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Nitrate removal from aqueous solution: Screening of variables and optimization

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ABSTRACT

The adverse effects caused by the increase in nitrate concentration in drinking water have prompted researchers to find green and economical methods for nitrate removal. Mineral materials are suggested for this purpose due to their economic and environmental benefits. In this study, Iranian natural zeolite was used for this purpose. An organic surfactant, HDTMA-Br, was used to modify the natural zeolite. Fourier-transform infrared spectroscopy (FTIR) verified that the surfactant was loaded on the zeolite surface. The influence of various parameters on adsorption was studied using the Taguchi method. They were screened by Taguchi's L_8 array, and four significant variables were determined: mass of adsorbent, particle size, contact time, and competing anion concentration. The Taguchi L_9 array was used to determine the optimum condition of these significant variables. Analysis of the results showed that the concentration of the competing anion was the most significant variable on the nitrate adsorption by the surfactant modified zeolite (SMZ). In the optimum conditions, SMZ removed about 90% of nitrate from the aqueous solution obtained at a 20 mg/L initial nitrate concentration, 10 min contact time, 15 g adsorbent, and without any competing anion. The study of the adsorption isotherms showed that the nitrate adsorption process by SMZ from the aqueous solution fits well with the Freundlich and linear models.

1. Introduction

Nitrate ions are among the most significant pollutants of surface and underground water sources originating from human, industrial, and agricultural wastewater. Nitrate ions are an indicator of groundwater pollution. The adverse effects of nitrate in humans occur as a result of its regeneration by bacteria in the digestive system and its conversion to nitrite [1]. In addition, the high concentration of nitrates in surface waters leads to the phenomenon of eutrophication in reservoirs, eliminating aquatic life due to a lack of oxygen [2]. The most common methods available to reduce nitrate are biological process [3,4] dilution [5] chemical reduction [6], ion exchange [7], reverse osmosis [8], electro dialysis [8], adsorption [2,9], etc. In general, the key factors in choosing a method are its applicability, simplicity of design, and economic feasibility. The adsorption

process enjoys such advantages and is suitable for removing nitrate from aqueous solutions [1]. Zeolites are commonly used for removing pollutants from aqueous solutions. Due to their alumina silicate structure, they are charged negatively, so it is necessary to get treated by a cationic surfactant to make it possible to adsorb the anionic pollutants like nitrate, sulphate, etc. [11]. In the present study, the statistical design of experiments was used to optimize nitrate removal from the aqueous solution via natural Sabzevar zeolite as a new, available, and economical adsorbent. The important process parameters were screened and optimized by L8 and L9 Taguchi arrays, respectively.

2. Materials and methods

Natural clinoptilolite zeolite from the Chah-e-Talkh region of Sabzevar, Iran, was used in this study. Hexa decyl tri methyl ammonium bromide (HDTMA-Br, $CH_3 (CH_2)_{15}N (Br) (CH_3)_3$, ≥98%) was obtained from the Sigma Aldrich Company.

2.1. Natural Sabzevar zeolite characterization and surfactant modified zeolite preparation and characterization.

The natural zeolite was milled and sieved based on the ASTM American standards. After washing and drying the meshed samples, they were stored in a desiccator for the next stage of the procedure. In order to identify and describe the elemental composition of the minerals of the Sabzevar natural zeolite, X-ray fluorescence (XRF) (CE3021, CECIL Instruments) was used [12]. Table 1 presents the chemical composition of the natural zeolite obtained by XRF. The results show the main characteristic, i.e., the ratio of Si to Al, was equal to 6.59, which was the same as that reported in the research of Guan et al. [13].
Transmission Electron Microscopy (CM120, Philips) and Philips X-ray diffraction (X' Pert PW 3040/60) were used to identify and describe the structure and the percentage of minerals of the Sabzevar natural zeolite. The zeolites have a natural negative

charge because of the Al-substituted within its framework structure. There are numerous anionic contaminants, such as nitrate, arsenate, phosphorus, etc. Generally, anionic contaminants cannot be effectively adsorbed with natural zeolite. Therefore, the surface chemical characteristics of zeolite should be modified with a cationic surfactant, such as HDTMA-Br [11]. The surfactant modified zeolite (SMZ) sample was prepared by modifying natural zeolite with HDTMA-Br. For this purpose, 10g of natural zeolite and 50 mL of 60 m mole /I surfactant solution were stirred at 150 rpm at $70°C$ for 20 h. Then the samples were filtered, washed, and dried at $70°C$ for 24 h [14]. The functional groups present in Sabzevar natural zeolite and the loading of surfactant on zeolite surface were verified by a Fourier transform infrared (FT-IR) (Shimadzu, Japan). For this purpose, the samples were first mixed with potassium bromide, then they turned into tablets. The spectra of the samples were determined using FT-IR.

