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# Removal of ammonium ions from aqueous solutions using zeolite synthesized from red mud

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## ABSTRACT

This study investigates the removal of ammonium from aqueous using zeolite synthesized from red mud. The zeolite was characterized with X-ray diffraction (XRD), scanning electron microscopy (SEM), the specific surface area, and the cation exchange capacity (CEC). SEM and XRD indicated that most of the synthetic zeolite was crystalline, with zeolite P and Analcime as the major components. The CEC increased from 81.9 to 111 mmol/100 g during the synthesis process. The effects of adsorbent dosage, shaking time, initial pH, initial ammonium ion concentration, and competitive cations were investigated by batch experiments. The result shows that the parameters mentioned above have great influence on the ammonium removal by using the synthesized zeolite, and the effect of cations follows the order $Na^+ > K^+ > Ca^{2+} > Mg^{2+}$. To understand the exchange process of ammonium by the synthesized zeolite, the adsorption dynamics was described by Ho's pseudo-second-order kinetic model. The Ho's pseudo-second-order kinetic model was found to provide excellent kinetic data fitting. Five models including Langmuir, Freundlich, Koble–Corrigan, Tempkin and D–R were used in this experiment to fit with the equilibrium isotherm data, and the Koble–Corrigan model gave the best fit. The maximum ammonium adosorption capacity obtained is 17.5 mg/g. The results implies that the zeolites synthesized from red mud is an efficient adsorbent for the removal of ammonium ion.

*Keywords:* Ammonium; Synthetic zeolite; Red mud; Adsorption

## 1. Introduction

Nitrogen in wastewater is an essential nutrient for the growth of photosynthetic algae and other biological organisms. However, excess nitrogen can lead to eutrophication of water bodies. Ammonium is the primary form of nitrogen pollution in municipal sewage and industrial wastewater. Increased concentrations of ammonium ions may be toxic to aquatic

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organisms, and increase oxygen demand and eutrophication in rivers and lakes [1]. Therefore, the amount of ammonium ions in domestic and industrial discharges must be controlled using wastewater treatment technology.

A variety of physicochemical and biological methods have been used for ammonium ion removal [2–4]. Biological nitrification/denitrification is the most widespread method for treating municipal and industrial wastewater. However, it does not respond well to shock loads of ammonium ions, and has other limitations as well. Physicochemical methods can be used to achieve stable treatments effect, but excessive sludge and salt concentrations in the water limit its large-scale applications. Zeolite is porous material with high cation exchange capacity (CEC), cation selectivity, higher void volume and great affinity for $NH_4^+$ [5,6]. Zeolites are aluminosilicate framework porous structure generated by corner-sharing $Al^{3+}$ and $Si^{4+}$oxygen tetrahedral. The small aluminum ions can occupy the position in the center of the tetrahedron of four oxygen atoms, and the isomorphous replacement of $Si^{4+}$ by $Al^{3+}$ produces a negative charge in the lattice. The net negative charge is balanced by the exchangeable cation (sodium, potassium and/or calcium, etc.). These exchangeable cations give rise to the ion-exchange or adsorption capability with $NH_4^+$. In recent years, a wide variety of natural, synthetic and modified zeolites have been reported as effective adsorbents for ammonium removal because of their low cost, selectivity, compatibility with natural environment and their relative simplicity of application and operation [7–11].

Red mud is a waste residue which is generated as a byproduct during the production of alumina. About 1–1.5 tons of red mud residues are produced for a ton of alumina [12]. Millions of tons of caustic red mud must be disposed of annually in China during recent years. Since the plant began to process, red mud has accumulated over years and causes a serious environmental problem due to its high alkalinity and large amount [13]. Many have studied the application of red mud in wastewater treatment, where it has been found to remove heavy metals and phosphates [12–15]. Red mud has become a suitable source for the synthesis of zeolite attributing to its high silicon and aluminum content, abundance and easy availability. Using red mud to synthesize zeolite might be a low-cost and effective way to treat wastewater polluted with ammonium ions. Roach and Cardile [16] synthesized 4A zeolite from red mud and it was used for the detergent industry; however, few investigations have been conducted on the performance of zeolite synthesized from red mud in ammonium removal.

The aim of the study is to examine the ability of zeolite synthesized from red mud using hydrothermal method to remove ammonium from aqueous solutions. The zeolite was characterized with X-ray diffraction (XRD), scanning electron microscopy (SEM), and the specific surface area (SSA) and CEC were determined. Adsorbent dosage, shaking time, initial pH, initial ammonium ion concentration, and competitive cations were investigated about their effects on ammonium ion removal. The adsorption kinetics and equilibrium isotherms of the adsorption of ammonium by the synthesized zeolite were also studied.

## 2. Materials and methods

### 2.1. Zeolite synthesis

Red mud used in this study was obtained from Shandong Aluminum Corporation (Shandong, China). The chemical composition is listed in Table 1. It was initially sieved and the particles smaller than 100 mesh were kept for zeolite synthesis. The hydrothermal method was adopted for the synthesis of zeolite. Extra silicon ($Na_2SiO_3{\cdot}9H_2O$, Nona hydrate of sodium silicate) was added to make the total mole ratio Si/Al = 4.5, and a NaOH solution was added to make ratio Na/Si = 1.3. The mixture was then heated in a homogeneous reactor for an 8 h aging time, and a 16 h crystallization time at a temperature of 120℃. After applying the above treatment, the precipitated samples were extracted and washed with distilled water until the pH of the samples was about nine. Finally, the samples were dried at 100℃ for 12 h for further studies. As seen from Table 1, the red mud contained high $Fe_2O_3$ content and so a large number of $[FeO_2]^-$ existed in the reaction system for zeolite synthesis. In the low alkalinity conditions, $[FeO_2]^-$ may hinder ion migration and ion compound of $[SiO_2(OH)_2]^{2-}$ and $[AlO_2]^-$ and reduce dissolution rate and solubility of the aluminosilicate gel, which is bad for zeolite synthesis [17]. High $Fe_2O_3$ content of red mud affects the purity and the CEC of the synthetic zeolite. In order

Table 1
The composition of the red mud (wt%)

| Composition | Content (%) |
|---|---|
| $SiO_{2s}$ | 14.44 |
| $Al_2O_3$ | 16.71 |
| $Fe_2O_3$ | 40.96 |
| MgO | 0.18 |
| CaO | 2.6 |
| $Na_2O$ | 6.6 |

to reduce the negative influence of high $Fe_2O_3$ content of red mud to zeolite synthesis, high alkalinity conditions were used for zeolite synthesis in this study.

