Removal of cadmium and humic acid from aqueous solutions using surface modified nanozeolite A

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ABSTRACT: The sorption of cadmium and humic acids from aqueous solutions using surface-modified nanozeolite A has been investigated under various examination conditions. The morphology of untreated and treated nanozeolite was studied under scanning electron microscope and transmission electron microscope. Isotherms of cadmium adsorption onto surface-modified nanozeolite A were studied at different pH, solid to liquid ratio, adsorbate concentration and interaction time. Kinetic and equilibrium studies were conducted and the equilibrium data have been analyzed using Langmuir and Freundlich isotherm models. The study revealed that experimental results were in agreement with the Freundlich model. The Langmuir monolayer adsorption capacity was found to be 1666.67 g cadmium and 6.75 g humic acid per gram of modified nanozeolite A, which is higher than that of reported value for other zeolites. The sorption ability was enhanced by surface modification and reduction in size and enabled the zeolite to adsorb cadmium. The adsorption of cadmium and humic acid on nanozeolite was found to be the highest at pH 6 and 3, respectively. Results showed that solid to liquid ratio and pH are the most important factors for cadmium and humic acid removal, respectively. Effect of competitive ions was studied and results showed that there is no competition between cadmium and humic acid sorption and presence of these ions.

Keywords: *Adsorption capacity; Adsorption isotherms; Competition; Modification; Nanozeolite*

INTRODUCTION

A promising alternative option to remove specific contaminants from aqueous solution could be the use of low-cost sorbent materials. Among the different minerals, which possess sorbent properties, zeolites appear to be one of the most promising sorbents for this purpose. The advantage of zeolites over resins, apart from their much lower cost, is their ion selectivity (Breck 1974; Ayuso *et al.,* 2003).

Zeolites are natural aluminosilicates having high surface areas, high cation exchange capacity and three-dimensional cage-like structures, four-cornered network of AlO_4 and SiO_2 tetrahedral with channel apertures on the order of a few Angstrom (Newsam, 1986). The tetrahedra are linked to each other by sharing of oxygen atoms to give rise to building blocks that are cubic, hexagonal, octagonal and polyhedral (Flanigen, 1980). Among various types of zeolites, zeolite A is one of the most important molecular sieves and is usually produced in sodium form. The zeolite unit cell formula is $Na_{12}[(AlO_2)_{12}(SiO_2)_{12}].27H_2O$. This zeolite has well cation exchange capacity and can easily exchange sodium ion with cations (Breck, 1974). Recently zeolites have been explored as effective adsorbents for cationic heavy metal (Zamzow *et al.,* 1990; Kesraoui-Ouki *et al.,* 1994; Wingenfelder *et al.,* 2005; Samarghandi *et al.,* 2007; Mahvi, 2008; Vinodhini and Narayanan, 2008) in water treatment because of their strong ion-exchange removal ability. Although some toxic metals may exist as cations, anions, non-ionized species and complex macromolecules in the aqueous phase, for example in the anionic form arsenic could be as a As (V) and non-ionized species as As (III). Another toxic metal in water is chromium, which could be cationic form as Cr^{3+} as Cr (III) and anionic form as chromate, CrO_4^{2-} as Cr (VI) (Sengupta 2001; Babel and Opiso, 2007; Nameni *et al.,* 2008). Therefore, materials capable of removing this

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type of metals simultaneously are of great importance.

Recently there are increasing interests in sorption of ions and neutral molecules by surface-modified zeolites (Zhang *et al.,* 2002). In order to sorb both anions and cations, the modified surface must possess positively and negatively charged exchange sites. A typical zeolite cannot remove or sorb the anion species due to anionic charges of surface. By treating with a cationic surfactant, an organic covering is created on the external zeolite surfaces and the charge is reversed to positive charge. Laboratory batch and column tests show that surface modified zeolite (SMZ) can simultaneously remove both inorganic anions (e.g. chromate) and hydrophobic organics (e.g. chlorinated solvents and fuel components) (Li *et al.,* 1998; Abdel-Ghani *et al.,* 2009). The most conventional surfactant to surface modification of zeolites is HDTMA (hexadecyltrimethylammonium) , the quaternary amine hexadecyltrimethylammonium cation with a long chain cationic surfactant that possesses a permanent positive charge (Nizam Nik Malek, 2007).

In view of the environmental significanc, sorption of a cation (cadmium) and a neutral organic (humic acid) on nanozeolite A has been investigated under different experimental conditions. The objective of this study was to gain an insight into the physico-chemical characteristics of Cd and HA on nanozeolite, in order to evaluate the optimal experimental conditions to be used in water treatment. Finally, the results were analyzed using statistical methods. This study was carried out in Isfahan University of Medical Sciences in 2009-2010.

MATERIALS AND METHODS
Instruments

Cadmium and humic acid analyses were carried out using an ICP-Integra XL-GBC (Australia) and a WPA Biowave II UV/Visible Spectrophotometer (UK) at 254 nm, respectively. A shaker was used to agitate the mixtures at the room temperature. A Metrohm pH meter model 525A was used for pH measurements. X-ray diffraction was performed on Bruker D8 Adavance X-radiation (CuK$_\alpha$ 1.5406Å). Samples were centrifuged with a Sigma 3K30 (Germany) running at 20,000 rpm. Morphology and particle size of the nanozeolite samples were examined using a Zeiss (LEO) 1455 VP (USA) scanning electron microscope (SEM) and a Philips CM10 (Germany) transmission electron microscope (TEM). SEM photographs were taken at different magnifications (in the range of 1000-20000 x). A number of microscope images were obtained for the unmodified and modified nanozeolite.