2.2. Influence of the surfactant modification

For a comparison of nitrate adsorption by the unmodified and surfactant modified zeolite, 10 g of each zeolite was added to 30 ml of the synthetic solution of nitrate. It was in contact with the zeolite for 60 min in a shaker incubator at 150 rpm and 30 °C. After 60 min, the zeolite was removed from the mixture, and the concentration of nitrate ions was measured using a UV-spectrophotometer (UV-2100, Unico) at 220 nm [14].

2.3. Screening of independent variables

The Taguchi method was used to screen the independent variables in the adsorption process and determine the optimum conditions [15,16]. According to reports published by other researchers and the obtained results from preliminary experiments, seven factors were selected for screening.

Table 1. The XRF results of the natural Sabzevar zeolite [12].

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

Level descriptions were determined according to the operational constraints and previous studies. In studying the effects of these seven factors, the Taguchi method suggested the L8 array. Table 2 shows the independent variables and their levels, and Table 3 shows the L8 orthogonal array. The batch experiments were carried out to investigate the effect of the seven variables (Table 3) on the nitrate removal efficiency from a water solution using SMZ. After the test time, the solid and liquid phases were separated by filtration, and the amount of nitrate absorption was measured using a UV-spectrophotometer (UV-2100, UNICO) with a detecting wavelength at 220 nm [14].

2.4. Statistical experimental design

According to the preliminary experiments, the initial nitrate concentration, mass of adsorbent, contact time, and competent anion concentration (SO_4^{2-}) were selected for further investigation. Therefore, the effects of these variables on the adsorption process were studied, and the optimum conditions of these variables were determined to maximize the removal efficiency of nitrate in the adsorption process. For this purpose, Taguchi's

method with the L_9 orthogonal array was used. The independent variables and their levels for the L_9 array are shown in Tables 4 and 5. The experiments were conducted according to L_9, and the results were analyzed by Qualitek-4 software. The batch experiments were carried out in sealed glass containers with 50 ml of nitrate solution (Table 5). After the specified time, the zeolite was removed from the mixture, and the amount of nitrate absorption was measured using a UV-spectrophotometer (UV-2100, Unico) with a detecting wavelength of 220 nm [14].

Table 2. Selected levels of independent variables for the Taguchi method.

Variables	Level1	Level2
Contact time (min)	10	180
Temperature (ᵒC)	25	45
Nitrate concentration (mg/L)	20	300
Mass of adsorbent (g)	5	30
Adsorbent Size (mesh)	50-80	8-10
Competing anion concentration (mg/L)	0	200
Agitation (rpm)	50	200

Table 3. L_8 array of Taguchi method for screening of independent variables for nitrate removal from aqueous solution.

Trial	Contact time (min)	Temperature (ᵒC)	Nitrate concentration (mg/L)	Mass of adsorbent(g)	Adsorbent size	Competing anion concentration (mg/L)	Agitation (rpm)
1	1	1	1	1	1	1	1
2	1	1	1	2	2	2	2
3	1	2	2	1	1	2	2
4	1	2	2	2	2	1	1
5	2	1	2	1	2	1	2
6	2	1	2	2	1	2	1
7	2	2	1	1	2	2	1
8	2	2	1	2	1	1	2

Table 4. Selected levels of variables for the L_9 array of Taguchi method for nitrate removal process from aqueous solution by SMZ.

Variables	Levels		
	1	2	3
Nitrate concentration (mg/L)	20	150	300
Mass of adsorbent (g)	5	15	30
Time (min)	10	180	360
Competing anion concentration (mg/L)	0	200	400

Table 5. L$_9$ orthogonal array and experimental results for nitrate adsorption by SMZ.

