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Cr (VI) adsorption from aqueous solution using a surfactant-modified Iranian zeolite: characterization, optimization, and kinetic approach

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ABSTRACT

The impact of various operating parameters, including pH (2–12), concentrations of modified zeolite (0.1–1.25 g/L), initial concentration of Cr (VI) (0.1–1.5 mg/L), and contact time (5–120 min), was investigated on the removal of Cr (VI) from water through different experimental runs in the batch system. The results showed that modified zeolite had best performance for the removal of Cr (VI) at the pH 7. The time required for the removal of 90.95% of the Cr (VI) from a 1 mg/L solution was about 80 min using modified zeolite. The equilibrium assessment illustrated that the Langmuir model is the best fit for the experimental data, which attains a maximum adsorption capacity of 4.4 mg/g. Pseudo-second-order kinetic model was found to adequately describe the adsorption process. In the final part of the study, the efficacy of modified natural zeolite was examined to simultaneously removal of Cr (VI) and As (V) from aqueous solution. In summary, modified natural zeolite is an efficient in performance, simple to operate, and economical process and thereby affordable technology for the removal of Cr (VI) from the contaminated water source.

Keywords: Adsorption; Hexavalent chromium; SMZ; pH; Aqueous solution

1. Introduction

Chromium is very toxic and exposure to this metal represents a serious hazard for human and other biological systems. Thus, its removal from polluted water or wastewater is a major concern. Industrial wastewater from plating industry and metallurgy, leather tanning, textile and dyes contain chromium [1,2]. In aqueous system, the chromium can be mainly found as Cr (III) and (VI), with the former being relatively insoluble and immobile and the latter species being soluble and having a great mobility in

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groundwater in the form of chromate under the given oxidation–reduction potential and pH. Cr (VI) is more toxic than Cr (III) and is strongly oxidative, which is dangerous for environmental and biological systems [3]. It is well known that while Cr (III) plays an essential role in plant and animal metabolism, Cr (VI) is considered to be extremely mutagenic and carcinogenic [4,5].

The most common methods employed to remove Cr (VI) from aqueous solution generally involves the chemical reduction to insoluble Cr (III) compounds [3]. Conventional methods, such as precipitation, oxidation–reduction, ion exchange, filtration, membranes, electrodialysis, and evaporation, are extremely expensive or inefficient for metal removal [6]. In other words, the most commonly applied technologies for chromium treatment are "removal–disposal" processes, like chemical precipitation or concentration [4], while the current research efforts are directed towards "recovery–reuse" technologies, in order to address both environmental and economical concerns. The adsorption processes are the most effective techniques for the removal of environmentally hazardous metals, because it is easy to remove the adsorbent from aqueous media after treatment. Further, the sorption technique is generally considered to be a promising method and has been proposed for chromate removal as well [6–8].

Natural zeolites are hydrated aluminosilicates materials having cage-like structure with internal and external surface areas of up to 100 m^2/g and cation-exchange capacity of up to several milliequivalents per gram. Natural zeolites consist of a tetrahedral framework of SiO_4 and AlO_4. Silicon is tetravalent and aluminum is trivalent, resulting in negatively charged framework structures. That is, each mole at aluminum produces one equivalent of cation-exchange capacity for zeolite framework. Because of this property, zeolite cannot adsorb chromate and other anions [9,10]. Natural zeolite modified by different reagents has already been used as adsorbents for inorganic anions and organic pollutants [11]. The cationic surfactants that are most commonly used to modify natural zeolites are usually long alkyl chains with a quaternary ammonium (HDTMA) bromide [12].

Recently, the utilization of natural zeolits particularly clinoptilolite modified with cationic surfactant to remove different types of pollutants from water has been studied by many researchers especially by Li and Bowman [13–15]. In addition, Prerez Cordoves et al. [16] showed that affinity distribution analysis combined with Freundlich-binding model allows the characterization of the surfactant modified zeolite (SMZ)-binding properties for Cr (VI). Moreover, the effect of surfactant type and concentration on modification of a natural zeolite (i.e. clinoptilolite-rich tuffs) modified by two cationic surfactants (i.e. hexadecyltrimethyl ammonium chloride (HDTMA-Cl) and *N*-cetylpyridinium bromide was reported by Torabian et al. [9]. As natural zeolite samples from different regions exhibit different adsorption (ion-exchange) processes [17], the modification of these zeolites can improve the capacity of adsorption.

However, the aim of this article was to study the adsorption of Cr (VI) from solution by micro-particles of SMZ (as a local modified zeolite). The impacts of various variables including solution pH, contact time, Cr (VI) concentration, and SMZ dosage were evaluated. A number of kinetic and isotherm models were also evaluated to describe the adsorption process/mechanism.

2. Materials and methods

2.1. Materials

The sample of zeolite rock used in this study was obtained from a mineral deposit located in the south of Semnan, Iran. The zeolites pieces were initially crushed and grinded and then sieved to the average particle diameter of 200–500 μm. Finally, the zeolite particles were repeatedly washed with distilled water to remove the impurities and debris, and dried, before being used in experiments. The water used in the batch experiment was prepared from mixing aliquots of potassium dichromate stock solution (5%) with distilled water. The stock solution of potassium dichromate was prepared by dissolving required amounts of $K_2Cr_2O_7$ into distilled water. The glassware used for experimental purposes was washed in 10% nitric acid to remove any possible interference by other metals.

