Optimization of ammonia removal by natural zeolite from aqueous solution using response surface methodology

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Abstract

Ammonium removal from aqueous solution was investigated using natural zeolite. Operating variables were optimized by statistical design for this process. Eight variables including pH, contact time, dose and size of adsorbent, initial ammonia concentration, temperature, agitation and concentration of other adsorbate were screened by Plackett–Burman design. The results indicated that particle size, contact time, dose of zeolite and initial ammonia concentration are effective on removal efficiency with *p*-value < 0.02. Optimizations of three important factors were conducted by response surface method. The optimal condition of ammonia removal in terms of removal efficiency was found to be at 0.18–0.4 mm particle size, 4 min contact time and 111 g L^{-1} dose of zeolite. The removal efficiency was found to be 98.25% at optimal condition. The maximum adsorption capacity of ammonium was 1.276 mg g^{-1} that was obtained at 0.18–0.4 mm zeolite size, 60 min contact time and 20 g L^{-1} zeolite dosage. The Langmuir and Freundlich isotherms adequately described the adsorption of ammonium ions by HCl-modified natural zeolite.

Keywords: ammonia removal, natural zeolite, Plackett–Burman design, Box–Behnken design, response surface method (RSM).

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Ammonia is one of the major pollutants in the environment which exists in a considerable quantity in sewages of industries such as petrochemicals. The removal of ammonia from wastewater and sewages is necessary because the existence of ammonium ion in water causes some problems, such as reducing the concentration of dissolved oxygen in water, accelerating the growth of algae and finally coating the surface of water resources which leads to changes in the taste and color of water [1]. Various biological, physical and chemical treatment methods have been used to remove ammonia from aqueous solution [2–11]. One of the proposed methods for ammonia removal from industrial wastewater is the use of low-cost adsorbents such as agriculture wastes [12] and silicate minerals like zeolite [13–17]. This method seems to be a good option for ammonium treatment due to high efficiency in removing ammonia, simplicity and low costs. Zeolites are alumino-silicate minerals with water, containing alkali and alkaline earth metals. Zeolites are commonly used in scientific and industrial fields because of their structural characteristics and chemical composition [18,19].

Optimization of physicochemical parameters of process is one method for increasing process yield and reducing process cost. To reduce the number of experiments, in regard to the large number of variables, statistical design of experiments have been used in many studies [20–23].

Some of batch adsorption parameters are pH, temperature, particle size and dose of adsorbent and initial concentration of adsorbate. Several studies have been conducted about removing ammonium from wastewater using zeolites. In some studies effective variables on adsorption process were considered and some important variables were recognized [14–17]. However in these studies, the statistical designs of experiments were not employed for optimization of the ammonia adsorption from aqueous solution.

In the present study, an Iranian natural zeolite which was extracted from Sabzevar region, for the first time, was used as adsorbent. In this work, the statistical design of experiments was applied for optimization of ammonia adsorption from aqueous solution. For this purpose, important process parameters were first screened and selected on the basis of the Plackett–Burman design (PBD). Subsequently, the significant variables were optimized by Response surface method (RSM) using Box–Behnken design (BBD).

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MATERIALS AND METHODS

Preparation and modification of zeolite

The natural zeolite was obtained from Sabzevar town, North East of Iran. The samples were grounded and sieved based on the U.S. standard mesh. After washing with distilled water and drying, zeolites were stored in the desiccators for the next stages. The prepared zeolites were modified using phosphoric, nitric, sulfuric and hydrochloric acids, separately, according to the following condition: 10 g zeolites were added into 250 mL acid solution (1 M) and shaken for 6 h at 60 °C and 150 rpm. The solid phase was separated by filter paper and was rinsed in hot distilled water, and then in cold distilled water until pH was adjusted to 7. Then, zeolites were dried for 24 h at 100 °C and kept in the desiccator to prevent moisture adsorption.

Adsorption

The ammonia solution was prepared by dissolving an accurately weighed sample of ammonium chloride (NH_4Cl) in deionized water. Batch adsorption experiments were carried out by shaking a series of bottles containing determined amounts of adsorbent and adsorbate solution at desired condition.