Trial	Variables				Removal efficiency		
	Nitrate concentration (mg/L)	Mass of adsorbent (g)	Time (min)	Competing anion concentration (mg/L)	Run 1	Run 2	S/N Ratio
1	1	1	1	1	69	68.2	36.73
2	1	2	2	2	53	55	34.64
3	1	3	3	3	50	54	34.30
4	2	1	2	3	27.5	23.9	28.13
5	2	2	3	1	82	77	37.99
6	2	3	1	2	52	46.7	33.83
7	3	1	3	2	26.5	31.4	29.14
8	3	2	1	3	55	51.3	34.49
9	3	3	2	1	75.5	77	37.64

2.5. Isotherms of adsorption

To study the adsorption isotherms, 50 ml of a series of nitrate solutions with a different initial nitrate concentration (C$_0$= 5-200 mg/l) were placed in contact with 15 g adsorbent (50-80 mesh) at 30°C and 50 rpm until reaching equilibrium. The agreement of the obtained results with the Linear, Langmuir, and Freundlich models was investigated. The equilibrium adsorption capacity (q$_e$) was determined according to the following equation:

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

where q$_e$ (mg/g) is the amount of nitrate adsorbed (mg) per the mass of beads (g), C$_o$ and C$_e$ (mg/L) are respectively the initial and equilibrium concentration of NO$_3$-N in the aqueous solution, V (L) is the volume of nitrate solution, and M (g) is the mass of beads (g) [17].

