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ORIGINAL ARTICLE

Optimization of ammonium removal from waste water by natural zeolite using central composite design approach

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Abstract The aims of the present study are to investigate removal of ammonium ion from wastewater using natural Western Azarbaijan zeolite and to optimize effective parameters by experimental design. In order to remove ammonium ions from aqueous solutions, experiments were carried out using column method as functions of the initial ammonium concentration, flow rate and pH of the solution. The results clearly confirmed that all mentioned parameters have vital affects on removing ammonium ions from wastewater and effluents, so got optimized. Central composite design with response surface methodology was applied for the optimization of main experiment parameters. The significance of the independent variables and their interactions were tested by the analysis of variance ANOVA and *f*-test statistics. Optimization of the variables for maximum removal efficiency by natural zeolite was performed using the quadratic model. The model predicted maximum removal efficiency under the optimum conditions including initial ammonium concentration of 30 mg l^{-1}; flow rate of 1 ml min^{-1} and pH 6, which was very close to the experimental value determined in column experiment. The cation exchange capacity of natural Western Azarbaijan zeolite was found to be 1.79 meq g^{-1}. Based on the experimental results, it can be concluded that the natural Western Azarbaijan zeolite has an excellent potential for removing ammonium ions from aqueous solutions and it is suggested as a suitable material for wastewater treatment.

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Introduction

Nitrogen compounds are undoubtedly considered as one of the most vital elements in living organism's life. The presence of excess nitrogen compounds causes environmental pollution and leads to harmful toxic symptom and puts the sea animal's life particularly fishes in danger. Therefore, monitoring its amount in environmental resources is inevitable and plays an important role in public health. Ammonia and ammonium ion are considered as the more commonly polluting nitrogen compounds in wastewaters and ground waters. Among the widely used processes for excluding nitrogen compounds [1–7], the biological nitrification–denitrification method is the most common method for the removal of high ammonium ion concentration from wastewater. However, since biological methods do not respond well to shock loads of ammonia, unacceptable peaks over the discharging levels may frequently appear in the effluent ammonium ion concentrations. In addition, this technique has practical limitations; pH should be controlled in cold weather treatment, the activity of nitrification bacteria declines and the treatment of nitrogen compound wastewater of low organic content by a biological process usually need to be supplemented with a carbon source, which may add to the treatment cost. In contrary, ion exchange process offers an alternative method for the removal of ammonium ion [8, 9].

Organic resins are very expensive to get employed in ion exchange processes; therefore, zeolites abundantly presents in nature, are preferred. Natural zeolites are the most important inorganic cation exchangers exhibiting high ion exchange capacity, selectivity and compatibility with the natural environment. Although zeolites can be employed for removal of ammonium ions from aqueous solution and waste water, other processes such as biological and chemical treatments are also very common [10].

There are more than 50 known naturally occurring zeolites [11]. Natural zeolites are hydrated aluminosilicates with comprising silica and aluminium tetrahedra which result in a stable three-dimensional framework. This honeycomb structure is generally very open, containing channels and cavities, which are filled with cations and water molecules [12]. The cations are bound by weaker electrostatic bonds, increasing their mobility and the capability of being exchanged with cations present in solution [13, 14].

The general formula of a zeolite is as follows:

$$(M_x^+, M_y^{2+})(Al_{(x+2y)}Si_{n-(x+2y)}O_{2n}) \cdot mH_2O$$

where, M^+ and M^{2+} are mono valent and divalent cations such as Na^+, K^+, and Ca^{2+}, Mg^{2+}, Ba^{2+}, respectively. These ions are called exchangeable cations.

The following order is suggested for cation selectivity arrange of natural zeolite [15]:

$$Cs^+ > Rb^+ > K^+ > NH_4^+ > Ba^{2+} > Sr^{2+} > Na^+ > Ca^{2+} > Fe^{3+} > AI^{3+} > Mg^{2+} > Li^+$$

Considering the former relation, natural zeolites approximately have a high selectivity for adsorption of ammonium ion. Clinoptilolite is the most abundant natural zeolite found in nature that has high affinity for adsorption some of cations such as ammonium ion. Clinoptilolite especially, is useful adsorbent due to their low cost, comfort of disposal and their high selectivity for ammonium ion [16, 17] and heavy metals [18, 19]. The main applications of zeolites are adsorption, separation and ion exchange operations as well as catalysis. The most suitable form of clinoptilolite for ammonium ion removal was found to be Na [20].

