

Removal of Hexavalent Chromium (VI) from Aqueous Solutions using Surface Modified Nanozeolite A

Tashauoei, H. R.^{1*}, Movahedian Attar, H.¹, Kamali, M.², Amin, M. M.¹, and Nikaen, M.¹

¹ Department of Environmental Health Engineering, School of Public Health, Isfahan University of Medical Sciences, Isfahan 14155-6359, Iran

² Faculty of Advanced Sciences and Technologies, University of Isfahan, Isfahan 81746-73441, Iran

Received 20 Feb. 2010;

Revised 10 March 2010;

Accepted 25 March 2010

ABSTRACT: Chromium (VI) adsorption behavior and capacity by surface modified nanozeolite A has been investigated. Surface modification was performed and the morphology of modified and unmodified nanozeolite was studied using Scanning Electron Microscope (SEM) and Transmission Electron Microscope (TEM). Adsorption isotherms were studied under different conditions (pH, adsorbent dose, adsorbate concentration and interaction time). The Langmuir monolayer adsorption capacity (q_m) was found to be 14.16 mg Cr(VI) per gram at pH = 3.0 at room temperature. Chromate adsorption on surface modified nanozeolite A was found to be inversely proportional to the pH. Effect of competitive ions was studied and it was found that there is no significant competition between chromate adsorption and presence of competitive ions. Results revealed that Langmuir model is in good agreement with experimental results. Results of examinations on a polluted natural sample showed that surface modified nanozeolite A could reduce chromium (VI) concentration to acceptable criteria. Based on results, surface modified nanozeolite A is an effective sorbent for removing chromate from aquatic solution and the adsorption ability is enhanced by surface modification.

Key words: Adsorption isotherm, Birjand, Chromate, Modification, Nanozeolite A

INTRODUCTION

Increasing levels of heavy metals in the environment pose serious threats to water quality, human health and living organisms (An *et al.* 2001; Wingenfelder *et al.* 2005; Vinodhini and Narayanan, 2008). Cr, Ni, Zn, Cu and Cd are considered as priority metals from the point of view of potential health hazards to human. Hexavalent chromium have high toxicity for humans and animals (McBride 1994; Ayuso *et al.* 2003; Babel and Opiso, 2007) and commonly interfere with beneficial use of effluents for irrigation and industrial applications. They are also the groundwater contaminants at industrial installations (Mier *et al.* 2001; Malakootian *et al.* 2009). In epidemiological studies, an association has been found between exposure to Cr(VI) by the inhalation and lung cancer. IARC has classified chromium (VI) in Group 1 (human carcinogen) (WHO 2004). Some cities in Iran have high amount of hexavalent chromium contents in ground water resources. Birjand, which is located in Southern Khorasan Province at the Eastern region of Iran, is one such ex-

ample (Fig. 1). Ground water resources in this region are contaminated with hexavalent chromium due to geological structure. The amount of this ion is in the range of 0.04 to 0.08 mg/L in autumn and 0.07-0.09 mg/L in winter, which is higher than WHO guidelines (0.05 mg/L) (WHO 2004).

Conventional method for industrial effluent treatment is physicochemical treatment including ion exchange, vacuum evaporation, solvent extraction and membrane technologies (Applegate 1984; Sengupta and Clifford 1986; Kentish and Stevens 2001). Among these, ion exchange is one of the most effective and economical methods (Tran *et al.* 1999; Nameni *et al.* 2008). Use of various sorbents such as bentonite (Zvinowanda *et al.* 2009), chitosan (Jha *et al.* 1988), perlite (Mathialagan and Viraraghavan 2002), coal (Karabulut *et al.* 2000), and activated carbon (Fan and Anderson 2005; Gueu *et al.*, 2007) have been reported for the removal of heavy metals including chromate from aqueous solutions. Among the different minerals with sorbent properties, zeolites are one of the most

*Corresponding author E-mail: tashauoei@hlth.mui.ac.ir

promising sorbents. The advantages of zeolites over resins are much lower cost and ion selectivity. Zeolites have many applications such as molecular sieves and water softeners (Breck 1974; Sand and Mumpton 1978; Kalló and Sherry 1988). They appear also as suitable sorbents for heavy metals; hence several investigations on sorbent behavior of natural (Mellah and Chegrouche 1997; Inglezakis *et al.* 2003; Dal Bosco *et al.* 2005; Chutia *et al.* 2009) and synthetic zeolites (Hertzenberg and Sherry 1980; Singh *et al.* 2000; Ríos *et al.* 2008) is implemented.