3. Results and discussion

3.1. Natural Sabzevar zeolite and surfactant modified zeolite characterization

Transmission Electron Microscopy (TEM), CM120 Philips and X-ray diffraction (XRD) showed that most of the Sabzevar zeolite was clinoptilolite. According to the XRD results in Figure 1, the employed zeolite had clinoptilolite and calcite with compositions of 76% and 24%, respectively. The other clinoptilolite samples analyzed had almost the same chemical compositions [13]. According to the TEM images in Figure 2, the range of zeolite particle size was between 50-870 nm. FTIR was used to ensure the surfactant layer formation on the zeolite, and the results are shown in Figure 3. It showed that the FTIR spectra of SMZ were different from that of natural zeolite (NZ). The HDTMA-Br spectrum had two peaks because of methylene tails and alkyl ammonium head groups [18]. The symmetric stretching mode of the tri methyl ammonium tail groups of CH$_2$-N showed two IR peaks at around 2914 cm^{-1} and 2844 cm^{-1}. These bands at 2840 and 2912 cm^{-1} in the SMZ sample spectra, which were absent in the spectrum of NZ, confirmed that HDTMA loaded onto the NZ surface [19]. The Si-O/Al-O stretching and bending vibration bands in the zeolite fundamental structure were located at the 1050 cm^{-1} and 400-600 cm^{-1} region, respectively [18,20]. All the IR symmetric and asymmetric stretching bands of NZ were also observed in the spectrum of SMZ, which indicated that modifying with HDTMA-Br did not affect the crystalline network of the raw zeolite.
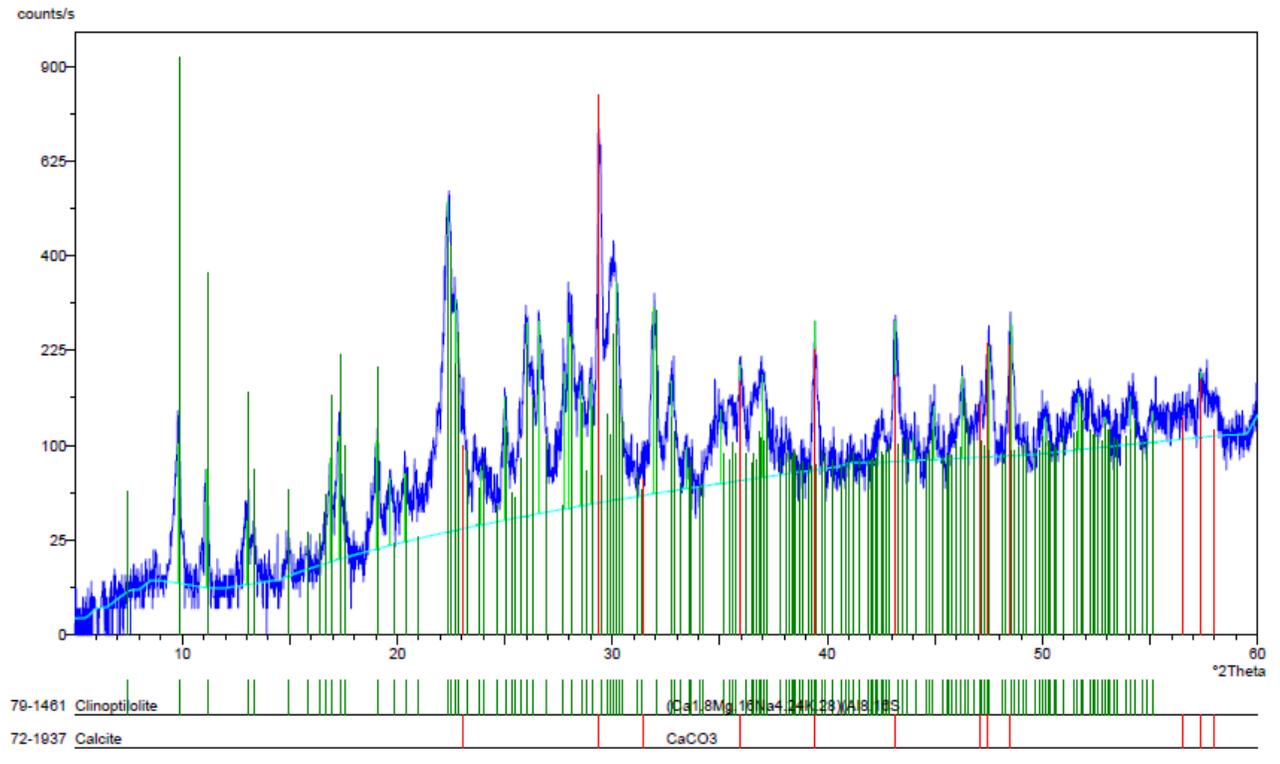
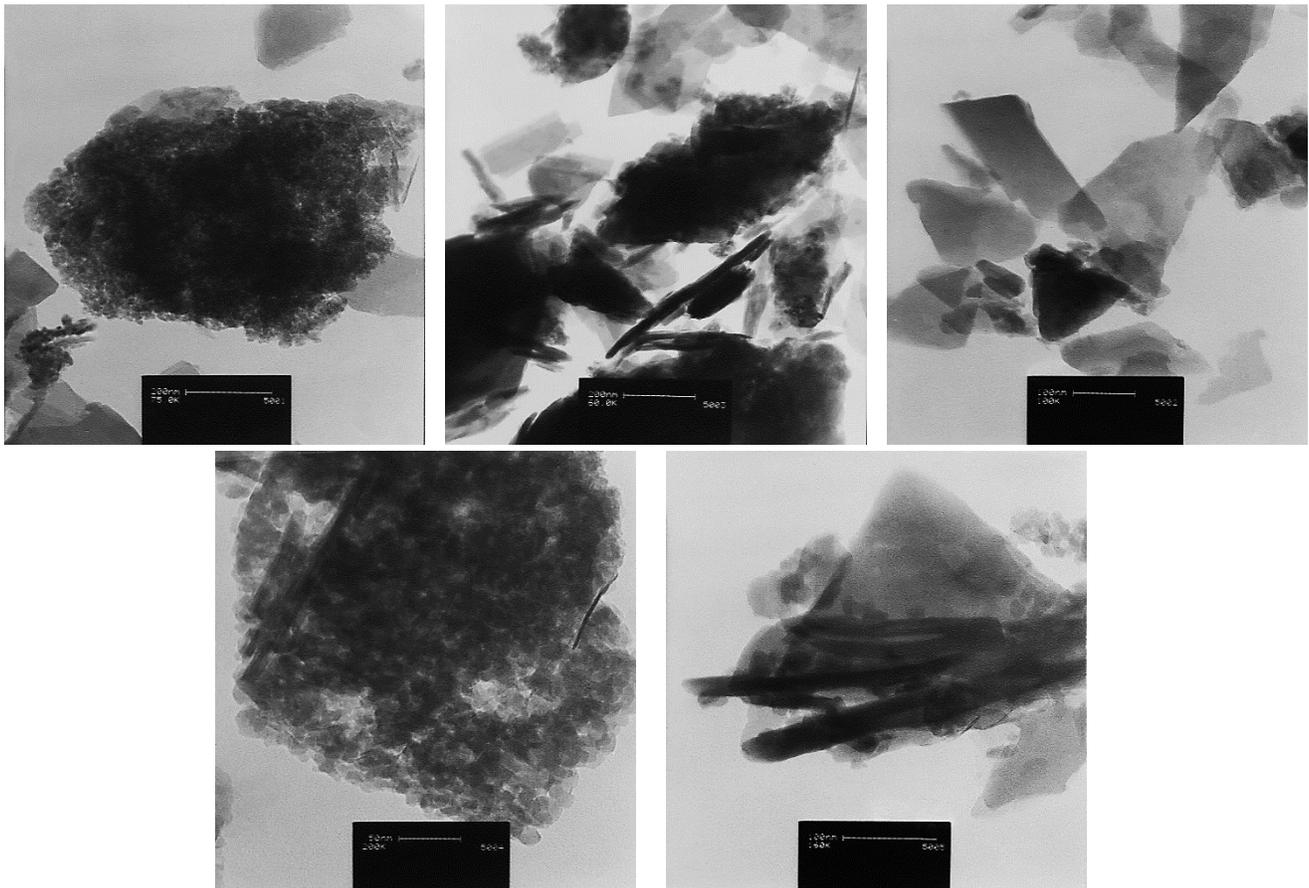**Fig. 1.** XRD results of natural Sabzevar zeolite powder.

