Abstract

High concentrations of nitrates in water can have a number of effects on human and aquatic health, therefore, control levels of nitrates are essential. In this work, adsorption of nitrate on beads of chitosan and zeolite composites were investigated. Accord to Transmission Electron Microscopy results, the employed zeolite has clinoptilolite and calcite with 50-870 nm particle size. The association between chitosan and zeolite was also verified by chemical and morphological characterizations. Results showed chitosan/acid modified natural zeolite composite beads (Ch/AMZ) exhibited higher nitrate adsorption than other ones. The adsorption of nitrate on Ch/AMZ as a function of pH, contact time, and bead concentration was optimized by a response surface method using batch experiments. According to the results, at the computed optimum operating conditions the maximum nitrate removal efficiency, 98.2% with Ch/AMZ and adsorption capacity, 22.48 mg g^{-1} were got. The presented nitrate removal technique with the proposed eco-friendly adsorbent can be considered as a very important approach for removing nitrate from drinking water and the possibility of using it on an industrial scale as a green and economic method for water and wastewater treatment.

Keywords: Adsorption; Nitrate; Chitosan; Sabzevar zeolite; Response Surface Method.

1. INTRODUCTION

Due to the increasing population of the world and the growing need for water, the exploitation of groundwater resources and saline water have been a necessity in recent decades [1, 2]. Since high nitrate concentration in drinking water can be harmful to health, especially for fetuses and infant, nitrate removal from groundwater resources is one of the essential needs in rural and some urban areas [3].

Technologies that are being used for the removal of nitrate include reverse osmosis [4], electro dialysis [5, 6], ion exchange [7, 8] and adsorption [9]. Among several technologies applied for nitrate removal, adsorption by sorbents (synthetic, bio and mineral sorbents) is one of the most effective because the technique uses equipment that is easily accessible, not energy-consuming, and straightforward to use and inexpensive [9-12]. Activated carbon [13, 14], Red mud [15], agriculture wastes [16-18], and biopolymers [11, 19, 20] were used to remove nitrate.

Chitosan is a low-cost biopolymer that found in the exoskeleton of crustaceans like crabs [21]. Reportedly, several studies focused on chitosan as an adsorbent because of its non-toxicity and biodegradability [9]. The chitosan amine and hydroxyl groups make it a promising material for nitrate sorption [22]. Using chitosan hydrogel beads is a method for obtaining nitrate from aqueous solutions [22-25]. However, chitosan dissolves easily in acidic wastewater, and its mechanical properties are weak, which bring limits on its application in wastewater treatment. Because of physical and chemical interactions between inorganic and organic components, chitosan's mechanical properties can be enhanced when it is combined with inorganic components [26], such as bentonite [27, 28], montmorillonite [29, 30], silica [31, 32], activated clay [33, 34], alumina [35], perlite [36], and zeolite [37-43].

Zeolites have also received more attention due to their many advantages such as easy access, low-cost, easy separation, recyclability and reuse. Actually, due to strong mechanical stability of zeolites, the chitosan mechanical strength and adsorption performance regarding different pollutants can be enhanced by synthesizing composites of chitosan/zeolite [37-44].

The novelty of the present study is that low-cost composite beads comprising the chitosan and modified Sabzevar zeolite was used as adsorbent in nitrate removal processes for the first time and optimal conditions were determined by response surface methodology (RSM).

2. MATERIALS AND METHODS

2.1. Materials

Chitosan with 99.95% purity and Hexadecyltrimethyl ammonium bromide (HDTMA-Br) were purchased from Sigma Company. The natural zeolite was prepared from a mineral deposit Chah-e Talkh village in Sabzevar town, North East of Iran.

2.2. Zeolite-modification

For the first, zeolite rock was crushed by a ball mill for 3 h at 500 rpm and then zeolite powder was washed with distilled water and dried, zeolites powder was stored in the desiccators for the next stages. The zeolite powder (Z) was activated by soaking into hydrochloric acids according to the following condition: 10 g of zeolite powder and 500 mL of HCl solution (1 N) were stirred at 150 rpm and 60°C for 24 h. Then the prepared mixture was centrifuged, and the solid powder was washed with distilled water to attain the neutral pH. The absence of Cl^- in the solid powder was confirmed by $AgNO_3$ solution 0.1mol/dm^3. The sample was dried in oven at 60°C overnight [45]. The prepared acid modified natural zeolite is named as AMZ. 10 g of zeolite powder and 100 mL of HDTMA-Br solution at the concentration 30 mmol L^{-1} were stirred at 150 rpm and 30°C for 24 h. Then centrifuged, and the solid residue was rinsed with distilled water two times and dried at 60°C overnight [46, 47]. The surfactant modified natural zeolite is named as SMZ.