In the first stage the adsorption of acid-modified zeolite and unmodified zeolite was examined at similar conditions of 1.0–1.7mm zeolite size, 50 g/L dose of the zeolite, 3 h contact time, 25 °C temperature, 200 rpm agitation, 25.6 mg/L initial ammonium concentration and pH 7.

In screening and optimization stage, adsorption condition was set according to experimental design and pH was adjusted by 0.1 M HCl or 0.1 M NaOH. After adsorption process, the adsorbent particles were separated from the suspensions by filtration through 0.43 µm filter paper and the residual concentration of ammonia was determined. In order to reduce the experimental errors, all experiments were conducted three times and the mean experimental data was reported.

To investigate the adsorption isotherms the series of NH_4^+ solutions with different initial ammonia concentration (C_0) (10–120 mg/L) were kept in contact with 20 g/L zeolite (0.6–0.85mm) at 35 °C and 50 rpm until arriving to equilibrium concentration. Then, the equilibrium adsorption capacity (q_e) was determined and agreement of obtained data with three isotherm models, Linear, Langmuar and Frendlich were studied.

Statistical experimental design

Review of published reports [14–17] showed that pH, contact time, dose and size of adsorbent, initial ammonia concentration, temperature, agitation and concentration of other adsorbate, may be effective on adsorption process. Ca^{2+} was studied as another adsorbate. Plackett–Burman design was used to screen these variables. Selected levels of variables are shown in Table 1.

Table 1. Selected levels of variables for PBD of ammonia removal from aqueous solution by HCl-modified natural zeolite

Variable		Coded value	
		(+1)	(–1)
d	Particle size, mm	1.7–3.35	Below 0.075
pH	pH	9	4
t	Contact time, min	180	10
m	Dose of zeolite, g/L	200	4
C_0	Initial ammonia concentration, mg/L	25.6	2.56
θ	Temperature, °C	45	25
S	Agitation, rpm	200	50
C_{Ca}	Concentration of other cation, mEq/L	5	0

After the identification of important variables, Box–Behnken design was used for optimization of process variables which were found to be important for ammonium adsorption while other factors were kept at a constant level. Selected levels of variables have been shown in Table 2. The results of the experimental designs were analyzed and interpreted using Minitab 16 statistical software.

Table 2. Selected levels of variables for BBD of ammonia removal from aqueous solution by HCl-modified natural zeolite

Variable		Coded value		
		+1	0	–1
d	Particles size, mm	1–1.4	0.6–0.85	0.18–0.3
t	Contact time, min	60	32	4
m	Dose of zeolite, g/L	160	90	20

Analysis techniques

The quantitative determination of major elements contained in the zeolite sample was carried out using the wavelength dispersive X-ray fluorescence (XRF) technique (model CE3021 made by CECIL Instruments, USA). The mineralogical composition of the natural adsorbent was determined by using Philips X'pert Modular Powder diffractometer (MPD). The concentration of ammonia in solution was measured using Phenat method [24].

RESULTS AND DISCUSSION

Identification of zeolite

Table 3 presents the elemental composition of the Sabzevar zeolite using XRF. According to these results the mass ratio of SiO_2/Al_2O_3 is equal to 6.55. Loss on ignition (L.O.I.) is the percentage of volatile components, mainly crystal bound water and organic carbon (as CO_2), driven off from a sample when heated at 1000 °C. Table 3 indicated 15.62% of zeolite is volatile components.

Table 3. Determined composition of zeolite sample using XRF

Component	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

The mineralogical composition of the natural adsorbent was determined by using Philips MPD; the results obtained were as follows: 76% clinoptilolite, 24% calcite.

Acid-modification

The removal of ammonia from aqueous solution using different acid-modified zeolite was determined and compared with unmodified zeolite (Table 4). According to Table 4, modification of zeolite significantly increased removal efficiency. When natural zeolites were modified with acid, aluminum ions were replaced by hydronium ions. Due to the replacement of protons with small radius (H_3O^+) by cations of larger radius (Al^{3+}), Si/Al ratio and pore size of zeolites increased. Among acid-modified zeolite, HCl-modified zeolite and H_3PO_4-modified zeolite had the highest adsorption amounts. HCl-modified zeolite was selected for further study.

