

Adsorption characteristics of ammonium exchange by zeolite and the optimal application in the tertiary treatment of coking wastewater using response surface methodology

Cui Zhao, Zhongyuan Zheng, Jing Zhang, Donghui Wen and Xiaoyan Tang

ABSTRACT

Natural zeolite is a favorable NH_4^+ -ion exchanger in the tertiary wastewater treatment. In this study, a natural Chinese zeolite was anatomized using the mercury injection method, X-ray diffraction, and scanning electron micrographs. The kinetic process of ammonium adsorption onto the zeolite was best described by the pseudo second order model; the adsorption equilibrium data fitted better to the Freundlich isotherm; and the exchange between ammonium and alkali/alkaline earth cations was in the order of $\text{Na}^+ > \text{Ca}^{2+} > \text{K}^+ > \text{Mg}^{2+}$. Finally, the zeolite powder was applied for the tertiary treatment of coking wastewater, which still contained high concentration of ammonium after the secondary treatment by a sequencing batch reactor. The Box–Behnken design was used to design the experimental protocol, and the response surface methodology (RSM) was used for the optimization of adsorption factors. The RSM analysis showed the optimal adsorption factors as particle size, 0.03 mm; initial dosage of zeolite powder, 50.0 g/L; and contact time, 24 h. The highest ammonium removal rate was 75.0% predicted by the RMS. Considering settleability of the zeolite powder, the particle size of 0.25 mm was recommended in practice with a little loss of the ammonium removal: 70.9% as the RMS predicted.

Key words | adsorption, ammonium removal, ion exchange, natural zeolite, response surface methodology

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INTRODUCTION

NH_4^+ -N is a common pollutant in industrial and domestic wastewater. With the growth of human population and rapid development of industry, ammonium with high concentration exceeding the discharge or reuse standards is frequently detected in wastewater even after a secondary biological treatment. As a result, the aquatic ecology is threatened by receiving such wastewater. Therefore, the effective removal of ammonium from wastewater is an important issue for environmental pollution control.

Because of their ammonium removal efficiency and economic cost, the biological technologies based on either traditional nitrification and denitrification or some new concepts of nitrogen biotransformation (Schmidt *et al.* 2003) are applied worldwide. However, in some cases, such as treated wastewater with low C/N ratio, industrial wastewater containing other toxic compounds

or requiring treatment with less retention time and land area, the physical and chemical technologies show great advantages over the biological ones. Among various physico-chemical technologies, adsorption is one superior choice (Koon & Kaufman 1975; Jorgensen *et al.* 1976), and natural zeolite is regarded as a low-cost adsorbent and ion exchanger for ammonium removal (Hedstrom 2001; Wang & Peng 2010).

The performance of zeolite in environmental pollution control relies on its physical and chemical characteristics. Natural zeolite is a non-metallic mineral with a specific micro-structure of tetrahedral skeleton frame. A general chemical formula of zeolite is $(M)_{x/n} [\text{Al}_x\text{Si}_y\text{O}_{2(x+y)}] \cdot p\text{H}_2\text{O}$, in which M is the monovalent or divalent cations (e.g. Na, K, Li, Ca, Mg, Ba, and Sr); n is the cation charge; x , y , and p are the number of elements or molecules, where

$y/x = 1-6$ and $p/x = 1-4$ (Wang & Peng 2010). Aluminosilicate constitutes the tetrahedron, and cations as well as water molecules are attached or coordinated in the frame pore and surface area. The cohesion between the cations and frame is not tight, which makes one significant characteristic, ion exchange, established. Colella summarized the ion exchange selectivity orders of several different zeolites (Colella 1996); the common recognition is as follows: $\text{Cs}^+ > \text{Rb}^+ > \text{K}^+ > \text{NH}_4^+ > \text{Ba}^{2+} > \text{Sr}^{2+} > \text{Na}^+ > \text{Ca}^{2+} > \text{Fe}^{3+} > \text{Al}^{3+} > \text{Mg}^{2+} > \text{Li}^+$ (Ames 1960). In recent years, many kinds of zeolites have been used for ammonium removal from wastewater in either an independent process of adsorption (Jorgensen & Weatherley 2003) or a combined process of adsorption and biological treatment (Chung *et al.* 2000; Jung *et al.* 2004; He *et al.* 2007).