2.3. Chitosan/zeolite composite beads synthesis

One gram of chitosan was added to 30 ml of 5% acetic acid solution to prepare chitosan solution.Then, this solution of chitosan and acetic acid were stirred by using a magnetic stirrer at 200 rpm for 4 hr to make sure complete dissolution of chitosan. The solution were injected into a 500 mL flask containing NaOH (0.50M) using a syringe pump equipped with a needle with 0.337 mm inner diameter and stirred at 150 rpm for 3 h to prepare the chitosan beads. The size of the beads was controlled using air compressor that injects high velocity air (9.6 m/s) into the needle head (Fig. 1). The beads formed were left for 30 minutes for proper formation of the beads, then filtered and washed several times with deionized water to reach a neutral pH.

To prepare chitosan/zeolite composite beads, 2.0 g chitosan were added to 60 ml of 5% acetic acid solution. After chitosan and acetic acid were mixed by magnetic stirrer, 1.0 g zeolites (Z or AMZ or SMZ) was added into this solution and stirred by using magnetic stirrer at 200 rpm for 4 hr to make sure complete dissolution of chitosan. The composite beads suspension were injected into a 500 Ml flask containing NaOH (0.50M), based on the method presented in the previous paragraph. The prepared chitosan/zeolite composite beads are named as Ch/Z, Ch/AMZ and Ch/SMZ.

2.4. Natural zeolite, chitosan, and chitosan/zeolite composite beads characterization

Natural zeolite was rinsed with distilled water and crushed by a ball mill for 3 h at 500 rpm then, the prepared zeolite powder was dried at 60°C for 24h. In order to identify and describe the composition, structure, elemental analysis, and the percentage of minerals of the Sabzevar natural zeolite, Transmission Electron Microscopy (TEM) (CM120, Philips), X-ray fluorescence (XRF) (CE3021, CECIL Instruments) and X-ray diffraction (XRD) (X' Pert PW 3040/60, Philips) were used. The functional groups present in the Chitosan, Sabzevar natural zeolite, surfactant, Ch/Z, Ch/AMZ, and Ch/SMZ in dried state were also recorded by a Fourier-Transform Infrared Spectroscopy (FTIR) (Shimadzu, Japan). The Brunauer-Emmett-Teller (BET) method was used to determine surface area and total pore volume for each composite beads by BET instrument (BELSORP mini II, BEL). Field Emission Scanning Electron Microscopy (FESEM) (MIRA III, TESCAN, Czech Republic) was used to studying the size and morphology of composite beads.

For measure the solubility of the beads in different acid solutions, 1.0 g of beads was put in 50 mL flasks containing various types of acid solutions (0.1 and 1.0 N HCl and 5% acetic acid and were shaking with 150 rpm at 25°C for 24h. A vacuum filtration technique used to separate beads from the solution and the weight of the remaining beads was measured. The beads were considered soluble when the weight loss was greater than 5%.

2.5. Selection of the "best" beads

In the first stage of adsorption experiments, four types of beads (Ch, Ch/Z, Ch/AMZ, and Ch/SMZ) were used in similar operating conditions (50 mg L^{-1} nitrate-nitrogen (NO_3-N), 12 g L^{-1} beads concentration, 1h contact time, 25 °C, 150 rpm, and pH =7). After adsorption process, the adsorbent particles were separated from the suspensions by filtration and the residual concentration of NO_3-N was determined using the UV-Vis spectrophotometer at 220 nm. In order to decrease the experimental errors, all tests were conducted three times, and the mean experimental data was reported.