Zeolite A has crystalline cubic lattice structure and is usually produced in sodium form. This zeolite is one of the most important molecular sieves, and has a good cation exchange capacity and can easily exchange sodium ion with cations (Breck 1974; Kamali *et al.* 2009). Nanocrystalline zeolites have unique properties in comparison to conventional micrometer-sized zeolite crystals. These materials have been reduced in size to just a few unit cells, this gives significant change in properties. The expected effects due to crystals' size reduction are: efficiency enhancement of very rapid reactions, and increasing the external surface (Zhan *et al.* 2002; Mintova *et al.* 2003).

Recently, interests on the adsorption of anions and neutral molecules by surface-modified zeolites is increased (Zhang *et al.* 2002). Zeolites in their original form could adsorb only cations, but some heavy metals such as chromium and arsenic are present in cations, anions, non-ionized species (Sengupta 2002). Hence, development of materials with capability to adsorb

anions, cations and neutral molecules is of high significance. Zeolites could be treated using a cationic surfactant in order to do this. By treating, an organic layer is created on the external surfaces and the charge is reversed to positive (Li *et al.* 1998). Generally, HDTMA is applied for zeolite treatment, which is a quaternary amine with a long chain cationic surfactant (Nizam Nik Malek 2007).

In view of the environmental significance, the chromate adsorption onto surface modified nanozeolite A has been investigated under different experimental conditions, i.e. pH: 3, 5, 7, and 8, solid: liquid (S:L) ratio: 0.5, 2, 3.5, and 5 g/L, adsorbent concentration: of 0.1, 1.0, 10.0 and 100.0 mg/L, and interaction time: 30, 60, 90, and 120 min. The objective of this study was to gain an insight into the physico-chemical characteristics of Cr (VI) adsorption on nanozeolite, in order to evaluate the optimal experimental conditions to be used in water treatment.

MATERIALS & METHODS

Morphology and particle size of the nanozeolite samples were examined using a Zeiss (LEO) 1455 VP scanning electron microscope (SEM) and a Philips CM10 transmission electron microscope (TEM). A number of microscope images were obtained for the unmodified and modified nanozeolite. X-ray diffraction was performed on Bruker D8 Advance X-radiation (CuK_α 1.5806 Å). Chromate analyses were carried out using the ICP-Integra XL-GBC (Australia). A Metrohm pH meter model 525A was used for pH measurements.

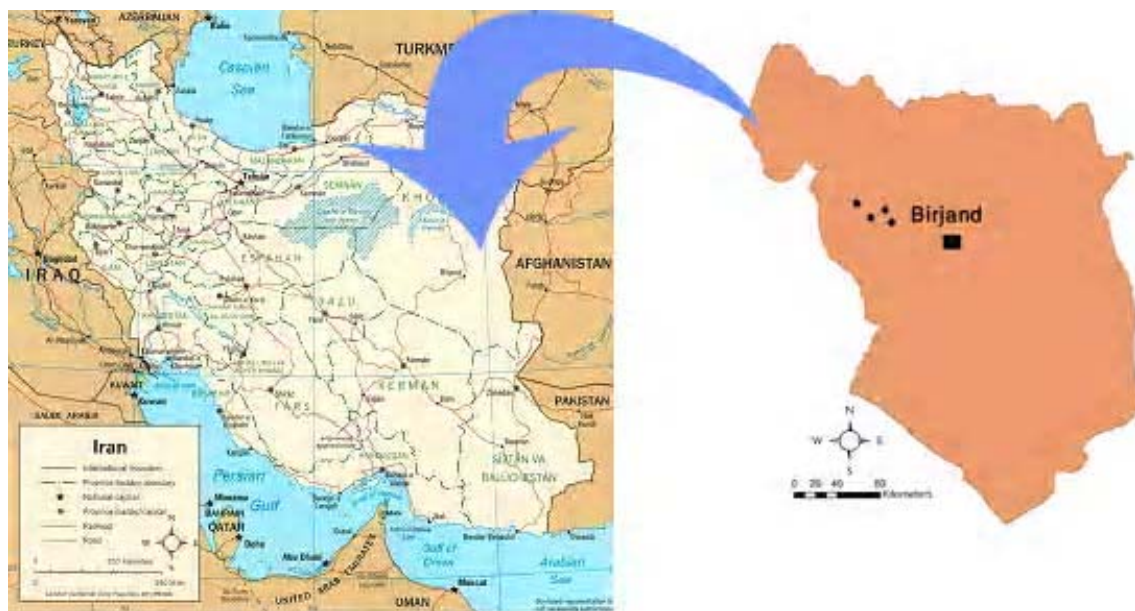


Fig. 1. Location of Birjan in Southern Khorasan Province (I%: polluted water wells)

The centrifugation was done with a Sigma 3K30 at 20,000 rpm.