HDTMA-Br, a model of cationic surfactants with a molecular formula of $(C_{16}H_{33})N(CH_3)_3Br$, was provided from Sigma Aldrich Co. The HDTMA-Br used in this study has a molecular weight of 365.45 g/mol and prepared 0.06 mol/L for modification of zeolite. All chemicals were of analytical grade.

2.2. Zeolite surfactant modification

The surface of the natural zeolite was conditioned by adsorbing the cationic surfactant HDTMA-Br according to procedure suggested by Li and Bowman [18]. In brief, the procedure was as follows: 20 g of powdered zeolite and 170 mL of 0.06 M HDTMA-Br solution was placed in a 500-mL bottle and shaken at room temperature for 10 h, a time sufficient to reach adsorption equilibrium.

The mixture was then centrifuged, and the solid was washed with distilled water in order to remove unreacted monomers. The material was then completely air-dried prior to further use.

The adsorption of a cationic surfactant on the surface of the natural zeolite can be governed mainly by cationic exchange and hydrophobic interaction [19]. At a low surfactant concentrations, the surfactant cations are exchanged with the exchangeable cations of natural zeolite until a monolayer of surfactant cations is formed at the surface. At concentrations above the critical micelle concentration, a bilayer of surfactant molecules (admicelle) is attached to the surface, where the outer layer of surfactant molecules is bound by hydrophobic interactions [20]. Thus, the surface charge of the SMZ is changed from negative into positive and now displays anion exchange capacity. A general model for modification of the zeolite surface by surfactant and adsorption of Cr (VI) is suggested in Fig. 1.

2.3. Adsorption experiments

Cr (VI) removal experiments with the prepared SMZ were carried out as the batch test in 100-mL flask while agitating on a shaker–incubator instrument (Pars Azma Co., Iran). Each test consisted of preparing a 50 mL of Cr (VI) solution with a desired initial concentration, and the initial pH of the solution was adjusted by adding 0.1 N HCl and NaOH solutions. Thirty microliters aliquots of the samples was then filtered through 0.45-μ*m* filters at various time intervals. The percentage of removal and the amount of Cr (VI) adsorbed by SMZ were calculated by the following equations:

$$\text{removal}\ (\%) = \frac{C_0 - C_e}{C_0} \times 100 \tag{1}$$

$$q_e = \frac{V}{M}(C_0 - C_e) \tag{2}$$

The pH, SMZ dosage, initial contaminant concentration, and contact time were the selected variables in this phase of the work. The experimental runs and the corresponded conditions are given in Table 1. Performance of the batch tests was evaluated as adsorption efficiency (%) of the contaminant. All experiments were conducted in duplicate to ensure the reproducibility of the results, and the average values are presented. Control experiments containing no SMZ particles were also prepared.

Water content (w/w) was obtained using loss on ignition (LOI) method at 1,050 °C for SMZ and natural zeolite. In addition, the LOI method was used to estimate the organic matter in SMZ.

2.4. Kinetic and isotherm experiments

Kinetic experiments were carried out using flasks containing 100 mL of Cr (VI) solution at concentrations of 1 and 1.5 mg/L. The procedure used in kinetic tests was similar to those conducted in the first part of the study. In each test, 100 mL of Cr (VI) solution with the desired concentration was added to each flask, and then, the pH was adjusted to 7. After the adjustments, 1 g of SMZ was added, and the resultant suspension was stirred at 120 rpm for 5–100 min at 24 °C in the shaker–incubator instrument (Pars Azma Co., Iran). Upon completion, the suspension was filtered, and the filtrate was then analyzed for residual Cr (VI). The

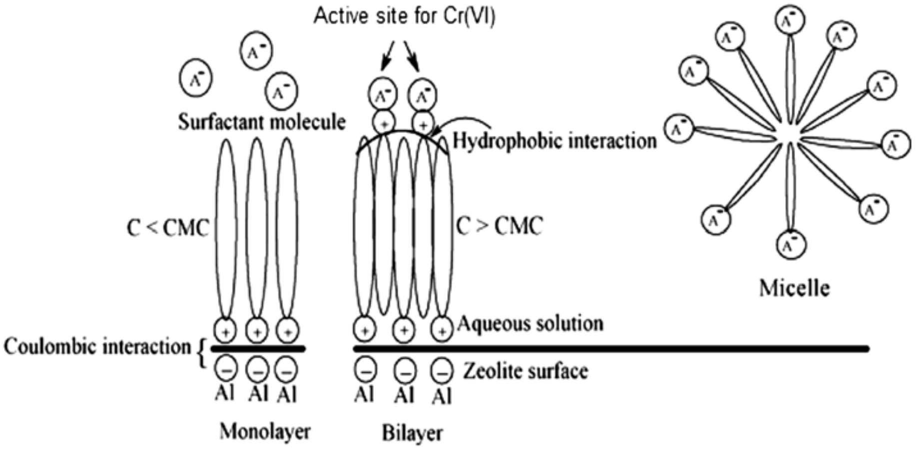

Fig. 1. A suggested model for the modification of zeolite surface by a surfactant and sorption of Cr (VI).

