

REMOVAL OF AMMONIUM FROM AQUEOUS SOLUTIONS USING SYNTHETIC ZEOLITE OBTAINED FROM COAL FLY-ASH

Yongchao Niu^{1,2}, Ying Zhao^{2,*}, Beidou Xi^{2,*}, Xiang Hu¹, Xunfeng Xia², Lei Wang², Dandan Lv¹, and Jiajuan Lu²

¹Beijing University of Chemical Technology, Beijing 100029, PR China

²State Key Laboratory of Environmental Criteria and Risk Assessment, Chinese Research Academy of Environmental Sciences, Beijing 100012, PR China

ABSTRACT

The purpose of this study was to investigate the removal of ammonium from aqueous solutions using a novel zeolite obtained from coal fly-ash. The zeolite was characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). Batch experiments were carried out to investigate adsorbent dosage, shaking time, initial pH, initial ammonium concentration, and competitive cations. Freundlich and Langmuir models were used to describe the equilibrium isotherm data. The SEM and XRD images indicated that most of the synthetic zeolite obtained from coal fly-ash was crystalline, and zeolite Na-P₁ was the major component. Adsorbent dosage, shaking time, initial pH, initial ammonium concentration, and competitive cations all affected NH₄⁺-ion removal from aqueous solutions. Equilibrium modeling data were fitted to linear Langmuir and Freundlich models. The results demonstrated that the novel zeolite obtained from coal fly-ash displayed a faster adsorption rate and higher adsorption capacity than did other zeolites reported in the literature. This implies that the zeolite has potential applications in removing ammonium pollutants from wastewater.

KEYWORDS:

Ammonia removal; Synthetic zeolite; Coal fly-ash; Adsorption

1. INTRODUCTION

Nitrogen in wastewater is one of the causes for growth of photosynthetic algae and other biological organisms in water bodies. Ammonium is the primary form of nitrogen pollution in various types of wastewater, including municipal sewage and industrial wastewater, and can be formed by decomposition of organic nitrogen compounds

in wastewater. Accumulation of ammonium in water may be toxic to aquatic organisms, and increase oxygen demand and eutrophication in rivers and lakes [1]. As awareness of the deleterious effects of ammonium increases, the laws restricting ammonium discharge from wastewater are becoming more stringent. Low-cost, effective methods are therefore needed for the treatment of waters polluted with ammonium.

In wastewater treatment, a variety of physicochemical and biological methods have been used for ammonium removal [2–5]. The biological nitrification/denitrification method is the traditional method for ammonium removal from municipal and industrial wastewater. However, this method has limitations. For example, it does not respond well to shock loads of ammonium. In cold weather, the low temperature of the wastewater precludes the use of this method for ammonium removal. Ion-exchange methods, for example using zeolites, are effective techniques for ammonium removal, and considered to be an attractive alternative to biological methods [6–9]. Removal of ammonium ions by selected natural and synthetic zeolites has been studied by many researchers [10–13].

Electricity-generating plants produce 500 million tons of fly-ash, a by-product of coal combustion, globally every year. However, only 16% is recycled, and most fly-ash is stored at the power plants or placed in landfills, causing severe environmental problems [14]. However, fly-ash can be useful and environmentally friendly. Recently, much attention has been paid to coal fly-ash as a potential material for ammonium removal, and there have been many reports [14–17] on the use of synthetic zeolites from fly-ash for ammonium removal.

The ability of a novel zeolite synthesized from coal fly-ash to remove ammonium from aqueous solutions is investigated in this study. The zeolite was characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM), and the effects of adsorbent dosage, shaking time, initial pH, initial ammonium concentration, and competitive cations on ammonium removal were investigated. Finally, the adsorption equilibrium isotherms of ammonium uptake by the zeolite were studied.

* Corresponding authors

2. MATERIALS AND METHODS

2.1 Raw materials

The zeolite synthesized from coal fly-ash used in this study was provided by the Beijing Daoshun International Technology Development Co., Ltd., Beijing, China. All of the other inorganic chemicals used in this study, i.e., ammonium chloride (NH₄Cl), sodium chloride (NaCl), sodium hydroxide (NaOH), and hydrochloric acid (HCl), were analytical grade reagents from the China National Pharmaceutical Group Chemical Reagent Co., Ltd. A stock solution (1000 mg·L⁻¹) was prepared by dissolving NH₄Cl in distilled water; the desired concentrations were obtained when needed by diluting the stock solution with distilled water. Diluted HCl and NaOH solutions were used for pH adjustment.

