in industrial wastewater and were prepared on a daily basis. The pH was adjusted by 0.1 M HCl and 0.1 M NaOH and measured by a digital pH meter (Model: Cyberscaneutech-instruments 5500).

Adsorbent preparation

Following zeolite preparation, the samples were milled and screened through ASTM standard sieves with the mesh No 40¹⁹. Then the zeolites were washed with distilled water to remove fine particulate matter and mineral salts. In order to remove any water soluble and magnetic impurities, the obtained powder was heated at 70°C in distilled water for 8 h on a magnetic stirrer²⁰.

This process was repeated three times. To remove moisture from the internal cavities of zeolite and creating space for sorption, the samples were heated for 24 hours at temperatures above 100°C¹³.

Experimental procedure

Experiments were done in 100-mL Erlenmeyer flasks as batch flow mode experimental reactors. The reactors were stirred using a shaker at 150 rpm and at room temperature (24–26°C). The operational parameters influencing Cr(VI) removal by zeolite including contact time, initial Cr(VI) concentration and adsorbent dosage were studied according to one factor at the time experimental design¹⁹. Results were analyzed according to removal efficiency using Eq. (1) as bellow:

$$\text{Removal (\%)} = (C_0 - C_t)/C_0 \times 100 \quad (1)$$

where C_0 and C_t are initial and final Cr (VI) concentration. In addition, the adsorption equilibrium in aqueous solution was determined using Eq. (2):

$$q = (C_0 - C_e)V/m \quad (2)$$

where, q is the amount of Cr(VI) adsorbed at equilibrium condition (mg/g), C_0 is the initial Cr(VI) concentration (mg/L), C_e is the equilibrium concentration of Cr(VI) (mg/L), m is the adsorbent mass (g) and V is the volume of solution (L)²¹. The study procedures are shown in Table 1. Also, reusability of clinoptilolite natural zeolite was studied through four adsorption–desorption cycles. For desorption study, used clinoptilolite zeolite was submerged in the 0.1 M H₂SO₄ and placed on a shaker at 150 rpm for 120 min at 25 ± 2°C. The Cr(VI) initial concentration of 50 mg/L was used in these experiments.

Adsorption isotherms

The adsorption isotherm indicates the amount of substance adsorbed by unit mass of adsorbent at a constant temperature in equilibrium conditions. The Langmuir, Freundlich, Temkin and Dubinin- Radushkevich (D-R) isotherms were studied for the experimental data. The

study of isotherm models were carried out in pH of the solution, adsorbent dosage, agitation speed and contact time of 2, 8 g/L, 150 rpm and 30 min, respectively.

Analytical methods

The Cr (VI) concentration was determined by flame atomic absorption spectroscopy (FAAS) (Model AAS vario 6). Samples were prepared according to standard methods for examination of water and wastewater²². The zeolite chemical composition was determined by X-ray diffraction (XRD) and X-ray Fluorescence (XRF). Surface morphology of the samples was characterized using scanning electron microscopy (SEM) via a XL30, Philips microscope. In addition, the specific surface area of as-prepared adsorbent was determined by BET analysis (MODEL: Nanosord, made in Iran).

RESULTS AND DISCUSSION

Characterization of natural clinoptilolite zeolite

According to XRD analysis, silica, aluminum, iron, potassium, magnesium and calcium were present in zeolite samples (Fig. 1). The main dominant peaks of natural clinoptilolite were placed at 2θ of 10.17°, 12.05°, 13.43°, 17.66°, 22.70°, 28.45°, 30.23° and 56.95° illustrating the presence of minerals like Al, Si, Na, K which is in good agreement with the standard JCPDS card no: (25-1349)²³. There are some similarities and also differences with other studied clinoptilolites in literature, for example in a sample studied by Derikvandi, and Nezamzadeh-Ejehieh (2017) for a zeolite obtained from Isfahan, Iran. Differences can be attributed to various origins of zeolites²⁴.