Adsorption kinetics and isotherm are significant in the adsorption study (Sarioglu 2005). A number of kinetic models and isotherm models were available to describe the $\text{NH}_4^+\text{-N}$ adsorption by zeolite, such as the kinetic models of linear regression and nonlinear regression (Ho & McKay 1998; Miladinovic *et al.* 2002; Kumar & Sivanesan 2006; Gunay *et al.* 2007; Saltali *et al.* 2007) and the Langmuir and Freundlich isotherms (Freundlich 1906; Langmuir 1918). In the treatment process, many operation factors including the contact time, zeolite particle size, dosage, and initial $\text{NH}_4^+\text{-N}$ concentration affect ammonium adsorption (Sarioglu 2005; Fachini & Vasconcelos 2006). Mathematical methods could be applied to obtain the optimal parameters for the most effective treatment. For example, the response surface methodology (RSM) is an empirical and statistical modeling method to describe the relationship between parameters and results (Annadurai 2000); and Box-Behnken design (BBD) is one experimental design for the RSM used in parameter optimization for many chemical and physical processes (Mohan *et al.* 2004).

In this study, coking wastewater, a kind of industrial wastewater that contains abundant $\text{NH}_4^+\text{-N}$ and nitrogen heterocyclic compounds (NHCs), was chosen to be the target wastewater. In the conventional biological process, ammonium could also be transformed from the NHCs as a metabolic intermediate product (Bai *et al.* 2010b, 2011; Zhao *et al.* 2011), so a common problem in the coking wastewater treatment is that the high concentration of ammonium destroyed the biological process and worsened the effluent. In order to solve the problem, based on the adsorption characteristics, a natural Chinese zeolite was chosen to remove ammonium from a biologically treated coking wastewater. The RSM was applied to determine and

optimize several more influential factors for ammonium adsorption by the zeolite.

MATERIALS AND METHODS

Zeolite and its characterization

Natural zeolite (clinoptilolite ore) was obtained from Jinyun, Zhejiang Province, China. The natural zeolite was sterilized by ultraviolet before use.

The micro-structure of the zeolite was detected with the mercury injection method using an AutoPore IV 9500 (Micromeritics, USA) (Bai *et al.* 2010b). The mineral constituents were examined by X-ray diffraction (XRD) using an X'Pert Pro MPD diffractometer (Philips, The Netherlands) equipped with Cu plate at 40 kV, 40 mA. The sample was scanned from 5° to 75° , 2θ with a stepping increment of 0.017° . The surface configuration was observed by scanning electron microscopy (SEM) using a FEI QUANTA 200 (The Netherlands), operated at 10.0 kV.

Ammonium adsorption in aqueous solution by the zeolite

The kinetics, isotherm, and ion exchange model of ammonium adsorption were investigated by batch experiments using a series of 250 mL Erlenmeyer flasks. Each flask contained 100 mL of solution with an $\text{NH}_4^+\text{-N}$ initial concentration of 126.55 mg/L for the kinetics and 0.25–165.00 mg/L for the isotherm. After 5 g of sterilized zeolite (4–6 mm) were added into each flask, all the flasks were sealed with seal film, shaken at 25°C at 110 rpm, and sampled periodically in the kinetic experiment or at the end of the isothermal experiment (96 h). Each sample was filtered through a $0.22\ \mu\text{m}$ membrane for ions analysis. The experiments were performed in triplicate. The average values of triple samples were shown as the experimental data.

Ammonium removal from biologically treated coking wastewater by the zeolite

The biological treatment of coking wastewater was carried out in a sequencing batch reactor (SBR), from which the effluent was further treated by the zeolite. The average quality analysis of the effluent was as follows: chemical oxygen demand (COD), 164 mg/L; total organic carbon (TOC), 74.5 mg/L; $\text{NH}_4^+\text{-N}$, 152.7 mg/L; and pH, 8.46.

A series of 250 mL Erlenmeyer flasks were used in the tertiary treatment experiments. Each flask carried 100 mL of the effluent and a certain amount of sterilized zeolite with certain particle size. All flasks were sealed with seal-film, shaken at 25 °C, 110 rpm, and sampled at the preset time. The BBD coupled with the RSM analysis was used for the design of experimental protocol and optimization of key factors. Every trial of the experiment was performed in triplicate. All average values of triple samples were shown as the experimental data.

Water quality analysis

The $\text{NH}_4^+\text{-N}$ concentration was analyzed by the salicylate-hypochlorous acid method (SEPA 1989). The concentrations of alkali and alkaline earth cations (K^+ , Na^+ , Ca^{2+} , and Mg^{2+}) were monitored by the ion chromatograph Dionex ICS-1500 (USA) with 20 mmol/L methanesulfonic acid as the mobile phase.

