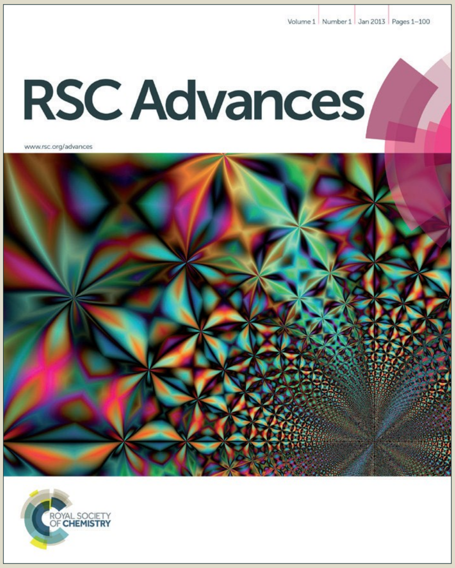
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Composite of activated carbon and Fe_2O_3 nanoparticles was synthesized as a novel adsorbent for nitrate removal.

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Parameters optimization for nitrate removal from water using activated carbon and composite of activated carbon and Fe_2O_3 nanoparticles

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Due to high solubility of nitrate in water, it is the most widespread contaminant in drinking water resources. In this study, activated carbon (AC) and composite of activated carbon and Fe_2O_3 nanoparticles (Fe-AC) were used for nitrate removal from water. AC and Fe-AC adsorbents were characterized using BET, SEM, FTIR and XRF analysis. Main operating parameters such as initial concentration (C_0), adsorbent dosage and pH have been optimized for maximum nitrate removal. Experimental design was carried out using Central Composite Design (CCD) with response surface methodology (RSM). Based on RSM analysis, the nitrate removal models proved to be highly significant with very low probability values (<0.0001). From the predicted models, maximum nitrate removal percentages by AC and Fe-AC were 68.45% and 95.56%, respectively. The optimum conditions for AC and Fe-AC were 0.53 g/50 mL adsorbent dosage, pH=3, C_0 = 147.31 mg L^{-1} and 0.53 g/50 mL, pH=5.1, C_0 = 69.16 mgL^{-1}, respectively. Model predictions fitted the obtained experimental results with relative errors of 6.94% and 4.44% for AC and Fe-AC, respectively. Equilibrium isotherms were analyzed using different models and data were fitted to the Langmuir isotherm. Analysis of kinetic data indicated that data followed second-order-rate model. The experimental results proved that Fe-AC as new adsorbent promotes the percentage of nitrate removal significantly.

Introduction

In the recent years, industrial activities, inappropriate treatment of wastewater and increasingly use of agricultural fertilizers have increased the toxic pollutants such as metal ions, organic and inorganic ions like nitrate in the environment.[1-3] Nitrate is one of the most worldwide contaminants due to its tendency to leach out from soil to water which pollutes drinking water resources especially ground waters that are the main source for rural regions.[1, 4] It is already well known that nitrate causes diverse kinds of cancers, diabetes, cyanosis among children, infectious diseases, potential formation of carcinogenic nitrosamines and blue-baby syndrome.[5, 6]

U.S. Environmental Protection Agency (U.S. EPA) has determined a maximum contaminant level (MCL) of 10 mg NO_3^--N L^{-1} or 45 mg NO_3^- L^{-1} in drinking water, and World Health Organization has a standard of 50 mg NO_3^- L^{-1} in drinking water.[7, 8]

In order to decrease the nitrate level in drinking water and meet these standards, some techniques have been analyzed and reported. These include biological de-nitrification[1, 9, 10], chemical reduction[1, 9, 11], reverse osmosis[1, 9, 10], electrodialysis[9, 10], ion exchange[1, 9, 10] and adsorption.[1, 12-15] Although each of these processes has their own advantages but they have some disadvantages as well. Biological de-nitrification may not be practically feasible for ground water treatment, because it is not effective at temperatures lower than 7 °C. Moreover, there would be the potential of incomplete de-nitrification and post treatment would be required due to microorganisms.[1, 13] Risk of nitrite formation and probability of releasing toxic compounds are disadvantages of chemical methods.[9, 13] In reverse osmosis, disposal of concentrate and pretreatment waste streams may be difficult and membranes are prone to fouling. Moreover, reverse osmosis has high operational costs and post treatment is necessary.[1, 10] Electrodialysis process can operate without fouling, scaling, or chemical addition and has long membrane life expectancy, but pretreatment would be required for high levels of Fe, Mn, H_2S, chlorine or hardness.[9, 10] In ion exchange method, potential for nitrate peaking, high chemical use (salt), brine waste disposal and final pH adjustment are the common disadvantages. Also, resins are still quite expensive and retain some sulfate and hydrogen carbonate, which change water composition significantly. It causes an increase in the chloride concentration in water due to replacing nitrate with chloride.[1, 9, 10]

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Adsorption is shown to be economical alternative for removing trace ions of different pollutants from water for its convenience, ease of operation and not complicated design.[1, 12, 16] Adsorbents play significant role for having economical and efficient separation process. A good adsorbent should have low price and provide high capacity and selectivity to the pollutants. Different adsorbents such as clay, zeolite, chitosan, agricultural wastes, industrial wastes and carbon based adsorbents have been suggested for nitrate removal.[1] Among these adsorbents, activated carbon is considered as a universal adsorbent in water treatment which has a large surface area (500–2000 m^2 g^{-1}). To increase the adsorption capacity or making the process more economical, modification of adsorbent is necessary. Depending on the application, there are different methods to modify activated carbon surface, which make the surface more accessible to variety of reactants.

These modification methods can be categorized in different classes named as chemical, physical, biological and electrochemical modifications.[17, 18] The chemical modification may be divided into two major categories. First type generates acidic or basic groups on adsorbent surface.[19] The second type of chemical modification is surface impregnation which can be done with active metals and their oxides.[19-21] The combination of activated carbon and iron would take advantage of the strength of these two materials.[22] Modified activated carbon with iron ions would provide high affinity for any negative ions such as nitrate (due to providing porous media that is charged with positive ions).[20, 22-25]

According to the published papers, this is the first study that reports the use of composite of activated carbon and Fe_2O_3 nanoparticles for nitrate removal. Moreover, removal process has been optimized using RSM to determine the optimum conditions and find a model for prediction of the amount of nitrate removal percentage versus process parameters.

The main objectives of the present study include the following:

1. To synthesize composite of activated carbon and Fe_2O_3 nanoparticles (Fe-AC) as a new adsorbent.
2. To investigate of the efficiency of AC and Fe-AC for nitrate removal from water.
3. To compare removal capacity of AC and Fe-AC
4. To determine the optimum operational conditions for the studied application.
5. To suggest a model for nitrate removal efficiency from water versus operational conditions using CCD in RSM package.
6. To find suitable models which describe isotherm and kinetic of adsorbents for nitrate removal.

Materials and methods

Chemicals

Commercial activated carbon based on coal was used as raw adsorbent. $NaNO_3$ was used for preparation of nitrate solution. $FeCl_3$ was used for preparing composite of activated carbon and iron nanoparticles. Diluted HCl and NaOH were applied for pH adjustment. Deionized water was used for making solutions prepared by Milli-Q. The reagents and salts used in the experiments were reagent-grade Merck products.

Adsorbent synthesis

The raw activated carbon was sieved to mesh 16-35 (0.50-1.19 mm) and dried at 110 ˚C and used for removal as AC. In order to prepare composite of activated carbon and Fe_2O_3 nanoparticles, 7 g of raw activated carbon were contacted with 140 mL of 3M $FeCl_3$ for 48 h at 56 ˚C using a shaker with 180 rpm, and after reacting time, adsorbents washed with deionized water repeatedly. Washing continued until reaching to a constant pH. Finally, the concentration of iron in washing water has measured using atomic absorption spectrophotometer to be sure there was not any unreacted iron. The adsorbent was then dried at 100 ˚C in an air oven overnight. AC and Fe-AC were kept in a desiccator for removal tests.

Characterization of adsorbents

Adsorbents were characterized by selected physical and chemical properties. The morphologies of AC and Fe-AC were examined by a scanning electron microscope (SEM, KYKY-EM3200). The BET specific surface area, pore volume and average pore radius of adsorbents were obtained by adsorption of nitrogen at 77 K (NOVA, Series1000- Quantachrome INSTRUMENTS).

pH_{pzc} (point of zero charge) of adsorbents were measured by adding 50 mg of adsorbent to 50 mL of a 0.1 N NaCl solution in 100 mL Erlenmeyer. Initial pH of the solution was adjusted by HCl or NaOH solutions. Samples were agitated on the shaker at 100 rpm for 24 h. After that, final pH was measured and compared with initial pH. If initial pH is pH_{pzc}, no change will be observed after adding adsorbent to NaCl solution.[26]

The XRF analysis was carried out using X-ray fluorescence (XRF, unisantis, XMF-104) in order to determine the amount of iron which coated on AC.