2.6. Response surface method (RSM)

The purpose of the optimization of the nitrate adsorption process is to maximize removal efficiency. Nitrate adsorption process depends on different variables. Therefore, a large number of experiments should be performed. Using an experimental design, the number of experiments is reduced In this research, RSM was utilized to explore the effect of effective variables [45, 48]. According to the preliminary adsorption experiments, it was found that the pH, contact time and the dose of adsorbent are the most important independent variables on the nitrate adsorption from aqueous solution. Level of variables were selected based on primary studies and have been shown in Table 1. Experimental design and data analysis was conducted using Design Expert. The independent variables for nitrate adsorption process (initial concentration 50 mg L^{-1} NO_3-N) were optimized RSM. Central composite design (CCD) was employed to optimize variables and predict the best value of the response using the Design Expert software version 7.0.

2.7. Adsorption isotherms

The adsorption isotherm experiments were conducted to evaluate removal efficiencies and maximum adsorption capacities. To investigate the adsorption isotherms, a series of bottles containing nitrate solutions with different NO_3-N concentration (C_o) between 10-200 mg L^{-1} and Ch/AMZ with 5.5 g L^{-1} concentration was kept at 25°C, 150 rpm, and pH= 6 until the equilibrium concentration is maintained. Agreement of experimental values with different adsorption isotherms were examined. The concentrations of the nitrate in the adsorbent phase at equilibrium was determined according to the following equation:

$$q_e = \frac{(C_o - C_e) \times V}{M} \tag{1}$$

In equation 1; qe (mg g−1) is the concentrations of the nitrate in the adsorbent phase at equilibrium (mg/g), Co and Ce (mg L−1) are the initial and equilibrium NO3-N concentration. V (L) is the volume of aqueous solution, and M (g) is the adsorbent mass [49].

3. RESULTS AND DISCUSSIONS

3.1. Natural zeolite, chitosan, and chitosan/zeolite composite beads characterization

According to the XRF results in Table 2, the mass ratio of SiO_2/Al_2O_3 in the natural zeolite is equal to 6.55 and 15.62% of loss on ignition (L.O.I.) that indicate the percentage of volatile components, mainly crystal bound water and organic carbon (as CO_2). XRD results show, the sabzevar zeolite has 76% clinoptilolite and 24% calcite. According to the TEM images in Fig. 2, the range of particle size of sabzevar zeolite was from 50 to 900 nm. The solubility of the various beads in acid solution is presented in Table 3. As can be seen, the addition of zeolite to chitosan reduces the solubility of chitosan in acidic solutions, so the produced composite beads are more stable than chitosan beads to treatment acidic effluents. The average diameter of wet non-spherical chitosan and chitosan/zeolite beads were 0.500 ± 0.080 and 0.550 ± 0.085 mm respectively.

According to the BET results in Table 4, The specific surface area of the natural zeolite (Z) increased after acid treatment from 22.52 to 41.74 $m^2 \cdot g^{-1}$. The greatest pore volume belonged to the AMZ with 0.1194 cm^3/g. The surface area and the total pore volumes of SMZ were 16.92 m^2/g and 0.0513 cm^3/g. The smaller surface area of SMZ compared with sabzevar zeolite represented the aggregation of the surfactant molecules on natural zeolite. The BET result shows that the surface area of Ch, Ch/Z, Ch/AMZ, and Ch/SMZ beads were found to be 18.92, 20.08, 38.04, and 15.72 m^2/g, respectively. The increased in the

BET surface area of comosite beads (Ch/Z, Ch/AMZ, and Ch/SMZ) than chitosan beads maybe attributed to the incorporation of more functional group.

According to the FTIR spectrum of zeolite (Fig. 3), the peaks of the broad 3471 and 1629 cm-1 correspond to vibration of water associated with K and Na in the channels and cavities of sabzevar zeolite The 1066, 669-678, 555 and 461 cm^{-1} bands correspond to Si-O stretching, Al-O-Si, Al-O and Si-O-Si bending vibrations in zeolite, respectively. The peaks of the broad 2354 cm^{-1} correspond to the CO_2 molecules in the atmosphere. The peak at 3431 cm-1 in FTIR spectrum of chitosan (Fig.3) correspond to a stretching vibrations of the hydroxyl group. The vibration band at 2889, 1425 and 1350 cm^{-1} in the FTIR spectrum of chitosan are due to the C-H stretching vibrations and those at 1155 cm^{-1} and 1081 cm^{-1} are due to asymmetry C-O-C stretching vibrations of CH-O-CH and C-O stretching vibration of the CH-OH, respectively. Three characteristics of adsorption bands observed in chitosan at 3400, 1652 and 1323 cm^{-1}, as in the given order are due to the N-H, amid I, and amid III groups.