Box-Behnken design of the factorial experiment

The most important factors, which greatly affect the efficiency of zeolite adsorption, were determined as the particle size (PS), initial dosage of zeolite (ID), and contact time (CT) (Sarioglu 2005). These were defined as the three variables for the layout of the zeolite adsorption.

The BBD was adopted in designing the experimental protocol with overall consideration of predictability, practicability, and economic feasibility. In addition, the BBD does not contain combinations of all three factors at their highest or lowest values at the same time, and therefore it avoids treatment combinations that are extreme (Ferreira et al. 2007). Therefore, the three variables were prescribed in three levels as PS of 0.03, 0.25, and 0.47 mm; ID of 1.00, 25.5, and 50.0 g/L; and CT of 3.0, 13.5, and 24 h. The experimental protocol included 17 trials for three variables with each at three levels. In the matrix cubic, the majority of the design points were situated on the midpoints of the edges, while the others were all at the center of the cubic. The experimental design based on BBD for the 3×3 factorial and star design with five central points are listed in Table 1. The BBD design was completed by the software Design Expert (Vers. 7.0, Stat-Ease Co, USA).

The statistical use of RSM

RSM was used for the model-fitting and statistical analysis of the factorial experimental results. The principle and

Table 1 | Experimental Box-Behnken design for determining the influence of three factors, zeolite particle size (PS, x_1), initial dosage of zeolite (ID, x_2), and contact time of zeolite and solution (CT, x_3), on the ammonium removal from the bio-treated coking wastewater

Trial No.	PS (mm)	ID (g/L)	CT (h)	Removal rate experimental (%)	Removal rate RSM predicted (%)
1	0.47	25.5	3.00	35.03	35.89
2	0.25	50.0	3.00	46.58	48.27
3	0.25	25.5	13.50	47.48	48.59
4	0.03	1.00	13.50	4.54	7.09
5	0.03	50.0	13.50	68.70	66.13
6	0.25	50.0	24.00	67.47	70.91
7	0.03	25.5	3.00	38.50	39.39
8	0.47	25.5	24.00	50.09	49.20
9	0.47	50.0	13.50	61.80	59.25
10	0.25	1.00	3.00	1.94	-1.50
11	0.03	25.5	24.00	56.99	56.13
12	0.25	25.5	13.50	50.23	48.59
13	0.25	25.5	13.50	44.82	48.59
14	0.47	1.00	13.50	0.97	3.54
15	0.25	25.5	13.50	48.33	48.59
16	0.25	1.00	24.00	7.61	5.92
17	0.25	25.5	13.50	52.11	48.59

fundamentals of RSM were reported by many researchers (Bradley 2007; Myers et al. 2009; Zhu et al. 2011). For the regression model-fitting for $\text{NH}_4^+\text{-N}$ adsorption by zeolite powder, an analysis of variance (ANOVA) was carried out by the same software Design Expert to analyze the experimental data and determine the best model. The interactions of the three variables were illustrated by three-dimensional (3D) contour plots, by which the important factors were optimized.

RESULTS AND DISCUSSION

Characterization of the natural zeolite

The structure of the natural zeolite detected by mercury injection showed that the total pore area was 8.617 m^2/g , the porosity was 15.34%, and the skeletal density was 2.21 g/mL . The surface configuration observed by SEM is shown in Figure 1, which showed that the zeolite had abundant microspores and macropores. The XRD pattern (Figure 2) revealed that the main component of the natural ore was clinoptilolite $((\text{Na,K,Ca})_{2-3}[\text{Al}_3(\text{Al,Si})_2\text{Si}_{13}\text{O}_{36}]\cdot 12\text{H}_2\text{O})$,

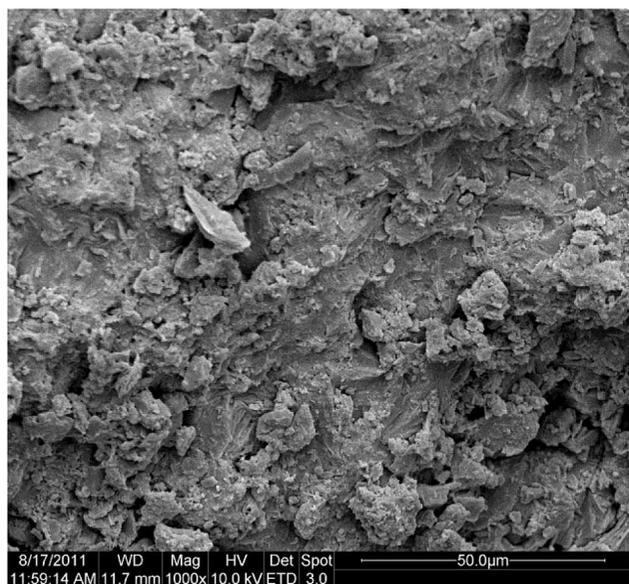


Figure 1 | The SEM image of the natural zeolite.