Potassium chromate (K_2CrO_4) was obtained as a commercial technical grade solid from Sigma-Aldrich. HCl and NaOH were purchased by Merck as analytical grade reagents. Doubly distilled water was used.

Nanozeolite A was supplied by the Fadak Group, Isfahan Science and Technology Town, I.R. Iran. The chemical composition of the this sample was SiO_2 35.58%, Al_2O_3 28.07%, Na_2O 17.21%, SO_3 1.08%, LOI

17.53% (Breck 1974; Kamali, Vaezifar *et al.* 2009). Fig. 2 displays the XRD patterns and Figs. 3 and 4 show SEM and TEM images of non-modified and modified nanozeolite A. Based on these figures, the particle size was in the range of 50-100 nm. Total cation exchange capacity (CEC) and the external CEC (ECEC) were measured according to Haggerty and Bowman method (Haggerty and Bowman 1994) and were found to be equivalent to 2.65 meq. of Na^+ /g (CEC) and 0.35 meq. of Na^+ /g zeolite (ECEC).

A homoionic material is required for examination, so 200 milliliters of 0.1M NaCl solution was placed in

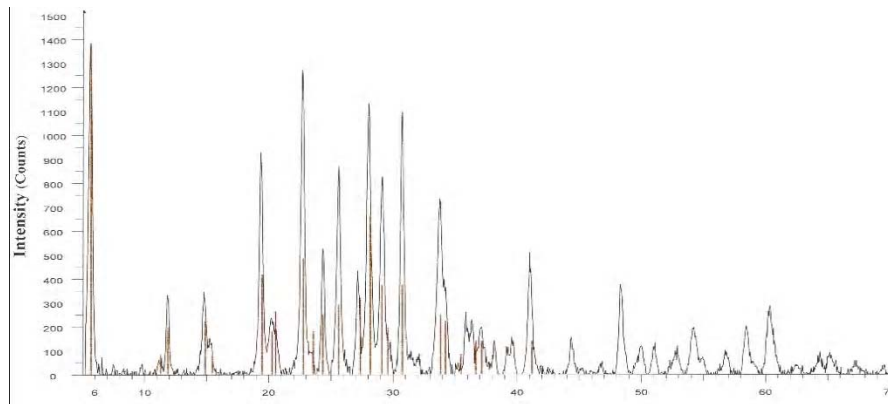


Fig. 2. XRD pattern of nanozeolite A

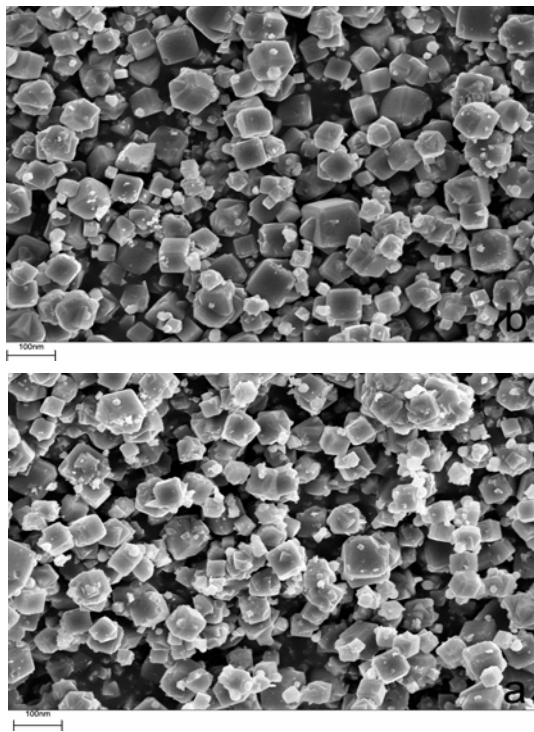


Fig. 3. SEM imaging of nanozeolite A: (a) unmodified and (b) modified

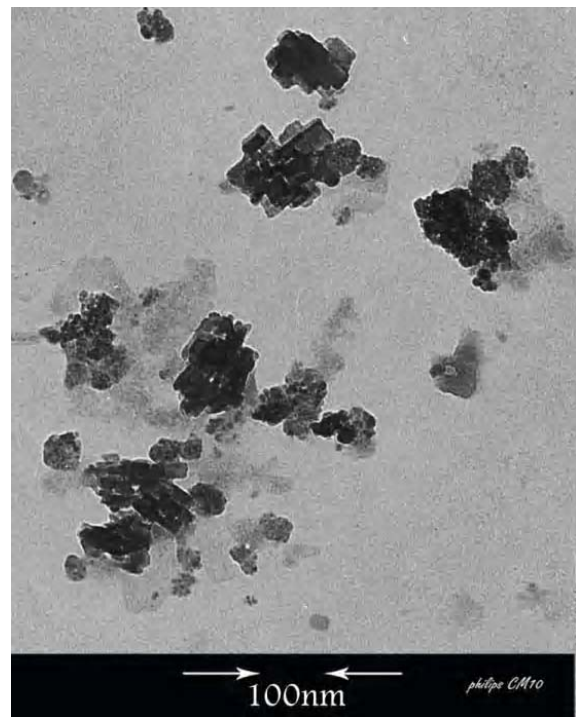


Fig. 4. TEM imaging of nanozeolite A

reflux with 10 g of nanozeolite at 85°C for 18 hours. Thereafter the solid and liquid phase was separated by centrifugation at 20000 rpm for 5 minutes. In order to obtain a chlorine free sample, the solids phase was washed triple and silver nitrate solution was used as a Cl⁻ indicator. After third sample washing, the solids phase was dried at 110°C for 18 hours (Ming and Dixon 1987; Diaz-Nava *et al.* 2005).

Modification of nanozeolite A was carried out using HDTMA-Br. In this stage, 10 g of raw nanozeolite was added to 100 mL of HDTMA-Br solution and shake for 24 h at 60°C. Preliminary experiments showed that a 24h shaking time is sufficient for equilibrium attaining and also HDTMA does not sorb labwares. Liquid and solids phases were separated using centrifugation at 20,000 rpm for 5 min. Resultant materials was washed by two portions of 100 mL deionized water, shaken at 150 rpm for 15 min and centrifuged at 20,000 rpm for 5 min. The pH of the final solutions was 7.0 ± 0.2. After the final washing, the sample was dried at 110°C for 24 hours. The HDTMA loading on the zeolite was 100% of CEC, which is the optimum for contaminant adsorption by SMZ (Li and Bowman 1997).