In this study, the main purposes includes: (1) to investigate the potential of natural Western Azarbaijan zeolite for removal of ammonium ion from wastewater. (2) To evaluate application of natural zeolite as an ion exchanger material for the exclusion of ammonium ion from wastewater and to optimize the effective parameters in column systems.

Central composite design (CCD) and response surface methodology (RSM) were applied as experimental strategies for modeling and optimization of the values of some effective parameters on removal of ammonium ion from water and wastewater using ion exchangers, zeolite. Furthermore, the influences of interactions between parameters on the responses were well identified and by using an experimental design, the time and the number of tests were also optimized [21, 22]. RSM is a useful method for studying the effect of several variables influencing the responses by varying them simultaneously and carrying out a limited number of experiments.

Materials and methods

Reagents

All chemicals used were of analytical grade and the solutions were prepared with freshly double distilled water. Synthetic wastewaters of (1–50 mg l^{-1}) ammonium ion concentrations were used in this study. At first, 1000 mg l^{-1} ammonium nitrogen stock standard is prepared from 3.819 g ammonium chloride and diluted to 1 l with distilled water. Then synthetic wastewaters by different ammonium ion concentrations were made from the stock solution.

Statistical software

Essential Regression and Experimental design for chemists and Engineers (EREGRESS), as a MS Excel Add-in software, was used to design the experiments and to model and analyze the results [23, 24].

Characteristic of clinoptilolite

The particular ion exchanger of interest in this study is clinoptilolite. As mentioned, clinoptilolite is an abundant zeolite found in nature that has high cation exchange capacity (CEC) and stability to set attrition, which make it qualitative for the removal of ammonium ion from water and wastewater [25]. The clinoptilolite used as an adsorbent in this experiment was obtained from Shahin Dejh City in the south of Western Azarbaijan, Iran. The clinoptilolite sample was characterized using Rigaku D-Max III X-ray diffractometer and chemical analysis. The chemical composition was determined by analytical methods usually applied for silicate materials. The chemical composition of the clinoptilolite used in this study is shown in Table 1.

The crystalline phase composition of the used natural zeolite was characterized by Scanning Electron Macrograph (VEGA II TSCAN Co. Czech. Republic). The SEM images are displayed in Fig. 1.

Table 1 Chemical and mineralogical composition of natural Western Azarbaijan zeolite

Parameter	Value (%)
SiO_2	67.5
Al_2O_3	12.5
Na_2O	3.1
K_2O	4.4
CaO	1.6
Fe_2O_3	0.2–0.9
L.O.I	10–13
XRD analysis	
Major mineral: Clinoptololite-Quartz-Cristobalite	
Minor mineral: Calesite-Montmonlonite	

The chosen clinoptilolite was sieved into three particle sizes: 0.5, 1 and 2 mm, then washed with distilled hot water to remove very fine particles and dried in an oven at 110°C for 24 h before using in the experiments. As mentioned earlier, the most suitable form of clinoptilolite for ammonium ion removal was found to be Na form. Hence, to convert to the sodium form, clinoptilolite was mixed with the solution of 0.1 mol l^{-1} sodium chloride and shaken at room temperature for 24 h, then thoroughly washed with distilled water and dried in an oven at 105°C prior to injection to column for measuring their adsorption capacity during ion exchange process.

Phenate method

Phenate method was carried out according to the procedure described in the ASM [26]. This method is one of the most widely used producers for the colorimetric determination of ammonium ions in aqueous solution in which alkaline phenate and hypochlorite are employed as the color reagent catalyst to form blue indophenol. The indophenol concentration is in direct proportion to the ammonium ion concentration.

