



Management and removal of nitrate contamination of water samples based on modified natural nanozeolite before determination by the UV-Vis spectrophotometry

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ARTICLE INFO:

Received 20 Nov 2021

Revised form 17 Jan 2022

Accepted 23 Feb 2022

Available online 28 Mar 2022

Keywords:

Removal,
Nitrate,
Adsorption,
Water samples,
Nanozeolite,
UV-Vis spectrophotometry

ABSTRACT

Nitrate is a hazardous substance for human health, the removal of which is an important environmental priority. Therefore, in this study, first, the sources of nitrate pollution of water were investigated, then the structure, role, and application of nanozeolites for the removal of nitrate ions were studied by the analytical method. Also, the presentation of management solutions, identification of polluting industrial sectors, different methods of removal and fabrication of ZSM-5/Fe/Ni nanosorbents, and the determination of optimal conditions for nitrate removal were investigated by experimental design software and graphical analysis of effective parameters. The results of graphical analysis of laboratory method showed us, the highest nitrate removal efficiency at a residence time of 150 minutes, pH 3, 4 g L⁻¹ adsorbent, and 40 mg L⁻¹ nitrate were achieved (%RE:91.5-97.4). Experimental results indicate the high efficiency, absorption capacity, and effectiveness of ZSM-5/Fe/Ni adsorbents for nitrate removal in waters. Finally, the absorbance values or nitrate concentrations between 20-120 mg L⁻¹ were measured by the UV-Vis spectrophotometry. The maximum absorption capacity of ZSM-5/Fe/Ni adsorbents for nitrate was obtained 136.7 mg g⁻¹. The developed method based on a novel ZSM-5/Fe/Ni adsorbents has many advantages such as simple, low cost, high efficiency, and favorite recovery of more than 90% for removal nitrate in water samples by nanotechnologies as compared to other reported methods.

1. Introduction

Nitrate and nitrite compounds are important factors in groundwater pollution. Due to the lack of nitrification of municipal, industrial and agricultural wastewater, its average amount is increasing. Therefore, various methods such as adsorption, ion exchange, reverse osmosis, chemical, and biological methods are used [1-3]. Banu et al Have

identified the chitosan beads (CS) technique as an efficient biosorbent for the removal of toxic anions from aqueous solutions. In this study, zirconium encapsulated quaternary chitosan beads (Zr@CSQ) were prepared and used to remove nitrate and phosphate ions from the prepared water. Zr@CSQ beads were identified by a sequence of analytical techniques, including XRD, SEM, EDAX, BET, FTIR, and TGA-DSC analysis. Various kinetic models and known Langmuir, Freundlich, and Dubinin-Radushkovich (D-R) isotherm models have been used to define the isotherm [4]. Revilla

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<https://doi.org/10.24200/amecj.v5.i01.165>

et al Studied the removal of nitrate from aqueous solutions using adsorption-activated biochar from municipal solid waste (MSWAB). Initially, municipal solid waste (MSW), another important source of environmental pollution, was used as a raw material for biochar production, which was activated using potassium hydroxide to produce MSWAB. MSWAB activation increased the level from 2.5 to 6.5 m²/g. Then, the effect of initial nitrate concentration (A), pH (B), and adsorbent dose (C) on nitrate removal was evaluated using a 2K factorial experimental design. The results showed that the initial nitrate concentration, pH, and bilateral interactions of AB and AC have a significant effect on nitrate removal [5]. Liyun Yang et al reported a new modified steel slag for nitrate removal from water. Steel slag (SS) has been used to remove nitrate pollution from the liquid phase. They prepared and activated SS by mixing steel with aluminum hydroxide and deionized water at 800 ° C. The physicochemical properties of steel scrap before and after modification were also investigated to compare the effect of their surface properties on nitrate adsorption behavior, contact time, adsorbent dose effects, and pH effects on it. The results showed that nitrate uptake was significantly increased due to the increase in the specific surface area of the modified waste compared to the unmodified type. They reported the optimal parameters for nitrate removal with this adsorbent: 20 mg L⁻¹ nitrate concentration, 1 g per 100 mL adsorbent, and 180 min residence time in Freundlich adsorption isotherm [6]. In another study, Caterji et al Investigated the uptake of nitrate on bisulfate-modified chitosan seeds. The results showed that cross-link and capacity modification increased uptake compared to conventional chitosan seeds. The maximum absorption capacity relative to the crosslink is 0.4. The maximum modified NaHSO₄ concentration capacity was reported to be 0.1 mM. The maximum nitrate uptake was 104 mg g⁻¹ at pH 5. It also corresponds to the Freundlich isotherm model [7]. Betangar et al used nano-alumina to remove nitrate from water. Their study studied the parameters of contact