### 2.2. Characterization of synthesized zeolite

Crystalline materials in the zeolite were identified by XRD using a PANnalytical X´Pert PRO MPD diffractometer (PANalytical, Eindhoven, The Netherlands), with Cu Kα ($\lambda = 0.154$ nm) radiation, operating at 40 kV and 40 mA and a step width of 0.026°. The morphological structures of the synthetic zeolite were identified by SEM, using a FEI-QUANTA200 (FEI Company, Brno, Czech Republic), operating in backscatter mode at an accelerating voltage of 15.0 kV.

The SSAs of the red mud and the synthetic zeolite were determined by nitrogen adsorption carried out at 77.3 K using a SB-091A apparatus (Cantata Instruments Co., USA). The Brunauer–Emmett–Teller equation was used to determine the SSA. The CECs of the red mud and the synthetic zeolite were measured according to the procedure of Li [18]. About 0.4 g of each sample was mixed with 40 mL of ammonium acetate (1 mol/L) five times to exchange cations. After continuous stirring for 30 min, the mixtures were centrifuged. The solid residues were washed five times with ethanol (95%) to remove excess ammonium acetate bound on the zeolite. The ammonium-saturated solid residues were then mixed five times with 40 mL of calcium chloride (0.5 mol/L) to extract the ammonium ions. After continuous stirring for 30 min, these suspensions were filtered with a 0.45-μm cellulose acetate membrane. The concentration of the extracted ammonium ions in the resulting supernatant was determined by the Nesslerization method. The CEC was then determined and denoted by mmol/100 g of adsorbents.

### 2.3. Ammonium ion adsorption

In order to examine the effect of the ammonium ion capacity and pH effect for the synthetic zeolite, batch experiments were performed in 250-mL stoppered conical flasks. The initial ammonium ion concentrations ranged from 5 to 500 mg/L in 200 mL solutions, and the zeolite dosage was varied from 0.5 to 25.0 g/L. The samples were agitated on a temperature-controlled oscillator with continuous shaking at 200 rpm. Equilibrium was established by monitoring absorbance changes at the 420-nm maximum with a UV spectrophotometer (UV-2100). The supernatant was then filtered with 0.45-μm membranes. The amounts of ammonium ions exchanged by the synthetic zeolite were determined by the Nesslerization method with the UV spectrophotometer. The ammonium ion removal was calculated as follows:

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

$$q_t = \frac{(C_0 - C_t)V}{W} \tag{2}$$

$$q_e = \frac{(C_0 - C_e)V}{W} \tag{3}$$

Here, $q_t$ and $q_e$ are the amounts of exchanged ammonium ions (mg/g); $C_0$, $C_t$ and $C_e$ are the initial, at time $t$, and the equilibrium ammonium concentrations of test solution (mg/L), respectively; $V$ is the solution volume (L); and $W$ is the weight of the zeolite (g). All the experiments were conducted in triplicate, and we report the average values where the error limit was <5%. Nona hydrate sodium silicate ($Na_2SiO_3{\cdot}9H2O$), ammonium chloride ($NH_4Cl$), sodium chloride (NaCl), sodium hydroxide (NaOH), and hydrochloric acid (HCl) were analytical grade reagents purchased from the China National Pharmaceutical Group Chemical Reagent Co., Ltd.

## 3. Results and discussion

### 3.1. Characterization of synthetic zeolite obtained from red mud

As shown in the SEM images of Fig. 1, the synthetic zeolite obtained from red mud is predominately crystalline, with some impurities. Many 10-μm round crystals and 7-μm polyhedral crystals are observed at different magnifications; although both round crystals and polyhedral crystals are major components, there are more polyhedral crystals present.

XRD patterns (Fig. 2) of the red mud and the synthetic zeolite have clear peaks. The synthetic zeolite data agree well with the characteristic peaks of zeolite P, Analcime, Sodalite and Hematite. Since the zeolite P and Analcime peaks were sharp and the intensities were relatively strong, they are most likely major components of the synthetic zeolite. This is consistent with the SEM images. Zeolite P and Analcime thus play major roles in $NH_4^+$-ion adsorption, especially the polyhedral crystals.

The obtained values of CEC and SSA of red mud were 81.9 mmol/100 g and 17.8 $m^2$/g, respectively, while those of the synthesized zeolite were 111 mmol/100 g and 28.1 $m^2$/g, respectively. This indicates that the CEC and SSA increased obviously following the conversion of

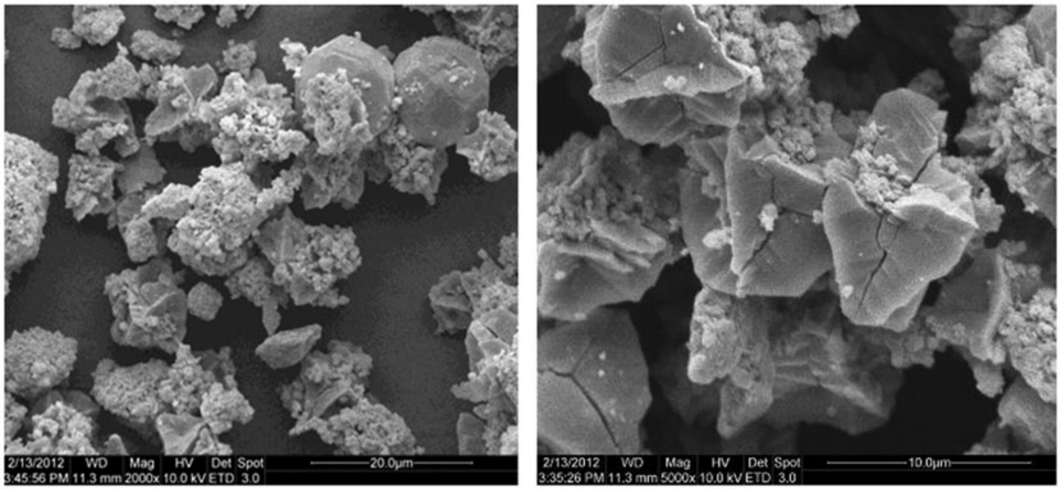

Fig. 1. SEM images of the synthetic zeolite synthesized from red mud.

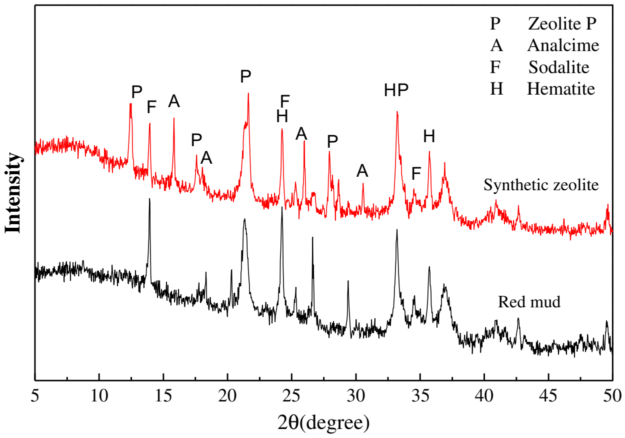

Fig. 2. The XRD diffraction pattern of the red mud and the synthetic zeolite synthesized under the optimal conditions (P is zeolite P, A is Analcime, F is Sodalite, H is Hematite).

red mud into zeolite. The zeolite pore channels provide a large surface area of active sites, and the channels can allow ions to penetrate into the structure and adsorb on the surfaces. Compared with some natural zeolites, the CEC of this synthetic zeolite is much larger, but it is not the best synthetic zeolite [10], the reason may be that the high iron contents of the red mud affect the quality, purity and the capacity of the synthetic zeolite [19]. Thus the synthetic zeolite has a significant potential for the adsorption of ammonium ions and other harmful ions.