Reagents and solutions

All the chemicals used were of analytical reagent grade. De-ionized water was used throughout the experi-mental studies. Cadmium chloride (CdCl$_2$) and humic acid (HA) were obtained as a commercial technical grade solid from Sigma-Aldrich. HCl and NaOH were purchased by Merck (Darmstadt, Germany). Hexadecyltrimethylammonium bromide (HDTMA, 98 % purity, Merck) dissolved in distilled water to obtain a 0.10 mol/L solution. A 1 g/L concentration of Cd and HA solution was prepared and stored for a short time.

Adsorbent

Samples of nanozeolite A were supplied by the Fadak Group, Isfahan Science and Technology Town, in Iran.

Zeolite treatments

In order to obtain a homoionic material, 10 g of nanozeolite were placed in reflux (358 K) with 200 mL 0.1 M NaCl solutions for 18 h, then the phases were separated using 5 min centrifugation at 13000 rpm. The materials were washed to achieve a Cl$^-$ free solution, using silver nitrate solution as an indicator. The resultant materials were dried at 110 °C for 24 h (Ming and Dixon, 1987; Diaz-Nava *et al.,* 2005).

Zeolite modification

Zeolite modification was carried out using HDTMA-Br. In this respect, 100 mL of HDTMA-Br solution and 10 g of raw nanozeolite were put into 500 mL polyethylene centrifuge bottles and shaken for 24 h at 60 °C. Based on preliminary experiments, this time was found to be sufficient for attaining sorption equilibrium. Experimental blanks showed that HDTMA did not sorb to plastic lab-ware including polyethylene. The mixture was then centrifuged at 20,000 rpm for 5 min followed by washing with two portions of 100 mL deionized water (Milli-Q system). In each washing phase, the bottles were shaken at 150 rpm for 15 min and centrifuged at 20,000 rpm for 5 min. Final sample was washed and then dried at 100 °C for 24 h. All the supernatants were analyzed for

concentration of HDTMA in aqueous solution. The amount of sorbed HDTMA was calculated from the difference between the initial and final concentrations. The HDTMA loading on the zeolite was 100 % of CEC, which is the optimum for contaminant sorption by SMZ (Li *et al.,* 1997). The pH value of the final solutions was 7.0 ± 0.2.

Adsorption procedure

Sorption by nanozeolite A was performed by a batch technique at room temperature.

To study Cd sorption, an accurate weight of 0.1000 and 0.1750 g of nanozeolite was shaken with 50.0 mL of 100 and 500 mg/L cadmium solutions for 30 and 60 min at different pH (6.0 and 7.0). To study HA sorption, an accurate weight of 0.0250, 0.1000, 0.1750 and 0.2500 g of nanozeolite A were shaken with 50.0 mL of 10.0, 20.0, 30.0 and 40.0 mg/L HA solutions for 30, 60, 90 and 120 min at different pH (3.0, 4.0, 7.0 and 9.0, respectively). Thereafter, aliquot of solution was then centrifuged at 20,000 rpm for 5 min and Cd and HA concentration in supernatant was measured by ICP and UV-Visible spectrophotometer (254 nm) according to the standard method (Eaton *et al.,* 2005). Blank solutions were treated similarly and the concentration at the end of each batch was taken as the initial one. For maintaining pH of the medium, either 0.01 N NaOH or 0.01 N HNO$_3$ was added dropwise before carrying out adsorption and the pH was monitored both before and after adsorption.

Adsorption isotherms

Cd and HA adsorption isotherm experiments using nanozeolite were conducted under a variety of conditions. The amount of adsorption at equilibrium, q$_e$ (mg/g) was calculated by mass balance equation (Doulia *et al.,* 2009):

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

where C$_o$ and C$_e$ are the initial and equilibrium concentration of cadmium solutions (mg/L), V is the solution volume (ml), and m is the adsorbent weight (g). The adsorption percent (%) was calculated using the equation (Doulia *et al.,* 2009):

$$Adsorption\ \% = \frac{(C_0 - C_e)}{C_0} \times 100 \qquad (2)$$

The sorption equilibrium data for cadmium on nanozeolite A was analyzed in terms of the Freundlich and Langmuir isotherm models. The Langmuir isotherm

equation could be written as:

$$\frac{q_e}{Q_m} = \frac{K_L C_e}{1 + K_L C_e} \qquad (3)$$

Where

q$_e$ = the equilibrium concentration on adsorbent (mg/g)
C$_e$ = equilibrium concentration in solution (mg/L)
Q$_m$ = maximum adsorption capacity (mg/g)
K$_L$ = adsorption equilibrium constant (mg/L).
This model is based on the assumption that the forces of interaction between sorbed molecules are negligible and once a molecule occupies a site no further sorption takes place.

Also, the logarithmic form of Freundlich equation may be written as:

$$q_e = K_F C_e^{1/n} \qquad (4)$$

q$_e$ = the equilibrium concentration on adsorbent (mg/g)
C$_e$ = equilibrium concentration in solution (mg/L)
K$_F$ = adsorption capacity
n = reaction energy

The Freundlich equation can 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 sorption isotherm is:

$$ln\ q_e = ln\ K_F + \frac{1}{n} ln\ C_e \qquad (5)$$

By plotting ln qe versus ln C$_e$, K$_F$ and n can be determined if a straight line is obtained.