time, pH, and nitrate concentration with a pseudo-second-order kinetic model. The highest nitrate removal was observed at a concentration of 4 mg/g, a temperature of 23-27°C, and a pH of 4.4. The Langmuir isotherm model was used to study nitrate uptake. This study showed that nano-adsorbent nanoalumina is useful and effective for the removal of nitrate from aqueous solutions [8]. Morado et al removed nitrate in water with zero-capacity iron and copper/iron nanoparticles. Zero-capacity iron and copper/iron particles in this study were fabricated by reducing sodium bromide at room temperature and atmospheric pressure. The results showed an increase in the rate of nitrate reduction by copper/iron particles so that the residence time of nitrate removal was reduced from 150 minutes to 60 minutes [9]. Hanache et al Developed an anion exchange ZSM-5 nanocatalyst modified with a cationic surfactant. This study showed that the larger the surface area of this nanocatalyst and the smaller the particle size, the higher its adsorption and properties. This modified nanocatalyst has been shown to have a high adsorption capacity and is modified by surfactants. The adsorption kinetics of this system is consistent with the Pseudo-Second isotherm model [10]. Due to the effectiveness of the adsorption method to remove nitrate and the existence of many sources of zeolites in our country, which can act as a suitable substrate for adsorption due to their high porosity and high specific surface area. In this study, the management strategies of nitrate ion removal by interviewing several experts and also the removal of this ion through adsorption by ZSM-5 nano zeolite functionalized with iron and nickel metals will be investigated. Also, in this study, the management methods of ion removal were reviewed and discussed through interviews with active experts in the water and wastewater industry. Several analytical methods such as high-performance liquid chromatography [11] and spectrophotometric [12] have been used for nitrate analysis in waters. The Association of analytical chemists announced that the spectrophotometric method is the favorite determination of Nitrite and Nitrate in waters [13]. The 3D image of nitrate ion

was shown in Figure 1.

Moreover, the metals such as Al, Sn, Zn, Fe, and Ni are effective agents for remediation of contaminated groundwater. Hence the present study was tested based on iron functionalized on ZSM-5 nanozeolite for removal nitrate in waters due to its availability, inexpensiveness, non-toxicity, high efficiency, and rapid reaction in the decomposition of contaminants. In addition, nitrate concentration was determined by the UV-Vis spectrophotometry and the optimal conditions based on effective factors for nitrate removal, including pH, contact time, and adsorbent dosage were evaluated.

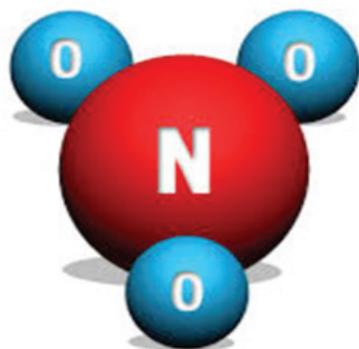


Fig.1. The 3D image of nitrate ion

2. Experimental

2.1. Material

The ZSM-5 nanozeolite powder (from the Zeolites family) was purchased from Sigma Aldrich with a crystal size of 0.5 μm and a pore size of 5.5 \AA . Ferric chloride (FeCl_3), sodium hydroxide (NaOH), potassium nitrate (KNO_3), hydrochloric acid (HCl), and %98 sulfuric acids (H_2SO_4) were also obtained from Merck Germany.