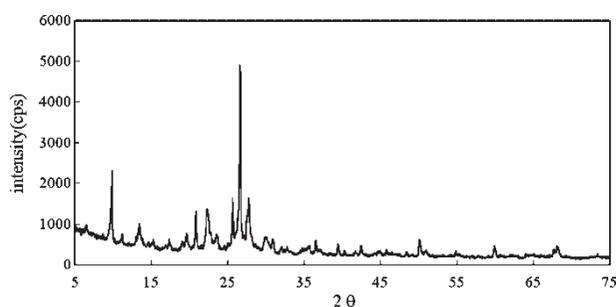


Figure 2 | The wide-angle powder XRD pattern of the natural zeolite.

CAS1318-02-1), and the proportion was 56%. The other two constitutions were quartz (SiO_2 , CAS 14464-46-1) and feldspar ((Na,K,Ca)-(AlSi₃O₈)), whose content were 26 and 18%, respectively.

Adsorption and ion exchange kinetics

Adsorption kinetics is important for determining the equilibrium time. The course of ammonium adsorption by the zeolite is presented in Figure 3, in which Figure 3(a) shows the adsorption kinetics and Figure 3(b) shows the ion exchange process.

The amount of NH_4^+ -N adsorbed on the zeolite, q_t (mg NH_4^+ -N/g zeolite), was calculated through the mass balance. Figure 3(a) indicated that the ammonium adsorption experienced fast surface sorption in the first 24 h, significantly

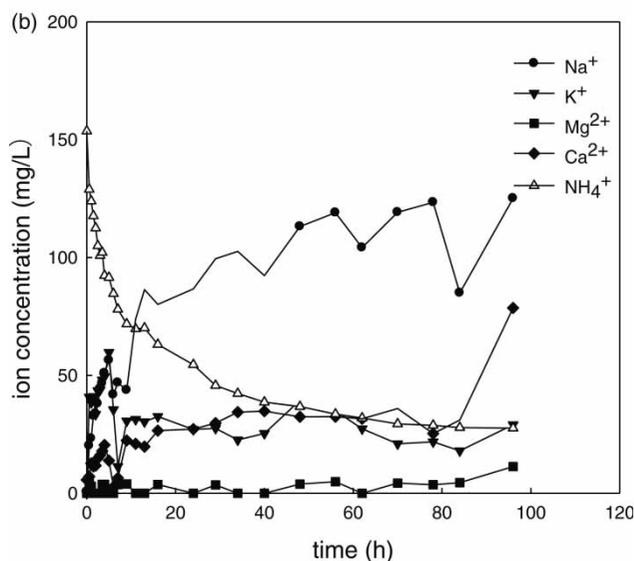
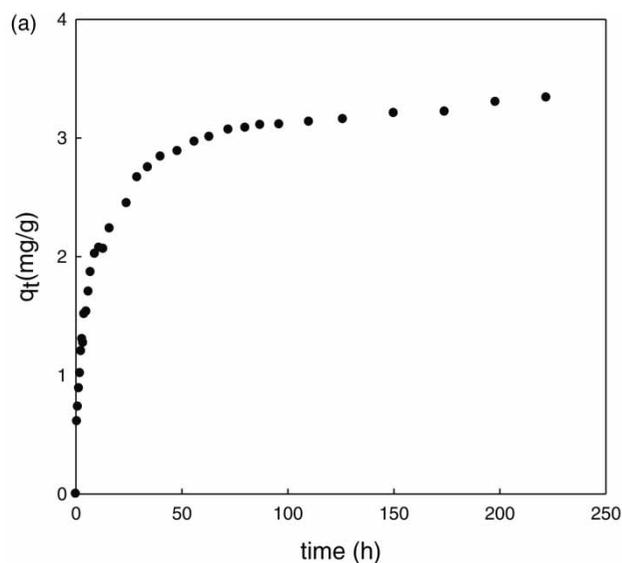


Figure 3 | The kinetics of (a) ammonium adsorption by the zeolite; and (b) ion exchange between ammonium in the solution and the alkali and alkaline earth cations in the zeolite.

declined to slow intraparticle diffusion thereafter, and gradually approached equilibrium after 96 h.