## 3.2. Removal of ammonium ions using synthetic zeolite

### 3.2.1. Effects of pH

In aqueous solutions, the pH can affect the removal of ammonium ions by zeolites. Initial pH values in the range 2–11 were investigated, and were adjusted to the desired pH (2–11) by using 0.2 mol/L HCl and 0.2 mol/L NaOH solutions. In the experiments, 200 mL of a 25-mg/L ammonium ion solution was agitated with 1.0 g of zeolite at 298 K. In Fig. 3, the ion removal efficiency decreased gradually as the pH was increased from 2 to 4, then there was a plateau over pH 4–7, followed by a rapid decrease for pH > 7. At pH < 4, the ammonium ion removal

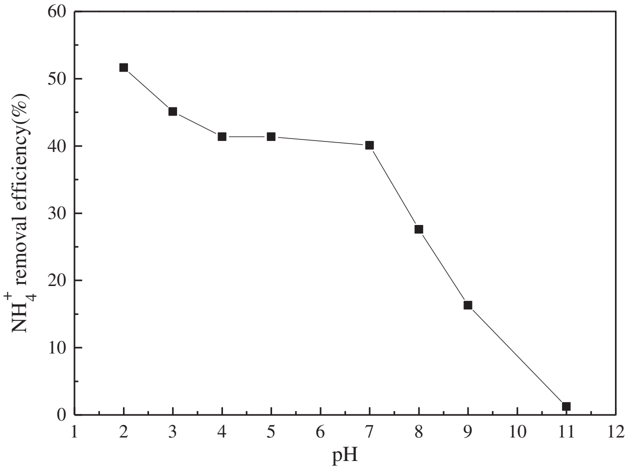

Fig. 3. Effects of pH at 298 K on ammonium adsorption of synthetic zeolite synthesized from red mud.

efficiency increased when the pH was reduced, which is most likely related to the impurity of the synthetic zeolites. When the pH is higher than 7, ammonium removal efficiency was decreased due to the reaction of $NH_4^+$ ions with $OH^-$ ions at higher pH values according to Eq. (4):

$$NH_4^+ + OH^- \leftrightarrow NH_3 \cdot H_2O \leftrightarrow NH_3 + H_2O \quad (4)$$

Also, $NH_4^+$ ions are reported to be converted to the $NH_3$ ions above pH 9 [6,17,20]. Partial dissolution of the zeolite in alkaline solutions may be another reason. As the optimum pH of the ammonium solution was near 6, the solution pH was not adjusted in the following experiments.

### 3.2.2. Effects of adsorbent dosage

To determine the balance between the ammonium-adsorption capacity and removal efficiency needed to achieve the optimum adsorbent dosage, the effects of varying the synthetic zeolite dosage on the ammonium removal efficiency were studied. In the experiments, the zeolite dosage was varied from 0.5 to 25.0 g/L for a series of 200-mL, 25-mg/L ammonium ion solutions and agitated at 298 K. As seen from Fig. 4(a), when the zeolite dosage increased from 0.5 to 25.0 g/L, the $NH_4^+$ removal efficiency increased from 22.0 to 46.6%, with a plateau at 5.0 g/L. This can be explained as follows. The increase in ammonium removal efficiency with the increase of the amount of synthesized zeolite can be attributed to the increase in surface area and exchange sites. With further increases of adsorbent dosage, higher solid/liquid ratios resulted in the formation of aggregates or precipitation of particles, resulting in a plateau at a concentration of 5.0 g/L of adsorbent. Aggregation that resulted from high sorbent concentration would lead to a decrease in total surface area of the sorbent and an increase in diffusional path length. From Fig. 4(b), it can also be seen that the ammonium ion adsorption capacity decreased as the synthetic zeolite dosage increased. This may be caused by a decrease in the ammonium ion concentration gradient per unit mass of adsorbent as the adsorbent dosage increased. The driving force generated from the concentration gradient also decreased accordingly. Consequently, less ammonium ions diffused though the liquid film and intra-particle channels to the exchangeable sites of the synthesized zeolite, and more sites remain unexchanged. Another reason for this may be due to the particle interaction, such as aggregation discussed above [10]. Particle interaction may also desorb some of the sorbate that is only loosely and reversibly bound to the sorbent surface.

### 3.2.3. Effects of initial ammonium ion concentration

Ammonium adsorption by the synthesized zeolite was studied under different initial ammonium concentrations, ranging from 5 to 500 mg/L. The zeolite dosage was kept at 5.0 g/L and the reaction temperature was kept at 298 K. The result was shown in Fig. 5. It can be seen that the initial ammonium concentration had an obvious effect on both the ammonium adsorption and the removal efficiency of ammonium. The ammonium adsorption capacity increased as the initial ammonium concentration increased. When the initial

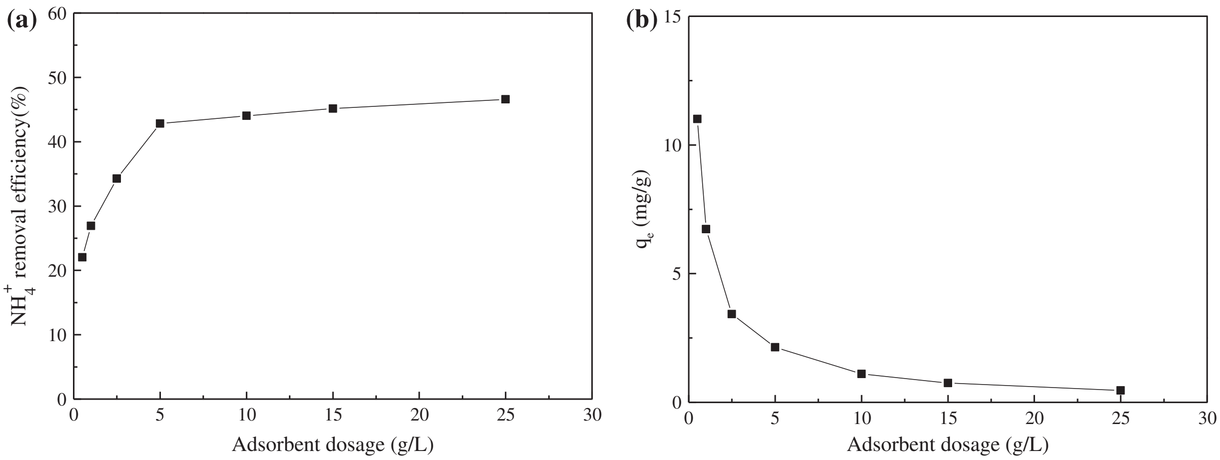

Fig. 4. Effects of adsorbent dosage on ammonium adsorption efficiency and adsorption capacities by synthetic zeolite synthesized from red mud at 298K.