Fig. 2. TEM micrographs natural Sabzevar zeolite powder with different magnification.
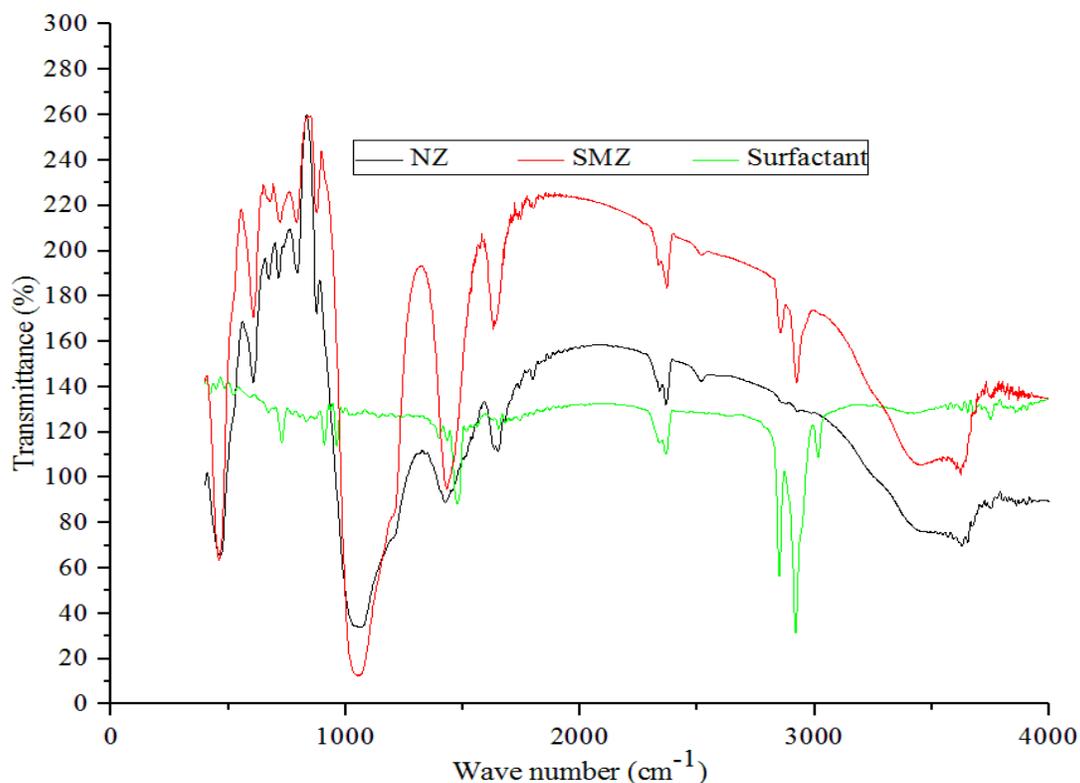
Fig. 3. FTIR spectra of HDTMA-Br, SMZ, and NZ

3.2. Influence of the surfactant modification

A comparison of nitrate adsorption by unmodified and surfactant modified zeolite indicated that the SMZs removed nitrate ten times more than the unmodified zeolites. This result is consistent with the results published by Guan et al. Their research showed that the surfactant modified zeolite removed nitrate 8–18 times more than the unmodified zeolites [13]. As outlined in the introduction, natural zeolites (NZ) usually have little affinity for anions due to the net negative charge on the framework. However, the positive charge caused by surfactants on the zeolite surface increases the adsorption of anionic pollutants by surfactant modified zeolite [21-24].

3.3. Screening of independent variables

For screening of independent variables, the experiments were carried out according to L8 orthogonal arrays (Tables 2 and 3). The results of the experiments in terms of removal efficiency are shown in Table 6. The results were analysed using Qualitek-4. The detailed method for analysis of

experimental data has been explained by many researchers [25-27]. Table 7 shows the ANOVA results for nitrate removal from aqueous solution by SMZ in terms of percent participation and the optimum level of the variables [28]. According to the results, the independent variables that had a greater contribution in the nitrate removal process were agitation and competing anion concentration, mass of adsorbent, and temperature.

Table 6. L_8 array results for nitrate removal from aqueous solution by SMZ in terms of sorption percentage.