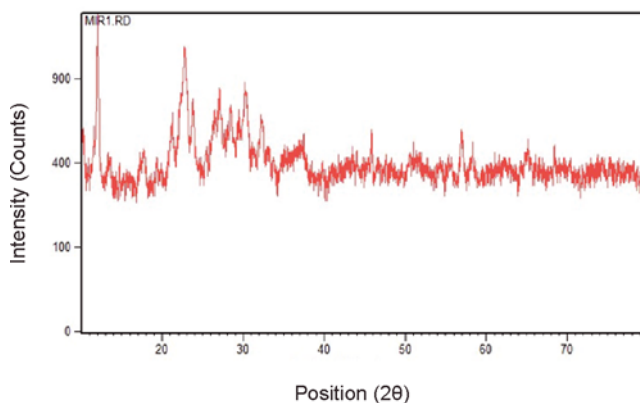


Figure 1. XRD patterns of natural clinoptilolite zeolite

The detailed view of the surface of zeolite taken by FE-SEM analysis is shown in Figure 2. The specific surface area of studied zeolite was 60.43 m²/g according to BET analysis which can be compared to value of 62.85 m²/g reported by in literature²⁵ for a natural

Table 1. Research experimental procedure and the ranges of variables

Parameter	Operational parameters					
	reaction time [min]	adsorbent dosage [g/L]	mixing speed [rpm]	temperature [°C]	initial pH	Cr(VI) [mg/L]
Adsorbent dosage	120	2–20	250	20–25	6	50
Initial pH	120	8	250	20–25	2–10	50
Reaction time	5–150	8	250	20–25	2	50
Initial Cr(VI)	30	8	250	20–25	2	10–100
Isotherm study	30	8	250	20–25	2	10–100
Kinetic study	30	8	250	20–25	2	10

clinoptilolite from Romania and 50 m²/g for one from Isfahan, Iran²⁴. The morphology of studied zeolite can be observed in Fe-SEM images (Fig. 2a) and based on elemental analysis through EDX (Fig. 2b), the zeolite was comprised mainly from Si and O followed by Al, K

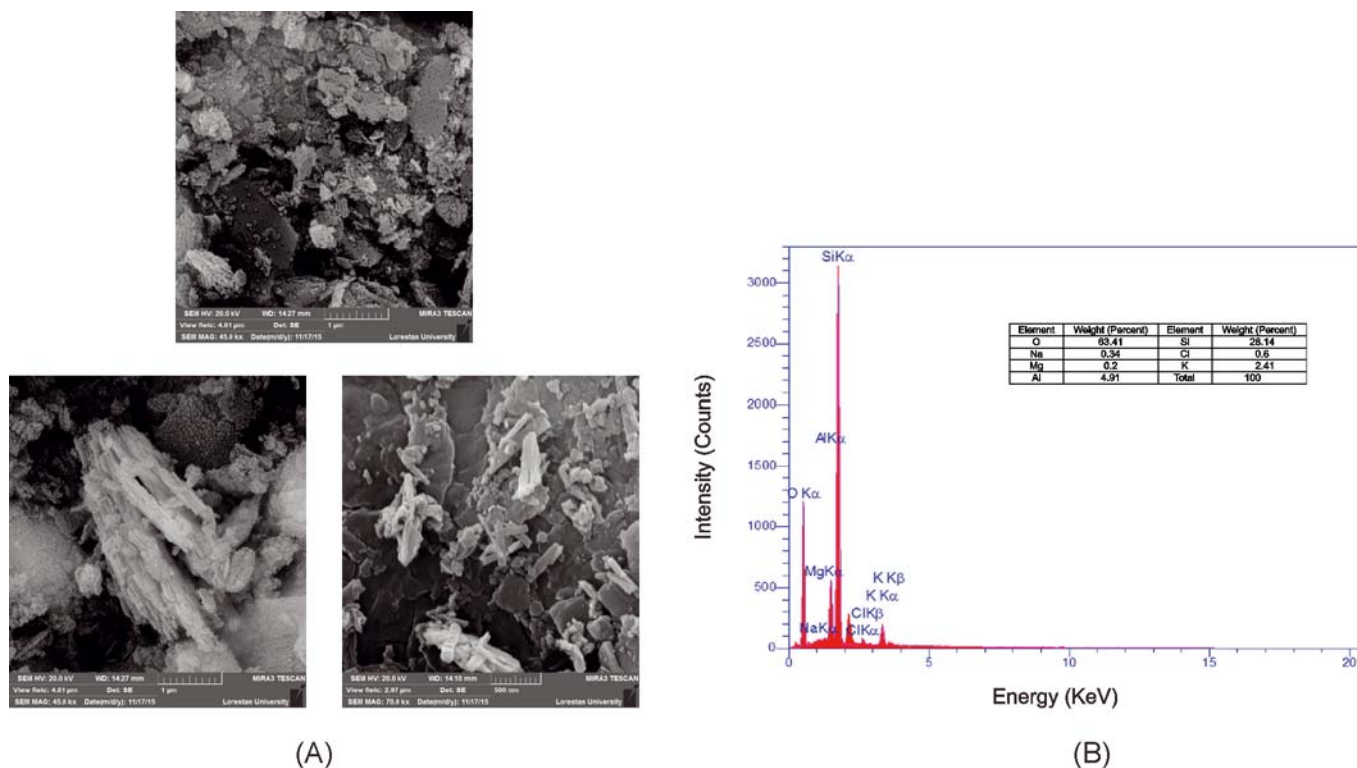


Figure 2. (a) FE-SEM images and (b) EDX spectrum of natural clinoptilolite zeolite