Si-O stretching vibration, Al-O-Si, Al-O and Si-O-Si bending vibrations in zeolite have shifted to 1064, 547, 676-692 and 464 cm^{-1} in Ch/Z (Fig.3). The peak at 719 cm^{-1} represents the stretching vibration of Si-C; this peak indicated bonding between chitosan and zeolite. The peaks of the N-H, amid I and amid III groups present in Ch/Z have shifted to 3400, 1650 and 1338 cm^{-1}. The peaks of the broad 1631, 1334, 1051, 790 cm^{-1} in FTIR spectrums of the AMZ correspond to Al-H, Al-OH or Al-OH_2, Si-O and Si-O-Si or Al-O-Al, respectively. Compared with the unmodified zeolite, bands of the AMZ at 1629 and 1334 cm^{-1} decreased sharply and the bands at 1051 and 790 cm^{-1} increased slightly. These are the powerful evidences for the dealumination process. For Ch/AMZ (Spectrum in Fig. 3) the bands corresponding to the Al-H, Al-OH or Al-OH_2, Si-O have shifted to 1652, 1029, 1041 cm^{-1}. The peaks of N-H, amid I and amid III groups in chitosan have shifted to wave numbers centered at 3425, 1652 and 1298 for Ch/AMZ.

The peaks of the broad 2850, 2918 cm^{-1} correspond to C-H stretches vibration modes of the methylene groups in surfactant (Fig.3). The surfactant modified zeolite, in contrast to unmodified zeolites has new bands at 2923 and 2856cm^{-1}, attributed to the antisymmetric CH_2 and symmetric CH_2, C-H stretching vibration modes of the methylene groups, respectively, which suggests that the surface of the natural zeolite is covered by the alkyl ammonium bromides. For Ch/SMZ, the bands corresponded to the antisymmetric CH_2 and symmetric CH_2, C-H stretching vibration modes of the methylene groups in SMZ have bands at 2923 and 2858 cm^{-1} and the N-H, amid I, and amid III groups present in chitosan peaks have shifted to wave numbers centered at 1303, 1650, 3413 cm^{-1}. The FTIR spectrum of Ch/Z and Ch/AMZ showed a broad band around 3500-3100 $cm^{-1,}$ showing enhanced hydrogen bonding. Absence of these bonds in the FTIR spectra of Ch/SMZ showed the formation of an electrostatic bond.

According to the results of FE-SEM in Fig. 4 , chitosan particles are observed on the surface of Ch/Z, Ch/SMZ and Ch/AMZ. According the element mapping results (Fig. 5) the zeolite was dispersed homogeneously in Ch/Z, Ch/SMZ and Ch/AMZ samples.

3.2. Selection of the “best” beads

Results of the nitrate removal from aqueous solution using the various beads showed modifications of zeolite increased the removal efficiency (Table 5). When natural zeolite was modified with acid, adsorption of the hydrogen ion on the zeolite structure led to the surface protonation. Protonation by acid is the main reason for dealumination or hydrolysis of the Al–O–Si that causes an increase in the Si/Al ratio and Si–OH groups in zeolite. Si–OH groups as the hydroxyl groups in zeolite are active sites for hydrogen bonding with nitrate ions, thus, the modification of zeolite by acid led to an increase in the nitrate removal efficiency. When natural zeolite was modified with surfactant, the surface charge changed from a net negative to a positive charge. Thus, electrostatic forces between the positively charged zeolite and negatively charged nitrate anions caused improve removal efficiency of nitrate. According to the results that presented in Table 5, the synthesized Ch/AMZ in this work showed the highest nitrate removal efficiency. Thus, the Ch/AMZ was selected for further nitrate removal studies in the present work.