The following equations of pseudo first order (Lagergren) (Ho & McKay 1999), pseudo second order (Ho & McKay 1998), and diffusion (Weber-Morris) (Weber & Chakraborty 1974) models were applied for describing the NH_4^+ -N adsorption kinetics:

$$\text{Pseudo first order model: } \ln(q_e - q_t) = \ln q_e - k_1 t \quad (1)$$

$$\text{Pseudo second order model: } \frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (2)$$

$$\text{Diffusion model: } q_t = C + k_p t^{1/2} \quad (3)$$

where q_e and q_t are milligrams of $\text{NH}_4^+\text{-N}$ absorbed per gram of zeolite at equilibrium and at time t ; k_1 (h^{-1}), k_2 ($\text{g}/\text{mg}\cdot\text{h}$), and k_p ($\text{mg}/\text{g}\cdot\text{h}^{1/2}$) are the rate constants for the three models. The results of model-fitting are shown in Table 2. Comparing the correlation coefficients (R^2), the pseudo second order model was much better than the other two models to describe the ammonium adsorption by the zeolite. The result was identical to our previous study (Wen et al. 2006b).

Ion exchange between NH_4^+ in the NH_4Cl solution and metal ions in the natural zeolite was the key mechanism of the adsorption, as indicated by Figure 3(b). In the whole course of ion exchange, Na^+ was the biggest contributor, followed by Ca^{2+} and K^+ , but Mg^{2+} was hardly involved. The results were coincident with the ion exchange sequence of zeolite (Ames 1960) and our previous study (Wen et al. 2006a). The exchange between ammonium and alkali cations happened mainly in the first 24 h, which was synchronous with ammonium fast surface sorption. Compared with the exchanged amounts at 96 h, 69.3% of Na^+ and 93.1% of K^+ had been exchanged at 24 h.

Adsorption isotherm

Adsorption isotherm is significant for evaluating the adsorption capacity and optimizing the dosage of adsorbent. The ammonium adsorption isotherm for zeolite is shown in Figure 4.

According to the data trend, the Langmuir and Freundlich isotherm models were used in data fitting. The Langmuir isotherm assumes that adsorption takes place at the specific homogeneous sites within the adsorbent (Langmuir 1918); and the Freundlich isotherm assumes that adsorption occurs on a heterogeneous surface with non-uniform distribution (Freundlich 1906). The equations of the two models are as follows:

$$\text{Langmuir isotherm: } q_e = \frac{K_L q_m c_e}{1 + K_L c_e} \quad (4)$$

Table 2 | The kinetic constants of three models for $\text{NH}_4^+\text{-N}$ adsorption by the natural zeolite

Model	Pseudo first order		Pseudo second order		Diffusion model	
	k_1 (h^{-1})	R^2	k_2 ($\text{g}/\text{mg}\cdot\text{h}$)	R^2	k_p ($\text{mg}/\text{g}\cdot\text{h}^{1/2}$)	R^2
Value	0.009	0.901	0.0502	0.998	0.197	0.808

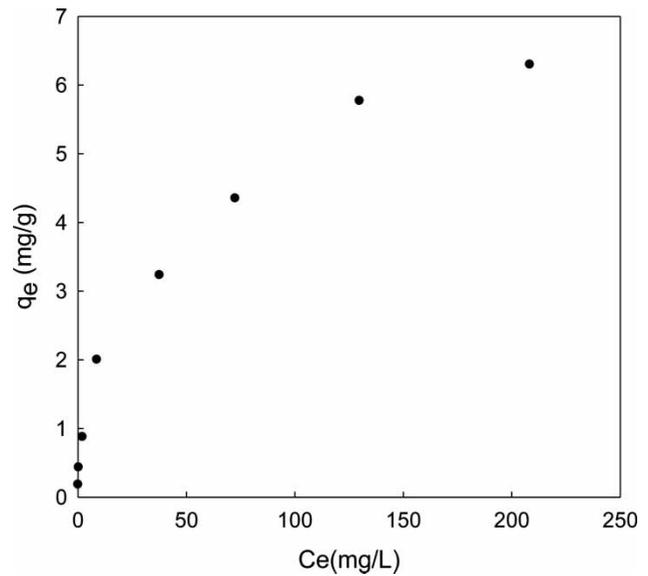


Figure 4 | The ammonium adsorption isotherm for zeolite.

$$\text{Freundlich isotherm: } q_e = K_F c_e^{1/n} \quad (5)$$

where q_m ($\text{mg}\ \text{NH}_4^+\text{-N}/\text{g}$ zeolite) is the maximum of the equilibrium $\text{NH}_4^+\text{-N}$ absorbed on one surface-layer per gram of the zeolite; c_e (mg/L) is the aqueous concentration of $\text{NH}_4^+\text{-N}$ at equilibrium; K_L (L/mg) is the constant of Langmuir model; K_F and n are the empirical constants of Freundlich model, and $1/n$, changing in the range of 0–1, is a measure of exchange intensity or surface heterogeneity. The results of data-fitting are shown in Table 3. Both fitted well to the experimental data ($R^2 > 0.98$).