and Na which is similar to other studied natural zeolites in literature^{26, 27}.

Effect of adsorbent dosage

Along with increasing the adsorbent dosage from 2 to 8 g/L, a rapid increase in removal efficiency was observed and then gradually till 20 g/L (Fig. 3). The most removal efficiency of 43.44% was observed for adsorbent dosage of 20 g/L. Also, the removal efficiency for adsorbent dosage of 8 g/L was 42.99%. Due to no significant difference in observed removal results for adsorbent dosages of 8, 10 and 20 g/L ($p > 0.05$) and the advantage of using less amounts of material, the adsorbent dosage of 8 g/L with the adsorption capacity 2.69 mg/g was selected as

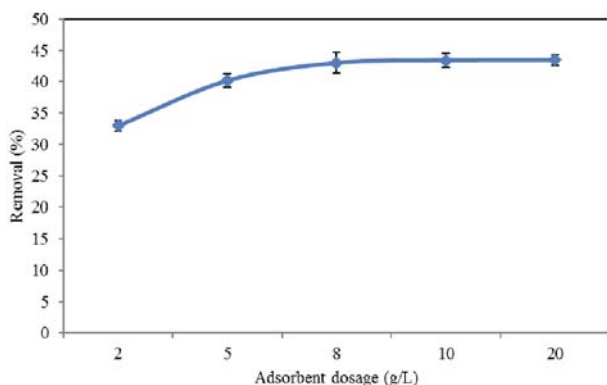


Figure 3. Effect of adsorbent dosage on Cr(VI) removal (initial pH: 6, Cr(VI) concentration: 50 mg/L and reaction time: 120 min)

the selective value for conducting the rest of experiments. Following the increase in adsorbent dosage, the specific surface area available for adsorption increases and improvement of removal efficiency is expected. It should be noted that the adsorption capacity decreased at the same time due to inter phase aggregation which

results in decreases available adsorption sites and also increasing unsaturated sites^{28–30} studied the humic acid removal with unmodified natural zeolite. Similar results were obtained in their study. Increasing the adsorbent dosages from 2 to 10 g/L, improved the removal efficiency from 30% to 80%. They claimed that increasing the adsorbent dosage would lead to increase of Van Der Waals and electrostatic attraction forces between molecules of humic acid and natural zeolite.

Effect of initial pH

Low pH values favored the Cr(VI) removal efficiency. According to Figure 4 the removal efficiency decreased till the initial pH value of 6 and then increased gradually. The most removal efficiency of 48.98% with the adsorption capacity of 3.06 mg/g was obtained at pH value of 2 and the minimum of 43.6% at initial pH of 6.

In the aqueous phase, Cr(VI) exists in different ionic forms (HCrO_4^- , $\text{Cr}_2\text{O}_7^{2-}$, CrO_4^{2-} , HCr_2O_7). The total concentration of Cr(VI) and pH of the equilibrium solution are effective in distribution of Cr(VI) species in aqueous phase. The CrO_4^{2-} anion prevails in basic or slightly acidic solution while the $\text{Cr}_2\text{O}_7^{2-}$ anion is dominant in acidic Cr(VI) aqueous solution³¹.

Low pH values lead to adsorption of oxyanions of Cr(VI) on the positively charged functional groups of zeolite. In addition, the HCrO_4^- ions are most easily exchanged with OH^- ions at active surfaces under acidic conditions. In high pH values, the interference by a high concentration of OH^- ions may lead to lower