2.2. Characterization

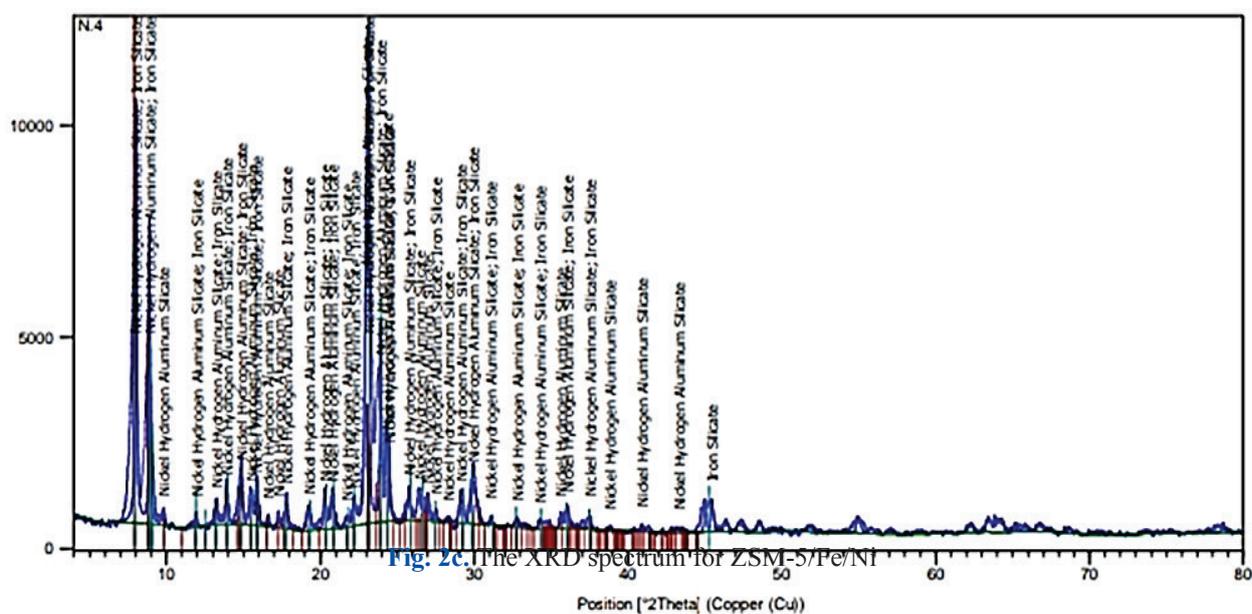
X-ray diffraction (XRD, STADI-P, the USA) was used to investigate ferrous (Fe) metals in the nanozeolite structure functionalized with these metals. Brunauer-Emmett-Teller (BET) surface area analysis (Belsorb apparatus, Japan) was used to determine the SSA of nanozeolite particles. The concentration of nitrate was measured with Spectrophotometer UV-Vis Hach model Dr2800 was used.

2.3. Preparation of ZSM-5/Fe/Ni nanosorbent

To Preparation the functionalized ZSM-5 nanozeolite, the first 2.5 g of ZSM-5 nanozeolite powder was placed in the furnace at a temperature of 500°C for 4 hours and calcined. Then, 0.5 g of ferric chloride (FeCl_3) powder was dissolved in distilled water twice for one hour, added to the calcined ZSM-5 nanozeolite powder and mixed for another 30 minutes, and filtered with a filter paper. The resulting powder was rinsed three times with distilled water and placed in an oven at a temperature of 80°C for 2 hours. Next, the powder was separated from the filter paper and re-calcined at a temperature of 500°C for 4 hours. To produce ZSM-5/Fe/Ni nanozeolite powder, ZSM-5 was first doped with Fe as previously mentioned, and then 0.5 g of nickel sulfate (Ni_2SO_4) powder was dissolved in deionized water for one hour. Next, the calcined ZSM-5/Fe nanozeolite powder was added and stirred for 30 minutes. Afterward, the solution was filtered and the powder was washed three times with distilled water and placed in an oven at a temperature of 80°C for 2 hours. The resulting powder was re-filtered and placed in the furnace at a temperature of 500°C for 4 hours [14].

2.4. Preparation of solutions and procedure

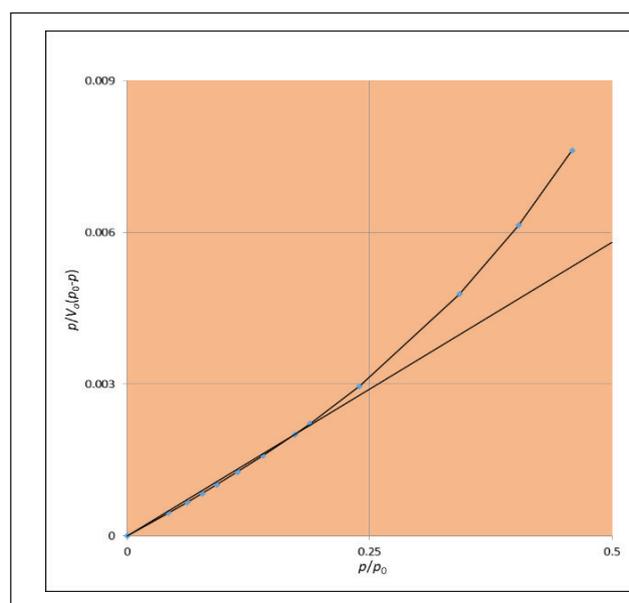
To prepare a standard concentrated potassium nitrate solution, 7 g of anhydrous KNO_3 was dried at 100°C for an hour. After cooling, 1.805 g of KNO_3 was dissolved in a volumetric flask and diluted to 250 ml, thus preparing a standard solution of 1000 mg L^{-1} or 1 mg mL^{-1} . HCl and NaOH solutions were prepared to set the pH values. Then, nitrate solutions with concentrations of 20, 40, 60, 80, 100, and 120 mg per liter were prepared from the standard solution of potassium nitrate 1000 mg L^{-1} [15]. In this research, the experimental design table was first provided using the effective variables of pH, contact time, and stirring speed in the intervals defined to RSM and the central composite design (CCD) by Design Expert.7 software. Then, the value of each parameter was provided according to the experimental design table and finally, the absorbance values or nitrate concentrations in