The absorbencies of solutions were measured at a wavelength of 640 nm with a Lamp UV/Visible Spectrophotometer (PG mode T80, Japan) and then ammonium ion concentration in solutions is determined by comparing the absorbance signal with calibration results obtained from prepared standard solutions. In order to improve sensitivity, sodium nitroprusside was used to provide deeper color for blue indophenol [27].

The column study

Ammonium ion exchange experiments were carried out using column with a diameter of 10 mm and height of 50 cm that was filled with fine zeolite (2.0 mm) and effects of flowrate, pH and initial ammonium concentration on the ammonium removal efficiency of zeolite were investigated. The ion exchange resin (swollen in water) is usually packed into a vertical tube. A synthetic solution of ammonium ion together with the resin form a homogeneous mixture in the column and then, the analyzed solution led to the column are passed down through the resin bed.

The column method of ion exchange process enable one to carry out quantitative exchange of ion from the solution as well as to separate ionic mixtures with maximum efficiency. At last, the initial and final ammonium concentrations remaining in solution were analyzed [28].

The removal efficiency (%) was calculated using Eq 1.

$$\text{Removal efficiency}\,(\%) = \frac{(C_0 - C_e)}{C_0} \times 100 \qquad (1)$$

where, C_0 and C_e are the initial and final concentrations of ammonium ion in solution (mg l^{-1}).

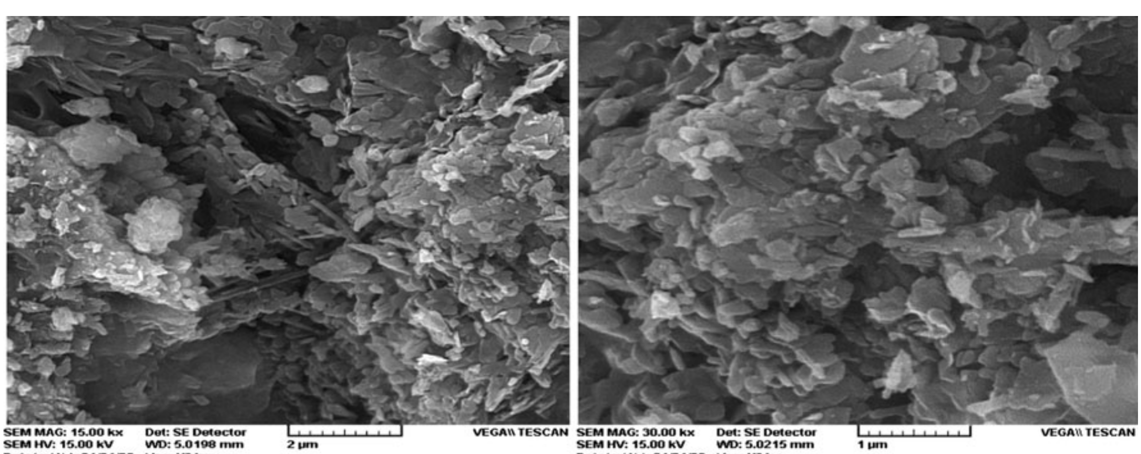

Fig. 1 SEM images of natural Western Azarbaijan zeolite

Central composite design (CCD)

CCD was used to optimize the experimental variables. Three independent factors, namely the initial ammonium concentration (F1), flow rate (F2) and pH (F3) were studied at five levels with four repeats at the central point, using a circumscribed CCD. For each of the three studied variables, high (coded value: +1.428) and low (coded value: −1.428) set points were selected as shown in Table 2.

Table 3 illustrates the coded and real values of designed experiments based on CCD methodology achieved using EREGRESS software. Essential regression and experimental design for chemists and engineers (EREGRESS), as a MS Excel Add-in software, was used to design the experiments and to model and analyze the results.