Table 1
Experimental runs and conditions

Run	Experiment	Operational conditions				
		pH	Cr (VI), mg/L	SMZ, g/L	Contact time, min	Temperature, ℃
1	Effect of pH of solution	2–12	0.5	0.5	80	24
2	Effect of SMZ dosage	7	1	0.1–1.25	80	24
3	Effect of contact time	7	1	1	5–120	24
4	Effect of Cr (VI) concentration	7	0.1–1.5	1	80	24
5	Simultaneous adsorption of Cr (VI) and As (V)	7	0.25–2	1	80	24
6	Adsorption isotherm	7	0.5–3.5	1	1,440	24
7	Kinetic study	7	0.5 and 1.5	1	5–80	24

results were analyzed for fitness with pseudo-first-order and pseudo-second-order models [21] to determine the order and rate constant of Cr (VI) adsorption onto SMZ. To evaluate the isotherms of Cr (VI) adsorption onto SMZ, a series of experiments were conducted. To this end, 100 mL of a solution containing 0.5–3.5 mg/L of Cr (VI) with a pH of 7 was poured into seven vessels. Thereafter, 1 g of SMZ was added to each flask. The flasks were subsequently stirred at a controlled temperature (24℃) for 1,440 min at 120 rpm to achieve equilibrium. Finally, the suspensions were filtered, and the filtrates were analyzed for residual Cr (VI). Three isotherm models were evaluated for fitness with experimental data.

2.5. Analysis

All analytical measurements were conducted according to the American Public Health Association (APHA) [22]. The concentration of Cr (VI) in water before and after treatment was measured colorimetrically by the reaction with diphenyl carbazide in acid solution as described in the standard methods [22]. Natural zeolite and SMZ were characterized for their chemical composition, crystallinity, and surface area. The mineral contents of natural zeolite and SMZ were obtained based on the X-ray fluorescence (XRF) technique by PW2404 X-ray spectrometer. The mineralogical phases and crystallinity of natural and SMZ were studied by X-ray diffraction (XRD). The XRD pattern was determined using a diffractometer, Pert MPD.α'. The characteristics including surface area, average pore diameter, and pore volume of natural zeolite and SMZ were determined by N_2-BET method using Belsorp Mini 2. The surface property of SMZ was analyzed using a Fourier transform infrared (FTIR, Perkin Elemer Model 1600). The pH of zero charge point (pH_{zpc}) of SMZ was determined according to the pH drift procedure.

3. Results and discussion

3.1. Chemical composition of natural zeolite and SMZ

Table 2 shows the chemical composition of natural zeolite and SMZ. The mineral contents of natural zeolite and SMZ were determined using XRF technique. The LOI 18.62% and 17.13% in SMZ are achieved after several hours of burning SMZ at high temperature for organic matter and water. Fig. 2 illustrates the XRD pattern of SMZ. The mineralogical phases and crystallinity of SMZ were studied by XRD. The crystalline species presenting in the SMZ were identified through comparing the characteristic peaks shown in the XRD pattern with the database of the diffractometer [16]. It was found that the largest intensity peaks correspond to clinoptilolite as the dominant species and quarts (SiO_2) was also identified as an impurity.

Table 2
Chemical properties of natural zeolite and SMZ

Composition (WT%)	P_2O_5	CaO	MgO	Fe_2O_3	Na_2O	K_2O	Al_2O_3	SiO_2	LOI[a]
Natural zeolite	0.023	1.3	0.507	1.026	3.727	3.618	9.85	68.61	12.83
SMZ	0.028	0.635	0.727	0.869	3.563	2.24	9.33	64.06	18.62

[a] Loss on ignition.

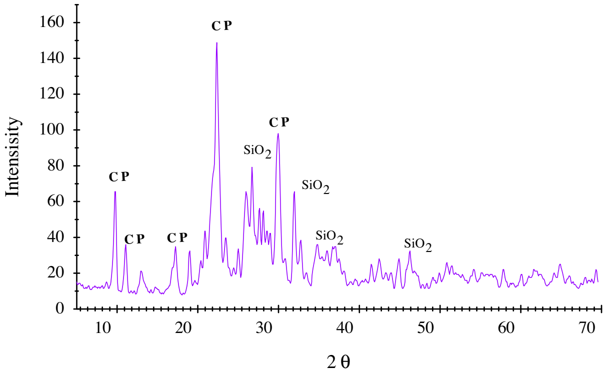

Fig. 2. XRD pattern of SMZ.

Table 3
Textural properties of natural zeolite and SMZ

Zeolite	Average pore diameter (nm)	Pore volume (cm^3/g)	Surface area (m^2/g)
Natural zeolite	26.66	0.051	13.7
SMZ	27.8	0.032	3.5

3.2. Textural properties of natural zeolite and SMZ

The results of BET method are showed in Table 3. The textural properties of natural zeolite and SMZ consist of the average specific surface area, pore volume, and average pore diameter of the natural zeolite and SMZ. These values are in the range of values reported in elsewhere [23]. The surface area and pore volume of natural zeolite decreased when it was modified with the surfactant. The decrease in the surface area and pore volume is because the surfactant obstructed some of the main channels of zeolite, thus impeding the diffusion of N_2 throughout these channels. Furthermore, the average pore diameter of zeolite increased when zeolite was modified with the surfactant. A probable reason is that the surfactant blocked in a greater proportion the smallest pore diameters, and therefore, the average pore diameter increased.

3.3. Morphology of natural zeolite and SMZ

The surface of the natural zeolite and SMZ particles were observed by using a SEM. This analysis revealed information about the surface and morphology of the particles. Fig. 3(a) presents a natural zeolite image that displays partially developed crystalline laminar habits and conglomerates of compact crystals different from those of the zeolite crystals that correspond to certain impurities such as feldspar and quartz. The laminar crystals in Fig. 3(b) cannot be seen clearly. This is because the surfactant was adsorbed on the surface of the zeolite crystals. This figure show that change in surface texture has occurred for certain regions of the used-SMZ grains (Fig. 3(b)). This change in surface texture is interpreted to be surface coatings.