Effect of experimental parameters on HA adsorption

Adsorption isotherm experiments were performed at 25 °C in order to examine the effect of nanozeolite dosage (S:L ratio), adsorbate concentration, pH and interaction time on the Cd and HA adsorption. In order to determine optimum conditions, the examinations were designed by QUALITEK-4 software using Taguchi method. This method uses a combination of parameters to determine the best condition. The best condition was determined based on four factors in four levels (Table 1). It must be noted that experiments on Cd sorption was carried out at first with 0.01, 0.1, 1 and 10 mg/L, but the remaining cadmium in supernatant reached to below the detection limits, due to high removal efficiency, thus, initial cadmium concentration was raised up to 500 mg/L. The designed examinations

using QUALITEK-4 are presented in Table 2.

RESULTS AND DISCUSSION

Adsorbent characterization

The chemical composition of sample utilized was SiO_2 35.58 %, Al_2O_3 28.07 %, Na_2O 17.21 %, SO_3 1.08 %, LOI 17.53 % (Kamali *et al.,* 2009). Fig. 1 shows the XRD pattern of nanozeolite A and Figs. 2 and 3 show SEM and TEM images of unmodified and modified nanozeolite A, respectively. These images show that particle size is in the range of 50-100 nm.

Total cation exchange capacity (CEC) and the external CEC (ECEC) were measured according Haggerty and Bowman method (Haggerty and Bowman, 1994). For the nanozeolite A used in this work, CEC was 2.65 meq. of Na^+ per g and ECEC was 0.35 meq. of Na^+ per g zeolite.

Adsorption of Cd and HA by nanozeolite A

Based on results, the estimated maximum contaminant uptake achieved by nanozeolite was 98.78 % at pH = 6, adsorbate concentration = 100 mg/L, S:L = 3.5 and 30 min interaction time for cadmium and 83.16 % at pH = 3.0, adsorbate concentration 10 mg/L, S:L = 0.5 and 30 min interaction time for humic acid (Table 3).

Effect of experimental parameters on Cd and HA adsorption

Effects of pH

Cadmium adsorption at different equilibrium solution pH values was studied. Adsorption of cadmium on nanozeolite A showed a decrease when pH increased from 6 to 7, i.e. from 96 to 94% by increasing pH from 6 to 7 (Fig. 4). Optimum cadmium adsorption occurred at pH 6 (Fig. 4) with no indication of precipitation of Cd (II)-hydroxide. Mathialagan and Viraragharan, (2002) carried out adsorption of Cd (II) up to pH 9.0 without any significant precipitation of the hydroxide. Dependence of heavy metal adsorption on the medium's pH is known (Panuccio *et al.,*2009) and Based on previous studies, the best pH for cadmium removal is 6 (Ayuso *et al.,* 2003; Gupta and Bhattacharyya, 2008; Panuccio *et al.,* 2009) and at low pH, cadmium sorption is very low (Chandra Rao *et al.,* 2006). In basic solution (pH > 7) the concentration of OH^- ions would be high, leading to precipitation of

Table 1: Factors and levels in experimental design

Factor	Humic acid				Cadmium	
	Level 1	Level 2	Level 3	Level 4	Level 1	Level 2
pH	3	5	7	8	7	8
Adsorbate concentration (mg/L)	10	20	30	40	100	500
S:L ratio (g/L)	0.5	2	3.5	5	2	3.5
Interaction time (min)	30	60	90	120	30	60

Table 2: Examination design using Taguchi method

Cadmium				Humic Acid			
pH	Adsorbate concentration (mg/L)	S:L ratio (g/L)	Interaction time (min)	pH	Adsorbate concentration (mg/L)	S:L ratio (g/L)	Interaction time (min)
6	100	2	30	3	10	0.5	30
6	100	3.5	60	3	20	2	60
6	500	2	60	3	30	3.5	90
6	500	3.5	30	3	40	5	120
7	100	2	60	5	10	2	90
7	100	3.5	30	5	20	0.5	120
7	500	2	30	5	30	5	30
7	500	3.5	60	5	40	3.5	60
				7	20	5	90
				7	10	3.5	120
				7	30	0.5	60
				7	40	2	30
				8	10	5	60
				8	20	3.5	30
				8	30	2	120
				8	40	0.5	90

the cations as their corresponding hydroxides rather than their adsorption on to the adsorbent surface. pH is one of the factors affecting the HA removal. Adsorption of HA nanozeolite A showed a decrease when pH increased from 3 to 5, a slight increase when pH increased from 5 to 7 and a decrease when pH increased from 7 to 8 (Fig. 5). Based on previous studies, the best pH for HA removal is 3 (Salman *et al.,* 2007; Terdkiatburana *et al.,* 2008; Wang *et al.,* 2008; Doulia *et al.,* 2009). At pH values below 3.0 the concentration of hydroxonium ions in the solution would be high and prevents any adsorption by the active sites on the substrate surface. Similarly, in basic solution (pH > 7) the concentration of OH⁻ ions would be high, leading to precipitation of the cations as their corresponding hydroxides, rather than their adsorption by the adsorbent surface.

Effects of solid to liquid (S:L) ratio

Data relating to the effect of S:L ratio on cadmium sorption by nanozeolite A is shown in Fig. 4. The figure indicates that amount of cadmium adsorbed per unit mass of nanozeolite increased with high nanozeolite loading and the best sorption occurs in S:L ratio of 3.5. Amount of metal ion adsorbed per unit mass of adsorbent increased with high nanozeolite loading (Fig. 4). This may be attributed to the 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 conse-quently, 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. As a result, the extent of adsorption comes down considerably, but the amount adsorbed per unit mass of the adsorbent rises. Similar results have also been reported by other researchers (e.g., Ni (II) by bagasse fly ash (Gupta *et al.,* 2003).