3.3. Response surface method (RSM)

The effect of pH, contact time and beads concentration on the nitrate removal efficiency was investigated by CCD method. The observed results are presented in Table 6. According to the results of the analysis of variance (ANOVA) using Design-Expert software, The quadratic and linear model was selected as the best model to fit the removal efficiency and adsorption capacity.

In this model for removal efficiency, the coefficient of determination (R^2) is 0.9321and the value of the adjusted coefficient of determination (R^2Adj) is 0.8709, and for adsorption capacity R^2 is 0.9883 and R^2Adj is 0.9778, these values show good agreements between the model prediction and the experimental data. As seen from Table 7, C, B2, and C2 for removal efficiency and BC and B2 for adsorption capacity are introduced as important parameters of the model (P-values<0.0500). According to the regression coefficients for actual factors (positive sign), the removal efficiency increases by increasing the bead concentration, contact time and pH; these results are similar to what was observed by Yunan Gao et al (2020) for bead concentration and contact time [50].Also, the high value of pH and the bead concentration coefficients indicated that these parameters have the greatest effect on the removal efficiency.

In the fitted model for adsorption capacity, the positive sign of the regression coefficients of contact time and pH indicates that adsorption capacity increases by increasing these variables. On the other, adsorption capacity decreases with increasing beads concentration. Also, the value of the coefficients indicated that the bead concentration parameter had the greatest effect on the adsorption capacity.

Table 8 presents a number of proposed solutions for optimizing the removal efficiency and adsorption capacity in different values of variables by Design Expert software. At the computed optimum operating conditions for removal efficiency (pH=7.75, 72.60 min contact time and 3.88 g L^{-1}), the maximum nitrate removal efficiency, 98.2% with Ch/AMZ was got and 99.3001% was predicted by the software. Also, at the optimum operating condition for adsorption capacity (pH= 4.30, 88.57 min contact time and 1.33 g L^{-1} beads concentration), the maximum adsorption capacity, 22.48 mg g^{-1} was got and 22.75 mg g^{-1} was predicted by the software. The close agreement of the observed and predicted response confirms the accuracy of the proposed model.

One of the things that should be considered in the design of any absorbent, the adsorption capacity and removal efficiency of that adsorbent compared to other common adsorbents. The maximum removal efficiency and adsorption capacity obtained here can be compared with the values mentioned in literature.

For removal efficiency, this value is 70.2% of chitosan cross-linked zeolite molecular sieve [50], 90% of Chitosan/polystyrene/zinc [51]. For adsorption capacity, this value is 23.58 for Chitosan/zeolite Y/nano ZrO_2 [43], 16.39 for Modified steel slag [52], 14.76 for HTDMA modified bentonite [53] and [81], as reported by other researchers. Therefore, the synthesized adsorbent has a significant adsorption capacity and removal efficiency, compared to another adsorbent.

Figs. 6-7 show the interaction between two parameters in the form of response surface 3D plot and contour plot for removal efficiency and adsorption capacity when the other independent variable is kept constant at median level. Fig. 6 a-b) shows the interaction between pH and contact time on the removal efficiency where bead concentration is kept constant at 3 g L-1. According to the results, the removal efficiency increases with increasing contact time, but increasing pH not have a significant effect on the removal efficiency, these results can also be seen in the figure 6 c-d). Fig. 6 e-f) shows that the removal efficiency increases with increasing bead concentration and contact time. At high bead concentration, the reaction efficiency increases with contact time with a very sharp slope. Fig. 7 a-b) shows the interaction between the parameters of pH and contact time on the adsorption where bead concentration is kept constant at their median level (3 g L^{-1}). This curve shows when the pH is constant, the adsorption capacity increases with increasing contact time and pH. Fig. 7 c-d) shows reducing bead concentration increases adsorption capacity and the trend of changes in adsorption capacity with increasing bead concentration is almost the same at different pH. Fig. 7 e-f) shows the interaction between contact time and bead concentration on the adsorption capacity. According to the graph, at higher beads concentration, increasing contact time doesn't have a significant effect on the adsorption capacity; however, at low concentration, increasing contact time increases the adsorption capacity.