The functional groups on the surface of AC and Fe-AC were determined before and after nitrate adsorption by using FTIR instrument (Nicolet, Nexus 670 spectrometer) with 4 cm^{-1} resolution within the range of 400–4000 cm^{-1}.

Experimental procedures

Nitrate removal was carried out with different rang of concentration and adsorbent dosages in 50 mL of nitrate solution. In these tests, the samples were shaked with constant speed of 100 rpm for 1 h with a shaker (FINEPCR, model SH30). In order to investigate the effect of pH on nitrate adsorption, pH of the $NaNO_3$ solution was adjusted to different values by diluted NaOH or HCl solutions using a pH-meter (GenWay, model 3345). pH of samples were measured after adsorption for knowing pH changes during the process. Due to analysis of interaction between pH and adsorbent particles, three different pH (3, 5.5 and 8) have been selected to investigate. The concentration of iron has been measured after nitrate adsorption and it was realized that there is no measurable amount of iron.

After 1 h of contact time, adsorbents were filtered with Whatman filter paper No.44 and nitrate concentrations were measured by Lovibond spectrophotometer (Spectro Direct). The removal percentage of nitrate was obtained using the eqn (1).

$$\text{Nitrate removal } \% = \frac{C_i - C_f}{C_i} \times 100 \qquad (1)$$

where C_i and C_f are the initial and final of nitrate concentration (mg L^{-1}).

Experimental design

Experiments have been done in different conditions of operating parameters such as pH, initial concentration and adsorbent dosage for both adsorbents. Table 1 shows the ranges for these parameters. The statistical analysis of the data was performed using Design Expert (version 7.0.0) software.[27] RSM is a combination of mathematical and statistical techniques used for developing, improving and optimizing the processes and can be used to evaluate the relative significance of several affecting factors even in the presence of complex interactions.[27-30]

In this study, CCD model that is the most frequently used based on RSM was carried out to assess a relation between response (nitrate removal %) and independent variables. Moreover, RSM was used to optimize the variables in order to predict the best value of response that was selected as maximum removal percentage of nitrate.[29] CCD has been selected because it is an effective design that is ideal for sequential experimentation, as it allows to test lack of fit when a sufficient number of experimental values are existed.[28]

Rotatability is one of the most important reasons for selecting the response surface design. Because RSM purpose is optimization and determination the location of the optimum response, so using a design that provides the equal precision of estimation in all directions is required. A central composite design is made rotatable by choosing of α. The α value for having a rotatable design depends on the number of the factorial points in design. By using $\alpha = n_f^{1/4}$, (where n_f is the number of factorial points which is 8 in this study) a rotatable central composite design was provided. According to mentioned formula, computed α was 1.68179.[27]

Based on our preliminary studies, three operation factors such as initial pH value (X_1), nitrate concentration (X_2) and the adsorbent dosage (X_3) were chosen as the variables [31]. The total number of experiments can be obtained using ($=2^K+2k+6$), where K is the number of factors ($K=3$). So, 20 experiments were formulated which consist of (2^K) 8 factorial points, six replicates at the central points and ($2K$) six star points. Each parameter was coded at five levels: $-\alpha$, -1, 0, 1, α at the determined ranges based on some preliminary experiments, which amount of α has important role for model to be rotatable. The ranges and levels of the actual form of coded variables from RSM studies have been listed in Table 1.

Table 1 Experimental ranges and levels of independent variables.

Independent variables	Actual form of Coded levels				
	$-\alpha$	-1	0	$+1$	α
X_1 (pH)	3	4	5.5	7	8
X_2 (nitrate concentration, mg L^{-1})	66	100	150	200	234
X_3 (adsorbent dosage, g/50 mL)	0.115	0.200	0.325	0.450	0.535

The optimum values of variables were determined by solving regression model.[32] To determine the optimum conditions, an experimental design as a function of the main parameters was developed. For description of process behavior, a model such as linear (eqn (2)), quadratic (eqn (3)) or cubic model (eqn (4)) might be required.

$$\text{Linear model} = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 \quad (2)$$

$$\text{quadratic model} = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_{12} X_1 X_2 + \beta_{13} X_1 X_3 + \beta_{23} X_2 X_3 + \beta_{11} X_1^2 + \beta_{22} X_2^2 + \beta_{33} X_3^2 \quad (3)$$

$$\text{Cubic model} = \text{quadratic model} + \beta_{123} X_1 X_2 X_3 + \beta_{122} X_1 X_2^2 + \beta_{133} X_1 X_3^2 + \beta_{211} X_2 X_1^2 + \beta_{233} X_2 X_3^2 + \beta_{311} X_3 X_1^2 + \beta_{322} X_3 X_2^2 + \beta_{111} X_1^3 + \beta_{222} X_2^3 + \beta_{333} X_3^3 \quad (4)$$

where β_0, β_i, β_{ii}, β_{iii} are the regression coefficients for intercept, linear, quadratic and cubic models, respectively. β_{ij} and β_{ijk} are interaction terms for quadratic and cubic models, and X_i, X_j and X_k are the independent variables. The quality of the fit of polynomial model was expressed by the value of correlation coefficient (R^2). As R^2 gets closer to 1, the provided results by the model will be more accurate. By using the amount of F-value (Fisher variation ratio), probability value (Prob > F), and Adequate Precision, the significance and adequacy of the final models have been analyzed.[27, 28, 33]

Equilibrium studies

In order to study the equilibrium isotherms, 50 mL of nitrate solutions with different initial concentration (25-200 mg L^{-1}) were prepared and shaked at 100 rpm for 24 h in 25, 35 and 45°C. pH and adsorbent dosage were set as their optimum conditions which were achieved by previous tests for AC and Fe-AC. After equilibrium time elapsed, the nitrate solution was filtered and the residual concentration of the nitrate was determined. The amount of nitrate adsorbed by adsorbents, q_e, was calculated by eqn (5).

$$q_e = \frac{V \times (C_0 - C_e)}{m} \quad (5)$$

where V is the volume of nitrate solution (L), C_0 and C_e are initial and equilibrium nitrate concentrations (mg L^{-1}), respectively and m is the amount of adsorbent (g).

Kinetic studies

Adsorption kinetic experiments were carried out by mixing 50 mL of nitrate solution with initial concentration, pH and adsorbent dosage set on their optimum conditions that obtained from Design Expert. Kinetic of adsorption was analyzed at different contact times from 0 to 60 min and shaking speed of 100 rpm. After adsorption time, the solution was filtered and residual was analyzed for nitrate concentration. The amount of nitrate adsorbed by adsorbent after elapsing *t* min, q_t, was obtained from eqn (6).

$$q_t = \frac{V \times (C_0 - C_t)}{m} \tag{6}$$

where *V* is the volume of the nitrate solution (L), C_0 and C_t are initial concentration and concentration at time t in mg L^{-1} and m is the amount of adsorbents (g).

Results and discussions

Characteristics of the adsorbents

In Fig. 1(a) and 1(b), SEM of AC and Fe-AC show the effect of loading iron on activated carbon. Accordingly Fig. 1, Fe-AC has less impurities compared to the AC which is the effect of the modification that removed them. Iron particles can be seen in Fig. 1(b), that were obtained in nano scale. Fig. 2(a) and 2(b) show the nitrate that adsorbed onto AC and Fe-AC. Improvement of nitrate adsorption is expected due to the effect of modification with iron components that washed impurities and increased the positive charges of activated carbon with Fe^{3+}. The positive charges create high affinity to nitrate ions with negative charge, so increase the amount of removing.

Physical and chemical properties of AC and Fe-AC are presented in Table 2. According to Table 2, modification has increased the specific surface area and total pore volume, which is probably due to removing of impurities from activated carbon.[20, 34] Moreover, pH_{pzc} of Fe-AC has decreased compared to AC which indicates more positive charge on the modified adsorbent.

The XRF results determined that 16.8% of the Fe-AC is belonged to Fe element which indicates iron coated on AC, effectively.