Jorgensen observed that the Langmuir model provided a better fitting than Freundlich's to the ammonium ion exchange equilibrium by clinoptilolite (Jorgensen & Weatherley 2003). However, more studies (Karadag et al. 2007; Wang et al. 2007; Bai et al. 2010a) proved that the Freundlich had better performance than the Langmuir. In this study, the Freundlich isotherm showed a little advantage, and the value of $1/n$ was 0.44, indicating a favorable condition for $\text{NH}_4^+\text{-N}$ adsorption, while Langmuir isotherm was not perfect because of its idealized assumptions.

Table 3 | The isothermal constants of two models for $\text{NH}_4^+\text{-N}$ adsorption by the natural zeolite

Model	Langmuir			Freundlich		
	q_m	b	R^2	K	n	R^2
Value	4.99	0.094	0.984	0.656	2.273	0.994

Optimization of ammonium adsorption by the zeolite using RSM

Response surface analysis in regression model-fitting

Based on the results of the factorial experiment for ammonium exchange from the biologically treated coking wastewater by zeolite (Table 1), different regression models were fitted to evaluate the ammonium removal rate (Y) with the particle size (PS, x_1), zeolite initial dosage (ID, x_2), and contact time (CT, x_3) as the independent variables. The quadratic model was suggested by the ANOVA, and expressed as follows:

$$Y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \beta_{11} x_1^2 + \beta_{22} x_2^2 + \beta_{33} x_3^2 + \beta_{12} x_1 x_2 + \beta_{13} x_1 x_3 + \beta_{23} x_2 x_3 \quad (6)$$

In Equation (6), β_0 is the constant; β_1 , β_2 and β_3 are the linear regression coefficients; β_{11} , β_{22} and β_{33} are the quadratic regression coefficients; β_{12} , β_{13} and β_{23} are the regression coefficients of the interaction between two corresponding variables.

Table 4 shows the statistical significance and indicators of the quadratic mode by the ANOVA. The model's F -value (70.67) indicated the quadratic model was significant, and there was only 0.01% (p -value, much lower than 0.05) of

chaos due to noise. The suitability of the suggested model was checked by the determination coefficient (R^2); the precision of the model was checked by the adjusted R^2 ; and the predicted R^2 was used to compare the observed and predicted dependent variable. In the second half of Table 4, the value of R^2 (0.99) indicated that 99% of the variation of ammonium removal rate could be explained by the independent variables of the quadratic model. The value of adjusted R^2 (0.98) was also high, indicating a high significance of the model. The predicted R^2 (0.88) was lower than the adjusted R^2 by only 0.10 ($< \pm 0.20$ (Montgomery 2000; Kumar et al. 2008)), which implied that the data-fitting and model-fitting were highly reasonable. Additionally, the low value of the coefficient of variation (8.88%) suggested the high precision and reliability of the experiment.

To get the equation of the quadratic model, the coefficient values and their significance levels of the regression were calculated, as shown in Table 5. The significance of β_2 , β_3 , and β_{22} were at a level of $p < 5\%$, indicating that the ID, CT, and the quadratic effect of ID were significant for the ammonium removal by zeolite. The $\text{NH}_4^+\text{-N}$ removal rate (Y) was expressed as:

$$Y(\%) = 48.59 - 2.60x_1 + 28.69x_2 + 7.51x_3 - 0.83x_1x_2 - 0.86x_1x_3 + 3.80x_2x_3 - 0.17x_1^2 - 14.42x_2^2 - 3.27x_3^2 \quad (7)$$

Using model Equation (7), the $\text{NH}_4^+\text{-N}$ removal rate under a set of given variables could be predicted. The predicted ammonium removal rates under the experimental conditions are also shown in Table 1. Comparing the experimental results with the predicted values, the reliability of

Table 4 | Analysis of variance (ANOVA) of the best-fitted quadratic polynomial model for the factorial experiment