3.4. FTIR spectroscopy

Fig. 4 presents that the FTIR spectrum of the Cr-SMZ is different from the pure HDTMA-Br. The peaks of the Cr-SMZ are of intermediate width, taking the range of breadth between those of the sharp one of the HDTMA-Br molecules. The following ionic vibrations can be observed in spectra of HDTMA-Br molecules: At 3,388 1/cm O–H and N–H stretching bands, 3,049 and 1,641 1/cm pyridine vibrations, 2,916 and 2,849 1/cm C–H stretching bands of CH and aliphatic C–H stretch, 1,487 and 1,378 1/cm aromatic C=C,

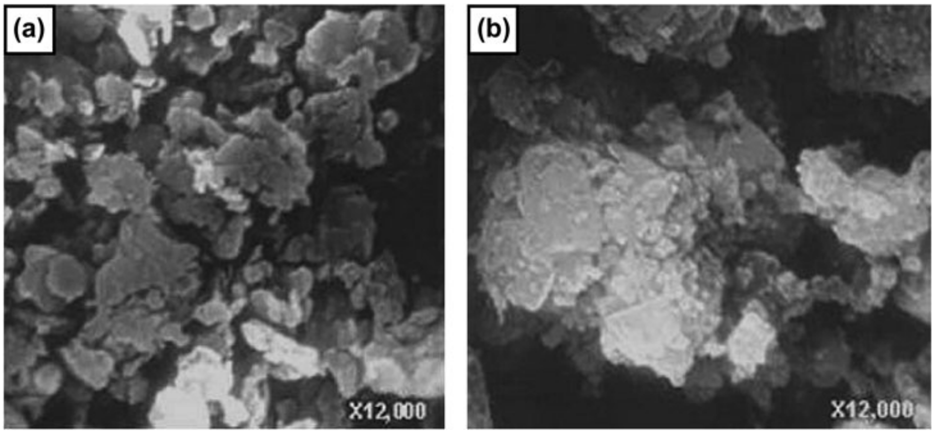

Fig. 3. SEM images of (a) natural zeolite and (b) SMZ.

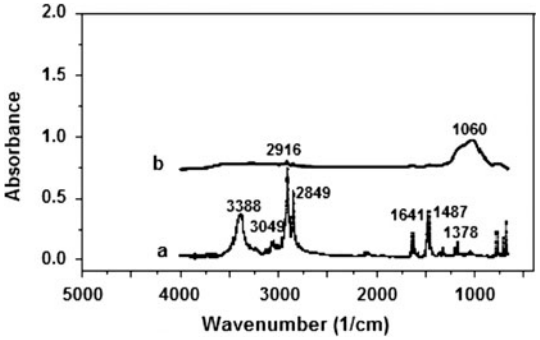

Fig. 4. FTIR spectra: (a) HDTMA-Br molecule and (b) Cr-SMZ.

aliphatic C–H stretching band [24]. In the Cr-SMZ spectra, the peak at wave number 1,060 1/cm is attributed to the association of HDTMA-Br$^+$ with zeolite. In addition, two pronounced C–H bands could be detected (2,849–2,916 1/cm). The vibration bands at 2,849 and 2,916 1/cm are attributed to symmetric and asymmetric CH_2-stretching vibration and their vibration frequencies changes with respect to surfactant surface configuration. Discrete OH-stretching bands of water (3,250–3,500 1/cm) are present in the HDTMA-Br molecules, whereas they are much broader in Cr-SMZ. Especially, for two Cr-SMZ samples, the absorption bands of the OH-stretching of water exhibit different positions. This shows that at least fractions of the water have different environments in the Cr-SMZ. Besides the hydration of HDTMA-Br cations in the interlayer space, water molecules may be associated with the uncovered part of the silicate surface [25].

Intercalated Cr (VI) ions in the interlayer region of SMZ result in only minor shifts in band positions of Si–O vibration of siloxane layers, while significant shifts in H–O vibration of adsorbed water molecules, indicating that Cr (VI) ions in the interlayer region do not basically change the configuration of the intercalated HDTMA-Br components. Moreover, the band position shift of adsorbed water molecules in Cr-SMZ may probably reflect the intercalated Cr (VI) ions in the interlayer region and the polarization of the interlayer H_2O molecules.

3.5. *Effect of solution pH on Cr (VI) adsorption*

The influence of solution pH ranging from 2 to 12 was evaluated on the removal of Cr (VI) using adsorption onto SMZ under the conditions presented in Table 1. As shown in Fig. 5, when the pH solution was raised from 2 to 7, the Cr (VI) removal efficiency increased from 83 to 94.91% while the efficiency decreased from 94.91 to 80.54% when the pH was raised from 7 to 12.

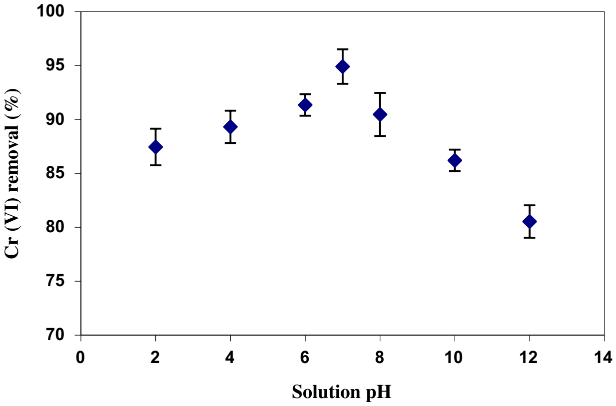

Fig. 5. Effect of solution pH on removal of Cr (VI) by SMZ.