The FTIR spectroscopic results of AC and Fe-AC before and after nitrate adsorption are shown in Fig. 3(a) and 3(b), respectively. The bands at 3430 cm^{-1} can be attributed to the absorption of water molecules due to the stretching of O-H.[35] The bands at 2920 are attributed to C-H interaction with the surface of activated carbon samples. The bands at 2850 cm^{-1} can be attributed to dimer of OH in carboxylic acid. In the region 1300-1750 cm^{-1}, amides can be distinguished on surface of the activated carbon samples.[36] The bands at 1100 cm^{-1} can be attributed to the stretching of C-O in carboxylic acid.[37] The bands between 500 and 700 cm^{-1} are due to the Fe–O stretching vibration. Moreover, the bands between 795 and 900 cm^{-1} can be attributed to Fe-O-H bending vibrations in α-FeOOH.[25] A new peak at 582 cm^{-1} was observed at Fig. 3(b), which shows a new group containing Fe. The intensity of these ranges at Fe-AC is higher than AC which indicates more iron accumulation. These functional groups which contain Fe, prove that Fe_2O_3 nanoparticles have been coated on activated carbon surface effectively. The change of intensity of bands at 3430 and in the ranges between 600 and 2850, indicate chemical interactions between adsorbents and nitrate.

Table 2 Characteristics of the adsorbents.

Parameter	AC	Fe-AC
BET ($m^2\ g^{-1}$)	922	1012
Average pore radius (Angstrom)	12.84	12.83
Total pore volume ($cm^3\ g^{-1}$)	0.614	0.649
pH_{pzc}	6.9	5.0

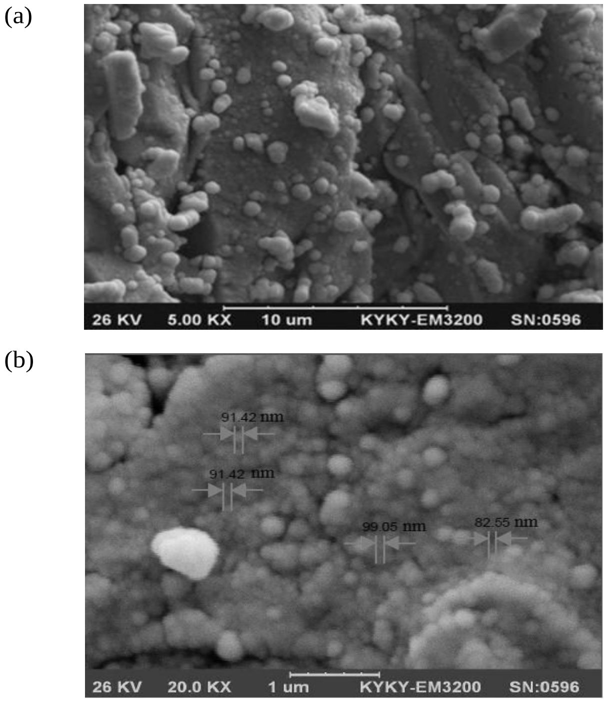

Fig.1 (a) SEM of AC at 5000 x, (b) SEM of Fe-AC at 20000 x.

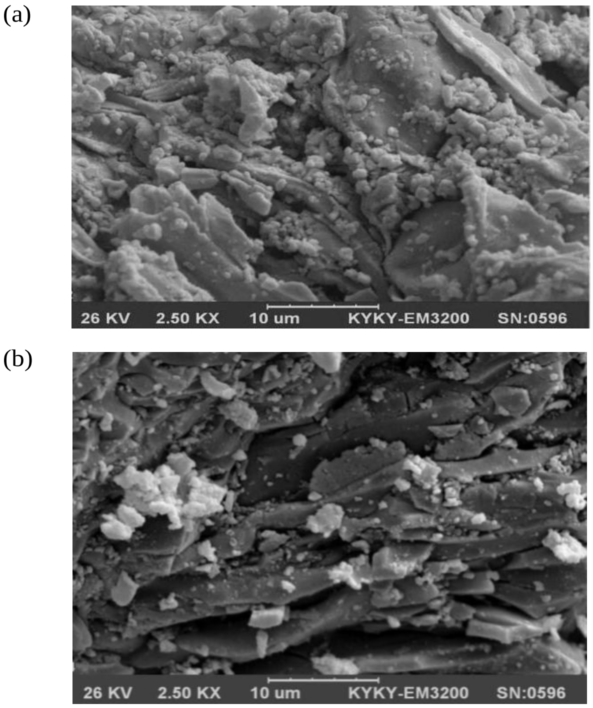

Fig.2 (a) SEM of AC, (b) Fe-AC after nitrate adsorption at 2500 x.

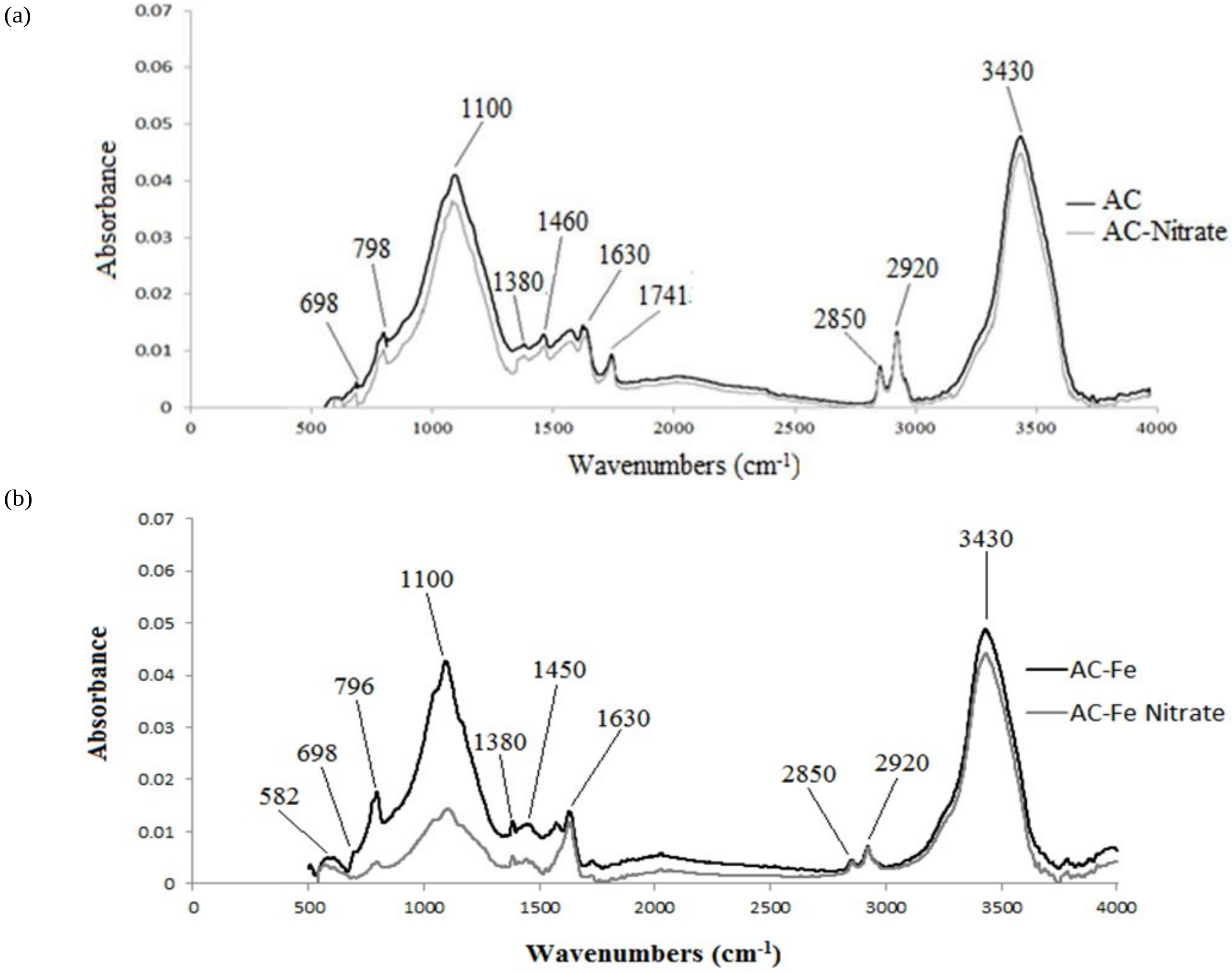

Fig.3 FTIR spectra before and after nitrate adsorption for (a) AC, (b) Fe-AC.