Variation	Sum of squares	Degree of freedom	F-value	p-value
Quadratic model evaluated by ANOVA:				
Model	8,102.77	9	70.67	<0.0001
Residual	89.18	7		
Lack of fit tests	58.59	3	2.55	0.1935
Pure error	30.59	4		
Total	8,191.95	16		
Statistical indicator:				
Standard deviation	3.57			
Mean	40.19			
Coefficient of variation (%)	8.88			
Adequate precision	26.447			
R^2	0.99			
Adjusted R^2	0.98			
Predicted R^2	0.88			

Table 5 | The regression coefficients and the corresponding significance level of the quadratic polynomial model

Coefficient	Estimated value	Standard error	p-value
β_0	48.59	1.60	
β_1	-2.60	1.26	0.0779
β_2	28.69	1.26	<0.0001
β_3	7.51	1.26	0.0006
β_{12}	-0.83	1.78	0.6550
β_{13}	-0.86	1.78	0.6455
β_{23}	3.80	1.78	0.0705
β_{11}	-0.17	1.74	0.9251
β_{22}	-14.42	1.74	<0.0001
β_{33}	-3.27	1.74	0.1020

the fitted quadratic model was further confirmed as it yielded accurate results of the ammonium removal rates.

Three-dimensional response surface plot

Corresponding contour plots facilitated the straightforward comparison of the effects of the independent variables on the response variable in the experiment (Yun *et al.* 2010). Therefore, to better understand both the main effects and the interactions between any of the two factors chosen from the three independent variables for the ammonium adsorption by zeolite, 3D response surface graphs were plotted based on Equation (7) and under the condition of two varying factors and one constant factor held at the center level for each graph, as shown in Figure 5.

Figure 5(a) shows the 3D response surface relationship between particle size (PS, x_1) and initial dosage of zeolite powder (ID, x_2) on the ammonium removal rate at the center level of contact time (CT, x_3), 13.5 h. The $\text{NH}_4^+\text{-N}$ removal rate increased rapidly as the ID increased, whereas the removal rate became better if smaller PS was applied. This was to be expected, because the larger zeolite surface area was gained by increasing the adsorbent dosage, decreasing its size, or both. However, the settleability of the zeolite was worse in the case of smaller PS. As a result, the effluent quality could deteriorate due to poor sedimentation of the zeolite powder. Therefore, an appropriate PS should be determined in the real application.

Figure 5(b) shows the 3D response surface relationship between PS (x_1) and CT (x_3) on the ammonium removal rate at the center level of ID (x_2), 25.5 g/L. The $\text{NH}_4^+\text{-N}$ removal rate increased markedly as the contact time increased; therefore, a longer CT could be chosen as long as the operation cost is affordable. The change of ammonium removal rate was relatively slow at different PS.

Figure 5(c) shows the 3D response surface relationship between ID (x_2) and CT (x_3) on the ammonium removal rate at the center level of PS (x_1), 0.25 mm. Both the increase of ID and CT contributed to the raising of $\text{NH}_4^+\text{-N}$ removal rate. However, except for the removal rate, an economic view is demanded for determining the appropriate values of ID and CT.

Optimization of the factors

From the experimental results, the ammonium removal by zeolite adsorption was higher in the following ranges: PS (x_1), 0.03–0.38 mm; ID (x_2), 48.3–50.0 g/L, and CT (x_3), 14.47–24 h. The highest RSM-predicted removal rate was