Trial	Sorption percentage		
	Run 1	Run 2	S/N ratio
1	62.50	64.50	36.05
2	14.25	16.65	23.70
3	13.74	18.30	23.83
4	52.20	57.00	34.72
5	25.10	27.10	28.31
6	54.70	55.00	34.78
7	20.70	26.75	27.29
8	37.16	11.67	23.94

Table 7. ANOVA results for nitrate removal from aqueous solution by SMZ in terms of percent participation and optimum level of variables.

Variables	df	Sums Of Squares	Percent participation	Optimum level	Optimum level description
Time (min)	1	15.428	5.022	2	180
Temperature (C°)	1	18.889	6.148	1	25
nitrate concentration (mg/L)	1	2.442	0.794	1	20
Mass of adsorbent (g)	1	35.011	11.396	2	30
Size (mesh)	1	3.587	1.16	1	0.1
Competing anion concentration (mg/L)	1	101.54	33.053	1	0
Agitation (rpm)	1	130.304	42.416	1	50

3.4. Statistical experimental design

The effects of the four variables selected by preliminary experiments and the reports of other researchers were investigated at three levels by the Taguchi method's L_9 array, and the results obtained as removal efficiency are exposed in Table 3. These results were analyzed by Qualitek-4 software. The main effects of variables, the effect of each variable separately, the contribution of each variable to the adsorption process, and optimized conditions were determined. The average of responses for each variable at different levels was calculated to investigate the effect of each variable.

3.4.1. The main effect of the variables

The main effect of each variable is indicated in Figure 4; the results show that increasing the initial nitrate concentration decreased adsorption efficiency. The same result, seen in Schick et al. [14]. As shown in the graph, the gradient of the adsorption percentage curve in terms of the initial levels was not much, so it showed that the initial concentration did not have much effect on the removal process in the range that has been studied. The decrease in the adsorption efficiency could be explained by the fact that adsorbents generally have a limited number of active sites, which eventually become saturated above a certain concentration [20]. The mass of adsorbent was investigated at three levels, and the results are shown in Figure 4. As expected, the higher the levels (15 and 30g zeolite), the more nitrate uptake. The increase of adsorption efficiency with a higher mass of adsorbent could be attributed to increased surface area [29]. This result is in accordance with previous studies from Schick et al. [14]. However,

an increase in the mass of adsorbent from 15 to 30 g did not lead to an increase in nitrate adsorption but caused a decrease in nitrate uptake an increase in the mass of adsorbent exceeding a given amount may lead to adsorbent aggregation, resulting in a decrease in active adsorbent sites [20]. Determining the optimum contact time is crucial for finding the maximum possible adsorption efficiency in the adsorption procedure. The contact time was studied at three levels (Figure 4). In the initial stage of nitrate adsorption, a large number of empty surface sites were available for adsorption. However, as the sorption progresses, the occupation of the empty sites becomes difficult because of the repulsive forces acting between the nitrate molecules present on the adsorbent surface and in the nitrate solution [16]. So, the best result was achieved at level 1, and it showed that the equilibrium time for nitrate adsorption was short, in accordance with Schick's study. His study was carried out in a fixed bed column; at the beginning of each experiment and after 3.5 minutes, the removal rates were very high, larger than about 95% [18]. Zhan's work showed that the adsorption efficiency increased with the increase of the reaction time until equilibrium was achieved (30 minutes) [19]. Figure 4 shows that the gradient of adsorption percentage in terms of contact time was small, so the nitrate uptake process was not affected much by the contact time in the investigated range. It is known that various anions in water and wastewater do not need to be removed. Therefore, it is necessary for the adsorbent to have selectivity only for nitrate ions. In the absence of competing anions, there are more available sites and pores for nitrate uptake. This study used sulfate (SO_4^{2-}) as a competing anion. As

expected, and in accordance with the research from other authors [19], nitrate adsorption decreased in the presence of competing anions (Figure 4.). The selectivity sequence for nitrate, chloride, sulfate and bicarbonate ions is $Cl^- \ll HCO_3^- < SO_4^{2-} < NO_3^-$, according to the reports from Schick [18].

3.4.2. Analysis of variance (ANOVA)

The analysis of variance of the L_9 array, in terms of removal efficiency, was carried out using Qualitek-4 according to an S/N ratio analysis with a 'higher-is-better' quality characteristic. Table 8 shows that competing anions and the mass of adsorbent were the most effective factors and had the highest proportion in the nitrate removal process by SMZ.