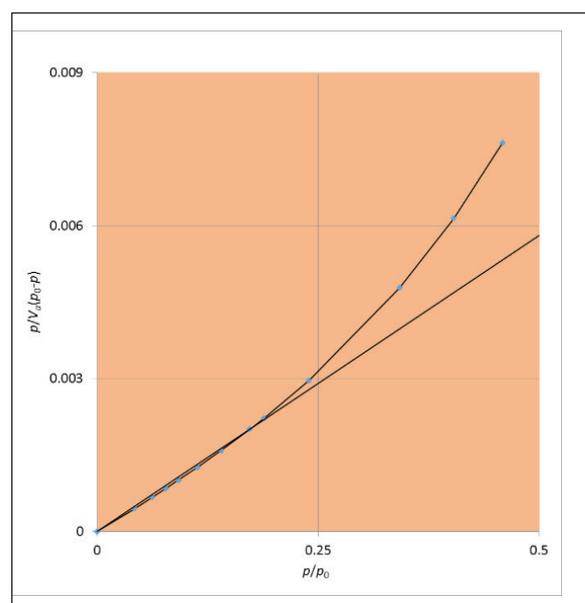
3.2. BET characterization

By comparing the BET parameter as in Figure 3 and Table 1. In each of the four BET analysis curves of the nanozeolite, the highest SSA was

related to the zeolite functionalized with Fe and Ni metal (ZSM-5/Fe/Ni, which was determined to be $418.76 \text{ m}^2 \text{ g}^{-1}$).



ZSM-5



ZSM-5/Fe/Ni

Fig. 3. BET curves of the prepared nanosorbent.

Table 1. The specific surface area of the prepared nanozeolite

Row	Nanocatalysts	BET	Unit
1	ZSM-5	374/66	m ² g ⁻¹
2	ZSM-5/Fe/Ni	418/76	m ² g ⁻¹

3.3. Optimization and experimental design

In this research, the experimental design using RSM in combination with the CCD method was performed to investigate the effects of influential variables of pH (range: 2-8) (A), contact time (30-180 minutes) (B), and adsorbent dosage (1-5 g L⁻¹) (C) on nitrate removal efficiency. Due to the extensive use of research on (A), (B), and (C) parameters for the nitrate removal process, these parameters as effective factors were used for optimizing nitrate removal [16-17]. The RSM method is a mathematical and statistical method used for the analysis and empirical modeling of problems where a given answer is influenced by several variables and the RSM can be calculated to determine the optimal conditions. One advantage of this method is to reduce the number of empirical tests which was performed to obtain statistically valid results. In addition, the RSM method can also analyze the interactions between variables. By optimizing parameters, the result can report more comprehensive and accurate data by performing the least number of experiments [18-19]. In this study, Table 2 showed the range of independent variables and design levels of the experiments examined. The results of the complete design of the test and the exact responses of the tests used are also listed in Table 3.

According to the results of the data analysis in Table 4, a quadratic function model can fit well to the empirical results. The fit of this model was evaluated by Analysis of Variance (ANOVA),

normal probability plot, and residual analysis. The quadratic function for nitrate removal efficiency is expressed as follows:

$$\begin{aligned} \% \text{ Removal Nitrate} = & 51.29 - (10.17 \times A) + (4.13 \times B) - (3.51 \times C) + (11.69 \times D) + (5.16 \times A \times B) + (3.69 \times A \times C) - (0.056 \times A \times D) + (2.84 \times B \times C) + 5.59 \times B \times D - (2.43 \times C \times D) + (0.47 \times A^2) + (0.83 \times B^2) + (2.81 \times C^2) - (1.28 \times D^2) \end{aligned}$$

In Table 4, the ANOVA analysis showed the importance of each parameter in response to nitrate removal by P and F values. The smaller the P-value, the higher its impact factor and its contribution to the response variable. The P values less than 0.05 indicate that the model expressions are significant. The P values of more than 0.1 indicate that the model terms are insignificant. Accordingly, the seven terms of (AC), (BD), and (C²) are significant parameters of the model and have the greatest effect on nitrate removal efficiency. The P values of the other terms were greater than 0.05, which means that their effect on the response model was not statistically significant.