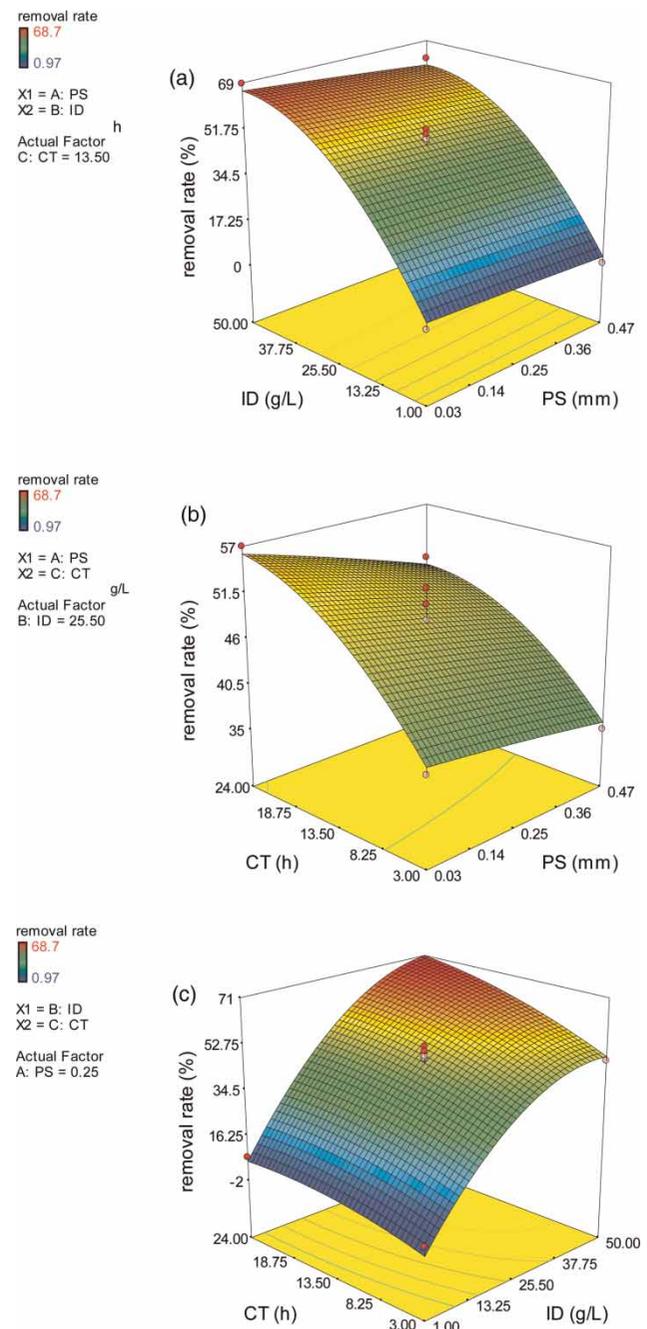


Figure 5 | The 3D response surface graphs: (a) the ammonium removal rate influenced by the particle size (x_1) and initial dosage of zeolite powder (x_2) at the center level of contact time (x_3); (b) the ammonium removal rate influenced by the particle size (x_1) and contact time (x_3) at the center level of initial dosage of zeolite powder (x_2); and (c) the ammonium removal rate influenced by the initial dosage of zeolite powder (x_2) and contact time (x_3) at the center level of particle size (x_1).

75.0% under the conditions of PS, 0.03 mm; ID, 50.0 g/L; and CT, 24 h. An experiment using 5.00 g of zeolite with particle size of 0.03 mm was conducted to treat 100 mL of the SBR effluent. The ammonium removal rate reached 78.5%

at the contact time of 24 h. However, after the adsorption, the zeolite powder was very hard to settle. The optimization of the factors needs further consideration with regard to technical application.

Taking settleability of the zeolite powder into account, particle size as large as 0.25 mm was suggested to be used in a practical operation. As shown in Table 5, β_1 and β_{11} were not significant for the ammonium removal by zeolite, indicating that PS was not as critical as ID and CT. Seen from Table 1, experimental trial No. 6, dosing 50.0 g/L of zeolite with particle size of 0.25 mm to treat the SBR effluent, reached an ammonium removal rate of 67.5% in the experiment, while 70.9% by the RSM analysis at the contact time of 24 h. This result confirmed that the suggested larger sized zeolite could yield an ideal $\text{NH}_4^+\text{-N}$ removal rate, which was closer to the highest output predicted by the RSM.

CONCLUSION

The physical and chemical characteristics of the Chinese natural zeolite benefit its ammonium adsorption. The adsorption kinetic process fitted better to the pseudo second order model than the pseudo first order and diffusion models. The adsorption isotherm fitted better to the Freundlich model. The ion exchange between ammonium in the aqueous solution and alkali and alkaline earth cations in the zeolite was in the order of $\text{Na}^+ > \text{Ca}^{2+} > \text{K}^+ > \text{Mg}^{2+}$. The zeolite powder was applied to remove ammonium from the SBR-treated coking wastewater. The BBD was employed for the experimental design in which particle size, initial dosage of zeolite powder, and contact time were taken as the most influencing factors. Based on the RSM analysis, the highest RSM-predicted $\text{NH}_4^+\text{-N}$ removal rate was 75.0% under the conditions of particle size 0.03 mm, zeolite dosage 50.0 g/L, and contact time 24 h. When the settleability was brought into account, the particle size 0.25 mm was suggested in the practical operation. These results indicate that, to enhance the removal of residue ammonia in the secondary effluent, adsorption using small zeolite particles can be a better choice for the tertiary treatment of industrial wastewater.

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