Data related to the effect of S:L ratio on HA sorption by nanozeolite A is shown in Fig. 5. The figures indicate that the amount of HA adsorbed per unit mass of nanozeolite increased with high nanozeolite loading, while the best sorption occurred at S:L ratio of 3.5 and 5 with a negligible difference and was low at ratios of 0.5 and 2.

Effects of adsorbate concentration

Results showed that increase of concentration could lead to a decrease in removal efficiency. On this regard, the highest cadmium removal occurs at 100 mg/L, although the difference this concentration and concentration of 500 mg/L is negligible (Fig. 4). Also the highest HA removal efficiency occurred at 10 mg/L and then slows down to reach the lowest sorption at 40 mg/L (Fig. 5). This could be attributed to saturation of sorption active sites on zeolite surface (Lin and Juang, 2002).
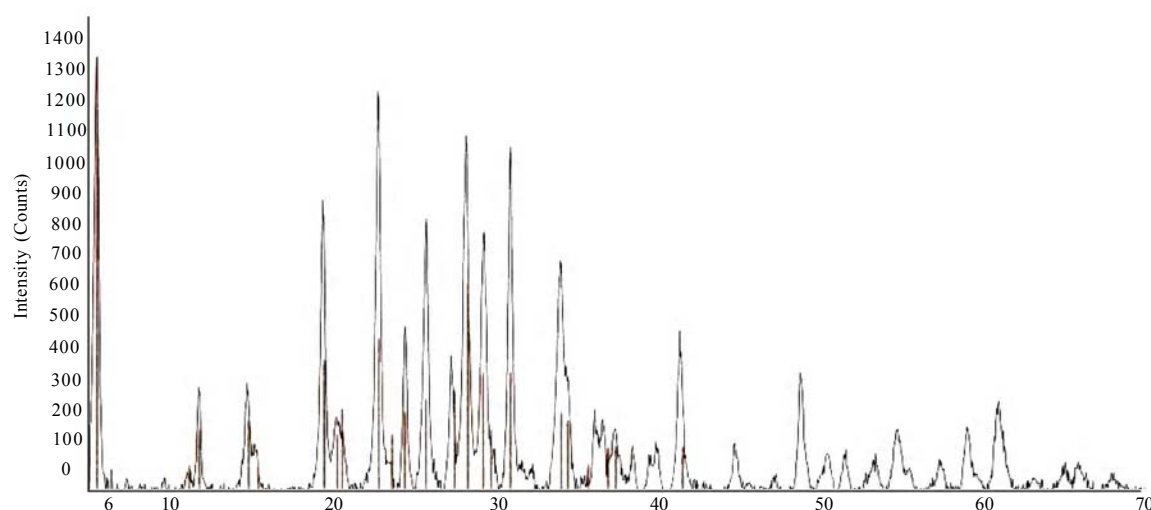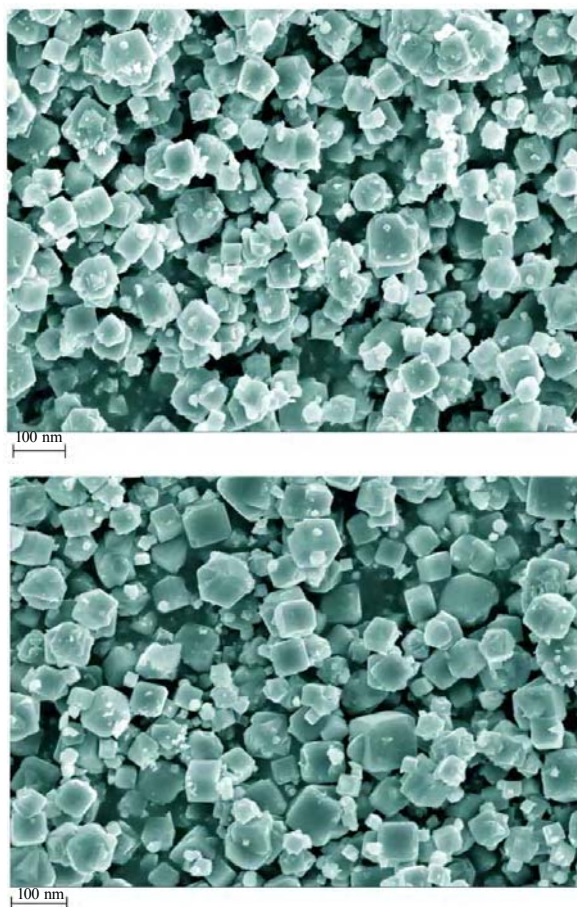
Fig. 1: XRD pattern of nanozeolite A