Figure 4 shows the residual curve in terms of the predicted response for the response of nitrate removal efficiency. This Figure shows that all empirical data are uniformly distributed around the mean response variable. This indicates that the proposed model is sufficient and there has

Table 2. Factors and levels for CCD study

Level	pH	Temperature	Time
-α	-22.4874	-4.31981	-13.7046
-1	3	5	1
+1	8	50	72
+α	472.487	59.3198	86.7046

Table 3. Experimental range and values of different variables studied.

standard	Run	Block	pH	Time (Min)	Nitrate (mg L ⁻¹)	Absorbent (g L ⁻¹)	%Removal Nitrate(mg L ⁻¹)
5	1	Block 1	7	60	40	4	46.62
7	2	Block 1	3	150	100	4	78.11
11	3	Block 1	5	105	70	3	51.42
8	4	Block 1	3	60	40	2	68.27
12	5	Block 1	5	105	70	3	51.19
1	6	Block 1	7	150	100	2	43.28
10	7	Block 1	5	105	70	3	49.41
3	8	Block 1	7	60	100	4	39.56
9	9	Block 1	5	105	70	3	54.12
6	10	Block 1	3	60	100	2	58.34
2	11	Block 1	7	150	40	2	30.47
4	12	Block 1	3	150	40	4	91.51
14	13	Block 2	8	105	70	3	29.19
17	14	Block 2	5	105	20	3	60.73
20	15	Block 2	5	105	70	5	57.16
22	16	Block 2	5	105	70	3	50.92
21	17	Block 2	5	105	70	3	51.69
15	18	Block 2	5	30	70	3	37.48
18	19	Block 2	5	105	120	3	45.33
13	20	Block 2	2	105	70	3	67.11
19	21	Block 2	5	105	70	1	18.81
16	22	Block 2	5	180	70	3	58.25

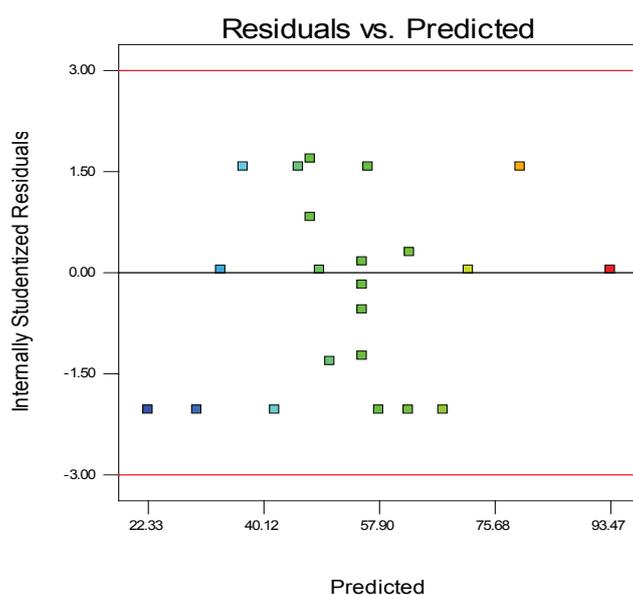
**Fig. 4.** The residual value curve in terms of the predicted response

Table 4. Experimental design and actual results of nitrate removal efficiency.