Polynomial equations and response surface for a particular response are produced using EREGRESS. For an experimental design with three factors, the model including linear, quadratic and cross-terms can be expressed as Eq. 2.

$$\begin{aligned}\text{Response} = {} & b0 + b1 \times F1 + b2 \times F2 + b3 \times F3 \\ & + b4 \times F1 \times F1 + b5 \times F2 \times F2 \\ & + b6 \times F3 \times F3 + b7 \times F1 \times F2 \\ & + b8 \times F1 \times F3 + b9 \times F2 \times F3\end{aligned} \qquad (2)$$

Within Eq. 2, F1, F2 and F3 are the variable parameters, and b0–b9 is the coefficient values obtained through multiple linear regressions (MLR) using EREGRESS. The response surface plots were obtained through a statistical process that described the design and the modeled CCD data. Response surface methodologies graphically illustrate relationships between parameters and responses that were used for obtaining an exact optimum [23, 24].

The statistical significance of the predicted models was evaluated by the analysis of variance (ANOVA) and least squares techniques. The ANOVA determines which of the factors significantly affects the response variables in study, using a Fisher's statistic test (*F* test). The significance and the magnitude of the estimated coefficients of each variable and all their possible interactions on the response variables were determined. Such coefficients for each variable represented the improvement in the response, in other words, it was expected the variable setting changes from low to high. Effects with less than 95% of significance (effects with a *p* value higher than 0.05) were discarded and pooled into the error term and a new analysis of variance was performed for the reduced model [29].

Table 2 The variables and values used for central composite design

Variable name	Coded factor levels: −1.428 (low)	−1	0	+1	+1.428 (high)
F1 Initial ammonium concentration (mg l^{-1})	1	8.34	25.5	42.6	50
F2 Flow rate (ml min^{-1})	1	1.3	2	2.7	3
F3 pH	4	4.75	6.5	8.25	9

Table 3 List of experiments in the CCD for model optimization (coded values)

Design points	Factor levels: F1	F2	F3	Response
1^{cp}	0	0	0	0.115
2	1	−1	1	0.08
3	−1	1	1	0.048
4	1	1	−1	0.143
5	−1	1	−1	0.09
6	1.428	0	0	0.125
7	0	0	1.428	0.075
8	−1	−1	−1	0.07
9	1	1	1	0.05
10	0	1.428	0	0.067
11	0	−1.428	0	0.096
12	−1.428	0	0	0.029
13	1	−1	−1	0.123
14	0	0	−1.428	0.13
15^{cp}	0	0	0	0.115
16	−1	−1	1	0.054
17^{cp}	0	0	0	0.115
18^{cp}	0	0	0	0.115

cp indicates 4 repeat of center points

Cation exchange capacity (CEC)

The CEC is a key characteristic of zeolite when it's applied in adsorption of cations such as ammonium ion. The CEC indicates the amount of cations should be accommodated by zeolite. To determine CEC, a Flame photometer (Corning Co., U.K.) was used via analyzing sodium ion concentration residual in the potassium chloride solution [30]. Subsequently, for extracting the experimental CEC of natural Western Azarbaijan zeolite, five grams of zeolite samples in sodium form was given into column and then, 100 ml 0.1 M KCl solution was added. Since zeolite is more selective to K^+ than Na^+, Na^+ was easily substituted with K^+ in the structure of zeolite. Finally, sodium ion concentration in KCl solution was measured with flame photometer to calculate CEC.

Results and discussion

Column study

Effect of flow rate on zeolite exchange

One of the important parameters in column design is the flow rate. The flow rate is inversely proportional to the retention time, hence by enhancing hydraulic retention time between particle sample and ammonium ion, much absorption will be occurred. It is shown in Fig. 2, as flow rate reduces, removal efficiency increases and at the flow rate of 1 ml min^{-1}, ammonium removal efficiency reaches to 99.43%.

Effect of initial ammonium concentration on zeolite exchange

In this study, the initial ammonium concentration in the column process was prepared in the range of 1–50 mg l^{-1}. As it can be seen from Fig. 3, increasing in the initial ammonium concentration of solutions leads to an enhancement in the removal efficiency. It was found that the removal efficiency increased rapidly in the range of 1–10 mg l^{-1} and then achieved to an optimum amount of 30 mg l^{-1}. This behavior can be explained that higher ammonium concentration in solution provides an important driving force for ammonium ions which occupy the cations sites on the effective pores of zeolite surfaces [22].