Stock chromate solutions with 1000 mg/L concentration were prepared by dissolving 0.3773 g of K₂CrO₄ in 1 L of doubly distilled water. Cr(VI) adsorption by surface modified nanozeolite A was performed by a batch technique at room temperature. 0.0250, 0.1000, 0.1750 and 0.2500 g of nanozeolite was shaken with 50.0 mL of 0.1, 1.0, 10.0 and 100.0 mg/L of Cr(VI) solutions for 30, 60, 90, and 120 min at different pHs (3.0, 5.0, 6.0, and 7.0). All of the solution was then centrifuged at 20,000 rpm for 5 min and Cr(VI) in supernatant was determined by ICP. In order to maintain the pH of the medium, 0.01 N NaOH or 0.01 N HNO₃ was added drop-wise before carrying out adsorption and the pH was monitored both before and after adsorption.

The adsorption amount at equilibrium, q_e (mg/g) was calculated by mass balance equation (Doulia *et al.* 2009):

where C_o and C_e are the initial and equilibrium chromate concentration (mg/L), V is the solution volume (mL), and m is the adsorbent weight (g). The adsorption equilibrium data was analyzed in terms of the Freundlich and Langmuir isotherm models (Glasstone 1981). The Langmuir isotherm equation could be written as:

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

where q_e is the equilibrium concentration on adsorbent (mg/g), C_e is equilibrium concentration in solution (mg/L), Q_m is maximum adsorption capacity (mg/g), and K_L is adsorption equilibrium constant (mg/L). The Langmuir isotherm is based on the assumption that the forces of interaction between adsorbed molecules are negligible and once a molecule occupies a site no further adsorption takes place. Also, the logarithmic form of Freundlich equation may be written as:

$$\frac{q_e}{Q_m} = \frac{K_L C_e}{1 + K_L C_e} \quad (2)$$

where q_e is the equilibrium concentration on adsorbent (mg/g), C_e is equilibrium concentration in solution (mg/L), K_F is adsorption capacity, and n is reaction energy. The Freundlich equation could be described by assuming a heterogeneous surface with adsorption on each class of sites. Although this expression is empirical, $1/n$ reflects the curvature in the isotherm and may represent the energy distribution of adsorption sites. The linearized form of Freundlich adsorption isotherm is:

$$q_e = K_F C_e^{1/n} \quad (3)$$

By plotting $\ln q_e$ versus $\ln C_e$, K_F and n can be determined if a straight line is obtained.

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (4)$$

Experiments on adsorption isotherm were performed at 25°C and the effect of nanozeolite dosage (S:L ratio), adsorbate concentration, pH, and interaction time on the chromate adsorption was examined. Taguchi method was applied in order to determine the optimum conditions of examinations (using QUALITEK-4 software). This method uses a combination of parameters to determine the optimum conditions. The optimum conditions were determined based on four factors at four levels (Table 1). The designed examinations using QUALITEK-4 along with results are presented in Table 2.