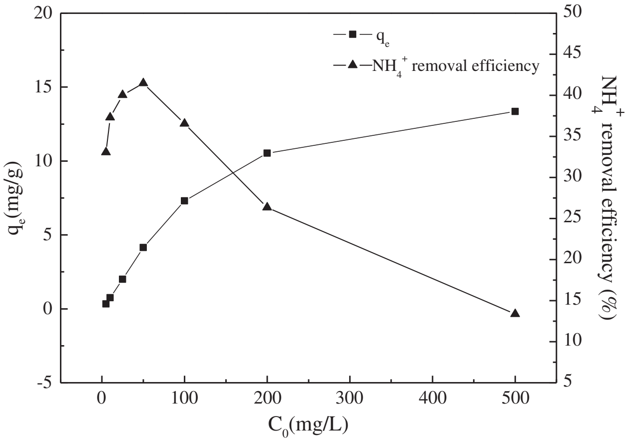

Fig. 5. Effects of ammonium initial concentration on adsorption on synthetic zeolite synthesized from red mud at 298 K.

ammonium concentration reached 500 mg/L, the ammonium adsorption capacity reached a maximum value of 13.3 mg/g. This is because higher concentrations can result in higher solute gradients, providing the necessary driving force for ammonium to replace cations in the medium framework. Fig. 5 also showed that the removal efficiency of ammonium strictly increased as the ammonium concentration increased up to 50 mg/L and thereafter, a decrease was observed. Maximum ammonium removal occurred at ammonium concentration of 50 mg/L. The increase in the first half was the result of the higher solute gradients, because the increase of the $NH_4^+$ gradient with the initial $NH_4^+$ concentration can generate more powerful driving force. The decrease in the latter half was the result of saturation of the limited number of exchange sites of the adsorbent. With an increase in initial ammonium concentration from 5 to 500 mg/L, the ammonium-removal efficiency first increased from 33.0 to 41.5% and then decreased to 13.3%.

### 3.2.4. Effects of competitive cations

Wastewater is usually contaminated with many other compounds, including inorganic salts. Therefore, it is necessary to investigate ammonium ion removal by the synthetic zeolite in the presence of various ions at similar concentrations, such as sodium ($Na^+$), potassium ($K^+$), calcium ($Ca^{2+}$), and magnesium ($Mg^{2+}$). The amount of adsorbent was 5.0 g/L, and the initial ammonium ion concentration was 25 mg/L (prepared by the deionized water). As shown in Fig. 6, the presence of the four metal ions significantly affected the ammonium ion removal efficiency at 298 K. Since the adsorption of ammonium ions is the result of ion-exchange between the aqueous solution and cations from the zeolite, the ammonium-adsorption capacity decreases as a result of competition with other inorganic cations for adsorption sites on the zeolite. Given identical concentrations of metal cations, the reduction in ammonium-adsorption capacity followed the order $Na^+ > K^+ > Ca^{2+} > Mg^{2+}$, indicating that the order of selectivity over ammonium of other cations on the synthetic zeolite was $Na^+ > K^+ > Ca^{2+} > Mg^{2+}$. It's consistent with the results of Sarioglu, Mc Veigh and Farkaˇs [21–23]. This was affected by properties of cations, such as the amount of charge, ionic radius and degree of hydration. The smaller the cationic radius, the stronger the ability of ion exchange. Though ionic radius of $Ca^{2+}$ is bigger than $Mg^{2+}$, the charge density of $Mg^{2+}$ is higher than that of $Ca^{2+}$. Therefore, the ability of ion exchange of $Mg^{2+}$ is weaker than that of $Ca^{2+}$. Lei et al. [5] and Huang et al. [6] reported similar results for the selectivity of natural zeolite. However, different results were reported by Zhang et al. [10]. The results from Zhang was that the reduction in ammonium ion uptake capacity followed the order $K^+ > Ca^{2+} > Na^+ > Mg^{2+}$ for identical concentrations. This is because different zeolites have different chemical compositions and structures, and thus different cation selectivities. As actual wastewater such as municipal and industrial wastewaters is always contaminated with various additives such as inorganic salts.If treating actual ammonia nitrogen wastewater, the $NH^{4+}$ removal efficiency will be lower than that under the experimental condition using the synthetic zeolite.

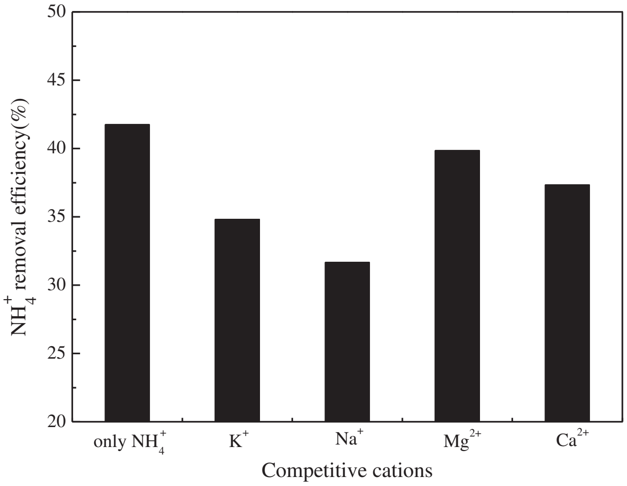

Fig. 6. Effects of competitive cations on adsorption on synthetic zeolite synthesized from red mud at 298 K.

### 3.2.5. Dynamics

The study of adsorption dynamics is necessary as it provides valuable insights into both the reaction pathway and the rate-controlling mechanism of exchange reactions. In order to determine the shaking time required to reach adsorption equilibrium, a 25-mg/L ammonium ion solution (500 mL) was shaken with 2.5 g of synthetic zeolite at 298 K. The equilibrium studies were performed at time intervals over the range 0–340 min. As seen in Fig. 7, the efficiency of ammonium ion removal reached 56.4% when the contact time was 5 min, and then showed a weak downward trend. The uptake reached a stable equilibrium after 70 min of reaction. The change in the rate of $NH_4^+$ ion removal may be explained as follows. On one hand, all the adsorbent sites are vacant and the solute concentration gradient is high [24]. When the synthetic zeolite was added in the first 5 min, ammonium ions were adsorbed rapidly by it. Thus the adsorption rate increased as time passed by. On the other hand, with the adsorption process proceeding, PH values will keep increasing which resulted in the decrease of removal efficiency of ammonium ion.