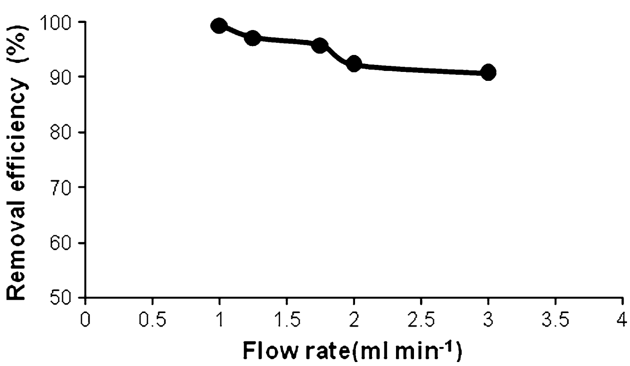

Fig. 2 The effect of flow rate on ammonium removal efficiency

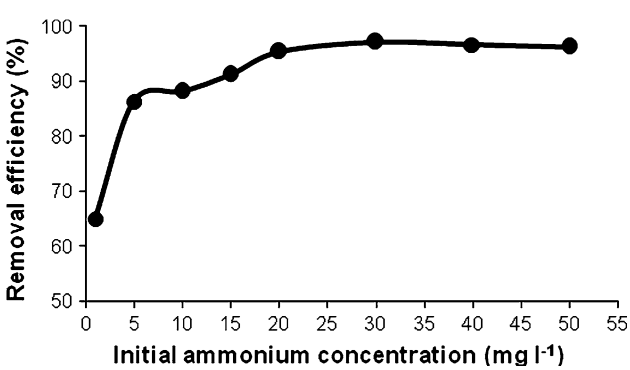

Fig. 3 The effect of initial ammonium concentration on removal efficiency

Effect of pH on zeolite exchange

The pH of aqueous solution is a significant factor on ammonium removal by ion exchange process because it can have influence both on the ions exchanging and characteristics of the zeolite. As shown in Fig. 4 ammonium removal from solution gets increased when the pH rises from 4 to about 6 and achieves to a maximum amount of 6. After this pH, the removal efficiency reduced slowly. The main reason is that at high at pH above 6, partial dissolution of the natural zeolite occurs, and it is also likely that ammonium is converted into ammonia and the ammonia molecules cannot exchange back into the resin and thus strips with air [31].

Central composite design (CCD)

Experimental design In order to optimize three independent factors in column method; initial ammonium concentration (F1), flow rate (F2) and pH (F3), the absorbance of samples in maximum wavelength of 640 nm were obtained. As discussed in previous sections, Tables 2 and 3 represent the levels of coded and actual experimental variables that were tested. The purposes of this CCD strategy were: (1) to study of the effect of initial ammonium concentration, flow rate and pH on removal efficiency of ammonium ion from synthetic solution in column method; (2) to calculate optimum amount of these effective variables and illustration of interactions between effective parameters.

In order to find the important factors and build a model to optimize the procedure, we started with a full quadratic model including all terms in Eq. 2 to obtain a simple and

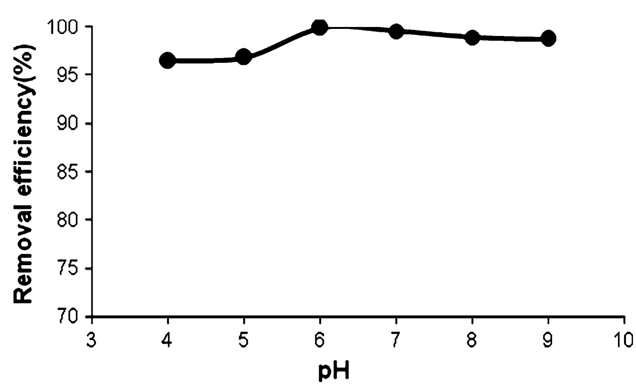

Fig. 4 The effect of pH on ammonium removal efficiency

realistic model. The insignificant terms ($p > 0.05$) were eliminated from the model via backward elimination process. Using all 10 parameters presented in Eq. 2 a relatively good fit is achieved. In this model, the regression coefficient R^2 for calibration (R^2) was 0.924. Although adjusted regression coefficient (R^2_{adj}) as well as that of prediction (R^2_{pred}) were very low.