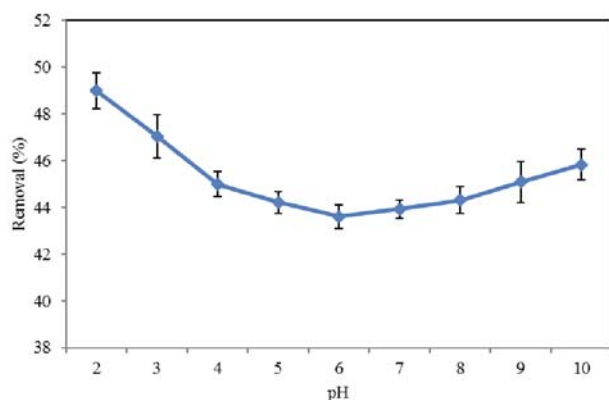


Figure 4. Effect of initial pH on Cr(VI) removal efficiency (adsorbent dosage: 8 g/L, initial Cr(VI) concentration: 50 mg/L and reaction time: 120 min)

removal efficiency. Increased amounts of OH^- , increases the competition between Cr(VI) and OH^- for occupying exchange sites in adsorbent pore^{32, 33}.

Effect of contact time

The Cr(VI) removal efficiency improved along with the reaction time and reached to 49.18% at contact time of 150 min (Fig. 5). Considering the inflection at the reaction time of 30 min and observation the equilibrium time, the reaction time of 30 min with removal efficiency of 47.46% (adsorption capacity of 2.96 mg/g) was determined as the optimum time. This optimum value was selected based on non-parametric Kruskal Wallis test, because of higher reaction times did not enhanced the removal significantly (p value 0.668). Metal removal rates were higher in the early stages due to the higher number of vacancies on the adsorbent surface. Over the time, the number of adsorptive sites reduced due to the occupation by the metal ions, leading to the increased repulsive forces between the adsorbed Cr ions with the same charge. Therefore, the removal or the metal ion adsorption decreases^{34, 35}. Esfehiani and Shamohammadi (2011) studied the manganese removal with natural and sodium zeolite. They observed that along with increasing the contact time to 25 min, the adsorption rate was high for both adsorbents. Thereafter, the adsorption rate decreased and reached to a constant value.

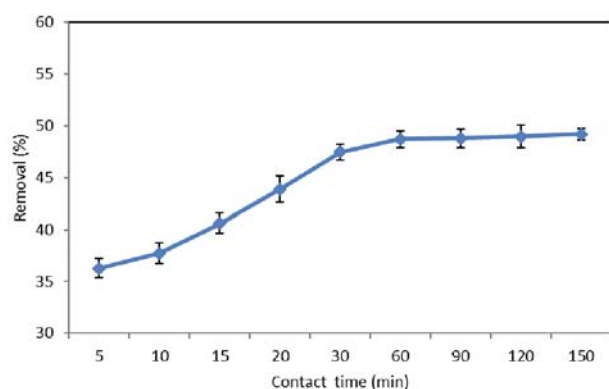


Figure 5. Effect of reaction time on Cr(VI) removal efficiency (adsorbent dosage: 8 g/L, pH: 2 and initial Cr(VI): 50 mg/L)

Effect of the initial Cr (VI) concentration

Along with the Cr(VI) concentration between 10–100 mg/L, removal efficiency varied from 98.53% to 44.94% respectively, but the amount of metal adsorbed per unit mass of adsorbent increased from 1.23 to 5.61 mg/g (Fig. 6). Removal efficiency has decreased along with increase in Cr(VI) concentration. According to Figure 6, enhancement of removal continues until the concentration of 50 mg/L and thereafter due to saturation of the active sites of the clinoptilolite zeolite for Cr(VI), no significant changes for the removing of Cr(VI) was observed³⁶. In a similar study performed by³⁷ on the use of clinoptilolite zeolite for the removal of heavy metals,

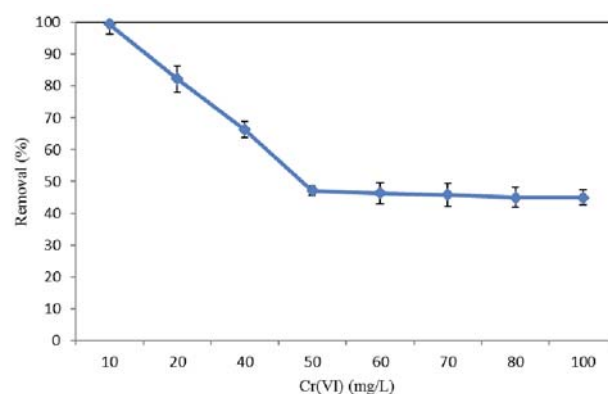


Figure 6. Effect of the initial Cr(VI) concentration (pH: 2, reaction time: 30 min and adsorbent dosage: 8 g/L)

the maximum adsorption capacities of 4.22, 27.7, 25.76 and 13.03 mg/g were obtained for cadmium, lead, copper and nickel, respectively.