Fig. 2: SEM images of unmodified (left) and modified nanozeolite A (right)
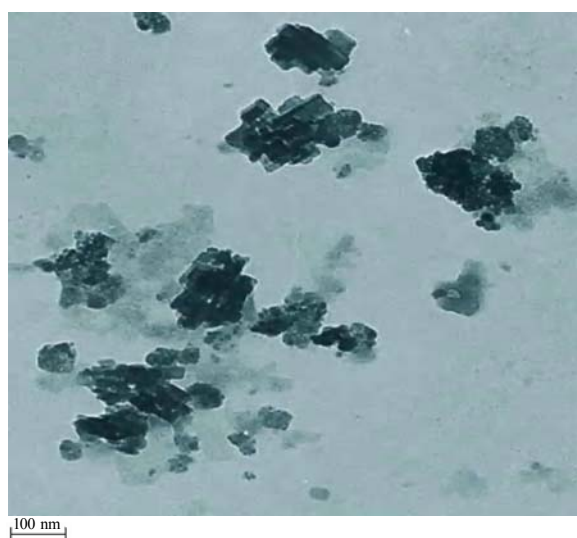

Fig. 3: TEM images of nanozeolite A

Effects of interaction time

Cadmium interacted with nanozeolite rapidly and the maximum uptake was observed within 30 min (Fig. 4). Afterwards, the interaction is stable. Attainment of equilibrium is influenced by several factors including the nature of adsorbent and adsorbate and the interactions between them. Results showed that increase of interaction time has no effect on removal efficiency and attainment of equilibrium is influenced other factors, mainly S:L ratio. HA interacted with nanozeolite rapidly, too, and the maximum uptake was observed within 30 min (Fig. 5). Afterward, the interactions slowed down up to 60 min and increased again after this time. Attainment of equilibrium is influenced by several factors such as nature of adsorbent and adsorbate and their interactions.

Analysis of variance and determining optimal conditions

Results were analyzed using ANOVA. The objective of this part was to determine variance of each factor in relation to total variance. Degree of freedom (DF), total DF of Cd and HA were 1 and 7 and 3 and 15, respectively. Results of this analysis are presented in Table 4. In this table, the most effective factors on cadmium and humic acid removal are S:L and pH, respectively (P value < 0.05).

Pearson correlation test showed that:

- There is no correlation between cadmium removal and pH (P_{value} = 0.306), but there is significant reverse correlation between HA removal and pH (P_{value} = 0.02, R = - 0.52);
- There is significant reverse correlation between cadmium and HA removal and S:L ratio (Cd: P_{value} = 0.035, R = -0.497; HA: P_{value} = 0.03, R = - 0.497);
- There is no correlation between cadmium removal and cadmium concentration (R = 0.269), but there is reverse correlation between HA removal and HA concentration (R = - 0.31, although this correlation is not significant);
- There is no correlation between cadmium and HA removal and interaction time (Cd: P_{value} = 0.997; HA: P_{value} = 0.43, R = - 0.05).

Multiple regression tests were applied in order to remove interaction effects of other factors in correlation between each factors and removal efficiency. The results confirmed Pearson correlation test and showed that there is not remove disarray effect.

Table 3: Results of Cd and HA adsorption by nanozeolite at various conditions

	Cadmium					Humic acid			
pH	Adsorbate aoncentration (mg/L)	S:L ratio (g/L)	Interaction time (min)	Removal efficiency (%)	pH	Adsorbate concentration (mg/L)	S:L ratio (g/L)	Interaction time (min)	Removal efficiency (%)
6	100	2	30	95.36	3	10	0.5	30	83.16
6	100	3.5	60	97.80	3	20	2	60	41.00
6	500	2	60	92.40	3	30	3.5	90	75.40
6	500	3.5	30	98.72	3	40	5	120	76.90
7	100	2	60	93.00	5	10	2	90	23.90
7	100	3.5	30	98.78	5	20	0.5	120	11.00
7	500	2	30	87.24	5	30	5	30	51.33
7	500	3.5	60	97.02	5	40	3.5	60	26.00
					7	20	5	90	69.20
					7	10	3.5	120	41.50
					7	30	0.5	60	4.33
					7	40	2	30	17.25
					8	10	5	60	46.00
					8	20	3.5	30	50.00
					8	30	2	120	18.67
					8	40	0.5	90	7.25