RSM and model fitting

According to the experimental design, 20 experiments have been done for investigation of nitrate removal. The results for both adsorbents are presented in Table 3. The obtained removal percentage of nitrate varies between 8.26 and 62.10% for AC, and 23.33 and 84.00% for Fe-AC. Tables 4 and 5 show the analysis of variance (ANOVA) of regression parameters of the predicted response surface models for AC and Fe-AC. F-values of 69.56 and 116.71 for AC and Fe-AC and their low p-value (<0.0001) indicate that the obtained models were significant. Values of Prob >F that are less than 0.0500 demonstrate that the model terms are significant, while values greater than 0.1000 indicate that the model terms are not significant.[38] Therefore, non-significant parameters have been omitted in the final model. Based on ANOVA Table, X_1, X_2, X_3, X_2X_3, X_1^2, $X_1X_2^2$ were significant model terms for AC and X_1, X_2, X_3, X_2^2 and X_3^2 were significant model terms for Fe-AC. In final model for nitrate removal using AC, parameter of X_2X_3 that is the interaction between initial concentration and adsorbent dosage has not been omitted, because it was observed that its considering in final model promote the adequacy of the model. The final regression models in terms of coded parameters are given by eqn (7) and (8).

$$\text{Removal percentage for AC} = 16.69 - 21.63\,X_1 - 5.25\,X_2 + 5.37\,X_3 - 1.57\,X_2X_3 + 20.94\,X_1^2 + 15.46\,X_1X_2^2 \quad (7)$$

$$\text{Removal percentage for Fe-AC} = 56.77 - 3.31\,X_1 - 7.92\,X_2 + 15.59\,X_3 + 2.93\,X_2^2 - 2.84\,X_3^2 \quad (8)$$

As it can be seen at eqn (7) and (8), final models agreed to non-complete cubic model and quadratic model for AC and Fe-AC, respectively. Complete cubic model is aliased which means that there are not enough parameters to fit the model properly. Therefore, non-important terms were reduced from the complete cubic model, and non-complete cubic model provided and used as final model. Nazghelichi used the same non-complete cubic model for optimization of an artificial neutral network using response surface.[39]

These models have been selected because of the following reasons. The "Adequate Precision" ratio of the models that measure the signal to noise ratio were 32.487 and 34.913 for AC and Fe-AC final models (Adequate Precision>4), which indicate an adequate signal for the models.[33, 40] Also, the F-values of lack of fits are not high which show the models are not very sensitive to systematic variation. High amounts of R-squared (0.9720 and 0.9782) of the models show that only 2.8 and 2.18% of total variation might not be explained by the predicted models (eqn (7) and (8)). It can be concluded that Response Surface methodology can create reasonable model for nitrate removal process, so it was used for prediction of maximum adsorption percentage. By applying the diagnostic plots, such as the predicted versus actual value plots, the models adequacy can be assessed to be sure if the selected models provide adequate approximation of the real system. Fig. 4(a) and (b) show the predicted values versus actual plots. According to these figures, the models explain the studied experimental ranges well as it is following a straight line.

Perturbation plots (Fig. 5(a) and (b)) show the comparative effects of all independent variables on nitrate removal efficiency. In Fig. 5(a) curvature in pH is the sharpest and effect of adsorbent dosage is sharper than initial concentration for AC which indicates that nitrate removal percentage is very sensitive to pH compared to initial concentration and adsorbent dosage. This can be realized from ANOVA table as well. As it was indicated in Table 4, the F-value of pH is higher than initial concentration and adsorbent dosage. In Fig. 5(b) curvature in adsorbent dosage is the sharpest for Fe-AC and initial concentration is sharper than pH which indicates that nitrate removal percentage is very sensitive to adsorbent dosage compared to the initial concentration and pH. As it was indicated in Table 5, the F- value of adsorbent dosage is higher than initial concentration and pH.

Nitrate removal efficiency

The 3D surface response figures for removal percentage of nitrate using AC and Fe-AC are illustrated in Fig. (6) and (7), respectively. In each plot, one parameter was kept constant at its final optimum amount, while the other two parameters varied within their experimental ranges.

As reported in Table 3, the maximum observed nitrate removal percentage by AC was 62.104 % at pH=3, C_0=150 mg L^{-1} and m=0.325 g/50 mL, meanwhile the minimum removal percentage was 8.256 % at pH=5.5, C_0=150 mg L^{-1} and m=0.115 g/50 mL. The maximum observed nitrate removal percentage by Fe-AC was 84.000% at pH=5.5, C_0=65.91 mg L^{-1} and m=0.325 g/50 mL meanwhile the minimum removal percentage was 23.333% at pH=5.5, C_0=150 mg L^{-1} and m=0.115 g/50 mL.

Table 3 The corresponding experimental conditions and obtained responses.

Run	X_1: pH	X_2: C_0(mg L^{-1})	X_3: m(g) in 50 mL	%Removal of AC	%Removal of Fe-AC
1	7.00	200.00	0.450	17.641	60.000
2	4.00	200.00	0.200	15.233	35.000
3	4.00	100.00	0.450	37.226	76.000
4	7.00	200.00	0.200	10.247	30.000
5	4.00	200.00	0.450	23.255	70.000
6	7.00	100.00	0.200	13.884	46.000
7	4.00	100.00	0.200	25.078	49.000
8	5.50	150.00	0.325	17.315	55.333
9	5.50	150.00	0.325	14.990	56.667
10	5.50	150.00	0.325	16.673	58.000
11	5.50	150.00	0.325	15.711	56.000
12	7.00	100.00	0.450	29.678	75.000
13	5.50	150.00	0.535	26.053	78.000
14	5.50	234.09	0.325	12.413	50.000
15	3.00	150.00	0.325	62.104	60.000
16	5.50	150.00	0.325	14.990	57.333
17	5.50	150.00	0.325	16.192	56.667
18	8.00	150.00	0.325	18.843	55.333
19	5.50	65.91	0.325	31.579	84.000
20	5.50	150.00	0.115	8.256	23.333

Table 4 ANOVA Table for AC.

Source	Sum of Squares	Degree of freedom	Mean Square	F-value	Prob> F
Model	2636.94	6	439.49	69.56	<0.0001
X_1	935.79	1	935.79	148.10	<0.0001
X_2	376.69	1	376.69	59.62	<0.0001
X_3	393.29	1	393.29	62.24	<0.0001
X_2X_3	19.61	1	19.61	3.10	0.1035
X_1^2	803.94	1	803.94	127.23	<0.0001
$X_1X_2^2$	280.12	1	280.12	44.33	<0.0001
Residual	75.82	12	6.32	-	-
Lack of Fit	71.93	8	8.99	9.24	0.0237
Pure error	3.89	4	0.97	-	-

Table 5 ANOVA Table for Fe-AC.

Source	Sum of Squares	Degree of Freedom	Mean Square	F-value	Prob> F
Model	4496.69	5	899.34	116.71	<0.0001
X_1	52.78	1	52.78	6.85	0.0213
X_2	856.94	1	856.94	111.21	<0.0001
X_3	3320.13	1	3320.13	430.86	<0.0001
X_2^2	124.92	1	124.92	16.21	0.0014
X_3^2	117.66	1	117.66	15.27	0.0018
Residual	100.18	13	7.71	-	-
Lack of Fit	96.06	9	10.67	10.39	0.0189
Pure error	4.11	4	1.03	-	-

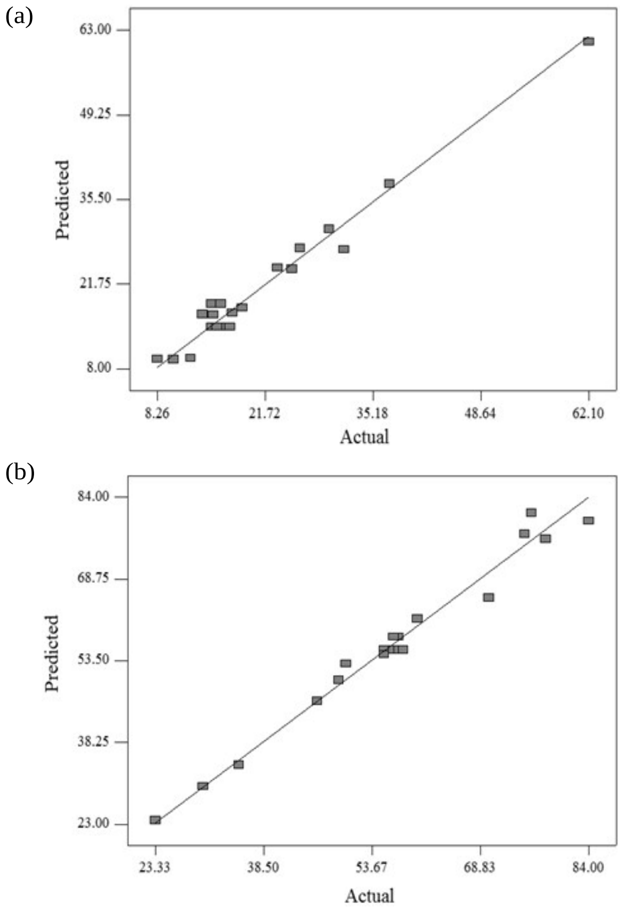

Fig.4 Predicted versus actual values plot for nitrate removal using (a) AC, (b) Fe-AC.