RESULTS & DISCUSSION

A batch method was applied for sorption experiments based on parameters determined by Taguchi method (Table 1). Based on the results, the estimated maximum chromate amount taken up by the nanozeolite was 82% (Table 2). The results were analyzed using Taguchi and statistical methods and

Table 1. Factors and levels in experimental design

| Factor | Level 1 | Level 2 | Level 3 | Level 4 |
|--------------------------------|---------|---------|---------|---------|
| pH | 3 | 5 | 7 | 8 |
| Adsorbate concentration (mg/L) | 0.1 | 1 | 10 | 100 |
| S:L ratio (g/L) | 0.5 | 2 | 3.5 | 5 |
| Interaction time (min) | 30 | 60 | 90 | 120 |

Table 2. Results of cadmium adsorption into surface modified nanozeolite A based on examinations designed by Taguchi method

| pH | Adsorbate concentration (mg/L) | S:L (g/L) | Interaction time (min) | Removal Efficiency (%) |
|----|--------------------------------|-----------|------------------------|------------------------|
| 3 | 0.1 | 0.5 | 30 | 22 |
| 3 | 1 | 2 | 60 | 51 |
| 3 | 10 | 3.5 | 90 | 37 |
| 3 | 100 | 5 | 120 | 43 |
| 5 | 0.1 | 0.5 | 30 | 23 |
| 5 | 1 | 2 | 60 | 45 |
| 5 | 10 | 3.5 | 90 | 41 |
| 5 | 100 | 5 | 120 | 38 |
| 7 | 0.1 | 0.5 | 30 | 15 |
| 7 | 1 | 2 | 60 | 43 |
| 7 | 10 | 3.5 | 90 | 28 |
| 7 | 100 | 5 | 120 | 32 |
| 8 | 0.1 | 0.5 | 30 | 20 |
| 8 | 1 | 2 | 60 | 34 |
| 8 | 10 | 3.5 | 90 | 29 |
| 8 | 100 | 5 | 120 | 32 |

results showed that the optimum conditions for Cr(VI) removal is pH of 3, 1 mg/L adsorbate concentration, S:L of 5 and 60 min interaction time. Results showed a decrease in Cr (VI) adsorption by increasing pH. Dependence of heavy metal adsorption on medium's pH is known (Panuccio *et al.* 2009) and it can be observed that the best chromate adsorption is at pH 3 (Mier, Callejas *et al.* 2001; Bajda and Klapyta 2006; Yusof and Malek 2009). Zeolites influence the solution's acidity, tending to neutralize the solutions by exchange of H⁺ with the cations initially present in their structures. The competitive exchange of H⁺ is considered to be the reason of lower retention of metals in more acidic environment. In addition, a decrease in initial pH decreases the probability of metal hydroxide precipitation because it also decreases the final pH resulting from the H⁺ exchange on zeolite, which explains the higher adsorption decrease shown for chromium. Zeolites, in general, are weakly acidic in

nature and therefore sodium form exchangers are selective for hydrogen (R - Na + H₂O → RH + Na⁺ + OH⁻), and this leads to high pH values when the exchanger is equilibrated with a relatively dilute electrolyte solution (Leinonen and Lehto 2001) making the metal hydroxide precipitation feasible. The extent of precipitation is clearly affected by the acidities of zeolites since they affect the bulk solution pH (Ayuso, Sanchez *et al.* 2003). As for the amount of zeolite, the highest chromate adsorption per unit mass of nanozeolite is the ratio of 5. This may be attributed to this fact that large adsorbent amount increases the adsorption sites. At low metal ion loading, the ratio of the number of metal ions to the number of available adsorption sites is small and consequently, adsorption is independent of initial concentration, but as the concentration of metal ions increases, the situation changes and the competition for adsorption sites becomes fierce.

Effects of pH. Chromate adsorption at different equilibrium solution pH values was studied. Adsorption of chromate on surface modified nanozeolite A showed a decrease with pH increasing from 3 to 8 (Fig. 5).

Effect of *solid to liquid S:L* ratio on chromate adsorption by surface modified nanozeolite A is illustrated in Fig. 6. Results indicate that the highest chromate adsorption per unit mass of nanozeolite occurred at S:L ratio of 5.

Chromate interacted with nanozeolite rapidly and the maximum uptake was observed within 30 minutes (Fig. 7). Results showed that the increase of interaction time could lead to the decrease of removal efficiency.

Results showed that the best Cr(VI) adsorption occurs at 10 mg/L and then slows down significantly to reach the lowest adsorption rate at 30 mg/L (Fig. 8).