Screening of variables

Eight variables pH, contact time, dose and size of adsorbent, initial adsorbate concentration, temperature, agitation and the presence of other adsorbate (Ca^{2+}) were evaluated using twelve matrix of PBD and the results of experiments are shown in Table 5. Table 6 displays the analysis results of the PBD using minitab16 software.

The statistically significant effect of each variable was screened by probability test and variables with a confidence interval greater than 98% (p-value < 0.02) were considered as a significant variable. According to Table 6, in terms of removal efficiency particle size, contact time, zeolite dosage and initial ammonium concentration are significant. Table 6, also, indicates that particle size, pH, contact time and presence of Ca^{2+} have negative effect on removal efficiency and other variables have positive effect. High negative effect of contact time shows that continuous process could obtain high removal efficiency. The results of the study are consistent with study of Huang et al. [15].

Table 4. The comparison of the removal ammonia by different acid-modified zeolite

Zeolite	Removal efficiency, %
Unmodified zeolite	29.59
HCl-modified zeolite	97.87
H_3PO_4-modified zeolite	97.51
HNO_3-modified zeolite	95.66
H_2SO_4-modified zeolite	92.78

In terms of adsorption capacity, only two variables, the initial ammonia concentration (C_0) and dose of zeolite (m) in studied range are significant with con-

Table 5. Plackett–Burman design matrix and corresponding results for ammonia removal from aqueous solution by HCl-modified natural zeolite

Trail	Coded factor[a]								Removal efficiency %	Adsorption capacity
	d	pH	t	m	C_0	θ	S	C_{Ca}		
1	1	–1	1	–1	–1	–1	1	1	23.83±0.39	0.1525±0.0025
2	1	1	–1	1	–1	–1	–1	1	66.99±1.76	0.0086±0.0002
3	–1	1	1	–1	1	–1	–1	–1	72.38±1.17	4.6325±0.0750
4	1	–1	1	1	–1	1	–1	–1	80.47±0.39	0.0103±0.0000
5	1	1	–1	1	1	–1	1	–1	95.25±0.06	0.1219±0.0001
6	1	1	1	–1	1	1	–1	1	48.42±1.04	3.0987±0.0662
7	–1	1	1	1	–1	1	1	–1	80.08±2.73	0.0102±0.0003
8	–1	–1	1	1	1	–1	1	1	97.89±0.04	0.1253±0.0000
9	–1	–1	–1	1	1	1	–1	1	97.71±0.14	0.1251±0.0002
10	1	–1	–1	–1	1	1	1	–1	97.95±0.02	6.2688±0.0012
11	–1	1	–1	–1	–1	1	1	1	97.05±0.49	0.6211±0.0031
12	–1	–1	–1	–1	–1	–1	–1	–1	75.39±0.78	0.4825±0.0050

[a]Factors refer to those in Table 1

Table 6. Analysis of PBD results for ammonia removal from aqueous solution by HCl-modified natural zeolite

Variable	Removal efficiency, %			Adsorption capacity, mg/g		
	Effect	*t*-value	*p*-value	Effect	*t*-value	*p*-value
Particles size (*d*)	–17.93	–3.85	0.002	0.611	1.28	0.220
pH	–2.18	–0.47	0.647	0.221	0.46	0.650
Contact time (*t*)	–21.21	–4.55	0.000	0.067	0.14	0.890
Dose of zeolite (*m*)	17.23	3.70	0.002	–2.476	–5.18	0.000
Initial ammonia concentration (C_0)	14.30	3.07	0.008	2.181	4.57	0.000
Temperature (θ)	11.66	2.50	0.024	0.768	1.61	0.128
Agitation (*S*)	8.45	1.81	0.090	–0.176	–0.37	0.717
Concentration of Ca (C_{Ca})	–11.60	–2.49	0.025	–1.232	–2.58	0.021

fidence interval greater than 98%. According to Table 6, dose of zeolite, agitation and presence of Ca^{2+} have negative effect on adsorption capacity and effects of other variables are positive. Du et al. studied the same variables for ammonia removal and found that all of these variables affect the adsorption process [14].