Adsorption isotherms

Exact mathematical description of the equilibrium isotherm in satisfactory absorption process is necessary to design effective adsorption systems³⁸. In the current study, Freundlich, Langmuir, Temkin and Dubinin–Radushkevich isotherms were examined.

Langmuir isotherm

The Langmuir isotherm which assumes that adsorption sites on the surface of the adsorbent are uniform with same energy is given as Eq (3):

$$q_e = q_m K C_e / (1 + K C_e) \quad (3)$$

Where, q_e is the amount adsorbed at equilibrium (mg/g), C_e is the equilibrium concentration (mg/L), K is the Langmuir constant for affinity of the binding sites (L/mg), q_m is the maximum adsorption capacity (mg/g). The linear presentation of Langmuir equation is Eq. (4):

$$q_e = q_m K C_e / (1 + K C_e) \quad (4)$$

The constant q_m and K can be determined by plotting (C_e/q_e) versus C_e ^{39, 25, 40}. Essential characteristic of Langmuir isotherm can be described in term of separation factor, R_L , as Eq. (5):

$$R_L = 1/(1 + C_e K) \quad (5)$$

The R_L values in the range of $0 < R_L < 1$ is favorable and $R_L > 1$ would be unfavorable. According to obtained R_L value range of 0.094–0.51 for initial Cr(VI) concentrations of 10–100 mg/L, the adsorption is favorable.

Freundlich isotherm

The Freundlich isotherm describes sorption on a heterogeneous surface with exponential distribution of energy Eq. (6).

$$q_e = K_f C_e^{\frac{1}{n}} \quad (6)$$

The linear representation of Freundlich isotherm is as Eq. (7)⁴¹:

$$\log q_e = \log K_f + 1/n \log C_e \quad (7)$$

where K_f (mg/g) is Freundlich constant related to adsorption capacity, n is constant related to sorption intensity, q_e (mg/g) is the amount of adsorbed metal ions per unit weight of adsorbent and C_e (mg/L) is the concentration of free metal ions in solution¹⁹. The constants K_f and n were obtained from the slope and intercept of the plot of $\log(q_e)$ versus $\log(C_e)$. The values of n range between 1–10 ($n > 1$ is favorable). According to n constant of 2.99, the adsorption is favorable.

Dubinin–Radushkevich (D–R) isotherm

The Dubinin–Radushkevich (D–R) isotherm model is used to determine whether the adsorption process is physical or chemical and assumes heterogeneity of the surface energies. The linear form of D–R isotherm model is as Eq. (8):

$$\ln q_e = \ln q_m - \beta \varepsilon^2 \quad (8)$$

Where q_m (mol/g) is the maximum sorption capacity, β is a constant related to the mean sorption energy (J^2/mol^2), ε is the Polanyi potential. The constants β and q_m can be obtained by plotting of $\ln(q_e)$ versus ε^2 . Polanyi potential can be calculated through Eq. (9):

$$\varepsilon = RT \ln(1 + 1/C_e) \quad (9)$$

Where R (8.314 J/mol K) and T (K) are the gas constant and temperature, respectively. The sorption energy E_s (kJ/mol), which represents the transport free energy of solute the surface of adsorbent, can be calculated by Eq. (10):

$$E_s = 1/(-2\beta^{0.5}) \quad (10)$$

For E_s values between 8 and 16 kJ/mol, the adsorption process would be considered as a chemical, while $E_s < 8$ kJ/mol, is a physical adsorption^{25, 39, 40}. For the adsorption of Cr (VI) onto clinoptilolite zeolite, the value of E was calculated 12.7 kJ/mol, indicating the adsorption process occurs chemically.

Temkin isotherm

Assumes that the reduction in absorption heat is linear and adsorption is characterized by a uniform distribution of binding energy. The linear representation of Temkin isotherm is as Eq. (11):

$$q_e = (q_m \ln K_T) + (q_m \ln C_e) \quad (11)$$

Where, q_e (mg/g) is the amount of adsorbed metal ions per unit weight of adsorbent, K_T is the Temkin constant (L/mol)^{39, 42}.