3.4. Adsorption isotherms

Table 9 shows equilibrium concentration and adsorption at different initial concentrations of NO_3-N. Eq. 1 was applied to describe the Linear isotherm:

$$q_e = aC_e + b \tag{1}$$

In Eq. 1 “a” and “b” is the Linear constants, “C_e” denotes the concentration of nitrate in aqueous solution at equilibrium conditions with scale mg/L; “q_e” means the amount of nitrate adsorbed at equilibrium time (mg/g).

Eq. 2 was applied to describe the Langmuir isotherm:

$$:q_e = \frac{q_m b C_e}{[1+bC_e]} \tag{2}$$

Where “C_e” denotes the concentration of nitrate in aqueous solution at equilibrium conditions with scale mg/L; “q_e” means the amount of nitrate adsorbed at equilibrium time (mg/g); “q_m” is the maximum adsorption capacity of the adsorbent; and “b” is the constant for the binding energy of the adsorption system.

Eq. 3 describes the Freundlich model. “K_f” and “n” in this equation are Freundlich constants

$$q_e = K_f C_e^{1/n} \tag{3}$$

The parameters of Linear, Langmuir and Freundlich models can be determined by regression of the experimental data (Table 9). According to the model parameters and correlation coefficients (R^2) (Table 10), high value of R^2 of the Freundlich isotherm (0.9732) represents better fitness of this model to the experimental data compared to other models. Table 11 show Comparative evaluation of the maximum nitrate adsorption capacities for adsorbents reported in previous literatures and this work

4 CONCLUSION

This study showed that chitosan is successfully mixed with Sabzevar zeolite, acid modified Sabzevar zeolite, and surfactant modified Sabzevar zeolite and formed chitosan/zeolite composite beads. The adsorption study showed that chitosan /acid modified zeolite composite beads could be effectively used to remove nitrate. The adsorption process depends on various parameters, such as pH, contact time and bead concentration. The optimum operating conditions to reach the maximum removal efficiency and adsorption capacity was determined by RSM design. According to the results, maximum nitrate removal of 97.32% and adsorption capacity of 5.62 mg g^{-1} were achieved at optimum operating conditions and the Freundlich isotherm model was superior to the other alternative models for the description of Ch/AMZ adsorption isotherm in the presence of nitrate compounds. As a final conclusion, the chitosan/Sabzevar zeolite composite beads synthesized in this work can be successfully used as a economical, eco-friendly adsorbent for removal of nitrate pollution.

Nomenclature

Acid modified natural zeolite	AMZ
Central composite design	CCD
Chitosan beads	Ch
Chitosan/acid modified natural zeolite composite beads	Ch/AMZ
Chitosan/ natural zeolite composite beads	Ch/Z
Chitosan/surfactant modified natural zeolite composite beads	Ch/SMZ
Field Emission Scanning Electron Micrographs	FE-SEM
Fourier-Transform Infrared Spectroscopy	FTIR
Natural zeolite	Z
Response Surface Methodology	RSM
Surfactant modified zeolite	SMZ
Transmission Electron Microscopy	TEM
X-Ray Diffraction	XRD
X-Ray Fluorescence	XRF

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Conflict of Interest:

The authors declare that they have no conflict of interest

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Table 1

The levels of the affective variables for nitrate removal from aqueous solution.

Variables	Variable code	Coded value				
		(-1.683)	(-1)	(0)	(+1)	(+1.683)
pH	A	3.64	5	7	9	10.36
Contact time (min)	B	19.55	40	70	100	120.45
Bead concentration (g L^{-1})	C	1.32	2	3	4	4.68

Table 2

The XRF results of the natural zeolite.

Elements	SiO_2	Al_2O_3	Na_2O	MgO	CaO	K_2O	TiO_2	MnO	P_2O_5	Fe_2O_3	SO_3	LOI
Perception	62.68	9.57	2.43	0.77	5.51	1.76	0.17	0.09	0.03	0.041	0.00	15.62

Table 3

Solubility of the various beads in various acid solutions.

Acid solution	Ch	Ch-Z	Ch-AMZ	Ch-SMZ
1.0 N HCl	soluble	soluble	soluble	soluble
0.1 N HCl	soluble	insoluble	insoluble	soluble
5% acetic acid	soluble	insoluble	insoluble	insoluble

Table 4

The BET results of the various zeolite and beads.