Ho's pseudo-second-order kinetic model [25] was employed to understand the exchange process of ammonium ions by the synthetic zeolite. The model is based on the assumption that the rate-limiting step may be chemical sorption or chemisorption involving sharing or exchange of electrons between the adsorbent and the adsorbate. It provides the best correlation of the data, and is represented by the following equation:

$$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{t}{q_e} \qquad (5)$$

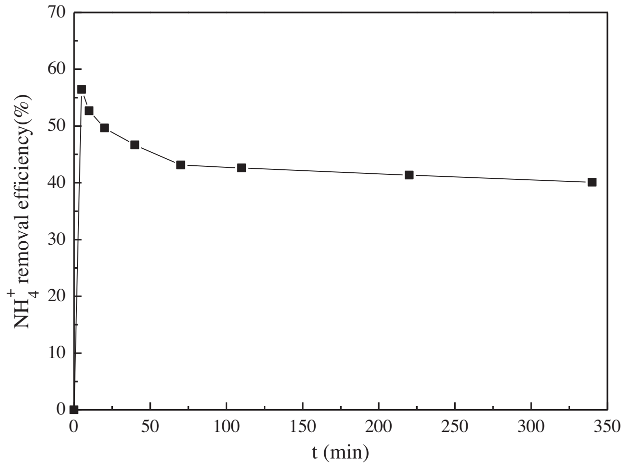

Fig. 7. Effects of contact time at 298 K for ammonium adsorption on synthetic zeolite synthesized from red mud.

where $q_t$ is the amount of exchanged ammonium ions (mg/g), $q_e$ is the maximum adsorption capacity (mg/g), $t$ is the contact time (min), and $k$ is the rate constant (g/mg min).

Fig. 8(A) shows that the coefficient of determination for the model was 0.9995, suggesting that chemisorption, i.e. the process of ion exchange, is the rate-controlling step for the uptake process of ammonium by the synthesized zeolite. The predicted value of $q_e$ was 1.918 mg/g, which was close to the experimental data (2.004 mg/g). The obtained rate constant $k$ was −0.6036 g/mg min, determined by desorption in the first half stage. Thus internal ion exchange played a decisive role in the adsorption of ammonium ions by the synthetic zeolite. Because of the small forces on the ion, adsorption by impurities and the zeolite surface was readily reversed.

## 3.3. Ammonium ions adsorption isotherms

Adsorption isotherms are important for describing how ammonium ions interact with the synthetic zeolite, and are useful in investigating the use of the zeolite as an adsorbent. The Langmuir [26], Freundlich [27], Koble–Corrigan [28], Pyzhev and Tempkin [29], and/or D–R [30] models are generally used to describe the equilibrium data. In this study, the above five models are used to fit with the experimental data to find the most suitable model.

### 3.3.1. Langmuir model

The Langmuir isotherm assumes that adsorption happens at specific homogeneous sites within the adsorbent, and there is no interaction between the adsorbate molecules. It is used to quantify the amount of adsorbate as a function of concentration at a given temperature. It considers the ideal adsorbate on an idealized surface. The linear form of the Langmuir model is:

$$\frac{C_e}{q_e} = \frac{1}{q_{\max}k} + \frac{1}{q_{\max}}C_e \qquad (6)$$

where $q_e$ (mg/g) is the equilibrium amount of ammonium ions adsorbed (mg) per unit mass of adsorbent (g), $C_e$ (mg/L) is the concentration of ammonium ions in the equilibrium solution, and $q_{max}$ (mg/g) and $k$ (L/mg) are the maximum adsorption capacity of the adsorbent and the adsorption energy coefficient, respectively.