3.4.3. Optimum condition

The Qualitek-4 can determine the optimum conditions and predict the desirable performance for these conditions. The optimum condition was obtained at an initial nitrate concentration of 20 mg/L, a mass of adsorbent of 15 g, a contact time of 10 min, and a sulfate concentration of 0 mg/L. The expected removal efficiency at the optimum condition was predicted by Qualitek-4 as 90.13%. Under the optimum condition, the removal efficiency was studied in triplicate, and the amount of 87% was obtained. This result verified the predicted result by the software.
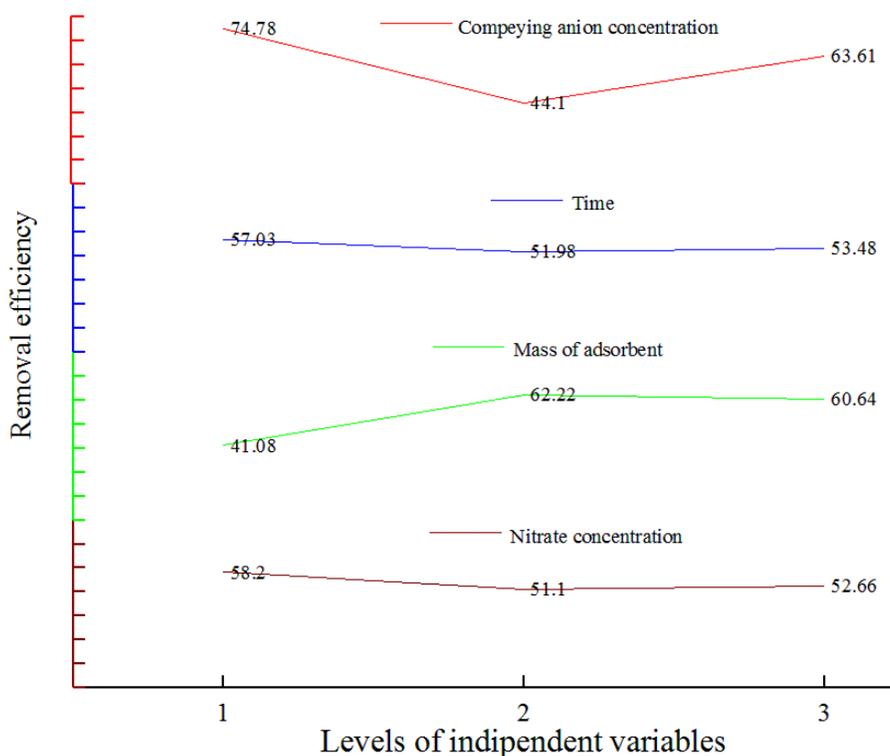

Fig. 4. The main effects of variables on nitrate removal SMZs from aqueous solution: a) Nitrate concentration; b) Mass of adsorbent; c) Time; and d) Competing anion concentration.

Table 8. Analysis of L_9 array results for nitrate adsorption by SMZ in terms of percent participation and optimum level of parameters.

| Term	df	Sums Of Squares	Variance	F-Value	Percent participation (%)	Optimum level	Optimum level description
Nitrate concentration (mg/L)	2	171.159	85.579	12.05	2.745	١	20
Mass of adsorbent (g)	2	1609.107	804.553	11.288	27.903	٢	15
Contact time (min)	2	72.901	36.45	5.132	1.026	١	10
Competing anion concentration (mg/L)	2	3798.778	1899.389	267.45	66.211	١	0

3.5. Isotherm adsorption

One of the important aspects of data analysis in adsorption studies is the fitting of experimental data to adsorption isotherm equations. This research used linear, Langmuir, and Freundlich isotherms to fit the experimental data (Table 9).

The model parameters and correlation coefficients (R^2) are summarized in Table 10. The correlation between the experimental data and the Freundlich model was evaluated by plotting log Q_e against log C_e (Figure 5). Higher values of R^2 is 0.8964. A better fit was observed in the Freundlich isotherm with the experimental data. The findings indicated that Freundlich and linear isotherms accurately describe the adsorption behaviors of nitrate on SMZ over the concentration ranges studied. To evaluate the correlation between the experimental data and a linear model, Q_e was plotted against the C_e (Figure 5). The correlation coefficient (R^2=0.8555) indicated that a better fit was observed in the linear isotherm with the experimental data. Also, C_e/ Q_e was plotted against C_e for examination of the Langmuir isotherm. According to Figure 5-b and the obtained R^2 (0.173), the Langmuir isotherm could not fit with experimental data.