Table 4: Analysis of variance

Factor		Cadmium					Humic acid			
	DF	Variance	F-ratio	Percent	P value	DF	Variance	F-ratio	Percent	P value
pH	1	0.000	1.413	1.917	0.306	3	0.149	58.209	43.355	0.003
Adsorbate concentration (mg/L)	1	0.001	2.208	5.609	0.269	3	0.044	17.181	12.262	0.019
Solids to liquid ratio (S/L) (g/L)	1	0.008	14.923	64.622	0.035	3	0.110	42.850	31.715	0.005
Interaction time, min	1	0.000	0.001	0.000	0.997					
Error	3	0.000		27.852						
Total	7			100%						
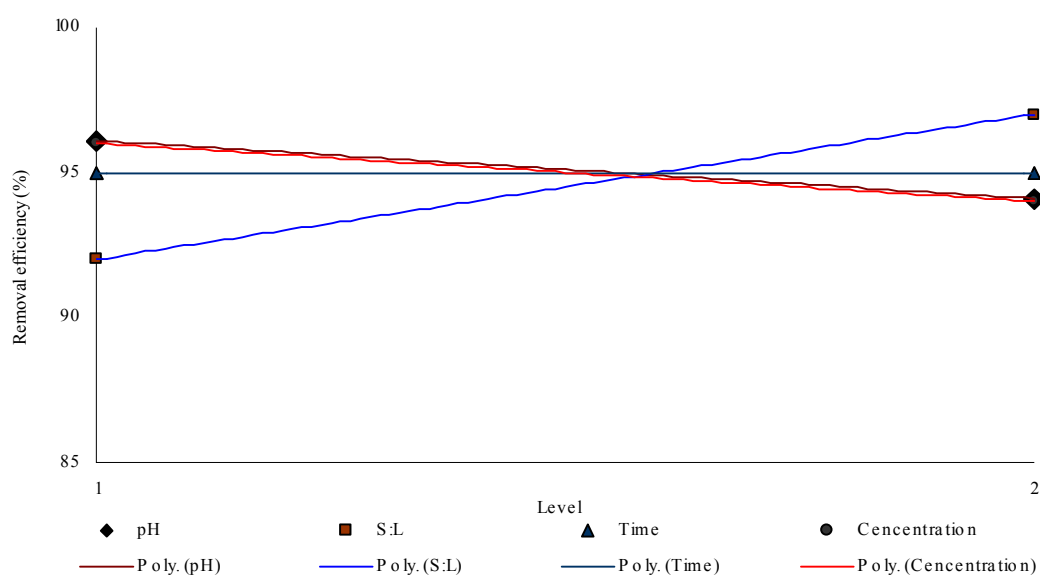
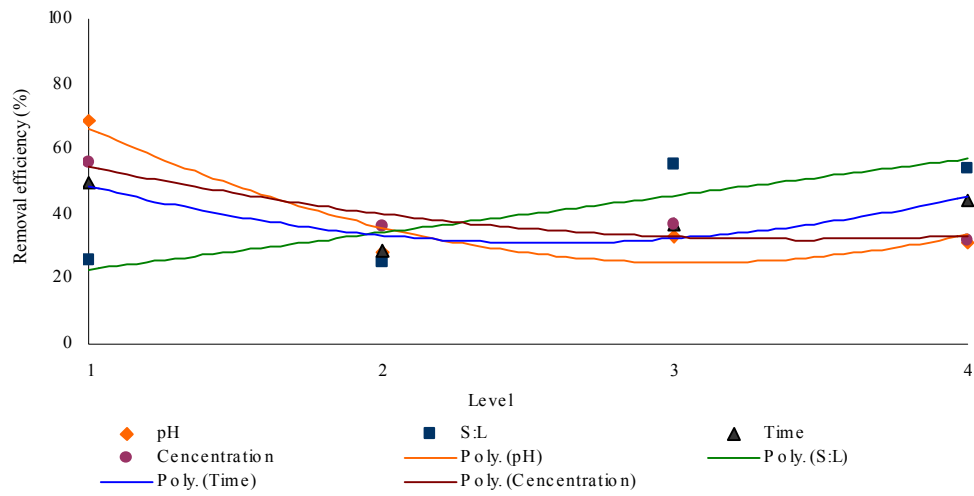Fig. 4: Average effects of experimental parameters on Cd removal

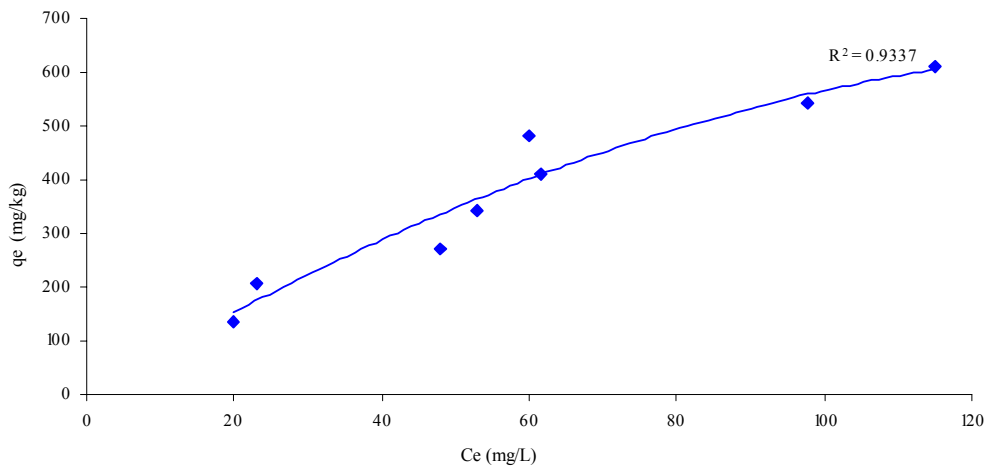Fig. 5: Average effects of experimental parameters on HA removal

Fig. 6: Adsorption isotherm for the sorption of Cd on nanozeolite A
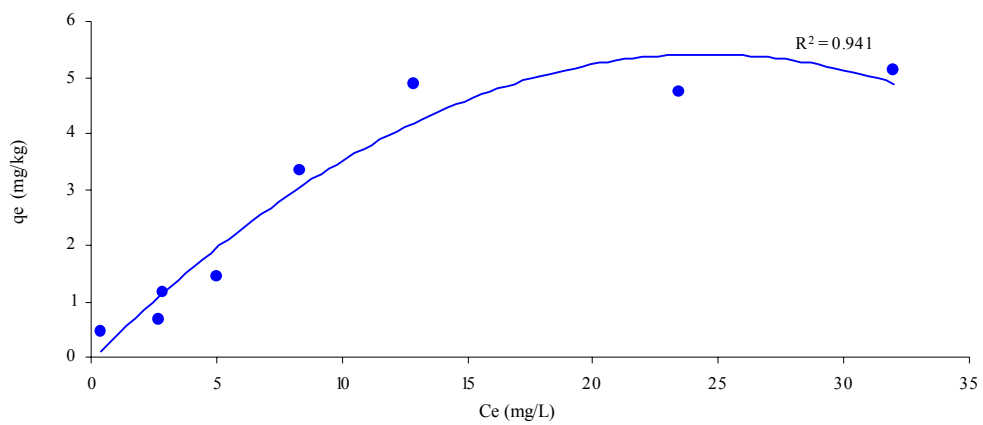