Some of these 10 regression variables have low significance and can be eliminated from the model. Since R^2 always decreases when a regression variable is eliminated from a regression model, in statistical modeling the R^2_{adj}, which take into account the number of regression variables, is usually chosen [32, 33]. Also R^2_{pred}, is selected for the same reason, which indicates the predictive power of the model. This parameter approximately uses prediction error sum of squares or PRESS calculating from residuals, which are based on a regression model with one data point removed. So R^2, R^2_{adj} and R^2_{pred} together are very convenient to get a quick impression of the overall accordance with the model and the predictive power based on one data point removed. In a good model, these parameters should not be too different from each other. However for small data sets, it is very likely that every data point is influential. In such cases, a high value for R^2_{pred} cannot be expected [23]. By the elimination of insignificant parameters from Eq. 2, R^2 decreased to 0.924 but R^2_{adj} and R^2_{pred} increased nearly to 0.870 and 0.656, respectively. Finally, the reduced model using significant linear, quadratic parameters which have interactions was obtained (Table 4). For this case, the R^2_{adj} was well within the acceptable limits and there were not important differences between R^2 values revealing that the experimental data shows an acceptable accordance with the third order polynomial equations.

Table 4 Some characteristics of the constructed models

		Coefficient	Value
Regression equation		b0	−0.299
Response = b0 + b1 × Conc		b1	0.0068
+ b2 × pH + b3 × Flow_Rate		b2	0.08661
+ b4 × Conc × Conc		b3	0.06331
+ b5 × Conc × Flow_Rate		b4	−6.14E−0.5
+ b6 × pH × pH		b5	−0.00113
+ b7 × pH × Flow_Rate		b6	−0.00518
		b7	−0.01075
R^2 for calibration	0.924		
R^2 adjusted	0.87		
R^2 for prediction	0.656		
Standard error	0.0121		
No. points	18		
PRESS[a]	0.01		

[a] Prediction error sum of squares

Response surface and selection of optimum conditions In order to gain insight about the effect of each variable, the three dimensional (3D) plots for the predicted responses were also formed, based on the model function to analyze the change of response surface. For example Fig. 5 illustrates some of response surface plots that show the 3D plots relationship between two variables and absorbance of samples while two other variables were kept in center levels. It has been shown in Table 4 several linear, squared and interaction parameters which are statistically significant. The selection of optimum conditions of the method is possible from the response surface plots.

These results demonstrate that the response surfaces have a flat optimum. The plots show the interaction between the mentioned factors when the remaining factors have been fixed using the constructed model by EREGRESS software. The results show an obvious dependency of absorbance to all of investigated experimental variables. Also these plots represent that there are significant interactions between initial ammonium concentration with flow rate and pH with flow rate (see also Table 4). Finally, the optimum conditions can be selected from the obtained model for further examinations (Table 5).

Cation exchange capacity (CEC)

Dimirkou et al. [34] found that the theoretical cation exchange capacity of zeolite is usually much higher than experimental amount of CEC. Sarioglu [35] concluded that impurities such as quartz and feldspar do not affect the amount of cation exchange capacity and adsorption ability. In this study, cation exchange capacity of natural Western Azarbajan zeolite was determined to be approximately 1.79 meq g^{-1}. It was demonstrated that the cation exchange capacity of the natural zeolite was strongly related to its structural characteristic, nature of cation and its concentration in solution [36].

Conclusion

The following are important points that can be concluded from the results obtained in this study:

- Natural Western Azarbijan zeolite has an excellent potential to be used as effective and low cost adsorbent for ammonium ion removal from aqueous solution.
- The pH value of the aqueous solution is an important controlling parameter in the adsorption and ion exchange process that significantly is influenced on ammonium removal efficiency.
- The maximum amount of ammonium removal efficiency was achieved at the lowest applied flow rate.