The results of the isotherm studies showed that the removal of Cr(VI) was consistent with Freundlich isotherm ($R^2 = 0.951$). The Freundlich isotherm indicates that the

adsorbed molecules form a single layer on the surface of adsorbent particles with the same energy. Each molecule is adsorbed only in assigned one location. Therefore, probably a uniform distribution of active adsorbent surface sites is expected. The result for the Freundlich isotherm indicates the constant n of greater than 1 that confirms the adsorption of Cr(VI) onto zeolite³⁹. But in term of adsorption capacity, experimental data (q_{max} : 5.61 mg/g) were best followed Langmuir isotherm with q_{max} value of 5.371 mg/g. Also, according to E value of 9.128 KJ/mole obtained from Dubinin–Radushkevich isotherm model, the absorption of Cr(VI) onto zeolite follows chemical mechanism³⁸. The maximum adsorption capacity in term K_f constant for Freundlich isotherm of was 1.93 mg/g, compared to 10.42 mg/g for D-R isotherm, 5.376 mg/g for Langmuir and 0.883 for Temkin isotherm. The results of the isotherms equations are shown in Table 2. The plot of Freundlich adsorption isotherm is presented in Figure 7. The maximum adsorption capacity of Cr(VI) onto clinoptilolite based on studied isotherm models are compared with findings of other researchers in Table 3.

Table 2. Isotherm parameters for Cr(VI) adsorption onto natural clinoptilolite zeolite

Isotherm model	Value	
Langmuir	q_{max} [mg/g]	5.376
	K [L/mg]	0.096
	R_L	0.094–0.51
	R^2	0.919
Freundlich	K_f [mg/g]	1.193
	n	2.99
	R^2	0.951
Dubinin–Radushkevich (D-R)	k [mol ² /J ²]	3.1×10^{-3}
	q_m [mol/g]	10.42
	E [kJ/mol]	12.7
	R^2	0.948
Temkin	q_m [mg/g]	0.883
	K_T [L/mg]	2.598
	R^2	0.878

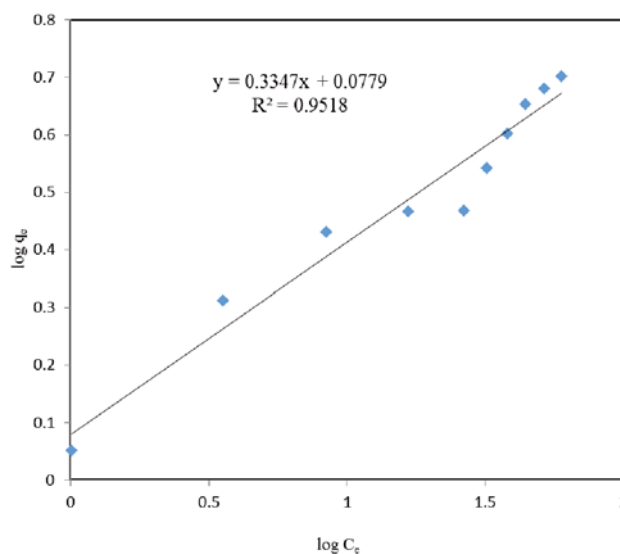


Figure 7. Freundlich, isotherm plot for Cr(VI) adsorption onto natural clinoptilolite Cr (VI) (concentration: 10–100 mg/L, contact time: 30 min pH: 2, adsorbent dosage: 8 g/L and agitation speed: 150 rpm)

Table 3. Maximum adsorption capacity of various adsorbents for Cr(VI) removal from aqueous solutions

Adsorbent	Maximum adsorption capacity [mg/g]	Reference
Biosynthetic Schwertmannite	38.82	(Gan et al., 2015)
Triethylenetetramine modified graphene oxide/chitosan composite	219.5	(Ge et al., 2015)
Aluminum-functionalized magnetic nanoparticles	263.2	(Yakout et al., 2015)
Sulphate-crosslinked chitosan	250.9	(Shekhawat et al., 2015)
Rice straw	15.82	(Wu et al., 2016)
Australian zeolite	5–11.2	(Nguyen et al., 2015)
Natural zeolites modified with <i>N,N</i> -dimethyl dehydroabietylamine oxide	69.94	(Liu et al., 2014)
Biomass material	227.3	(Zhong et al., 2013)
Chitosan/polymethylmethacrylate composite	92.5	(Li et al., 2015)
Current study (natural clinoptilolite)	10.42	–

Adsorption kinetics

In adsorption studies it is important to predict the adsorption rate which is useful in modeling of the adsorption process³⁸. The kinetic study was carried out at an initial Cr(VI) concentration of 10 mg/L, adsorbent dosage of 8 g/L, initial pH of 2 and a contact time of 30 min. In the current study, Lagergren pseudo-first and pseudo-second order kinetic models were studied to determine the adsorption mechanism.