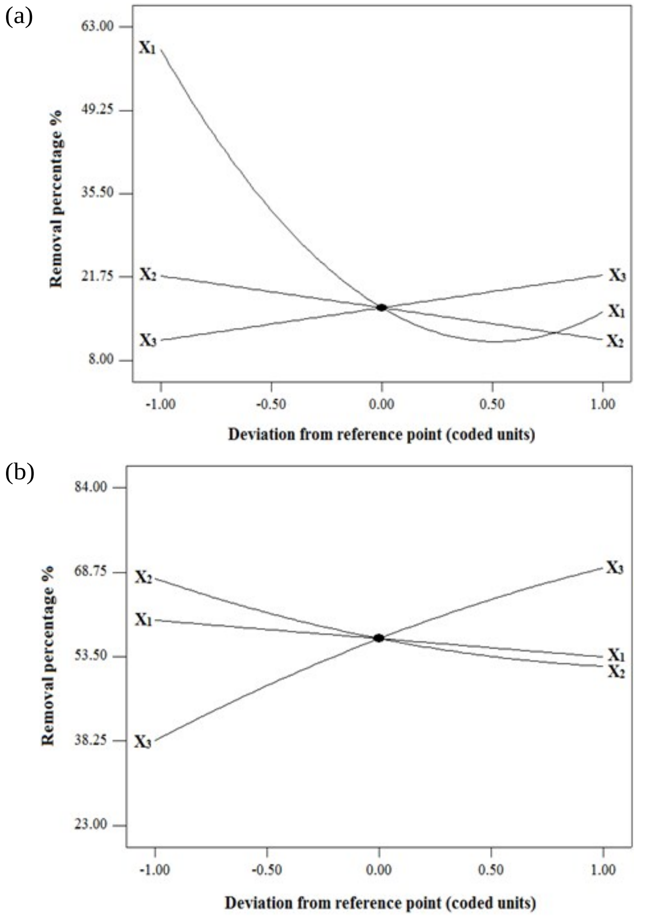

Fig.5 Perturbation plot for nitrate removal at central point of design parameters (pH=5.5, C_0=150 mg L^{-1}, m=0.325 gr/50 mL) using (a) AC, (b) Fe-AC.

Optimization of operational parameters

The goal of the process (nitrate removal percentage) has been set as maximum while the process parameters (adsorbent dosage, initial concentration and pH) have been set as "within the range", then response surface method was used to optimize the process versus process parameters. Accordingly, the optimum amount of parameters and respective percent removal efficiencies were established.

Based on the optimum conditions, 68.45% nitrate removal was predicted by the model under operational conditions of (adsorbent dosage 0.53 g/50 mL, initial concentration of 147.31 mg L^{-1} and pH=3) for AC. Similarly, 95.56% nitrate removal was predicted under operational conditions of (adsorbent dosage 0.53 g/50 mL, initial concentration of 69.16 mg L^{-1} and pH=5.1) for Fe-AC. The desirability function values were found as 1.0 for both predicted optimum conditions. This optimum predicted results were checked by repeating experiments, and it was observed that the experiment and model results were in good agreement with relative errors of just 6.94 and 4.44% for AC and Fe-AC, respectively.

The ranges of nitrate removal percentage with other adsorbents have been presented in Table 6. As it is seen in Table 6, the maximum removal percentage of this study adsorbents (especially Fe-AC) are comparable to other studies. According to the results, it can be concluded that modification with iron particles improved removal percentage significantly.

Adsorption isotherms

Isotherms of adsorption help to understand the adsorbate-adsorbent interaction. Langmuir and Freundlich isotherms are the most common isotherm models for describing adsorption characteristics of the adsorbents.[41] In this study, equilibrium data were analyzed with the Langmuir, Freundlich, Dubinin-Radushkevich and Temkin isotherms. The parameters values of these models have been reported in Table 7.

In Langmuir isotherm theory, the basic assumption is that the adsorption takes place at monolayer coverage of adsorbate over a homogeneous adsorbent surface. The linear form of Langmuir isotherm equation is given as eqn (9).[13]

$$\frac{C_e}{q_e}=\frac{1}{k_l}+\frac{a_l}{k_l}C_e \qquad (9)$$

Table 6 Nitrate removal percentage of different adsorbent.

Adsorbent	pH	Adsorbent dosage (g/50 mL)	Initial concentration (mg L^{-1})	Removal %	References
C-Cloth	7	-	115	8.7	12
Acid treated C-Cloth	7	-	115	29.5	12
Activated carbon	2-10	0.250-1.000	100	54.3-71.0	14
Sepiolite	2-10	0.250-1.000	100	29.3-35.4	14
Sepiolite activated by HCl	2-10	0.250-1.000	100	76.4-99.6	14
Activated carbon prepared from sugar beet bagasse	3	0.100	100	41.2	42
Zinc chloride treated activated carbon	3-12	0.5	50	16-28.5	43
Carbon residue	6	0.25	25-125	1.9-21.6	44
Activated carbon residue	6	0.25	25-125	12.8-29.9	44
Commercial activated carbon	4	0.25	25-125	31.1-81.3	44
AC	3-8	0.115-0.535	66-234	8.3-63.8	This study
Fe-AC	3-8	0.115-0.535	66-234	23.3-91.3	This study