Optimization of effective variables

The most important parameters which affect the efficiency of ammonia removal are particles size *(d)*, contact time (*t*) and dose of zeolite (*m*) and initial ammonium concentration (C_0). Further study was conducted with initial constant ammonium concentration because it is constant in actual process. Then, the other three variables were optimized in initial concentration 25.6 mg L^{-1} at 30 °C and 50 rpm without the presence of Ca^{2+} and adjusting pH. RSM was employed to investigate the combined effect of these factors to reveal the optimum conditions for ammonia removal and to build models. BBD was applied to evaluate the interactive effects of adsorption variables and optimize the ammonia removal process. The range and levels of variables are coded according to Eq. (1) and summarized in Table 2.

$$x = \frac{X - X_0}{\Delta X} \quad (1)$$

where *x* and *X* are the coded and the real values of variables. X_0 and ΔX are the center point of *X* and the step change in *X*, respectively. The results of experiments were measured according to BBD of three independent variables and were reported in Table 7. The results were analyzed using minitab16 software. The experimental results of removal efficiency (%) and adsorption capacity were fitted with a second order polynomial equation.

The fitted equations (in terms of coded values) for removal efficiency (Y_1) and adsorption capacity (Y_2) were as follows:

$$\begin{aligned} Y_1 &= 65.895 + 5.602m + 0.884t - 5.387d - \\ &-1.199m^2 + 3.855t^2 + 22.618d^2 - \\ &-0.559mt + 5.450md + 1.031td \end{aligned} \quad (2)$$

$$\begin{aligned} Y_2 &= 0.1874 - 0.3961m + 0.0220t - 0.0544d + \\ &+0.3046m^2 - 0.0328t^2 + 0.1082d^2 - 0.0500mt + \\ &+0.1006md + 0.0029td \end{aligned} \quad (3)$$

The coefficients of the regression model (Eqs. (2) and (3)) that appear as one constant, three linear, three quadratic and three interaction terms are listed in Table 8.

Table 7. Box–Behnken design matrix and corresponding results for ammonia removal from aqueous solution by HCl-modified natural zeolite

Trail	Coded factors[a]			Removal efficiency, %	Adsorption capacity
	m	*t*	*d*		
1	–1	–1	0	53.65±0.41	0.6867±0.0052
2	1	–1	0	67.02±0.44	0.1072±0.0007
3	–1	1	0	71.20±0.49	0.9113±0.0063
4	1	1	0	82.34±0.86	0.1317±0.0014
5	–1	0	–1	98.64±0.12	1.2626±0.0016
6	1	0	–1	97.89±0.30	0.1566±0.0005
7	–1	0	1	65.84±0.37	0.8427±0.0047
8	1	0	1	86.88±0.57	0.1390±0.0009
9	0	–1	–1	99.67±0.08	0.2835±0.0002
10	0	1	–1	84.71±0.47	0.2410±0.0013
11	0	–1	1	97.96±0.05	0.2786±0.0001
12	0	1	1	87.13±0.42	0.2478±0.0012
13	0	0	0	65.70±0.09	0.1869±0.0002
14	0	0	0	65.89±0.01	0.1874±0.0000
15	0	0	0	66.10±0.07	0.1880±0.0002

[a]Factors refer to those in Table 1

The significance of each coefficient was determined by p-values. The *p*-values imply that the first order main effects of particles size and zeolite dosage and second order main effects of particles size are significant in terms of the removal efficiency. Therefore,

Table 8. Analysis of BBD results for ammonia removal from aqueous solution by HCl-modified natural zeolite

Term	Removal efficiency (%)			Adsorption capacity		
	Coefficient	*t*-value	*p*-value	Coefficient	*t*-value	*p*-value
Constant	65.895	19.538	0.000	0.1874	5.801	0.000
Dose of zeolite (*m*)	5.602	2.712	0.013	–0.3961	–20.018	0.000
Contact time (*t*)	0.884	0.428	0.673	0.0220	1.111	0.280
Particle size (*d*)	–5.387	–2.608	0.017	–0.0544	–2.751	0.012
m^2	–1.199	–0.394	0.697	0.3047	10.460	0.000
t^2	3.855	1.268	0.219	–0.0328	–1.128	0.273
d^2	22.618	7.440	0.000	0.1081	3.713	0.001
mt	–0.559	–0.191	0.850	–0.0500	–1.788	0.089
md	5.450	1.866	0.077	0.1006	3.594	0.002
td	1.031	0.353	0.728	0.0029	0.105	0.918

they can act as limiting adsorption. There is not any significant interaction for removal efficiency. In terms of adsorption capacity, the main effects of zeolite dosage and particles size, quadratic variables zeolite dosage and particles size and interaction between zeolite dosage and particles size are effective on process.