The behavior of Cr (VI) removal as a function of solution pH can be explained by considering the change in density of hydrogen ions, the dominant ionic species of chromium and the surface charge of zeolite as a function of solution pH. According to the literature [4], various Cr (VI) species such as H_2CrO_4, $HCrO_4^-$, CrO_4^{2-}, and $Cr_2O_7^{2-}$ are in solution phase as a function of solution pH. Within the pH range of 2–7, $HCrO_4^-$ and $Cr_2O_7^{2-}$ are predominant, whereas at pH higher than 7, the dominant species is CrO_4^{2-}. Since all Cr (VI) species in solution are in the form of anion, so it is clear that SMZ is suitable to adsorb Cr (VI) species in solution. However, at pH higher than 7, Cr (VI) removal by SMZ is not efficient. As reported by other researcher [26], the effect of solution pH can be attributed to the electrostatic interactions between the Cr (VI) species present in the solution and the SMZ surface and also to the selectivity of SMZ for the Cr (VI) species. The electrostatic attraction phenomenon can take place more easily as follows:

$$2SMZ^+ + HCrO_4^- + Cr_2O_7^{2-} \rightarrow SMZ^+HCrO_4^- + SMZ^+Cr_2O_7^{2-} \tag{3}$$

The surface charge of an adsorbent is indicated by its point of zero charge (pH_{pzc}). As shown in Fig. 6, the pH_{zpc} of the SMZ was found to be 7.4, implying that zeolite particle's surface is uncharged at solution pH of 7.4; zeolite particle's surface has positive charge at solution pH below 7.4, and it is negatively charged at solution pH above 7.4. That is, the SMZ surface was negatively charged at $pH > 7.4$, and the anionic Cr (VI) species were repelled by SMZ surface. The SMZ surface was positively charged at $pH < 7.4$ and the anionic Cr (VI) species were well attracted to the

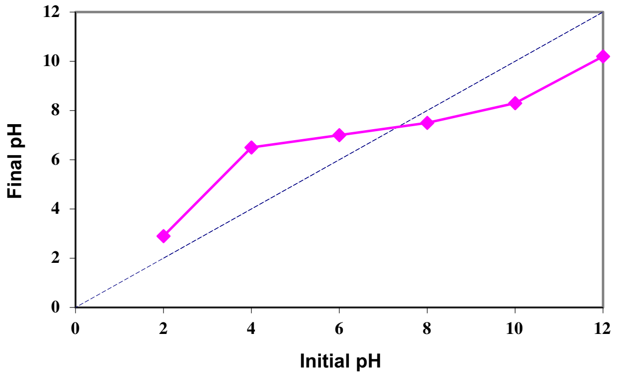

Fig. 6. Initial pH *vs.* final pH for determining the pH_{zpc} of SMZ.

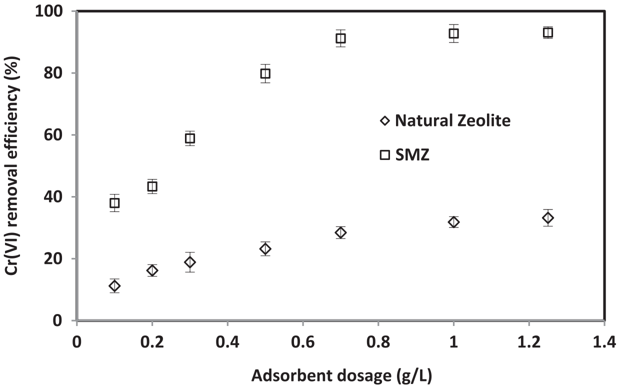

Fig. 7. Effect of adsorbent dosage on Cr (VI) adsorption by natural and modified zeolite.

SMZ. Therefore, the maximum adsorption of the SMZ was remarkable when the pH was around 7. Attaining the maximum Cr (VI) adsorption at pH 7 is of great importance from application point of view, since the pH of natural water is usually neutral. This overcomes the necessity of pH manipulation for maximizing the adsorption, which in turn makes the treatment more cost-effective. Therefore, pH 7 was selected for the rest of experiments through the study.

Several authors have found differences in the pH dependency of Cr (VI) adsorption on organo-modified clays and zeolites. Li [27] obtained an optimum pH range of 5–9 for Cr (VI) on organo-kaolinit. In other words, reports [28,29] revealed the pH intervals of 2–6 for Cr (VI) adsorption on surfactant-modified bentonit and chabazite. Leyva-Ramos [30] reported maximum adsorption of chromates on HDTMA-modified zeolite at pH 6. Majdan et al. [28] found the pH ranges of 2–6 and 5–7 for chromate adsorption on surfactant-modified bentonit and chabazite, respectively. In our study, the higher Cr (VI) adsorption capacity occurred at pH 7. As mentioned, optimum pH at which the maximum Cr (VI) adsorption could be attained has been reported to be contradictory. This contradiction in the literatures can be related to the difference in the adsorbent as well as in the experimental circumstances.