Source	Sum of Squares	dF	Mean Square	F Value	p-value Prob > F
Block	346.13	1	369.12		
Model	5119.11	13	331.08	18.81	0.0007 <i>significant</i>
A-pH	714.14	1	713.46	35.61	0.0007
B-Time	121.42	1	121.29	6.59	0.0354
C-gr nitrate	176.02	1	176.14	11.41	0.0181
D-gr adsorbent	809.74	1	783.41	42.12	0.0005
AB	94.18	1	95.13	4.26	0.0576
AC	105.00	1	106.63	5.09	0.0413
AD	0.011	1	0.011	6.417E-004	0.9563
BC	73.61	1	66.57	3.94	0.0791
BD	107.46	1	103.34	7.16	0.0465
CD	62.52	1	58.49	2.83	0.1017
A ²	3.93	1	3.83	0.62	0.6173
B ²	13.17	1	13.41	0.51	0.4019
C ²	157.63	1	162.83	7.68	0.0238
D ²	43.08	1	47.19	2.36	0.1609
Residual	105.38	5	19.04		
Lack of Fit	83.59	3	40.56	8.17	0.0381 <i>significant</i>
Pure Error	18.53	3	4.69		
Cor Total	5568.06	23			

been no deviation from the hypotheses made. As can be seen in Table 5, the difference between the adjusted R^2 and the predicted R^2 is less than 0.2 and the precision of the model is 19.461 (which is greater than 4), indicating the used model is accurate.

Figure 5 shows a comparison between the actual response values obtained from the empirical

results and the predicted response values obtained from the quadratic function model equation. It is observed that the model describes the empirical results and data fairly accurately, meaning that it has been successful in comparing the correlations between the three variables. In addition, there is a sufficient correlation with the linear regression coinciding with the R-value of about 0.94612.

Table 5. Model equation statistical parameters for ANOVA model for nitrate removal efficiency

Type of variables	Value
Std. Dev.	3.79
R-Squared	0.94612
Mean	51.14
Adj R-Square	0.9056
C.V. %	7.18
Pred R-Squared	-3.0346
PRESS	25147.62
Adeq Precision	19.461

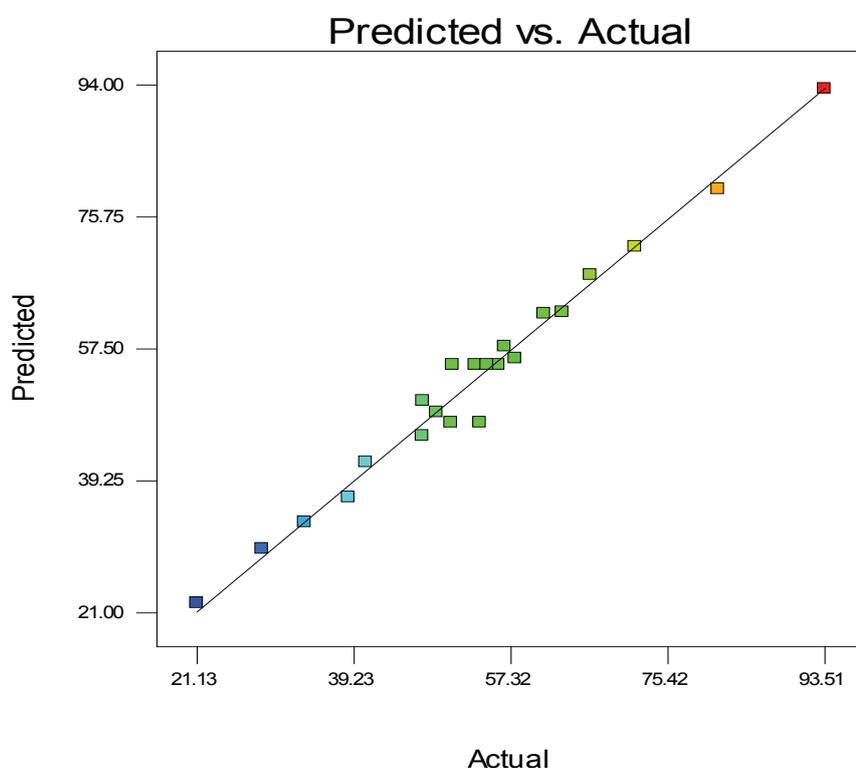
**Fig. 5.** Comparison between predicted and actual empirical values of nitrate removal efficiency.

Figure 6 shows the three-dimensional interaction curves of contact time, pH, adsorbent dosage, and initial nitrate concentration for nitrate removal efficiency. The highest nitrate removal efficiency was reported at the contact time of 150 min, pH

value of 3, an adsorbent dosage of 4 g L⁻¹ and an initial concentration of 40 mg L⁻¹. Analysis of the diagrams in Figure 6 revealed higher nitrate removal efficiency at lower pH values and longer contact times.