The linear equation of the pseudo- first order kinetic model is as Eq. (12)

$$\log(q_e - q_t) = \log q_e - (k_{1,ads}/2.303)t \quad (12)$$

Where q_t (mg/g) is the amount of adsorbed Cr(VI) at time t and $k_{1,ads}$ (1/min) is the rate constant. By plotting $\log(q_e - q_t)$ versus time q_e and k_1 are obtained (Fig. 8a). The linear equation of the type 1 pseudo-second order kinetic model is as Eq. (13):

$$(t/q_t) = 1/k_2 q_e^2 + (1/q_e)t \quad (13)$$

Where k_2 (g/mg min) is the rate constant of the equation⁴³. By plotting t/q_t versus time, q_e and k_2 are obtained (Figure 8b).

Also, the linear equations of the type 2 pseudo-second order kinetic model is as Eq. (14):

$$(1/q_t) = 1/q_e + (1/k_2 q_e)(1/t) \quad (14)$$

By plotting $1/q_t$ versus time $1/t$, q_e and k_2 are obtained (Fig. 8c).

The linear equations of the type 3 pseudo-second order kinetic model is as Eq. (15)⁴⁴:

$$(1/t) = (k_2 - q_{e2}/q_t) - (k_2 - q_{e2}/q_e) \quad (15)$$

By plotting $1/t$ versus time $1/t$, q_e and k_2 are obtained (Fig. 8d).

Reaction time and dimensions of the reactor depend on the adsorption kinetics⁴⁵. The kinetic parameters and correlation coefficients of pseudo-first order and pseudo-second order kinetic models are presented in Table 4. In the current study, experimental data were best fitted to type 1 pseudo-second order model for Cr(VI) adsorption onto natural clinoptilolite zeolite ($R^2 = 1$ and also the affinity of calculated q_e to the experimental q_e). It is believed that adsorption involves mechanisms such as chemical and electrostatic interactions between adsorption sites and metal ion being adsorbed. Consequently, pseudo-second order model provides the best correlation for chemical adsorption. In the case of metal adsorption via diffusion through a boundary layer, the kinetic of process should follow the pseudo-first order model³⁴.

Desorption

In order to predict reusability of clinoptilolite natural zeolite, four adsorption–desorption cycles were considered. The Cr(VI) initial concentration of 50 mg/L was studied. Desorption ratio (DR %) was determined through Eq. (16)^{46, 47}:

$$DR\% = \frac{\text{Amount of desorbed metal ion}}{\text{Amount of adsorbed metal ion}} \times 100 \quad (16)$$

It was observed that 74.31% of the adsorbed Cr(VI) was desorbed in the first adsorption–desorption cycle, and decreased to 41.69% in the fourth cycle. The total reduction after four cycles was 32.62%, demonstrating the acceptable reusability of used clinoptilolite zeolite for full-scale applications considering its low cost and ease of access.

Table 4. Kinetic parameters of Cr(VI) adsorption

Kinetic models		Coefficient	Value	$q_{e \text{ exp}}$ [mg/g]
Pseudo-first order		K_1 [L/g]	0.099	1.25
		$q_{e \text{ cal}}$ [mg/g]	0.155	
		R_2	0.943	
Pseudo-second order	Type(I)	K_2 [g/mg · min]	1.39	1.25
		$q_{e \text{ cal}}$ [mg/g]	1.26	
		R_2	1	
	Type(II)	K_2 [g/mg · min]	1.37	
		$q_{e \text{ cal}}$ [mg/g]	– 0.57	
		R_2	0.979	
	Type(III)	K_2 [g/mg · min]	1.362	
		$q_{e \text{ cal}}$ [mg/g]	1.26	
		R_2	0.982	