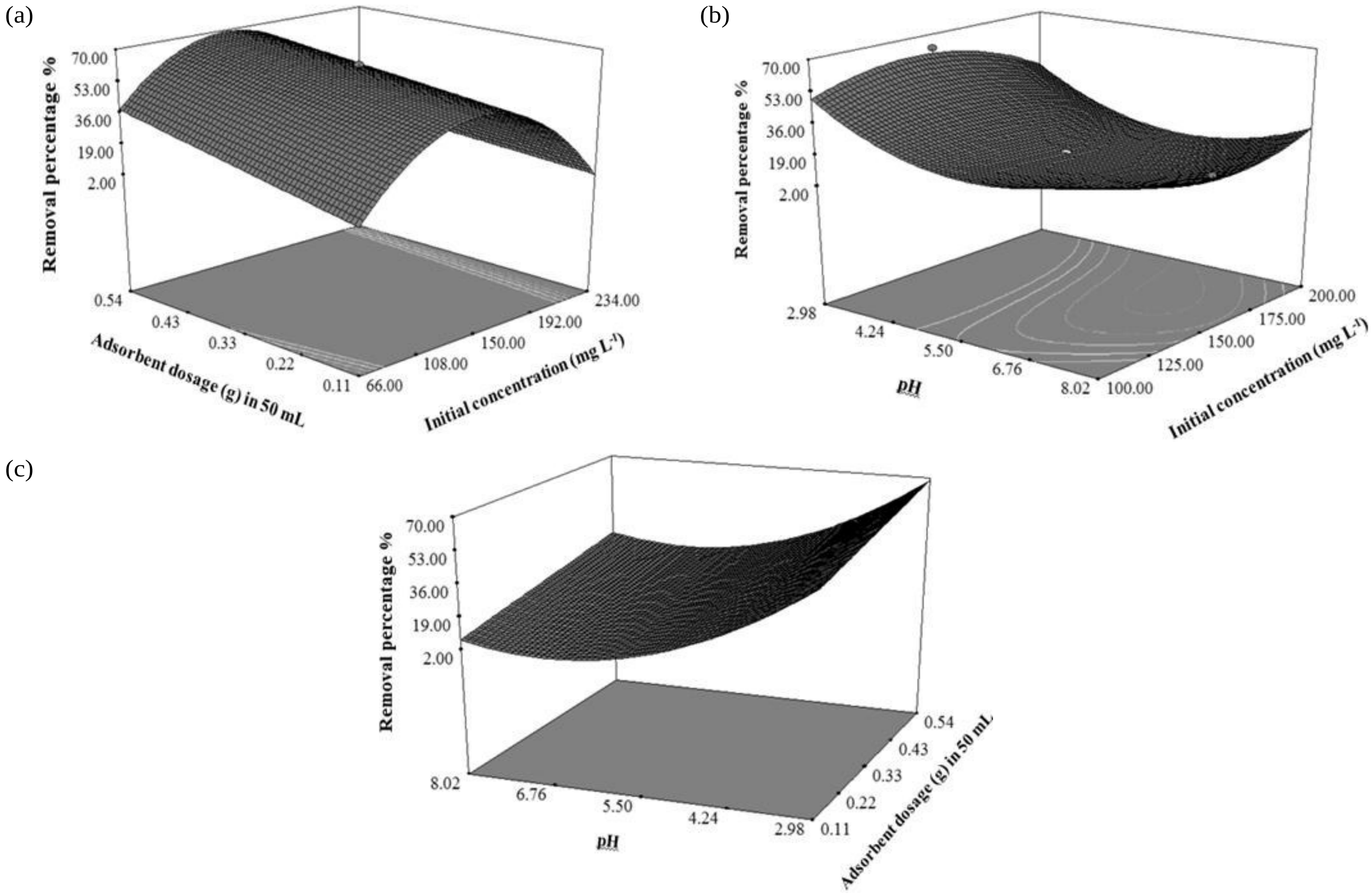

Fig. 6 3D Surface Response for nitrate removal with AC versus (a) adsorbent dosage and initial concentration at pH=3, (b) pH and initial concentration at adsorbent dosage=0.53 g/50 mL, (c) adsorbent dosage and pH at initial concentration=147.31 mg L^{-1}.

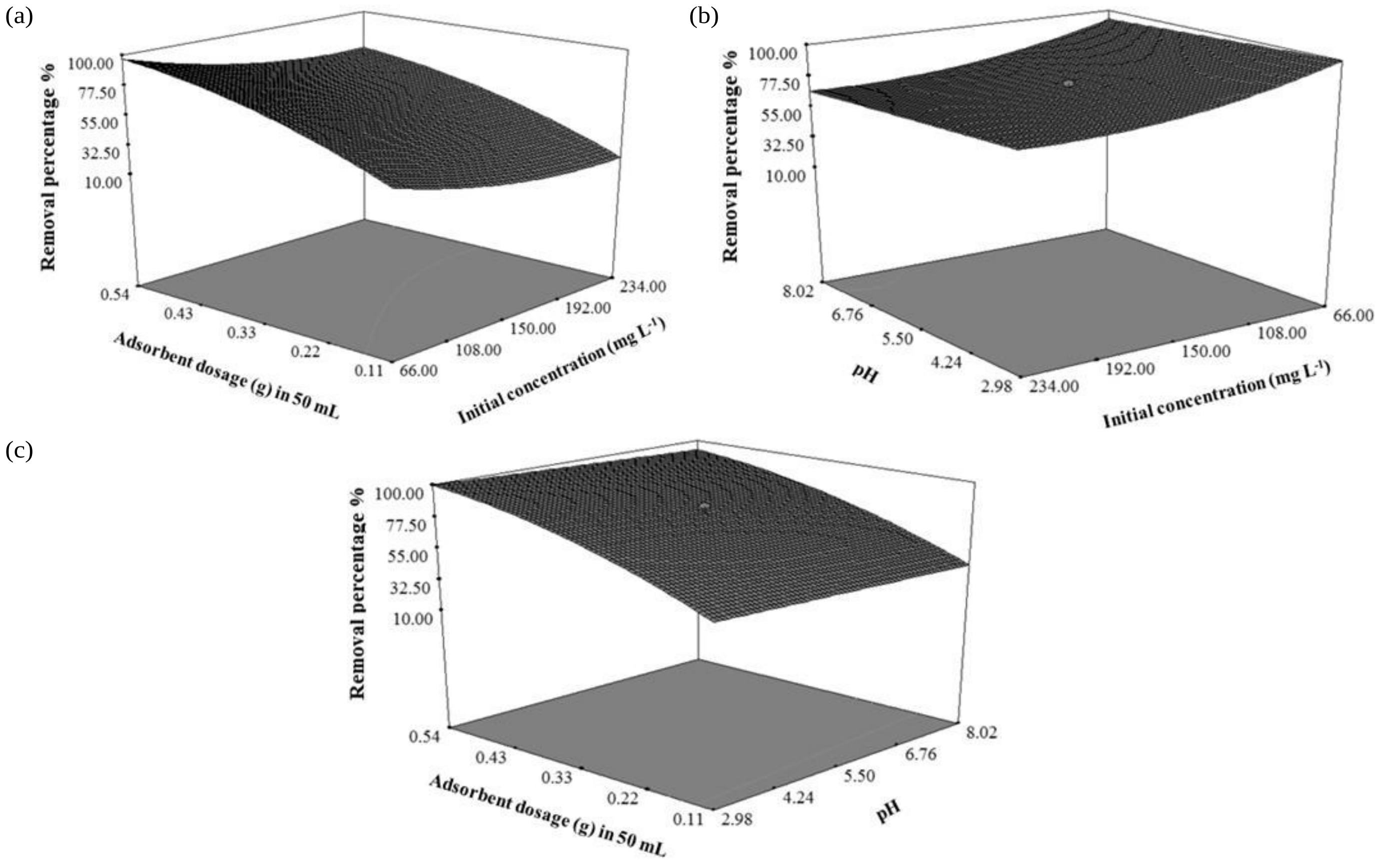

Fig. 7 3D Surface Response for nitrate removal with Fe-AC versus (a) adsorbent dosage and initial concentration at pH=5.1, (b) pH and initial concentration at adsorbent dosage=0.53 g/50 mL, (c) versus adsorbent dosage and pH at initial concentration=69.16 mg L^{-1}.

where q_e is the amount of nitrate adsorbed on activated carbon (mg g^{-1}), C_e is the equilibrium concentration (mg L^{-1}), a_l (L mg^{-1}) and k_l (L g^{-1}) are Langmuir constants. The characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless equilibrium parameter (R_L) [41] which is presented by eqn (10).

$$R_L = \frac{1}{1 + a_l C_0} \qquad (10)$$

where a_l is the Langmuir constant and C_0 is the initial nitrate concentration (mg L^{-1}). The value of R_L indicates the type of isotherm to be either unfavorable (R_L>1), linear (R_L=1), favorable (0<R_L<1), or irreversible (R_L=0).[13] The R_L values for nitrate adsorption at different temperatures indicate that the adsorption is a favorable process.

The Freundlich isotherm is an empirical equation, that assumes the adsorption process takes place on heterogeneous surfaces.[45] The linear form of Freundlich isotherm equation is given as eqn (11).

$$\log q_e = \log k_f + \frac{1}{n} \log C_e \qquad (11)$$

where C_e is the equilibrium concentration of the adsorbate (mg L^{-1}), q_e is the amount of nitrate adsorbed per unit mass of adsorbent (mg g^{-1}), k_f and n are Freundlich constants. k_f (mg g^{-1} $L^{1/n}$ $mg^{-1/n}$) is roughly an indicator of the adsorption capacity of the adsorbent and n indicates favorability of adsorption. As *1/n* gets closer to zero, it becomes more heterogeneous. Using the slope of *1/n* (which changes between 0 and 1), adsorption intensity or surface heterogeneity can be measured. According to the results, the values of n are greater than 1 which shows a favorable adsorption condition.[46]

Dubinin–Radushkevich[47] (D-R) isotherm is an empirical model which uses to distinguish the physical and chemical adsorption. The D–R equation has the linear form which is given as eqn (12).

$$\ln q_e = \ln q_m - \beta \varepsilon^2 \qquad (12)$$

where q_m is the maximum amount of ion that can be sorbed onto unit weight of adsorbent (mol g^{-1}), β is the constant related to the sorption energy (mol^2 kJ^{-2}), and the parameter ε is polanyi potential that can be calculated using eqn (13).

$$\varepsilon = RT \ln(1 + \frac{1}{C_e}) \qquad (13)$$

where R is the gas constant (kJ mol^{-1} K^{-1}), and T is the absolute temperature (K). Mean free energy E (kJ mol^{-1}) of sorption is the free energy that changes when one mole of nitrate ion is transferred to the surface of the adsorbent from infinity in the solution and it can be calculated from eqn (14).

$$E = (-2\beta)^{-1/2} \qquad (14)$$

This parameter indicates adsorption mechanism is ion exchange or physical adsorption. If the magnitude of E is between 8 and 16 kJ mol^{-1}, the adsorption process is governed by ion-exchange, while for the values of $E < 8$ kJ mol^{-1}, the adsorption process is affected by physical forces. According to the results, the nature of both adsorptions was ion exchange (chemical adsorption) in this study.