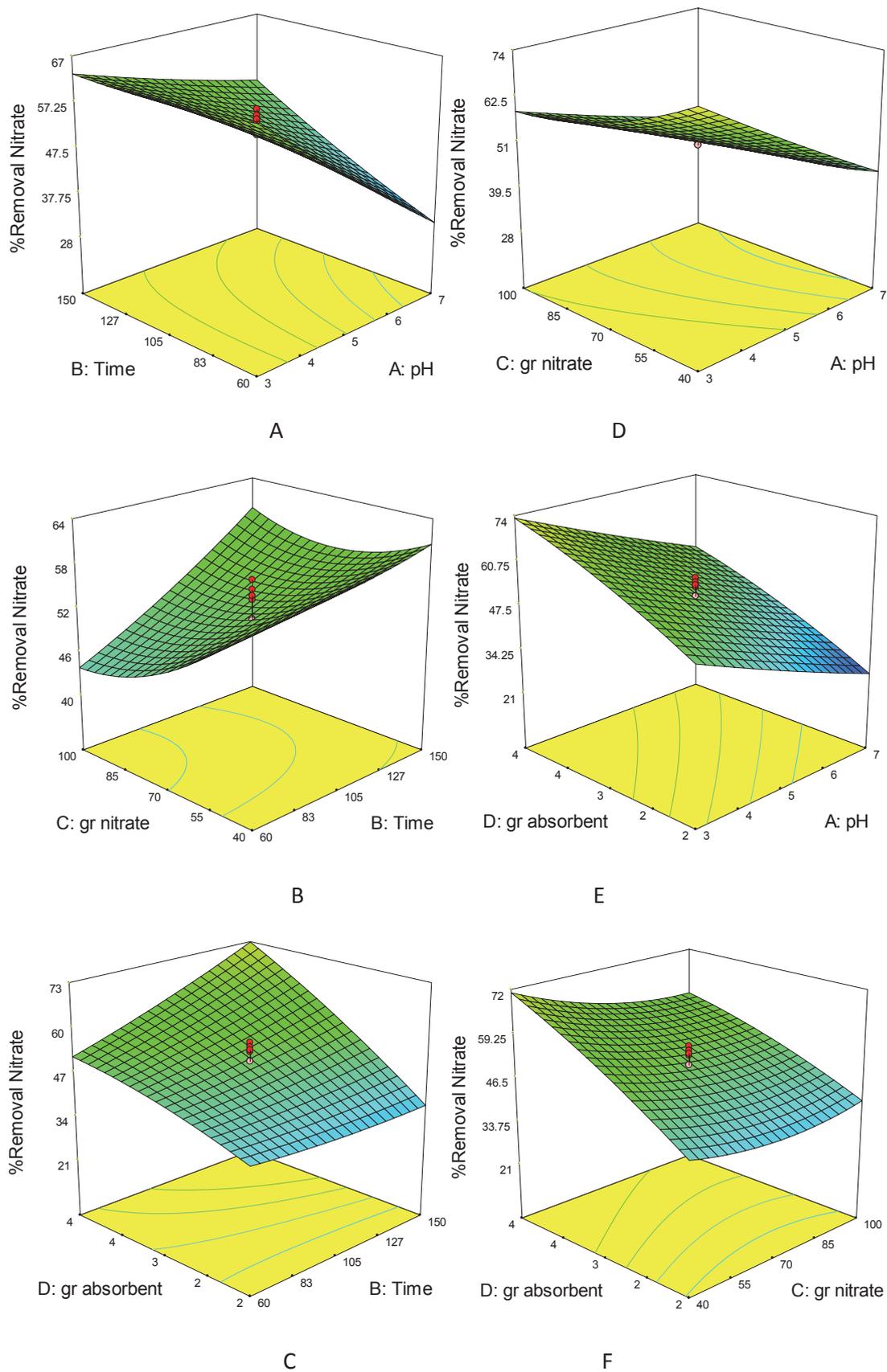


Fig. 6. 3D response surface method curves of nitrate removal efficiency

4. Management

According to the interviews conducted with active experts in the water and wastewater industry, the following items can be suggested as management strategies to remove and monitor nitrate ions from the source. According to the survey and statistical analysis of the interviewees, the highest amount of suggestions was related to the use of new technologies and nanosorbents (%85). Also, this procedure can be suggested as a management strategy to remove and monitor nitrate ions from the source. According to the survey and statistical analysis (Fig. 7 and Table 6), the highest number of suggestions was related to using new technologies and nanosorbents (%85).