Coefficients of correlation were determined by the analysis of variance using Minitab16 software. R^2 = = 78.92 for removal efficiency shows there are relatively good agreement between the experimental results and the predicted results by the model and for adsorption capacity the R^2 = 96.48 indicates a very good agreement of model prediction data with experimental data.

The 2D contour plots are the graphical representations of the regression equation and are plotted to understand response variation with variation of two variables, while the other independent variable is constant. Moreover, the 2D cotour plots indicate the interaction of these variables and locate the optimum level of each variable for maximum response. Figures 1 and 2 indicate contour plots for removal efficiency and adsorption capacity, respectively.

According to Figure 1a and c, at low levels of particles size, removal efficiency is relatively independent of zeolite dosage and contact time, but at high levels of particles size, the removal efficiency is dependent on zeolite dosage (increasing of removal efficiency with increasing of dose of zeolite) and the response is independent of contact time. This shows that zeolite dosage and particles size have interaction in removal efficiency (Figure 1c). Figure 1a shows there is not any interaction between particles size and contact time and in constant contact time at low levels and high levels of zeolite dose, removal efficiency is higher than middle levels.

Contour plot of adsorption capacity versus contact time and particle size at optimal value of dose of zeolite shows adsorption capacity rises with increasing particles size and reducing contact time and maximum adsorption capacity exists at maximum contact time and minimum particle size (Figure 2a). Figure 2b indicates reducing particle size and zeolite dosage increases adsorption capacity. According to Figure 2c, in constant dose of zeolite, adsorption capacity relatively doesn't vary with variation of contact time.

The optimum condition for maximum response was obtained using Minitab16 software. In the studied range of variables, the optimum condition for removal efficiency were $d = -1$, $t = -1$ and $m = 0.3$ means 0.18––0.4 mm particle size, 4 min contact time and 111 g/L dose of zeolite. Under this condition, predicted removal efficiency by software was 98.19% and for the experimental study it was 98.25% for removal efficiency which indicates consistent results and proves the validity of the model. The optimum condition for adsorption capacity, in the studied range of variables, were $d = -1$, $t = 1$ and $m = -1$; in terms of coded value or the 0.18–0.4 mm size of zeolite, 60 min contact time and 20 g/L zeolite dosage in terms of actual value. Predicted adsorption capacity by software at optimum condition was 1.2 mg NH_3/g zeolite. Experimental adsorption capacity in this condition yielded 1.276 that is very close to predicted value and validates the model.

Adsorption isotherms

Fitting of adsorption isotherm equations to experimental data is often an important aspect of data analysis. In this study, three typical isotherms Linear, Langmuir and Freundlich models were used for fitting the adsorption experimental data. Table 9 indicates equilibrium concentration and adsorption in different initial ammonia concentration. Experimental data of Table 9 were fitted with three isotherm model, linear, Langmuir and Freundlich.

Parameters of these models can be determined by linear regression of the experimental data. The model parameters and correlation coefficients (R^2) are summarized in Table 10. Higher values of R^2 (0.9886) for