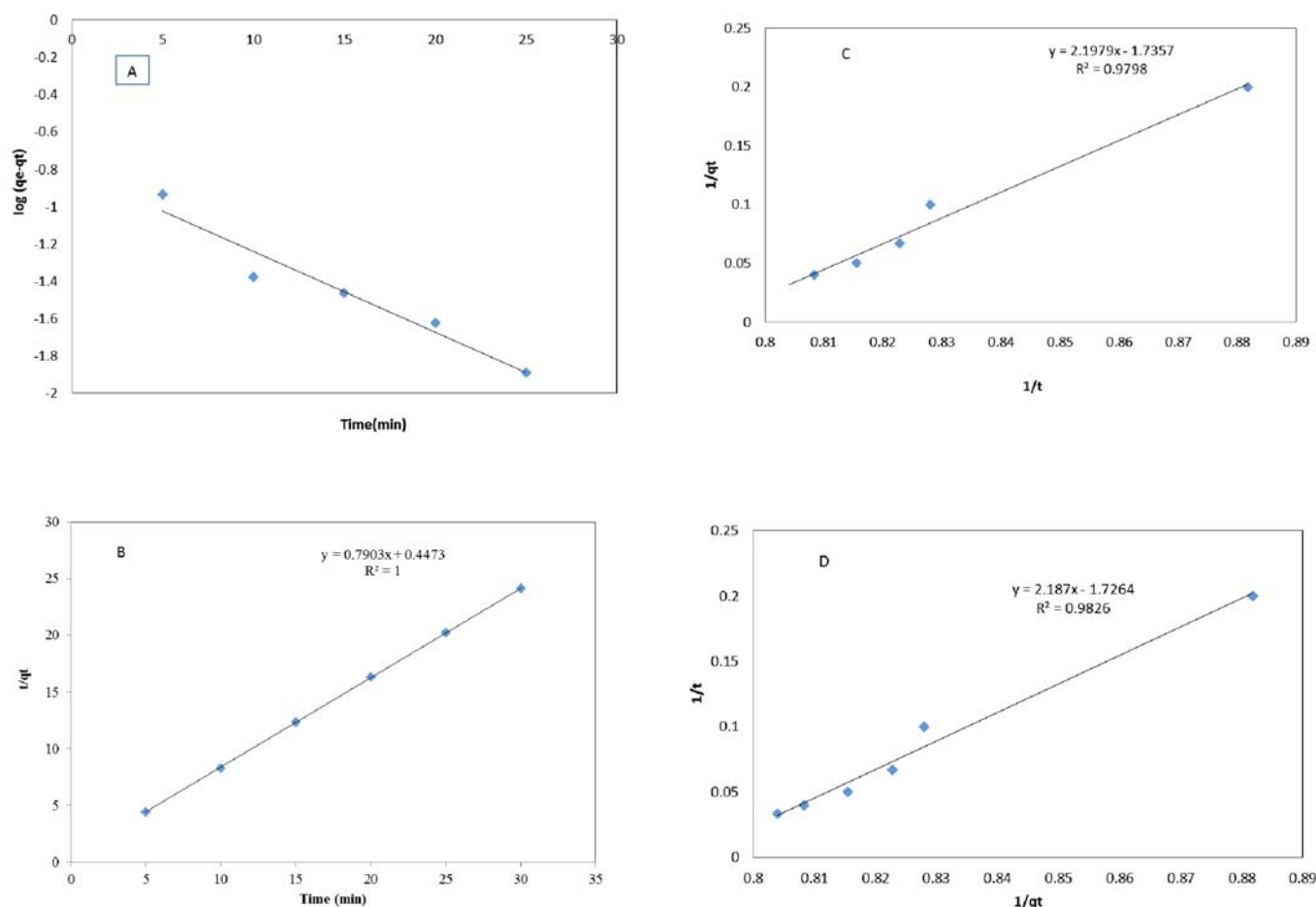


Figure 8. The fitting of different kinetic models for Cr(VI) adsorption on clinoptilolite zeolite with concentration of 10 mg/L: (a) pseudo-first order; (b), (c), (d) type 1–3 pseudo-second order, respectively

CONCLUSION

In the current study, capability of a natural clinoptilolite zeolite was studied for Cr(VI) adsorption in aqueous solution. Results indicated acceptable capability of studied zeolite for removal of Cr(VI) under determined condition. Freundlich isotherm model was best fitted with experimental data, indicating that the adsorption of Cr(VI) onto the clinoptilolite zeolite was multilayer adsorption. Negative charges of Cr(VI) along with positive charges of zeolite surface in initial pH value of 2, led to a chemical binding in adsorption process. The chemical adsorption of Cr(VI) was confirmed by Calculated E value of 9.128 KJ/mole for D–R isotherm. The kinetic data closely follow the type I pseudo-second order kinetic model. Since natural Clinoptilolite zeolite is a low-cost and naturally available adsorbent and based on findings of current study, it can be considered as an efficient, viable and reliable adsorbent for removal of Cr(VI) from aqueous solutions.

CONFLICT OF INTREST

The authors declare that they have no conflict interest.

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LITERATURE CITED

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