*Identification of nitrate pollution-producing industries through sampling and testing

*Continuous instantaneous monitoring of effluents of different industries

*Establishment of nitrification unit in the effluent reservoirs of petrochemical industries and use of expert experts to manage it

*Transfer of effluent to the central treatment plant of industrial sites for re-treatment

*Designing the capacity of the central treatment plant in proportion to the amount of input and pollution of petrochemical units in the region to apply the conditions of complete nitrification

*Perform frequent inspections of various industries

*Prevent the activity of polluting industries

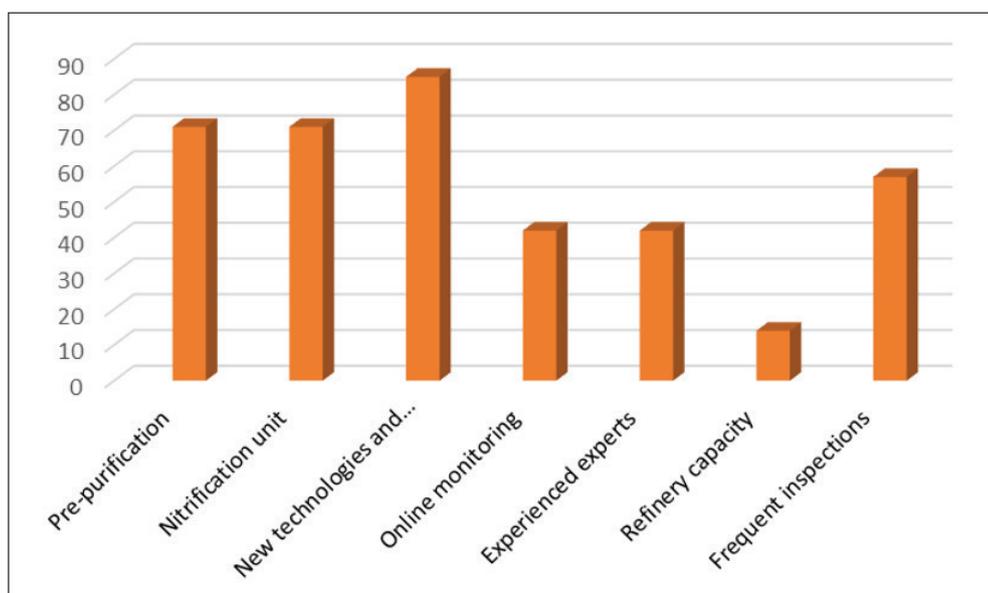


Fig.7. The percentage of importance of the proposed solutions of the interviewees to remove nitrate

Table 6. Percentage of the importance of the proposed solutions of the interviewees to remove nitrate

Cases	Percentage
Pre-purification	71
Nitrification unit	71
New technologies and nanosorbent materials	85
Online monitoring	42
Experienced experts	42
Refinery capacity	14
Frequent inspections	57

5. Conclusions

This study showed that the use of chemical fertilizers, lack of control of wastewater, including municipal, industrial, especially wastewater from food production plants and animal waste, and the entry of treatment plant effluents without applying the nitrification process are important sources of mixing nitrate with groundwater. It can be controlled by the following management methods. It can be eliminated by various executive methods such as adsorption, ion exchange, reverse osmosis, chemical and biological methods such as thermal hydrolysis, solar photocatalysis, and microbial fuel cells. According to the results of the analysis of three-dimensional diagrams, the highest nitrate removal efficiency (91.51%) was reported at a residence time of 150 minutes, pH 3 and 4 g L⁻¹ of sorbent, and 40 mg L⁻¹ nitrate which indicates the high efficiency and effectiveness of this nanosorbent in nitrate removal. Therefore, nanosorbent (ZSM-5 /Fe/ Ni) can be introduced as a promising adsorbent to remove nitrate from effluents. As compared to other studies, this nanosorbent is cheaper due to its abundance in the soils of our country, and in most cases, has a higher efficiency than others in removing nitrate. Another advantage of the proposed method is to use of the experimental design method with Design Expert.7 software, which will reduce the number of experiments performed by statistical and software methods. By procedure, the use of materials and nanosorbents was greatly reduced. The main difference and advantage of ZSM-5 /Fe/ Ni nanosorbents with other adsorbents is completely green and environmentally friendly. Another advantage of the present study is the management methods for removing this ion through interviews and the presentation of management solutions.

6. Suggestions

Due to the widespread use of nanozeolites as adsorbents for nitrate, nitrite, and heavy metals from aqueous media in various articles, it can be used in future research for the removal of heavy metals in waters.

7. Acknowledgments

The authors would like to thank and appreciate Dr. Mostafa Hassani.

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