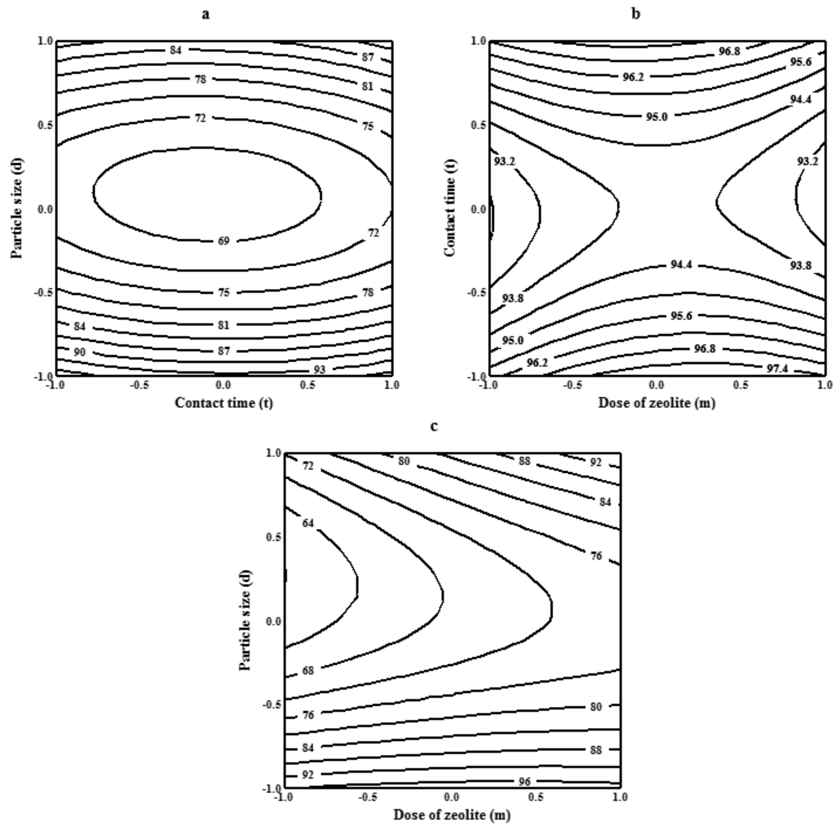

Figure 1. Contour plots of removal efficiency (a) vs particle size and contact time, (b) vs particle size and adsorbent amount and (c) vs adsorbent amount and contact time at optimal levels of other components (d, t and m are coded variables).

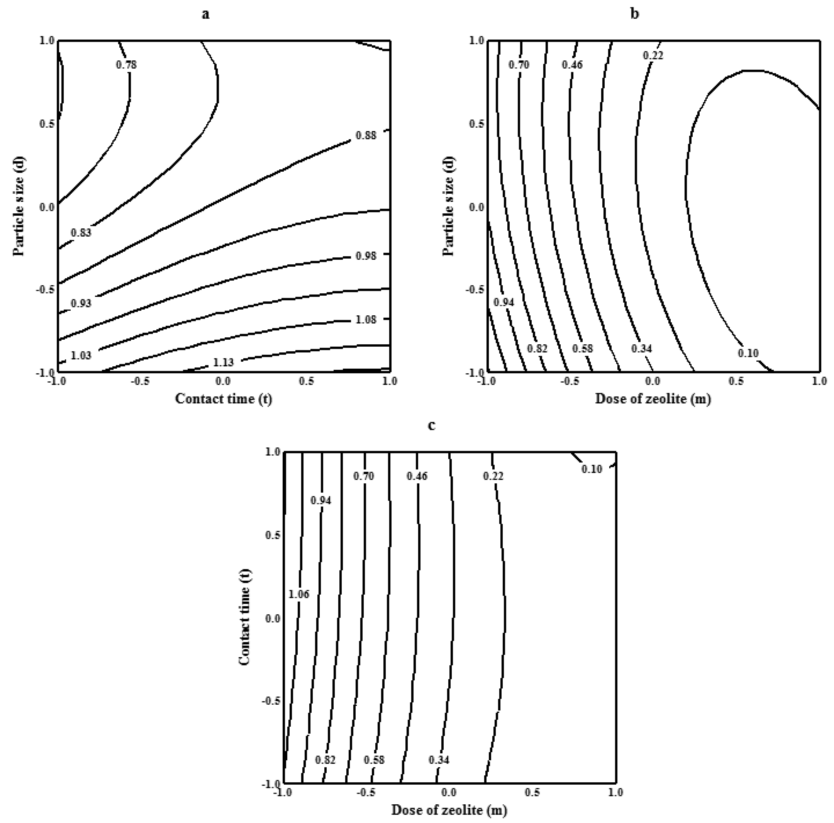

Figure 2. Contour plots of adsorption capacity (a) vs particle size and contact time, (b) vs particle size and dose of zeolite and (c) vs dose of zeolite and contact time at optimal levels of other components (d, t and m are coded variables).