Fig. 7: Adsorption isotherm for the sorption of HA on nanozeolite A

Effect of competitive ions

The presence of competitive ions affects the sorption of cadmium. For example calcium could compete with cadmium sorption; and cadmium and chromate could compete with humic acid sorption (Barros *et al., 2003* ; Chandra Rao *et al., 2006;* Terdkiatburana *et al., 2008*). The effect of calcium competition with cadmium was investigated by adding 100, 200, 500, 1000, 2000 and 1000 mg/L to a solution containing 100 mg/L of Cd. Results showed that there is no competition in cadmium sorption and there is no change in adsorption by increase of competitive ion calcium up to 10,000 mg /L. The effect of the cadmium and chromate on humic acid removal was investigated by adding 0.05, 0.1, 0.15, 0.2, 0.25 and 0.3 ppm of chromate and 0.01, 0.05, 0.1, 0.15, 0.25, 0.3 ppm of cadmium to a solution containing 10 ppm of HA. Results showed that there is no competition between HA sorption and the presence of competitive ions.

Sorption isotherm

The sorption isotherms for the removal of Cd and HA from aqueous solutions onto nanozeolite A is shown in Figs. 6 and 7, respectively. The isotherms are regular, positive, and concave with respect to the concentration axis. These results show efficiency of nanozeolite A for cadmium removal from aqueous solution. The

sorption studies were carried out at 298K to determine the sorption isotherms. The Langmuir and Freundlich isotherms for the sorption of the cadmium on the prepared zeolite material are presented in Figs. 8-11, respectively.

The isotherm parameters were evaluated using Langmuir and Freundlich isotherm models. The Freundlich equation can 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 straight lines obtained for the two sorption isotherms indicate that the sorption of HA and Cd fits with two investigated isotherm models. The corresponding Langmuir and Freundlich parameters along with correlation coefficients are given in Table 5. The slope of the Freundlich isotherm was more than Langmuir isotherm, hence, sorption isotherm fits better with Freundlich model.

Several investigations have been conducted to obtain adsorption capacity of Cd and HA on natural zeolite. Chandra Rao *et al.* (2006) reported that adsorption capacity of cadmium with an initial concentration of 25 ppm is 0.088 mmol/g with zeolite 4A and 0.086 mmol/g with zeolite 13X. Wang *et al.* (2006) reported a fulvic acid adsorption capacity of 2 mg/g by clinoptilolite. Kaneco *et al.* (2003) found that synthetic
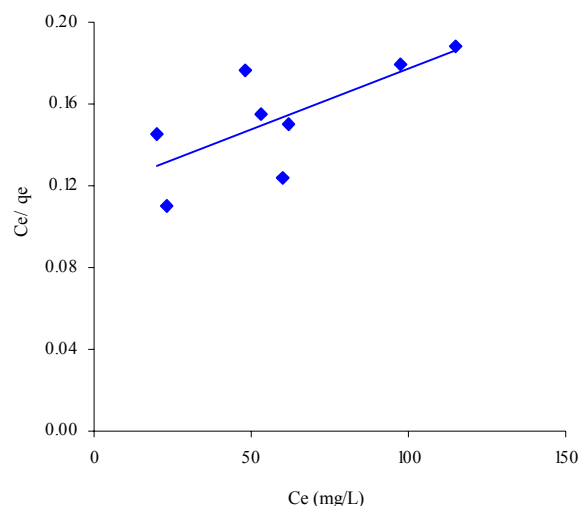

Fig. 8. Linear plot of Langmuir isotherm for the adsorption of Cd on nanozeolite A
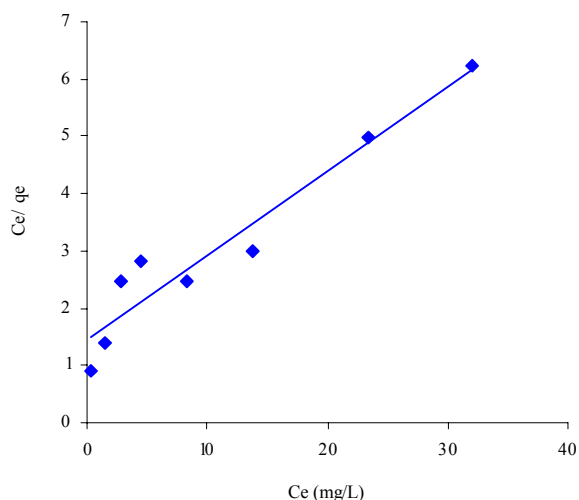

Fig. 9. Linear plot of Langmuir isotherm for the adsorption of HA on nanozeolite A