The presence of competitive ions such as sulfates can affect on the adsorption of Cr(VI) (Bowman 1996). The

effect of this competition was investigated by adding 100, 200, 500, 1000, 2000 and 10000 mg/L of sulfate ion to a solution containing 100 mg/L of Cr(VI). Results showed that there is no significant competition up to 1000 mg/L of sulfate (up to 99% chromate removal), but the removal efficiency decreases slightly by increasing the competitive ion to 10000 mg/L (decreasing of removal efficiency to 93%) (Fig. 9). Based on results chromate adsorption could be affected slightly only at very high sulfate concentrations (10000 mg/L) which is several times higher than the contents of natural waters.

Adsorption was determined at 25°C and the adsorption isotherms are shown in Fig. 10. According to this figure, it is being shown that data is better fitted by Langmuir isotherms. The linear forms of these isotherms are plotted in Figs. 11 and 12 to calculate respective coefficients. The corresponding Langmuir and Freundlich parameters along with correlation coefficients are given in Table 3.

Several investigations have been conducted to obtain the adsorption capacity of chromate on zeolite. Ayuso *et al.* (Ayuso *et al.*, 2003) found that the maximum Cr

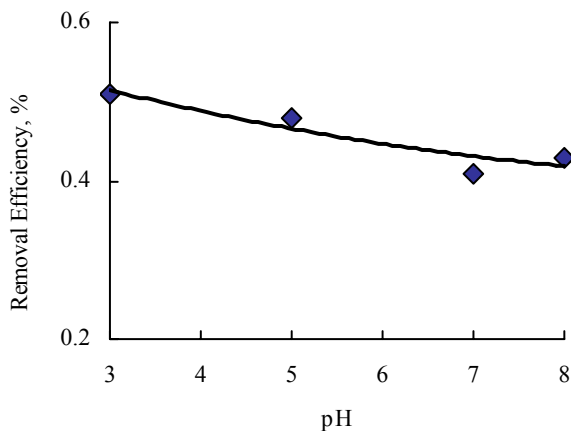


Fig. 5. Average effects of pH on chromate removal

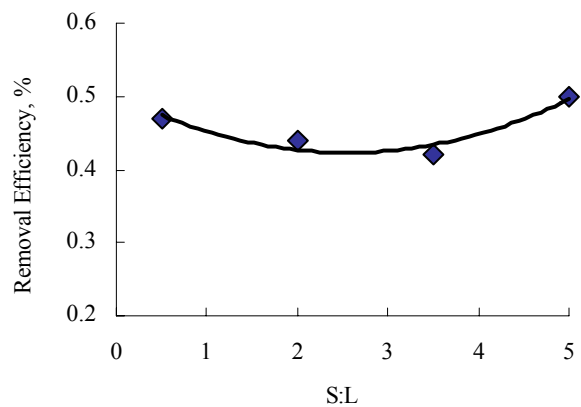


Fig. 6. Average effects S:L ratio on chromate removal

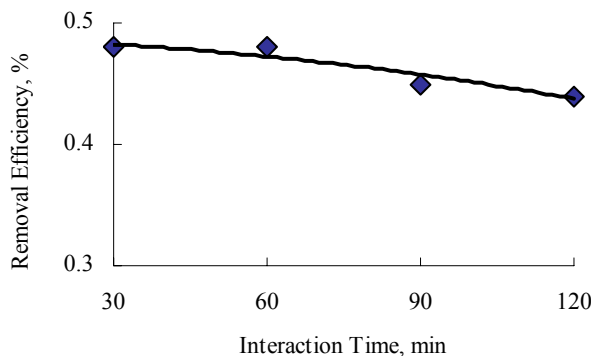


Fig. 7. Average effects of interaction time on chromate removal

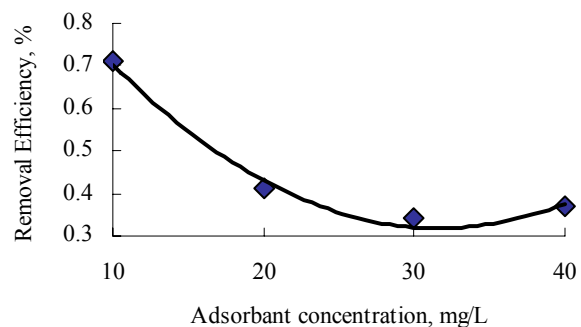


Fig. 8. Average effects of adsorbant concentration on chromate removal

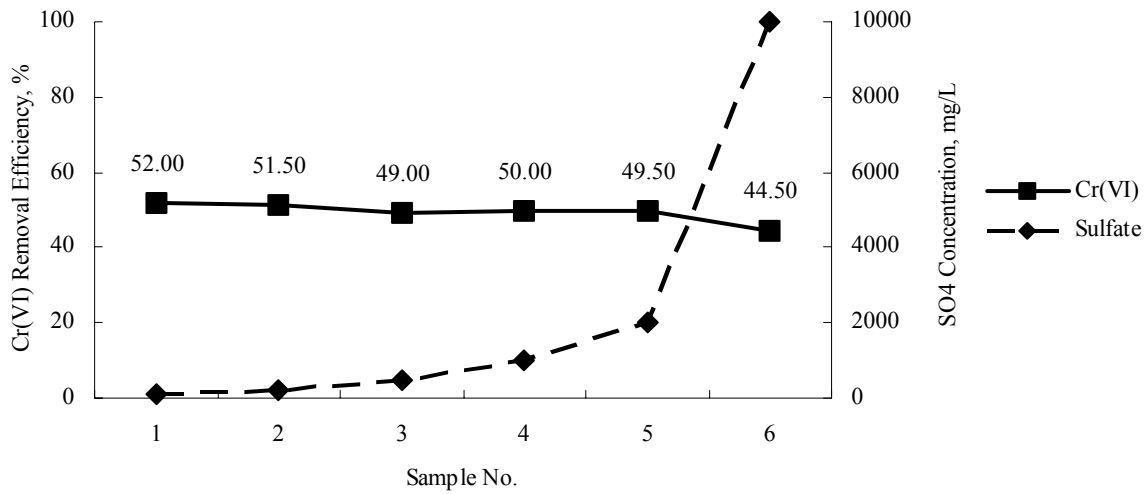


Fig. 9. Competition of sulfate ion with chromate adsorption

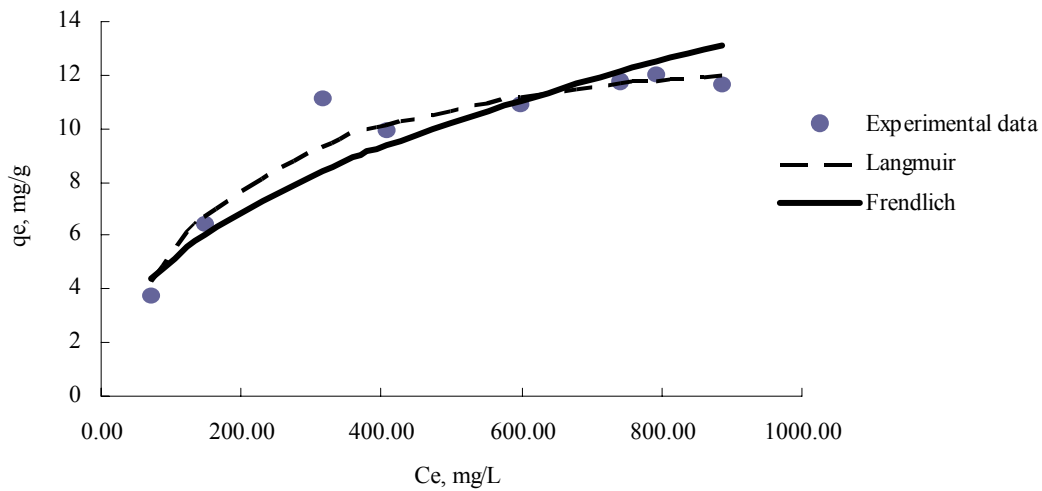


Fig. 10. Adsorption isotherm for the adsorption of chromate on surface modified nanozeolite A

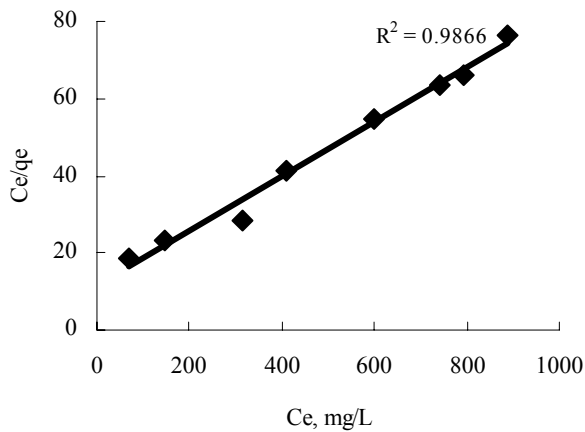


Fig. 11. Linear plot of Langmuir isotherm for the adsorption of chromate on surface modified nanozeolite A