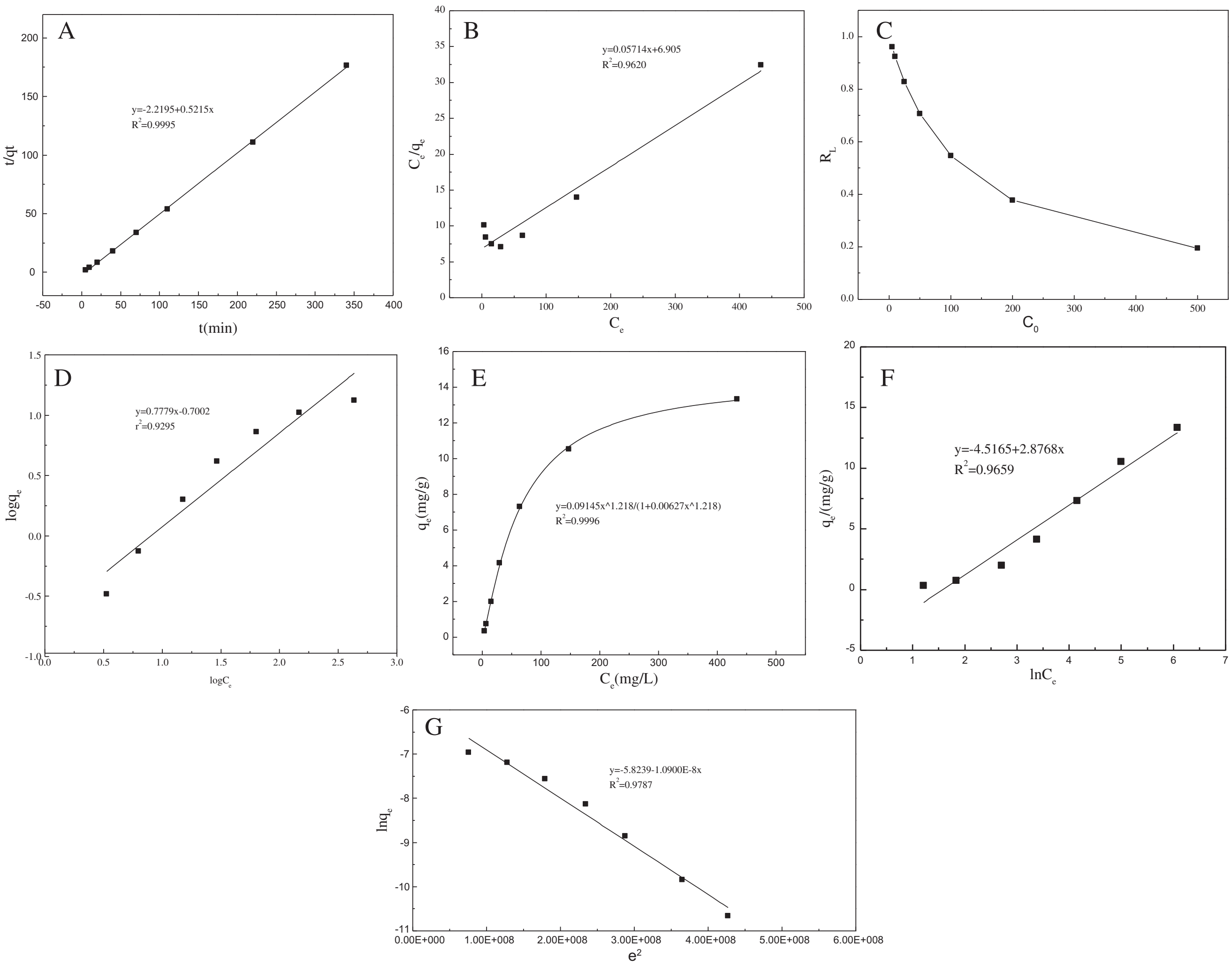

Fig. 8. Adsorption dynamics and isotherms (A) Plots of kinetics of ammonium ion removal by the red mud zeolite: Ho's pseudo-second-order model; (B) isotherm models at 298 K for ammonium adsorption on synthetic zeolite obtained from red mud: Langmuir model; (C) RL; (D) isotherm models at 298 K for ammonium adsorption on synthetic zeolite synthesized from red mud: Freundlich model; (E) isotherm models at 298 K for ammonium adsorption on synthetic zeolite synthesized from red mud: Koble-Corrigan isotherm model; (F) isotherm models at 298 K for ammonium adsorption on synthetic zeolite synthesized from red mud: Tempkin isotherm model; (G) isotherm models at 298 K for ammonium adsorption on synthetic zeolite synthesized from red mud: D-R isotherm model.

The essential features of the Langmuir isotherm can be expressed in terms of the dimensionless separation factor constant $R_L$:

$$R_L = \frac{1}{1 + kC_0} \tag{7}$$

where $C_0$ (mg/L) is the initial concentration of ammonium ions and $k$ is the Langmuir constant (L/mg). There are four possibilities for the $R_L$ value: for favorable adsorption conditions, $0 < R_L < 1$; for unfavorable adsorption conditions, $R_L > 1$; for linear adsorption, $R_L = 1$; and for irreversible adsorption, $R_L = 0$ [31].

The parameters for the Langmuir plots for ammonium ion adsorption on the synthetic zeolite are given in Table 2. The Langmuir model fits the experimental data with a good coefficient of determination of 0.9620 as shown in Fig. 8(B). The maximum adsorption capacity and the Langmuir constant ($k$) deduced from the Langmuir isotherm are 17.50 mg/g and 0.008275 L/mg, respectively. $R_L$ is between 0 and 1 as shown in Fig. 8(C), suggesting that the adsorption process was a favorable one. The $R_L$ values also demonstrate that synthetic zeolite from red mud is a potential adsorbent for ammonium ions in aqueous solutions. Fungaro et al. [3] found that the maximum adsorption capacity of zeolite

Table 2
Isotherm constants for ammonium adsorption on synthetic zeolite obtained from red mud at 298 K

| Isotherm models | Equation | Parameters | | $R^2$ |
|---|---|---|---|---|
| Langmuir | $C_e/q_e = 6.905 + 0.05714\ C_e$ | k (L/mg): 0.008275 | $q_{\max}$ (mg/g): 17.50 | 0.9620 |
| Freundlich | $\log q_e = -0.7002 + 0.7779 \log C_e$ | $K_f$ (mg/g): 0.1994 | $1/n$: 0.7779 | 0.9295 |
| Koble–Corrigan | $q_e = 0.09145 \times {}^{1.218}/(1 + 0.00627 \times {}^{1.218})$ | $a$: 0.09145 | $b$: 0.00627 | 0.9996 |
| Tempkin | $q_e = -4.5165 + 2.8768 \ln C_e$ | $b_T$: 861.2 | $A_T$ (L/g): 0.2081 | 0.9659 |
| D–R | $\ln q_e = -5.8139–1.0900\text{E-}8\varepsilon^2$ | $E$: 6.773 kJ/mol | $Q_m$ (mmol/g): 3 | 0.9787 |

13X was 8.61 mg/g at 298 K. Juan et al. [32] found that the maximum adsorption capacity of a zeolite synthesized from fly-ash using a hydrothermal method was 7.02 mg/g at 298 K. Lebedynets et al. [33] and Karadag et al. [34] reported that the maximum amounts of exchanged $NH_4^+$ using the transcarpathian clinoptilolite and natural Turkish clinoptilolite were 11.5 and 8.121 mg/g at 25°C, respectively. Weatherley and Miladinovic [35] found the maximum amounts of exchanged $NH_4^+$ by New Zealand clinoptilolite and mordenite to be 6.588 and 9.479 mg/g, respectively. Saltalı et al. reported that the maximum amount of exchanged $NH_4^+$ by natural Turkish (Yıldızeli) zeolite was 9.64 mg/g at 21°C [36]. Compared with these zeolites, the synthetic zeolite from red mud thus showed better ammonium ion adsorption.

### 3.3.2. Freundlich model

The Freundlich model is the most important multisite adsorption isotherm for rough surfaces, and is therefore applied to non-ideal adsorption on heterogeneous surfaces. The linear form of the Freundlich model is:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \tag{8}$$

where $K_f$ is the Freundlich constant (mg/g), the measure of the adsorption capacity of the adsorbent, and $1/n$ is the heterogeneity factor, a constant related to the adsorption intensity or surface heterogeneity. High values of $K_f$ indicate high affinities for ammonium ions, and $0.1 < 1/n < 1$ indicates favorable conditions for adsorption [37]. Calculated Freundlich constants are given in Table 2. The 0.9295 coefficient of determination indicated that the model did not fit the experimental data very well as shown in Fig. 8(D). The value of $1/n$ is less than 1 (0.7779 at 298 K), and therefore represents favorable removal conditions. The constant $K_f = 0.1994$, whereas Sarioglu [38] and Weatherley and Miladinovic [35] had 2.23 and 2.27, respectively, for the adsorption of ammonium ions, which indicated less affinity.

### 3.3.3. Koble–Corrigan model

The Koble–Corrigan model is an empirical model that combines the Langmuir and Freundlich isotherm models. Its form is given below:

$$q_e = \frac{aC_e^n}{1 + bC_e^n} \tag{9}$$

where, $a$, $b$, and $n$ are the Koble–Corrigan parameters, respectively. $C_e$ and $q_e$ are the same as those in the Langmuir isotherm model.