Temkin isotherm[48] suggests that the heat of adsorption of all the molecules in the layer would decrease linearly rather than logarithmic with coverage if the concentration of the solution was not very high or low. The linear form of Temkin isotherm is presented by the eqn (15).

$$q_e = \beta \ln k_t + \beta \ln C_e \qquad (15)$$

where k_t is the equilibrium binding constant (L mg^{-1}) corresponding to the maximum binding energy and constant β (J mol^{-1}) is related to the heat of adsorption. Because of Temkin model results, it can be concluded that the heat of adsorption decreases linearly with surface coverage.

Fig. 8 and 9 illustrate the predicted equilibrium adsorption values versus equilibrium concentration at different temperatures using isotherm models for AC and Fe-AC, respectively. These figures show that Langmuir isotherm has the best fit to experimental equilibrium adsorption data for both adsorbents. This is also confirmed by the higher value of R^2 in case of Langmuir model compared to other models for all investigated temperatures. This indicates that the adsorption of nitrate onto both adsorbents take place as monolayer adsorption on a homogeneous surface. According to the Langmuir isotherm, maximum adsorption capacities were 11.0132 and 17.7305 mg g^{-1} for AC and Fe-AC, respectively.

Adsorption kinetics

Kinetic modeling is analyzed to investigate the mechanism of adsorption and the potential rate controlling processes, such as, mass transfer and chemical reaction. The adsorption kinetics of nitrate onto AC and Fe-AC were investigated by three common models named, pseudo-first-order model, pseudo-second-order model and intraparticle diffusion model.

A simple kinetic analysis of adsorption is the Lagergren's pseudo-first-order differential equation[49] that can be expressed as eqn (16).

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \qquad (16)$$

where q_e and q_t are the amount of nitrate adsorbed at equilibrium and at time t (mg g^{-1}), respectively. k_1 (min^{-1}) is the equilibrium rate constant of pseudo-first-order model.

The experimental data were tested by the second order model[41] using eqn (17).

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (17)$$

where q_e and q_t are the amount of nitrate adsorbed at equilibrium and at time t (mg g^{-1}), respectively. k_2 (g mg^{-1}min^{-1}) is the equilibrium rate constant of pseudo-second-order model.

Table 7 Isotherm model parameters for nitrate adsorption onto AC and Fe-AC adsorbents.

Isotherm models	Parameters	AC			Fe-AC		
		25 ºC	35 ºC	45ºC	25 ºC	35 ºC	45ºC
Langmuir	q_m(mg g^{-1})	11.0132	10.2881	9.9305	17.4216	17.6367	17.7305
	a_l (L mg^{-1})	0.0733	0.0514	0.0469	0.0643	0.0785	0.1034
	k_l (L g^{-1})	0.8074	0.5286	0.4661	1.1198	1.3841	1.8328
	R_L	0.0638-0.3530	0.0887-0.4377	0.0963-0.4601	0.2205-0.8811	0.2031-0.8792	0.1802-0.8775
	R^2	0.9971	0.9922	0.9968	0.9992	0.9991	0.9980
Freundlich	n	2.1587	2.1906	2.1482	1.7596	1.7986	1.8681
	k_f	1.3642	1.1439	1.0332	1.5849	1.8315	2.2090
	R^2	0.9422	0.9725	0.9722	0.9778	0.9740	0.9665
D-R	q_m(mg g^{-1})	36.5898	29.9512	29.1125	75.8357	77.7399	78.1061
	β(mol^2 kJ^{-2})	4.70E-03	4.40E-03	4.20E-03	5.40E-03	4.80E-03	4.30E-03
	R^2	0.9657	0.9865	0.9867	0.9906	0.9880	0.9828
	E (kJ mol^{-1})	10.3	10.7	10.9	9.62	10.2	10.8
Temkin	β(J mol^{-1})	2.3666	2.1243	1.8336	3.6031	3.6358	3.6217
	k_t(L mg^{-1})	0.7522	0.5800	0.6100	0.7504	0.9202	1.2279
	R^2	0.9802	0.9910	0.9960	0.9917	0.9936	0.9959

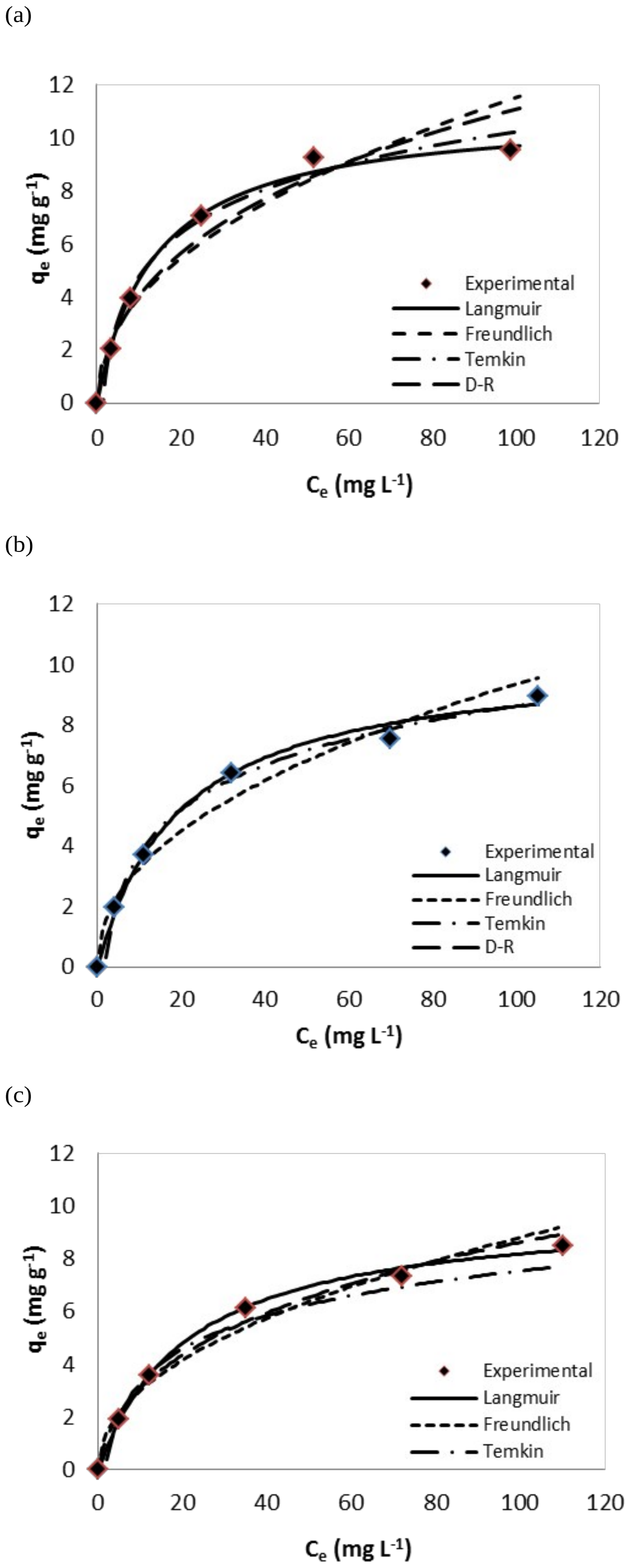

Fig. 8 Isotherm plots for the adsorption of nitrate onto AC at (a) 25˚C, (b) 35˚C, and (c) 45˚C.