Beads	Surface Area (m^2 g^{-1})	Total pore volume (cm^3 $.g^{-1}$)
Z	22.52	0.0807
AMZ	41.74	0.1194
SMZ	16.92	0.0513
Ch	18.92	0.0612
Ch/Z	20.08	0.0845
Ch/AMZ	38.04	0.9581
Ch/SMZ	15.72	0.0501

Table 5

The comparison of the removal nitrate by different beads.

Beads	Removal efficiency (%)
Ch	70.5%
Ch/Z	73.5%
Ch/AMZ	95.0%
Ch/SMZ	88.0%

Table 6

Central Composite Design matrix for the experimental design with corresponding results.

Trail	pH	Contact time	Bead concentration	Removal efficiency (%)	Adsorption capacity (mg g^{-1})
1	9.00	40.00	2.00	76.1	19.02
2	5.00	100.00	2.00	83.8	20.95
3	9.00	100.00	2.00	91	22.75
4	7.00	120.45	3.00	99.3	16.48
5	5.00	40.00	2.00	72.88	18.22
6	7.00	70.00	3.00	94.4	15.73
7	7.00	70.00	4.68	98.7	10.55
8	7.00	70.00	3.00	94.9	15.82
9	5.00	100.00	4.00	95.7	11.96
10	7.00	70.00	3.00	98.9	16.55
11	5.00	40.00	4.00	89.9	11.25
12	7.00	70.00	1.32	59.4	22.55
13	7.00	19.55	3.00	82.4	13.73
14	10.36	70.00	3.00	97.8	16.30
15	9.00	100.00	4.00	98.6	12.26
16	3.64	70.00	3.00	95.4	15.90
17	7.00	70.00	3.00	98.7	16.45
18	7.00	70.00	3.00	99.3	16.52
19	7.00	70.00	3.00	99.3	16.47
20	9.00	40.00	4.00	84.1	10.51

Table 7

ANOVA of second-order polynomial models for removal efficiency and first-order polynomial models for adsorption capacity.

	Removal efficiency (%)						
Term	Sum of Squares	df	Mean Square	F-value	p-value	Regression coefficients for actual factors	
Model	2124.14	9	236.02	15.24	0.0001		Significant
A	19.60	1	19.60	1.27	0.2868	3.527	
B	0.055	1	0.055	0.0036	0.9535	0.491	
C	609.79	1	609.79	39.39	< 0.0001	58.212	
AB	20.10	1	20.10	1.30	0.2811	0.026	
AC	22.18	1	22.18	1.43	0.2590	-0.832	
BC	3.81	1	3.81	0.25	0.6306	-0.023	
A^2	7.10	1	7.10	0.46	0.5136	-0.175	
B^2	107.90	1	107.90	6.97	0.0247	-0.003	
C^2	697.59	1	697.59	45.06	< 0.0001	-7.132	
Constant						-38.977	
Residual	154.83	10	15.48				
Lake of Fit	128.62	5	25.72	4.91	0.0528		Not significant
Pure Error	26.21	5	5.24				
Cor Total	2278.97	19					

	Adsorption capacity						
Term	Sum of Squares	df	Mean Square	F-value	p-value	Regression coefficients for actual factors	
Model	243.44	9	27.05	93.82	< 0.0001		Significant
A	1.01	1	1.01	3.51	0.0905	0.571	
B	1.20	1	1.20	4.17	0.0685	0.116	
C	0.37	1	0.37	1.28	0.2843	-1.94	
AB	0.52	1	0.52	1.79	0.2104	0.004	
AC	1.16	1	1.16	4.01	0.0731	-0.194	
BC	1.99	1	1.99	6.91	0.0252	0.004	
A^2	0.044	1	0.044	0.15	0.7035	-0.017	
B^2	2.38	1	2.38	8.27	0.0165	-0.014	
C^2	0.052	1	0.052	0.18	0.6810	-4.516	
Constant						0.061	
Residual	2.88	10	0.29				
Lake of Fit	2.18	5	0.44	3.11	0.1196		Not significant
Pure Error	0.70	5	0.14				
Cor Total	246.32	19					

Table 8

A number of proposed solutions for optimizing the removal efficiency and adsorption capacity in different values of variables by Design Expert software.