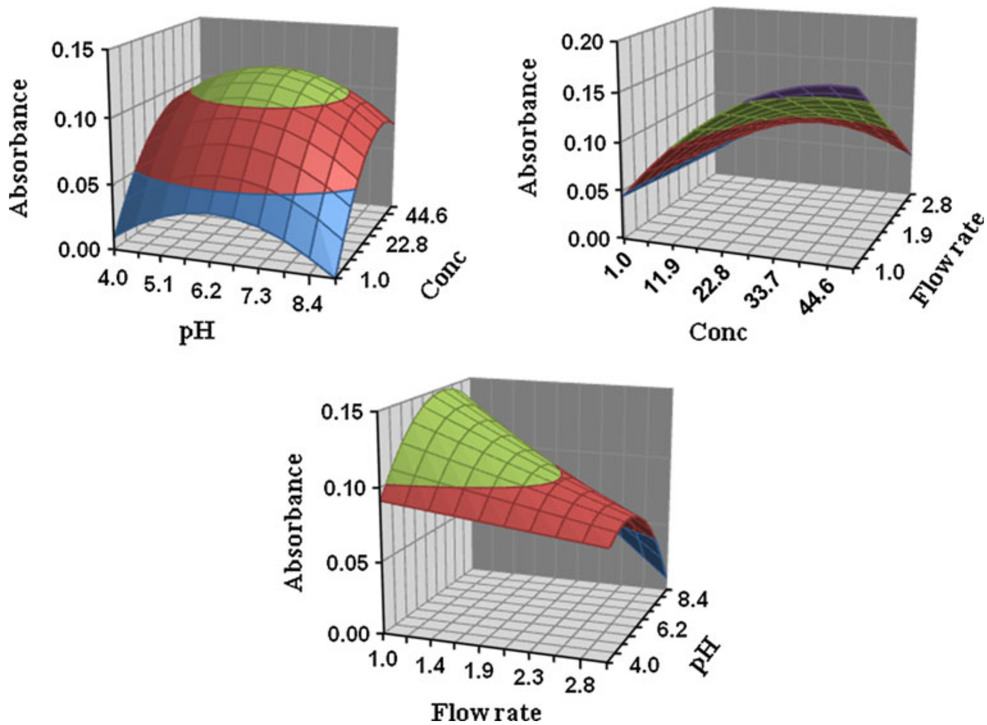

Fig. 5 Response surface of initial ammonium concentration (Conc.) (F1), flow rate (F2) and pH (F3)

Table 5 Optimum conditions obtained by response surface modeling for ammonium removal from solution by ion exchange in column method

	Variable name	Optimum values	Selected values
F1	Initial ammonium concentration (mg l^{-1})	28–33	30
F2	Flow rate (ml min^{-1})	1–1.2	1
F3	pH	5.7–6.8	6

- The ammonium removal efficiency was considerably dependent on initial ammonium concentration in solution. As the initial ammonium concentration rises, selectivity of the zeolite samples for removal of ammonium ions from aqueous solutions increases.
- By using CCD and subsequently RSM, the effect of parameters such as initial ammonium concentration, pH and flow rate on removal efficiency of ammonium in column method was studied and the optimum conditions were obtained. Also, the possible interactions between these effective parameters were shown.
- Optimization of the independent variables to maximize the removal efficiency was performed using the quadratic model within the studied experimental range. The optimization modeling suggested that the optimum values of the three selected independent variables of the process including the initial ammonium concentration 30 mg l^{-1}; pH 6 and flow rate 1 ml min^{-1}; to achieve the maximum amount of ammonium removal efficiency from waste water, which are very close to the experimentally determined removal efficiency.
- This paper shows that the use of experimental design enabled a subsequent advantage in terms of labor time and number of experience to optimize the conditions of experiments for ammonium removal from aqueous solutions and wastewater.

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