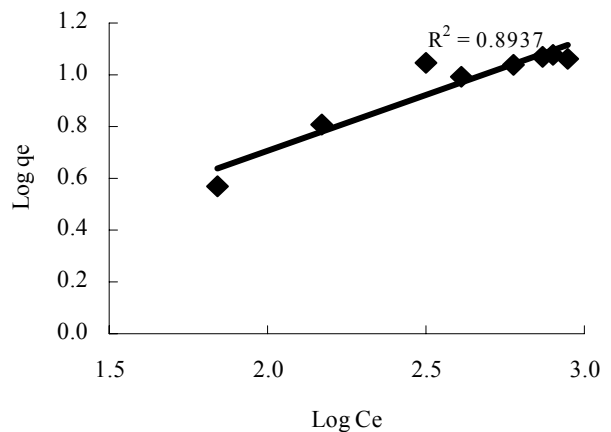


Fig. 12. Linear plot of Freundlich isotherm for the adsorption of chromate on surface modified nanozeolite A

Table 3. Isothermal parameters of chromate adsorption

| Langmuir isotherm | | | Freundlich isotherm | | |
|-----------------------|----------------------|----------------|---------------------|-------------------------|----------------|
| Q _m (mg/g) | K _L (/kg) | R ² | 1/n | K _f (mmol/g) | R ² |
| 14.16 | 6.11 | 0.987 | 2.3 | 1.43 | 0.894 |

(VI) adsorption capacities by synthetic zeolite is 14.16 mg/g. Ghiaci *et al.* (Ghiaci *et al.*, 2004) found that the maximum capacity of clinoptilolite and ZSM-5 is in the range of 0.8-3.2 and 0.7-2.7 mg/g, respectively. Other researchers found a 7.3 mg g⁻¹ (Yusof and Malek, 2009) and 2.92 mg/g (Misaelides *et al.*, 2008).

Results of examinations were analyzed using Pearson correlation test to determine the effects of each experimental parameter on the removal efficiency. Pearson correlation test showed that:

- there is significant reverse correlation between chromate removal and pH ($P_{\text{value}}=0.05$, $R=-0.415$)
- there is no significant correlation between chromate removal and S:L ratio ($P_{\text{value}}=0.302$)
- there is significant correlation between chromate removal and chromate concentration ($P_{\text{value}}=0.244$)
- there is no significant correlation between chromate removal and interaction time ($P_{\text{value}}=0.471$)

Multiple regression tests were applied in order to remove interaction effects of other factors in correlation between each factor and the removal efficiency. The results confirmed Pearson correlation test and showed that there is no removal disarray effect.

In order to evaluate the efficiency of surface modified nanozeolite A in removing Cr(VI) from natural polluted waters, an examinations were carried out on a samples from one of the most polluted Birjand's water wells. Based on surveys, the highest chromate amount in Iranian polluted waters is about 100 µg/L. The average amount of this ion during sampling from Birjand's water wells was about 85 µg/L, and examinations were carried out twice under optimum conditions based on results from Taguchi designed examination (pH = 3, adsorbate concentration = 1 mg/L, S:L = 5 and 60 min of interaction time). Results showed surface modified nanozeolite A could reduce Cr(VI) concentration to 46.7 µg/L (45 % removal efficiency), which is lower than the WHO guidelines.

CONCLUSION

The purpose of this work was to study the feasibility of chromate removal from aqueous solutions by adsorption onto surface modified nanozeolite A. It could be assumed that modifying zeolite could enable nanozeolite to adsorb chromate and lead to

considerable decrease in its concentration. The data reported here showed that surface modified nanozeolite A is an effective sorbent for removing chromate from aquatic solution. The adsorption capacity of nanozeolite was higher than the reported value for zeolites and the adsorption ability was enhanced by surface modification, which enables zeolite to adsorb Cr(VI). Equilibrium studies were conducted for the adsorption of Cr(VI) from aqueous solutions onto surface modified nanozeolite A. pH was the most important factor in Cr(VI) adsorption, and other factors had little effect. The equilibrium data have been analyzed using Langmuir and Freundlich isotherm models and the results revealed that Langmuir model is in good agreement with experimental results. Results showed that surface modified nanozeolite A is an efficient tool in removing Cr(VI) from natural water containing Cr(VI) ion in concentrations lower than 90 µg/L under optimum conditions. Also the results showed no significant competition between chromate adsorption and chromate and chromate ions.

ACKNOWLEDGEMENTS

Authors gratefully acknowledge the generous support provided by Isfahan University of Medical Sciences (No. 5141600); Fadak Group and Nanotek Spadana for nanozeolite A and Mr. M.J. Hesami, Faculty of Advanced Sciences and Technologies, University of Isfahan and A.R. Shahnoush, Department of Chemistry, University of Isfahan; Mr. F. Karakani, Iranian Elites Foundation and Mrs. Vahid Dastjerdi for their kind cooperation.

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