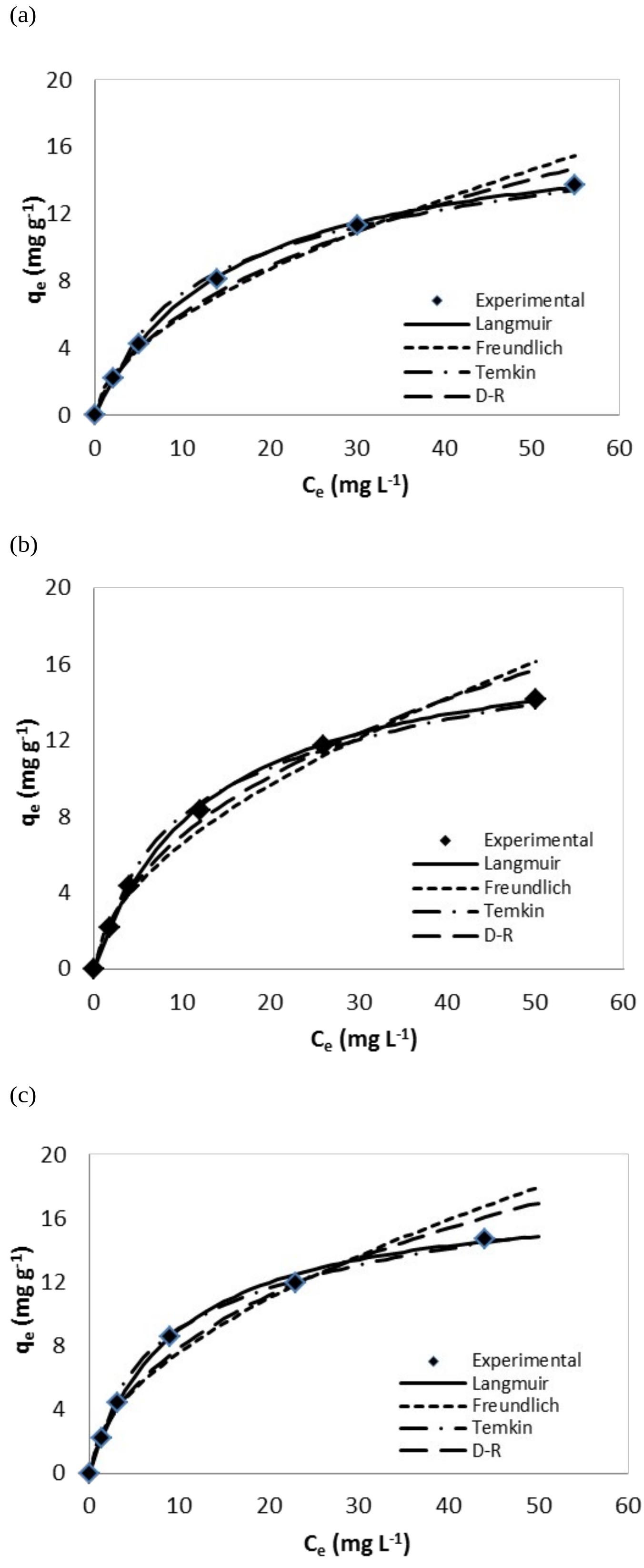

Fig. 9 Isotherm plots for the adsorption of nitrate onto Fe-AC at (a) 25˚C, (b) 35˚C, and (c) 45˚C.

Intraparticle diffusion[50] is the diffusion across the liquid film surrounding the adsorbent particles like external diffusion or film diffusion. Weber-Morris found that in many adsorption processes, solute uptake almost proportionally with $t^{1/2}$ in comparison with t, and presented the model by eqn (18).

$$q_t = k_3 t^{1/2} + c \tag{18}$$

If the regression of q_t against $t^{1/2}$ is linear and passes through the origin, intraparticle diffusion will be the only rate limiting mechanism. Otherwise, the other mechanisms are involved with intraparticle diffusion. The intercept gives an idea about the thickness of boundary layer. As larger intercept result the greater effect of boundary layer.

Fig. 10 illustrates the linear plots of mentioned kinetic models. Parameters of these models and their R^2 values have been listed in Table 8. Results demonstrate that there is a good agreement of the experimental data with the pseudo-second-order model compared to the other models. This suggests that the adsorption of nitrate process was controlled by chemisorption which proved the results that had been obtained by D-R isotherm.[46, 51] High R^2 value of intraparticle diffusion model shows the part of intraparticle diffusion in adsorption process and because of not passing through the origin, it is not the only rate limiting process.

Conclusions

In order to improvement of nitrate removal from water, composite of activated carbon and Fe_2O_3 nanoparticles as a new adsorbent has been prepared. FTIR, XRF and SEM analysis proved that Fe_2O_3 nanoparticles coated on activated carbon surface effectively. Our results indicated that the composite of activated carbon and Fe_2O_3 nanoparticles (Fe-AC) has high potential for nitrate removal and improved the removal percentage significantly compared to activated carbon. Based on RSM results at optimum conditions, AC could achieve 68.45% of nitrate removal after 1 h contact under the adsorbent dosage of 0.53g/50 mL, initial concentration of 147.31 mg L^{-1} and pH of 3. Similarly, Fe-AC was able to nitrate removal about 95.56% after 1 h contact under the adsorbent dosage of 0.53g/50 mL, initial concentration of 69.16 mg L^{-1} and pH of 5.1. These predicted results were fitted well with experiments with relative errors of 6.94% for AC and 4.44% Fe-AC, respectively. The final models were validated using predicted versus actual plots and R-squared of the models to be sure about the optimum experimental conditions which were predicted by the models. The adsorption equilibrium data fitted well with the Langmuir isotherm. The trends of the adsorption kinetics data followed pseudo-second-order model, demonstrating that chemisorption was mechanism that controlled nitrate adsorption. According to this study, adsorption process is practical for removing nitrate from water.

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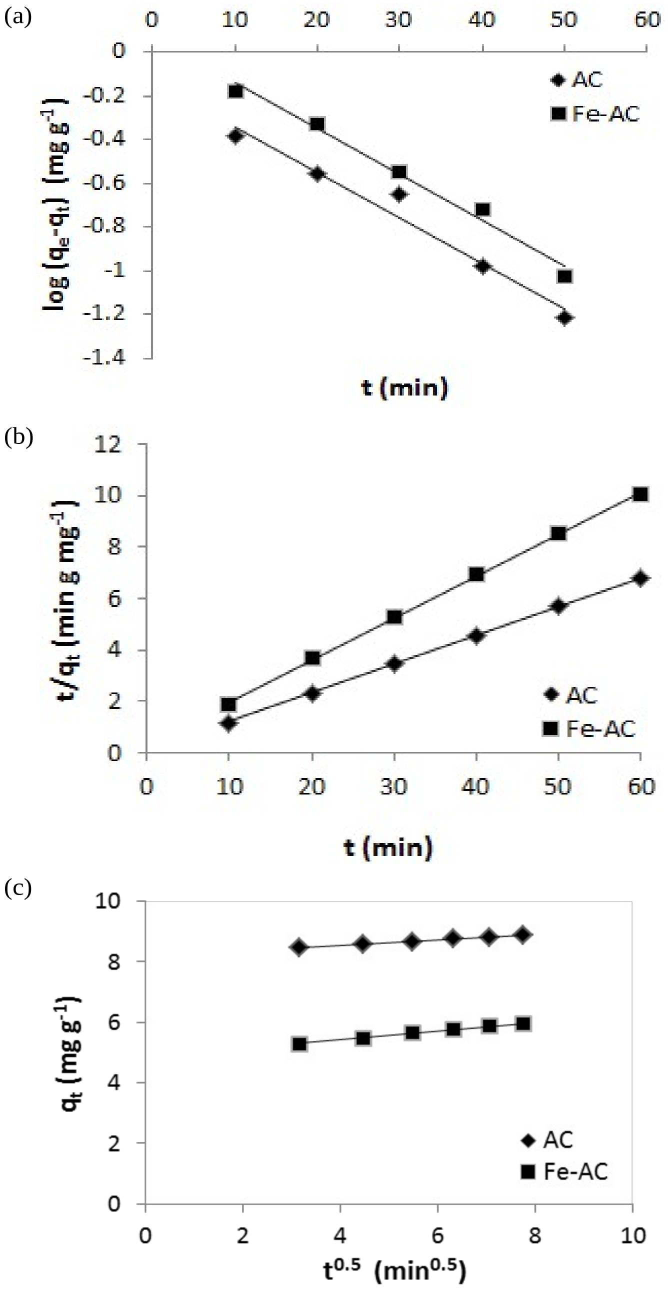

Fig.10 (a) pseudo-first-order model; (b) pseudo-second-order model; and (c) intraparticle diffusion model at their optimum conditions.

Table 8 Kinetic model parameters for nitrate adsorption.

Adsorbent	experimental	First-order kinetic model			Second-order kinetic model			Intraparticle diffusion		
	q_e (mg g^{-1})	k_1(min^{-1})	q_e (mg g^{-1})	R^2	k_2 (g mg^{-1} min^{-1})	q_e (mg g^{-1})	R^2	k_3	c	R^2
AC	8.8704	0.0479	0.7377	0.9665	0.1348	8.9606	0.9999	0.0898	8.1777	0.9907
Fe-AC	5.9574	0.0479	1.1633	0.9841	0.0790	6.1162	0.9996	0.1442	4.8502	0.9955

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