The predicted equilibrium data and values of $a$, $b$, and $n$ are listed in Table 2. The coefficient of determination was 0.9996 as shown in Fig. 8(E), which indicates a better fit to the experimental data relative to those by the Langmuir and Freundlich models. This indicates a combination of heterogeneous and homogeneous adsorption occurred for ammonium ions adsorption by the synthetic zeolite. Comparing with the coefficients of determination of the Langmuir and Freundlich models, it can be deduced that homogeneous adsorption was the primary mechanism of ammonium ion adsorption.

### 3.3.4. Tempkin model

The Tempkin isotherm model takes into account indirect adsorbent–adsorbate interactions and assumes that the heat of adsorption decreases linearly with coverage due to the interactions. The form of the Tempkin equation is given as:

$$q_e = B_T \ln A_T + B_T \ln C_e \tag{10}$$

$$\text{where } B_T = \frac{RT}{b_T} \tag{11}$$

The constant $b_T$ is related to the heat of adsorption, $A_T$ is the equilibrium binding constant (L/g) corresponding to the maximum binding energy, $T$ (K) is the absolute temperature, $R$ is the universal gas constant (8.314 J/mol K), and $C_e$ and $q_e$ are as defined above.

Calculated Tempkin constants are given in Table 2, where $A_T = 0.2081$ at 298 K, and the $B_T = 861.2$. The coefficient of determination was 0.9659 as shown in Fig. 8(F). Thus, the Tempkin isotherm model fits the experimental data better than the Langmuir and Freundlich models, but it was not as good as the Koble–Corrigan model.

### *3.3.5. D–R model*

The D–R (Dubinin–Radushkevich) isotherm is used to describe the adsorption process of microporous adsorbents and the characteristic sorption curve is related to the porous structure of the sorbent. The D–R equation is described as:

$$\ln q_e = \ln Q_m - K\varepsilon^2 \tag{12}$$

$$\varepsilon = RT \ln\left(1 + \frac{1}{C_e}\right) \tag{13}$$

where $K$ (mol$^2$/kJ$^2$) is a constant related to the adsorption energy, $Q_m$ (mol/g) is the maximum adsorption capacity, and $T$, $R$, $C_e$, and $q_e$ are defined as before. The mean free energy of adsorption E can be calculated by:

$$E = \frac{1}{\sqrt{2K}} \tag{14}$$

The D–R model is used to estimate $E$. Based on the principle of this model, if $1 < E < 8$ kJ/mol, physical adsorption prevails; if $8 < E < 16$ kJ/mol, chemisorption prevails. Calculated constants are listed in Table 2, and $Q_m = 3$ mmol/g at 298 K and $E = 6.773$ kJ/mol. Since $E < 8$ kJ/mol, physical uptake of ammonium ions prevailed for the synthesized zeolite. Fig. 8(G) shows that the obtained coefficient of determination at 298 K was 0.9787, smaller than that obtained from the Koble–Corrigan model but bigger than those obtained from other models (Table 2). This indicates that the D–R model was not as good as the Koble–Corrigan model, but it fits the experimental equilibrium data better compared to other models.

### *3.3.6. Summary of the adsorption isotherm studies*

The above analyses indicated that the Koble–Corrigan model yields a better fit than the other models. The D–R, Tempkin, and Langmuir models also describe the uptake process, while the Freundlich model relatively failed to express the equilibrium relation. The adsorption was single layer (physical), and homogeneous uptake was most likely the primary mechanism of ammonium ion adsorption. Finally, adsorbent–adsorbate interactions should be taken into account.

A comparison of the ammonium adsorption capacities by various zeolites has been discussed in Section 3.3.1. It may be difficult to compare the ammonium adsorption of the synthesized zeolite in our study to those found by other authors, as doing so would require that the experiments are carried out under the same experimental conditions. However, it is generally true to say that the synthesized zeolite had a good capacity for ammonium uptake. As a synthesized material from red mud, it is easily-available and high-efficient as an adsorbent for ammonium removal.

## 4. Conclusion

The novel zeolite adsorbent obtained from red mud was characterized and its adsorption behavior with respect to removal of ammonium from aqueous solutions was investigated. SEM and XRD indicated that the major components of the zeolite were zeolite P and Analcime. CEC increased significantly from 81.9 mmol/100 g of raw red mud to 111 mmol/100 g of synthesized zeolite after conversion. Adsorbent dosage, pH, shaking time, initial ammonium ion concentration, and competitive cations influenced ammonium removal from aqueous systems by the zeolite. The kinetics of ammonium uptake by the synthesized zeolite followed the Ho’ pseudo-second-order model, suggesting that ion exchange was the rate controlling step. The uptake data fit the Koble–Corrigan model best, indicating that heterogeneous and homogeneous uptake co-occurred for ammonium uptake by the synthesized zeolite. In conclusion, this synthetic zeolite obtained from red mud has potential applications in the removal of pollutant ammonium ions from wastewater.

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## References

[1] M. Gholamreza, T. Sadegh, F. Mehrdad, Removal of ammonium from water by adsorption onto synthetic zeolites NaA and NaX: A comparative parametric, kinetic, and equilibrium study, Desalin. Water Treat. 51 (2013) 28–30.

[2] E. Saifeddine, K. Hamadi, J. Naceur, D.H. Ben, Ammonium nitrogen removal from synthetic water by treatment with Tunisian natural clay, Desalin. Water Treat. 49 (2012) 227–233.

[3] D.A. Fungaro, M. Bruno, L.C. Grosche, Adsorption and kinetic studies of methylene blue on zeolite synthesized from fly ash, Desalin. Water Treat. 2 (2009) 231–239.

[4] Y. Feng, Y.Z. Yu, Q.N. Duan, J. Tan, C.H. Zhao, The characteristic research of ammonium ions removal in grain-slag biological aerated filter (BAF), Desalination 263 (2010) 146–150.

[5] L.C. Lei, X.J. Li, X.W. Zhang, Ammonium ions removal from aqueous solutions using microwave-treated natural Chinese zeolite, Sep. Purif. Technol. 58 (2008) 359–366.

[6] H.M. Huang, X.M. Xiao, B. Yan, L.P. Yang, Ammonium ions removal from aqueous solutions by using natural Chinese (Chende) zeolite as adsorbent, J. Hazard. Mater. 175 (2010) 247–252.

[7] D. Karadag, Y. Koc, M. Turan, B. Armagan, Removal of ammonium ions ion from aqueous solution using natural Turkish clinoptilolite, J. Hazard. Mater. 136 (2006) 604–609.

[8] M.L. Zhang, H.Y. Zhang, D. Xu, L. Han, D.X. Niu, L.Y. Zhang, W.S. Wu, B.H. Tian, Ammonium ions removal from aqueous solution by zeolites synthesized from low-calcium and high-calcium fly ashes, Desalination 271 (2011) 46–53.