	Proposed solutions for optimizing the adsorption capacity					Proposed solutions for optimizing the removal efficiency				
No	Independent variables code			Adsorption capacity	Desirability	Independent variables code			Removal efficiency	Desirability
	A	B	C			A	B	C		
1	7.60	73.53	1.54	22.75	1.000	7.75	72.60	3.88	99.3001	1.000
2	7.82	100.30	1.81	22.75	1.000	9.62	100.71	4.11	99.2999	1.000
3	9.99	107.71	2.02	22.75	1.000	4.22	93.87	3.60	99.3	1.000
4	10.19	67.06	1.63	22.75	1.000	10.18	83.74	2.83	99.3002	1.000
5	9.34	72.13	1.65	22.75	1.000	8.95	71.99	3.68	99.2998	1.000
6	8.26	96.67	1.82	22.75	1.000	8.96	81.47	3.97	99.3	1.000
7	6.48	85.67	1.57	22.75	1.000	4.30	76.31	3.84	99.2999	1.000
8	5.17	81.22	1.38	22.75	1.000	4.43	82.79	3.95	99.2999	1.000
9	3.95	97.98	1.34	22.75	1.000	7.59	114.69	2.83	99.3002	1.000
10	4.30	88.57	1.33	22.75	1.000	4.86	103.88	3.43	99.2999	1.000

Table 9

Variation of equilibrium concentration and adsorption capacity at different initial NO_3-N concentration for nitrate adsorption from aqueous solution by Ch/AMZ beads.

C_0 (mg L^{-1})	C_e (mg L^{-1})	q_e (mg NO_3-N /g beads)
10	0.5	1.7272
25	4	3.8181
40	8	5.8181
65	14	9.2727
80	17	11.4545
100	25	13.6363
120	28	16.7272
150	40	20.0000
180	50	23.6363
200	70	23.6363

Table 10

Model parameters and correlation coefficients (R^2) of Linear, Langmuir and Freundlich isotherms for NO_3-N adsorption from aqueous solution by Ch/AMZ beads

Isotherm model	Equation	Model parameters		R^2
Linear	$q_e = aC_e + b$	a	0.3426	0.8916
		b	4.4757	
Langmuir	$q_e = \frac{q_m bC_e}{[1 + bC_e]}$	q_m	22.026	0.8776
		b	0.0736	
Freundlich	$q_e = K_f C_e^{1/n}$	K_f	2.1607	0.9732
		n	1.71	

Table 11

Comparative evaluation of adsorption capacity of some different adsorbents based on chitosan for nitrate removal

Materials	Initial nitrate concentration	pH	Dose	Temperature	Contact time	Adsorption capacity	Reference
Chitosan-zeolite (Ch-Z)	3,100 mg/L	–	0.4 g/250 mL	4°C	72 h	37.2 mg/g	[24]
Chitosan-zeolite (Ch-Z)	620 mg/L	3	0.4 g/250 mL	20°C	72 h	45.8 mg/g	[24]
Chitosan/Zeolite/nano ZrO_2	20 mg/L	3	0.02 g/L	35°C	60 min	42.5%	[43]
Surfactant modified Sabzevar zeolite	50 mg/L	-	15 g/50 mL	30°C	10 min	0.34 mg/g	[54]
Chitosan-acid modified Sabzevar zeolite composite beads	200 mg/L	6	5.5 g/L	25°C	80 min	23.6363 mg/g	This work

Figure Captions:

Figure 1 Experimental set-up for production of chitosan/zeolite beads

Figure 2 TEM micrographs natural Sabzevar zeolite powder with different magnification

Figure 3 FTIR spectra of natural zeolite, chitosan, Ch/ Z, AMZ, SMZ, Ch/AMZ and Ch/ SMZ

Figure 4 Scanning electron micrographs of (FE-SEM) for Ch/Z, Ch/SMZ, and Ch/AMZ

Figure 5 Element mapping results for Ch/Z, Ch/SMZ, and Ch/AMZ

Figure 6 Response surface 3D plot and contour plot for the interaction of two parameters on the removal efficiency when the other parameters at the middle level

Figure 7 Response surface 3D plot and contour plot for the interaction of two parameters on adsorption capacity when the other parameters at the middle level