Table 9. Variation of equilibrium concentration and adsorption versus different initial ammonia concentration for ammonia adsorption from aqueous solution by HCl-modified natural zeolite

C_0 / mg L^{-1}	C_e / mg L^{-1}	q_e / mg NH_3 (g zeolite)$^{-1}$
10.000	0.135	0.493
20.000	0.300	0.985
40.000	0.480	1.976
80.000	3.263	3.837
100.000	6.045	4.698
120.000	9.334	5.533

Table 10. Model parameters and correlation coefficients (R^2) of Linear, Langmuir and Freundlich isotherms for ammonia adsorption from aqueous solution by HCl-modified natural zeolite

Isotherm model	Equation	Model parameters		R^2
Linear	$q_e = aC_e + b$	a / L g^{-1}	0.5185	0.8925
		b / mg g^{-1}	1.2304	
Langmuir	$q_e = \frac{q_m b C_e}{1 + bC_e}$	q_m / mg g^{-1}	6.2189	0.9886
		b/ L mg^{-1}	0.6429	
Freundlich	$q_e = k_f C_e^{\frac{1}{n}}$	k_f / L g^{-1}	1.9102	0.9378
		n	1.8815	

Langmuir isotherm indicate better fitness of Langmuir isotherm to the experimental data.

CONCLUSION

Process variables of ammonia removal from aqueous solution using HCl-modified natural zeolite were optimized by statistical design. Screening of variables by PBD indicated four factors particle size, contact time, dose of zeolite and initial ammonia concentration are effective on removal efficiency. Three important factors were optimized by RSM. Quadratic models, counter plots and optimum conditions were obtained for this design using Minitab 16 software. It was observed that decrease in particle size and increase in adsorbent dose and contact time increased removal of ammonia by zeolite. Also, it was found that reduction in particle size and dosage of adsorbent and increase in contact time increased adsorption capacity of ammonium by zeolite. In optimum condition of 0.18–0.4 mm particle size, 4 min contact time and 111 g L^{-1} dose of zeolite, 98.25% of ammonium was removed. The Langmuir and Freundlich isotherm models were used to investigate the adsorption equilibrium of HCl-modified natural zeolite for ammonium adsorption. Adsorbent showed that it fits better to Langmuir isotherm which suggests that adsorption is homogeneous in nature. Ammonia removal from aqueous solution using HCl--modified natural zeolite is an inexpensive, effective and suitable process.

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IZVOD

OPTIMIZACIJA UKLANJANJA AMONIJAKA IZ VODENOG RASTVORA PRIRODNIM ZEOLITOM KORIŠĆENJEM METODE POVRŠINSKOG ODZIVA

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(Naučni rad)

U radu je ispitivano uklanjanje azota iz vodenog rastvora korišćenjem prirodnog zeolita. Operativne promenljive (ili uslovi u sistemu) su optimizovane primenom statističke analize. Praćeno je i analizirano, Planet–Burkman metodom, osam parametara: pH, vreme kontakta, doza i veličina adsorbenta, početna koncentracija amonijaka, temperatura, mešanje i koncentracija drugih adsorbata. Rezultati su pokazali da vreme kontakta, doziranje zeolita i početna koncentracija amonijaka utiču na efikasnost uklanjanja amonijaka sa *p*-vrednošću <0.02. Optimizacija tri važna parametra izvršena je metodom površinskog odziva. U pogledu efikasnosti uklanjanja azota postavljeni su optimalni uslovi: veličina čestica 0,18––0,4 mm, vreme kontakta 4 min, doziranje zeolita 111 g L^{-1}. Utvrđeno je da je efikasnost uklanjanja azota 98,25% od optimalne vrednosti. Maksimalni adsorpcioni kapacitet amonijaka bio je 1,276 mg g^{-1} dobijen na zeolitu veličine 0,18–0,4 mm, sa vremenom kontakta 60 min i doziranjem zeolita od 20 g L^{-1}. Adsorpcija amonijum jona na prirodnom zeolitu modifikovanom hlorovoroničnom kiselinom opisana je Langmuiri Freundlich izotermama.

Ključne reči: Uklanjanje amonijaka • prirodni zeolit • Plackett–Burman dizajn • Box–Behnken dizajn • Metoda površinskog odziva