[9] A.M. Yusofa, L.K. Keata, Z. Ibrahimb, Z.A. Majida, N.A. Nizamb, Kinetic and equilibrium studies of the removal of ammonium ions from aqueous solution by rice husk ash-synthesized zeolite Y and powdered and granulated forms of mordenite, J. Hazard. Mater. 174 (2010) 380–385.

[10] M.L. Zhang, H.Y. Zhang, D. Xu, L. Han, D.X. Niu, B.H. Tian, J. Zhang, L.Y. Zhang, W.S. Wu, Removal of ammonium ions from aqueous solutions using zeolite synthesized from fly ash by a fusion method, Desalination 271 (2011) 111–121.

[11] W. Franus, M. Wdowin, Removal of ammonium ions ions by selected natural and synthetic zeolites, Gospod. Surowcami. Min. 26 (2010) 133–148.

[12] Y. Zhao, J. Wang, Z.K. Luan, X.J. Peng, Z. Liang, L. Shi, Removal of phosphate from aqueous solution by red mud using a factorial design, J. Hazard. Mater. 165 (2009) 1193–1199.

[13] Y. Zhao, J. Wang, C.J. Liu, Z.K. Luan, N. Wei, Z. Liang, Characterization and risk assessment of red mud derived from the sintering alumina process, Fresenius Environ. Bull. 18 (2009) 989–993.

[14] Y. Zhao, L.Y. Zhang, F. Ni, B.D. Xi, X.F. Xia, X.J. Peng, Z.K. Luan, Evaluation of a novel composite inorganic coagulant prepared by red mud for phosphate removal, Desalination 273 (2011) 414–420.

[15] Y.R. Li, J. Wang, Y. Zhao, Z.K. Luan, Research on magnetic seeding flocculation for arsenic removal by superconducting magnetic separation, Sep. Purif. Technol. 73 (2010) 264–270.

[16] G.I.D. Roach, C.M. Cardile, Zeolite Production From Dsp in Red Mud Feedstock [A]. Light Metals: Proceedings of Sessions, TMS Annual Meeting (Warrendale, Pennsylvania) [C], Miner. Met. Mate. Soc (TMS). (1993) 51–57.

[17] L.H. Xia, B.Z. Dong, N.Y. Gao, C. Chang, Study on ammonia-nitrogen and organics removal using modified zeolites, J. Tongji Univ. (Natural Science) 33 (2005) 78–82.

[18] Y.Q. Li, Studies on the Optimization of Synthesis Conditions for Fly-Ash Zeolite and its Preliminary Applications [D], Shanghai Jiao Tong University, Shanghai, 2007, p. 1.

[19] X.H. Zhang, H.W. Ma, J. Yang, H.B. Qi, Influences of $Fe_2O_3$ on synthesis and properties of 13X zeolite molecular sieve, Earth Sci. Front. 12 (2005) 157–163.

[20] E. Maranon, M. Ulmanu, Y. Fernandez, I. Anger, L. Castrillon, Removal of ammonium ions from aqueous solutions with volcanic tuff, J. Hazard. Mater. 137 (2006) 1402–1409.

[21] M Sarioglu, Removal of ammonium from municipal wastewater using natural Turkish (Dogantepe) zeolite, Sep. Purif. Technol. 41 (2005) 1–11

[22] A. Farkaˇs, M. Rozic, Z. Barbaric-Mikocevic, Ammonium exchange in leakage waters of waste dumps using natural zeolite from the Krapina region, Croatia, J. Hazard. Mater. B117 (2005) 25–33.

[23] R.J. Mc Veigh, The Enhancement of Ammonium Ion Removal onto Columns of Clinoptilolite in the Presence of Nitrifying Bacteria, Ph.D. Research Dissertation, Department of Chemical and Process Engineering, The Queen's University of Belfast.

[24] N. Murayama, S. Yoshida, Y. Takami, H. Yamamoto, J. Shibata, Simultaneous removal of $NH_4^+$ and $PO_4^{3-}$ in aqueous solution and its mechanism by using zeolite synthesized from coal fly ash, Sep. Sci. Technol. 38 (2003) 113–129.

[25] Y.S. Ho, G. McKay, Pseudo-second order model for sorption processes, Process Biochem. 34 (1999) 451–465.

[26] I. Langmuir, The adsorption of gases on plane surfaces of glass, mica and platinum, J. Am. Chem. Soc. 40 (1918) 1361–1367.

[27] H.M.F. Freundlich, Uber die adsorption in losungen, Z. Phys. Chem. 57 (1906) 385–470.

[28] R.A. Koble, T.E. Corrigan, Adsorption isotherm for pure hydrocarbons, Ind. Eng. Chem. 44 (1952) 383–387.

[29] M.J. Pyzhev, V. Tempkin, Kinetics of ammonia synthesis on promoted iron catalysts, Acta Physicochim. URSS. 12 (1940) 217–256.

[30] M.M. Dubinin, L.V. Radushkevich, Equation of the characteristic curve of activated charcoal, Chem. Zentralbl. 55 (1947) 331–337.

[31] V.K. Gupta, A. Mittal, A. Malviya, J. Mittal, Adsorption of carmoisine a from wastewater using waste materials-bottom ash and deoiled soya, J. Colloid Interface Sci. 335 (2009) 24–33.

[32] R.H. Juan, A. Susana, J.M.R. Carmen, Ion exchange uptake of ammonium ions in wastewater from a sewage treatment plant by zeolitic materials from fly ash, J. Hazard. Mater. 161 (2009) 781–786.

[33] M. Lebedynets, M. Sprynsky, I. Sakhnyuk, R. Zbytniewski, R. Golembiewski, B. Buszewski, Adsorption of $NH_4^+$ ions onto a natural aeolite: transcarpathian clinoptilolite, Adsorpt. Sci. Technol. 22 (2004) 731–741.

[34] D. Karadag, Y. Koc, M. Turan, B. Armagan, Removal of ammonium ion from aqueous solution using natural Turkish clinoptilolite, J. Hazard. Mater. B 136 (2006) 604–609.

[35] L.R. Weatherley, N.D. Miladinovic, Comparison of the ion exchange uptake of ammonium ions ion onto New Zealand clinoptolite and mordenite, Water Res. 38 (2004) 4305–4312.

[36] K. Saltalı, A. Sarı, M. Aydın, Removal of ammonium ion from aqueous solution by natural Turkish (Yıldızeli) zeolite for environmental quality, J. Hazard. Mater. 141 (2007) 258–263.

[37] C. Raji, T.S. Anirudhan, Batch Cr(VI) removal by polyacrylamide-grafted sawdust: Kinetics and thermodynamics, Water. Res. 32 (1998) 3372–3780.

[38] M. Sarioglu, Removal of ammonium ions from municipal wastewater using natural Turkish (Dogantepe) zeolite, Sep. Purif. Technol. 41 (2005) 1–11.