Table 9. Equilibrium concentration and adsorption in different initial nitrate concentration for nitrate removal by SMZ

C_0 (mg/L)	C_e (mg/L)	Q_e (mg nitrate/g zeolite)
5.00	1.79	0.01
20.00	11.25	0.03
50.00	16.47	0.11
100.00	63.91	0.12
200.00	98.19	0.34

(A)

(B)

(C)
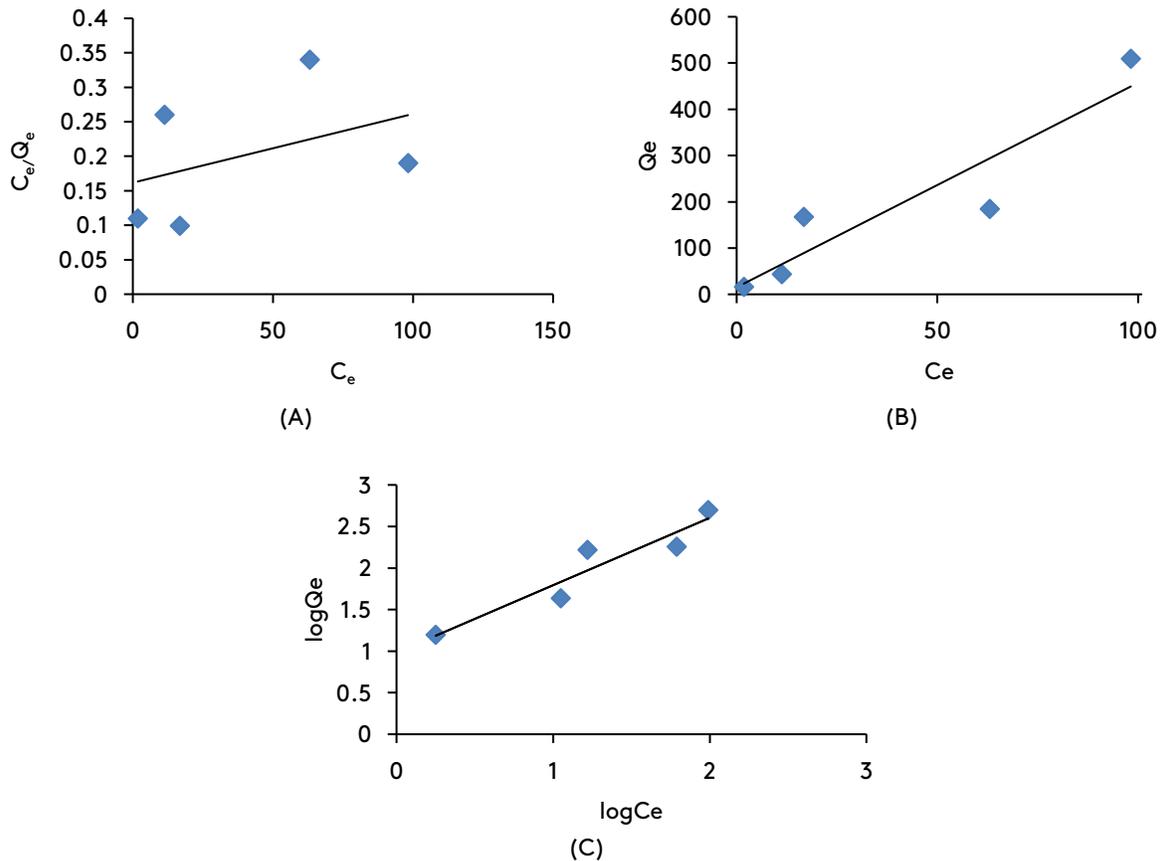
Fig. 5. Comparison of (a) Linear, (b) Langmuir, (c) Freundlich isotherms with experimental data.

5. Conclusions

According to the results of this work, modified Sabzevar zeolite displayed great promise in the area of nitrate uptake ions from aqueous solutions and is worthy of further investigation. The results of FTIR spectroscopy indicated that the HDTMA-Br was loaded and immobilized on the Sabzevar zeolite surface without changing the crystalline composition of this adsorbate. Four independent

variables were chosen and investigated through preliminary and complementary experiments, and the optimized conditions were determined. In optimum conditions, the removal efficiency of nitrate was 87%. The surfactant modified zeolite removed ten times more nitrate than the unmodified zeolite, and the experimental data of the nitrate adsorption process fit well with Freundlich and linear models. In conclusion, the surfactant modified Sabzevar zeolite can be successfully used as a low-cost, eco-friendly adsorbent for nitrate adsorption from hazardous aqueous solutions.

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