3.6. Effect of adsorbent dosage on Cr (VI) adsorption

Since the adsorption of Cr (VI) by SMZ occurs during a reaction at the adsorbent surface, it was suggested that the quantity of adsorbent strongly influenced the efficiency of Cr (VI) adsorption. The effects of modified and natural zeolite dosage in the range of 0.1–1.25 g/L were investigated on adsorption of Cr (VI) under the conditions given in Table 1. As illustrated in Fig. 7, the trend of Cr (VI) removal is same for both adsorbents. It was observed that the adsorption efficiency of Cr (VI) by SMZ increased from 38% to 91.2% with the increase in the SMZ dosage from 0.1 to 0.7 g/L. The enhancement of Cr (VI) adsorption with higher adsorbent dosage may be attributed to the increased surface area of adsorbent and availability of more active adsorption sites [31]. However, further increases in SMZ to 1 and 1.25 g/L did not lead to a remarkable increase in Cr (VI) adsorption (92.78 and 93.08%, respectively). This is due to the fact that an increase in adsorbent dosage at constant concentration of Cr (VI) and volume of solution leads to unsaturation adsorption sites [31]. Similar results were reported by Senturk et al. [31] and Zhan et al. [32].

3.7. Effect of contact time on Cr (VI) adsorption

The contact time between adsorbate and adsorbent is the most important parameter that affects the performance of adsorption processes. In this study, the adsorption of Cr (VI) on SMZ was investigated as a function of contact time in the range of 5–100 min under the conditions specified in Table 1. The results are shown in Fig. 8. Fig. 8 shows the removal efficiency of Cr (VI) increased from 12.4% in 5 min to 90.95% in 80 min and after that increasing the contact time, that is, 100 and 120 min, did not led to significant Cr (VI) adsorption (93.78 and 93.93%, respectively). It is evident that saturation was reached almost after 80 min. Hence, 80 min was selected as the period of contact time for the rest of experiments through the study. Similar observations have been reported by Majdan et al. [28], Perez Cordoves et al. [16], and Campos et al. [33]. Other researchers such as Ghiaci et al. [29] and Bowman [8] found that equilibrium for Cr (VI)-HDTMA-modified clinoptilolite system was obtained when contact time was much

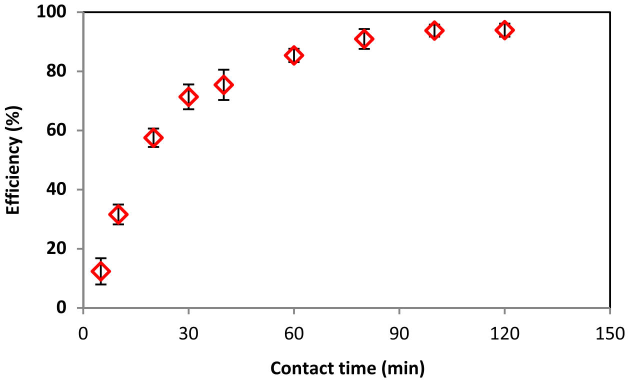

Fig. 8. Effect of reaction time on Cr (VI) adsorption onto SMZ.

longer. However, the relatively long time to reach the adsorption equilibrium is a propellant to develop other zeolite modification methods to reducing the optimal contact time.

3.8. Effect of initial concentration of Cr (VI) on Cr (VI) adsorption

It is important to study how the initial Cr (VI) concentration affects the performance of SMZ in the removal of Cr (VI). The effect of initial concentration of Cr (VI) between 0.1 and 1.5 mg/L was studied under the conditions given in Table 1. The relationship between the initial Cr (VI) concentration and the removal efficiency of Cr (VI) is presented in Fig. 9. It can be seen that increasing of the initial concentration Cr (VI) from 0.1 to 1.5 mg/L had no effect on Cr (VI) removal efficiency. However, as the initial concentration of Cr (VI) anion increased did not cause rising in removal efficiency, which may be due to low concentration of Cr (VI) available at fixed adsorbent dose [34].

3.9. Adsorption isotherm modeling

To obtain more insight on the adsorption of Cr (VI) onto SMZ, the results of equilibrium experiments were evaluated with the models of Langmuir, Freundlich, and Dubinin–Radushkevich (D–R). The information obtained from isotherm modeling is summarized in Table 4. The results revealed that the R^2 of the Langmuir isotherm was greater than the other models, indicating that the Langmuir isotherm better represented the adsorption of Cr (VI) onto SMZ. This result proposed that the adsorption of Cr (VI) occurred on a monolayer of the SMZ surface. Conformity of the experimental data to the Langmuir model is in agreement with most previously published experiments [16,23,35]. The maximum adsorption capacity of Cr

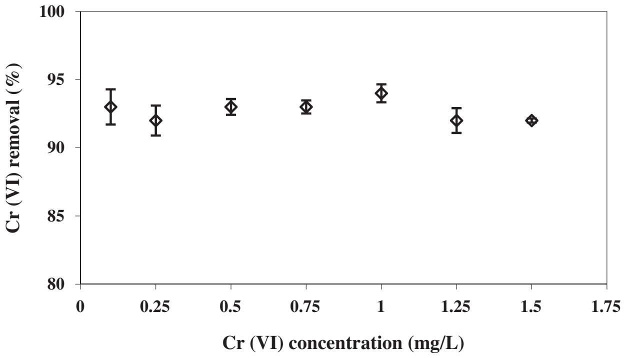

Fig. 9. Effect of initial Cr (VI) concentration in the percent of Cr (VI) removal by SMZ.

(VI) onto SMZ, obtained from the fitted Langmuir model, was 4.4 mg/g (see Table 4), which is greater than most of the zeolites reported for the adsorption of chromium [16,23].