Table 5: Isothermal parameters of cadmium adsorption

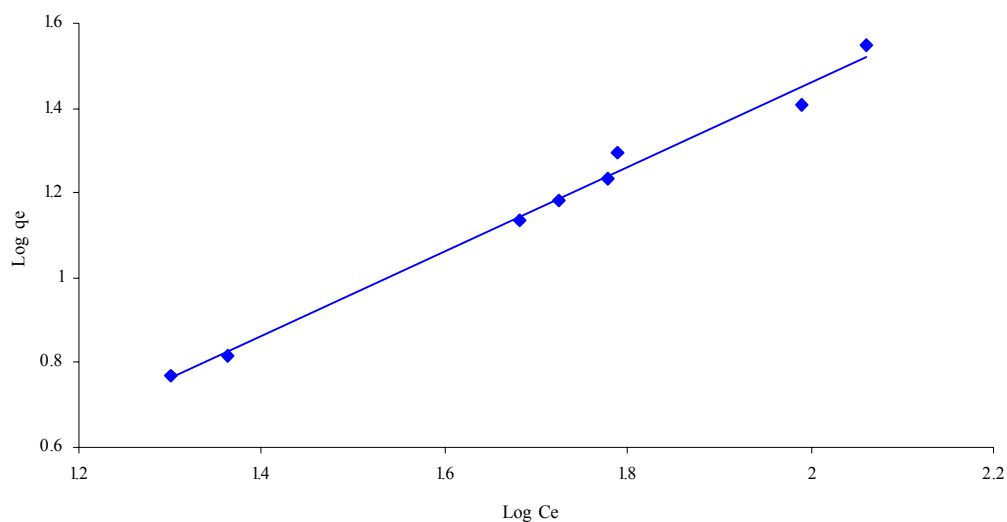|	Langmuir isotherm			Freundlich isotherm		
	Q_m (mg/g)	K_L (/mg)	R^2	1/n	K_F (mmol/g)	R^2
Cd	1666.67	0.0051	0.85	1	0.2857	0.99
HA	6.75	0.1039	0.9281	0.5951	0.760	0.9631

Fig. 10: Linear plot of Freundlich isotherm for the adsorption Cd on nanozeolite A
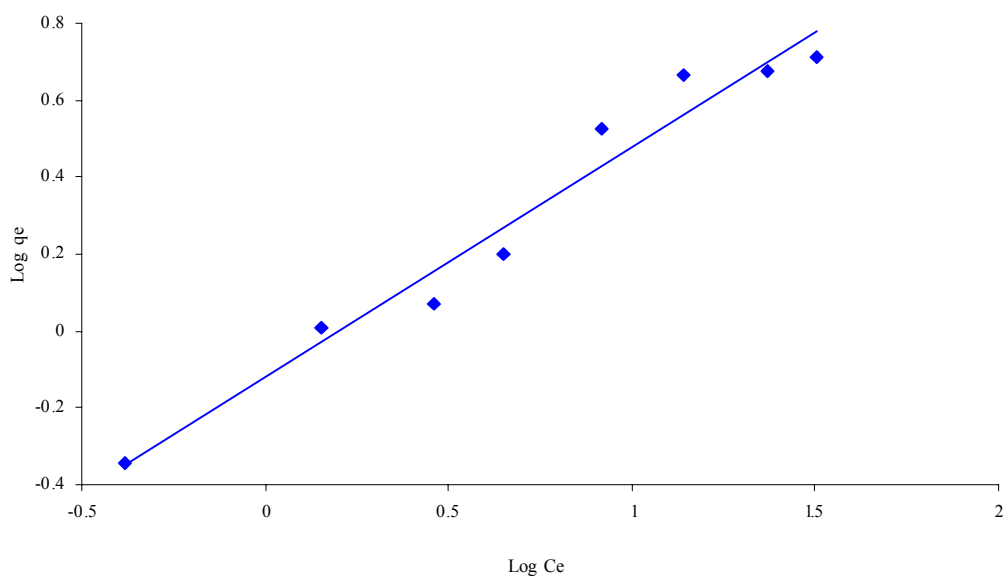

Fig. 11: Linear plot of Freundlich isotherm for the adsorption HA on nanozeolite A

zeolite and molecular sieve 5A exhibited low adsorption (< 0.03 mg/g) for fulvic acid.

Based on results (Table 4), sorption capacity of modified nanozeolite A is 0.286 mmol/g, i.e. more than three times for Cd sorption. This capacity is much higher than what was reported by Gupta and Bhattacharyya (2008) who showed an adsorption capacity of 6.8–11.5 mg/g (Kaolinite) and 21.1–31.1 mg/g (montmorillonite): 1666.67 mg/g by modified nanozeolite A. Also, HA adsorption on nanozeolite A is much higher in this study. It should be mentioned that unmodified nanozeolite A used in this study could remove only 16.7 % of HA at optimum conditions.

CONCLUSION

The purpose of this work was to study the possibility of removing Cd and HA from aqueous solutions through sorption by surface modified nanozeolite A. We assumed that zeolite modification could enable nanozeolite to adsorb non-ionic species such as HA, which would lead to a considerable decrease in its concentration.

The data reported here, show that nanozeolite A is an effective sorbent for removing Cd and HA from aquatic solutions. The sorption capacity of nanozeolite was higher than the reported value for other zeolites. Equilibrium studies were conducted for the adsorption of Cd and HA from aqueous solutions by surface modified nanozeolite A. The adsorbed amounts of HA increased with a decrease in pH and was reach to maximum at pH value of 3 and the highest cadmium sorption occurred at pH of 6. The equilibrium data have been analyzed using Langmuir and Freundlich isotherm models, and results showed that sorption of Cd and HA fit better to Freundlich isotherm model. Furthermore, the results showed no competition between Cd and HA sorption and the competitive ions. Regarding high efficiency of surface modified nanozeolite A in removing various contaminants from aqueous solutions and presence of natural zeolite resources in Iran and possibility of economic production of nanozeolite, it could be planned to use nanozolite potential to economic polluted water treatment by establishing these particles onto various beds such as polymeric membranes.

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