According to the data provided in Table 4, the value of the constant 1/n in the Freundlich model is greater than unity, which confirms the suitability [36]

Table 4
Results of Cr (VI) adsorption isotherm modeling

Isotherm	Unit	Information
Langmuir model		$C_e/q_e = 1/k_L q_{max} + C_e/q_{max}$
Plot	–	(C_e/q_e) vs. C_e
Fitted model	–	$C_e/q_e = 0.5629 + 0.2278 C_e$
q_{max}	mg/g	4.389
k_L	L/mg	0.407
R^2	–	0.997
$R_L = 1/1 + k_L C_i$	–	0.15–0.76
Freundlich model		$\ln q_e = \ln K_F + 1/n \ln C_e$
Plot	–	$\ln q_e$ vs. $\ln C_e$
Fitted model	–	$\ln q_e = 1.008 + 1.0925 \ln C_e$
k_f	–	2.74
n	$(mg/g(L/mg)^{1/n})$	0.915
R^2	–	0.875
Dubinin–Radushkevich model		$\ln q_e = \ln q_m - K_{DR}\varepsilon^2$
Plot	–	$\ln q_e$ vs. ε^2
Fitted model	–	$\ln q_e = 2.16 - 0.0037\ \varepsilon^2$
K_{DR}	mol^2/kJ^2	0.0037
$E = 1/(2K_{DR})^{0.5}$	kJ/mol	11.62
R^2	–	0.851

of SMZ as an adsorbent for Cr (VI) adsorption from wastewater. The favorability of Cr (VI) adsorption onto SMZ was further evaluated by the dimensionless parameter, R_L, which was derived from the Langmuir model. As shown in Table 4, the R_L values (0.15–0.76) for Cr (VI) adsorption onto SMZ are between 0 and 1, indicating that the adsorption process is favorable. Based on the results of the D–R model (Table 4), the amount of free energy in Cr (VI) adsorption by SMZ is 11.62 kJ/mol. The value of E lie in the range of 8–16 kJ/mol indicates chemisorption is the dominant process under the experimental conditions [37,38].

3.10. Adsorption kinetics

The kinetic adsorption data were beneficial to understand the dynamics of the adsorption reactions in terms of the order of the rate constant. Therefore, the parameters of kinetics provide informative data for designing and modeling the adsorption process. The experimental kinetic data of Cr (VI) adsorption onto SMZ were analyzed by using three kinetic models: pseudo-first-order, pseudo-second-order, and intra-particle diffusion as described in Table 5.

The conformity between the experimental data and the model-predicted values was ascribed by the correlation coefficients (R^2). Besides the value of R^2, the applicability of the kinetic models to describe the adsorption process was further validated by the normalized standard deviation, Δq (%), which is defined as follows:

$$\Delta q\,(\%) = 100\sqrt{\frac{\sum[(q_{\exp} - q_{\mathrm{cal}})/q_{\exp}]^2}{N-1}} \tag{4}$$

The kinetic information obtained from the models is summarized in Table 5. According to Table 5, the correlation coefficients for the three kinetic models were greater than 0.867, which led us to believe that the kinetic models provided good correlation for the adsorption of different concentrations of Cr (VI) onto SMZ. The Δq values gained for the pseudo-second-order model was 4.2%, and 3.9% for Cr (VI) concentrations of 1, and 1.5 mg/L, respectively, which was lower compared with other presented kinetic models. Considering that the models presented high values of R^2, the applicability was based on the lowest Δq % values, so the pseudo-second-order model was the most suitable equation to describe the adsorption kinetics. Furthermore, Table 5 showed that the values of the rate constant k_2 decrease with increasing initial concentration of Cr (VI). The reason for this phenomenon can be attributed to the high competition for the

Table 5
Results of Cr (VI) adsorption kinetic modeling

Model	Pseudo-first-order		Pseudo-second-order		Weber and Morris	
Equation	$\ln(q_e - q_t) = \ln q_e - k_1 t$		$t/q_t = (1/k_2 q_e^2) + t/q_e$		$q_t = k_{id} t^{0.5} + C$	
Plot	$\ln(q_e - q_t)$ vs. t		(t/q_t) vs. t		q_t vs. $t^{0.5}$	
Concentration	1	1.5	1	1.5	1	1.5
Fitted model	$\ln(q_e - q_t) = 0.215 - 0.065t$	$\ln(q_e - q_t) = 1.012 - 0.035t$	$t/q_t = 0.037 + 0.077t$	$t/q_t = 0.048 + 0.065t$	$q_t = 0.21\, t^{0.5} + 10.21$	$q_t = 0.36\, t^{0.5} + 16.34$
R^2	0.867	0.901	0.9984	0.9987	0.976	0.972
Constant	$k_1 = 0.065\,\mathrm{min}^{-1}$	$k_1 = 0.035\,\mathrm{min}^{-1}$	$k_2 = 0.16$ mg/(g min)	$k_2 = 0.088$ mg/(g min)	$k_{id} = 0.21$	$k_{id} = 0.36$
Calculated q_e, (q_{cal})	1.24 mg/g	2.75 mg/g	12.98 mg/g	15.38 mg/g	–	–
Experimental q_e, (q_{exp})	13.1 mg/g	18.2 mg/g	13.1 mg/g	18.2 mg/g	–	–
Δq	52.14%	23.13%	4.50%	3.9%	–	–

adsorption surface sites at a high concentration, which leads to higher adsorption rates.

The adsorption mechanism is usually demonstrated by four steps: transport of adsorbate from bulk liquid to the liquid film or boundary layer surrounding the adsorbent, transport of adsorbate from the boundary film to the external surface of the adsorbent (surface diffusion), transfer of ions/molecules from the surface to the intra-particle active sites (pore diffusion), and adsorption of ions/molecules by the active sites of adsorbent. Because the first step is not involved with the adsorbent and the fourth step is a very rapid process, they do not belong to the rate-controlling steps. Therefore, the rate-controlling steps mainly depend on either surface or pore diffusion [39]. The Weber and Morris model is a widely used intra-particle diffusion model, to predict the rate-controlling step [40].

As shown in Table 5, the experimental data were fitted to Weber and Morris's model to evaluate whether intra-particle diffusion controlled the rate of Cr (VI) adsorption onto SMZ. High values of R^2 were obtained for both concentrations of Cr (VI) (1 and 1.5 mg/L), suggesting that intra-particle diffusion was involved in the adsorption of chromium ions by SMZ under the experimental conditions. However, the regression lines did not pass through the origin of the plot and a positive intercept was observed at both concentrations, indicating that another process was also involved in adsorption [41] of Cr (VI) onto SMZ. Considering the concentration of Cr (VI) in solution, mass transfer of ions from boundary layer to adsorbate was not likely limiting the rate of adsorption. Therefore, both intra-particle diffusion and chemical sorption were assumed to control the adsorption of Cr (VI) onto SMZ particles under the experimental conditions. The low slope of the plots (Table 5) indicated that adsorption approaches equilibrium in 80 min, illustrating a high rate of Cr (VI) adsorption onto SMZ. The rate constants for intra-particle diffusion, k_{id}, obtained from the plots [42] are included in Table 5. The k_{id} increased with an increase in Cr (VI) concentration, which validated the observed reduction in the pseudo-second-order constant and the increase in the rate of adsorption as a function of ion concentration. Moreover, the value of the constant C (intercept) was higher for a chromium concentration of 1.5 mg/L than 1 mg/L (Table 5), indicating that chemisorption effects were more significant at higher ion concentrations.

3.11. Simultaneous adsorption of Cr (VI) and As (V) onto SMZ

Effect of initial As (V) and Cr (VI) concentration on percent anion removal was studied under the conditions specified in Table 1. It is shown in Fig. 10 that the As (V) percentage removal increased with increasing As (V) concentration in the initial solution, whereas a different trend was observed for Cr (VI). The removal efficiency was independent of initial concentration under the experimental conditions studied. It was about 77–81%. The removal of oxyanions from aqueous solution is probably taking place by anion exchange mechanism and the trend corroborates with that reported in the literature. In a study by Li and Bowman [12], HDTMA-Br modified zeolite was found to be more selective for chromium than arsenic and the removal mechanism suggested was ion exchange. The lower selectivity for arsenic can explain by probable competition from OH^- for adsorption sites.

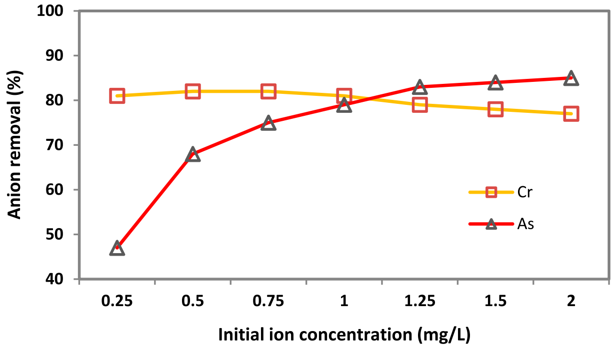

Fig. 10. Simultaneous adsorption of Cr (VI) and As (V) by SMZ.

4. Conclusions

This study reports the efficacy of an Iranian modified zeolite on removal of Cr (VI). Influence of various variables including solution pH, concentration of SMZ, concentration of contaminant, and adsorption time on removal of chromium ion was evaluated. The following results can be derived from the experimental findings of this study:

- Majority of Cr (VI) adsorption in an aqueous solution can be achieved in the 80 min in presence of SMZ particles under condition with no pH control during reaction time.
- The maximum adsorption of Cr (VI) was obtained at SMZ dosage of 1 g/L.
- The pH_{zpc} of SMZ was found to be 7.4, and the maximum chromium adsorption was obtained at natural solution.
- The results showed that equilibrium data fitted well with the Langmuir model with maximum adsorption capacity of 4.4 mg/g.

- The adsorption kinetic analysis indicated that pseudo-second-order reaction had best fitness with the experimental data of adsorption.

Therefore, the Iranian modified zeolite was found to be a very efficient adsorbent for the removal of Cr (VI) and thus a promising option for the treatment of contaminated water source.

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Nomenclature

C_0 — initial Cr (VI) concentrations (mg/L)
C_e — Cr (VI) concentrations at equilibrium (mg/L)
C_t — Cr (VI) concentrations at a time t (mg/L)
E — adsorption free energy (kJ/mol)
k_1 — pseudo-first-order rate constant (1/min)
k_2 — pseudo-second-order rate constant (mg/g min)
K_{DR} — D–R constant (mol^2/kJ^2)
K_F — Freundlich adsorbent capacity (mg/g(L/mg)$^{1/n}$)
k_{id} — the intra-particle diffusion rate constant (mg/(g min$^{0.5}$))
k_L — Langmuir affinity constant (L/mg)
M — mass of SMZ (g)
N — the number of data points
n — the reciprocal of reaction order
q_{max} — maximum adsorption capacity (mg/g)
q_{cal} — the calculated adsorption capacity (mg/g)
q_e — adsorption capacity at equilibrium (mg Cr (VI)/g SMZ)
q_{exp} — the experimental adsorption capacity (mg/g)
q_t — adsorption capacity at time t (mg/g)
R^2 — coefficient of determination
R_L — constant separation factor
T — time of contact (min)
V — volume of the Cr (VI) solution (L)
Δq — the normalized standard deviation (%)
ε — Polanyi potential (J/mol)

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