2.2 Methods characterization

The synthetic zeolite obtained from fly-ash was characterized by XRD and SEM. Crystalline materials in the zeolite were identified by XRD using a PANalytical X τ Pert PRO MPD diffractometer (PANalytical, Eindhoven, The Netherlands) with Cu K α ($\lambda = 0.154$ 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 specific surface area of the synthetic zeolite obtained from fly-ash was determined by the nitrogen adsorption method. Nitrogen sorption experiments were carried out at 77 K using a NOVA4200e apparatus (Cantata Instruments Co., USA). The Brunauer–Emmett–Teller equation was used to determine the specific surface area.

2.3 Ammonium-adsorption experiments

Batch experiments were performed in 250-mL stoppered conical flasks using 200 mL of solutions with different initial concentrations of ammonium and adsorbent doses. The initial ammonium concentrations ranged from 5 to 100 mg·L⁻¹, and the zeolite dosage was varied from 0.5 g·L⁻¹ to 15.0 g·L⁻¹. The samples were agitated on a temperature-controlled shaker with continuous stirring at 200 rpm. After equilibrium had been reached, the supernatant was filtered using 0.45- μ m membranes. The initial and final ammonium concentrations in solution were determined, using a UV spectrophotometer (UV-2100), by monitoring the absorbance changes at the maximum absorbance wavelength (420 nm).

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

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

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

where q_t and q_e are the amounts of exchanged ammonium (mg·g⁻¹); C_0 , C_t and C_e (mg·L⁻¹) are the initial, time t , and equilibrium concentrations, respectively, of the ammonium solution; V (L) is the solution volume; and W (g) is the weight of synthetic zeolite. All treatments were conducted in triplicate, and we report the average values. The limit of error of the triplicate samples was lower than 5%.

3. RESULTS AND DISCUSSION

3.1 Characterization of synthetic zeolite obtained from coal fly-ash

Fig. 1 shows the XRD pattern of the synthetic zeolite obtained from coal fly-ash. All the XRD peaks agree well with the characteristic peaks of zeolite Na-P₁, mullite, quartz, and phillipsite. The zeolite Na-P₁ peak is sharp and the intensity is comparatively strong. This indicates that zeolite Na-P₁ is the major component of the synthetic zeolite and would play the major role in NH₄⁺-ion adsorption.

Analysis of the XRD pattern suggests the following composition for the synthetic zeolite: Na-P₁ 71.9%, mullite 17.8%, quartz 9.9%, and phillipsite 0.4%.

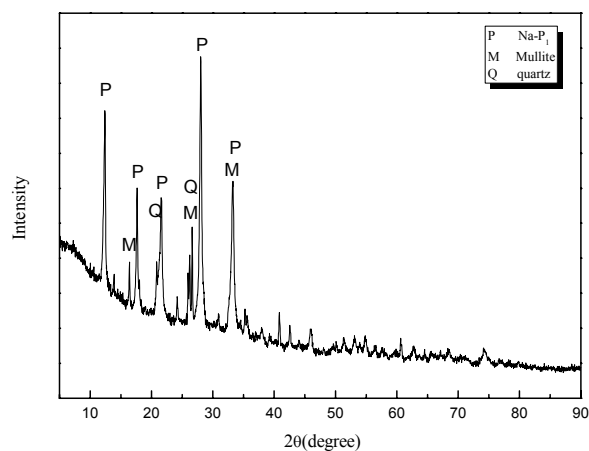


FIGURE 1 - XRD diffraction pattern of synthetic zeolite obtained from coal fly-ash

Fig. 2 shows the SEM images of the synthetic zeolite obtained from coal fly-ash; a large number of round crystals with strip-shaped surfaces can be easily observed at different magnifications. The particle size is estimated to be about 2 μ m; some impurities can be observed.

The potential adsorption capacity is reflected to some extent by the specific surface area. The obtained value of the specific surface area of the synthetic zeolite obtained from coal fly-ash was 22.60 m²·g⁻¹. The pore channels in the zeolite, which can allow ions to penetrate into or adsorb on the surface, provide a large surface of active sites. This kind of zeolite therefore has significant potential applications in the adsorption of harmful ions such as ammonium.

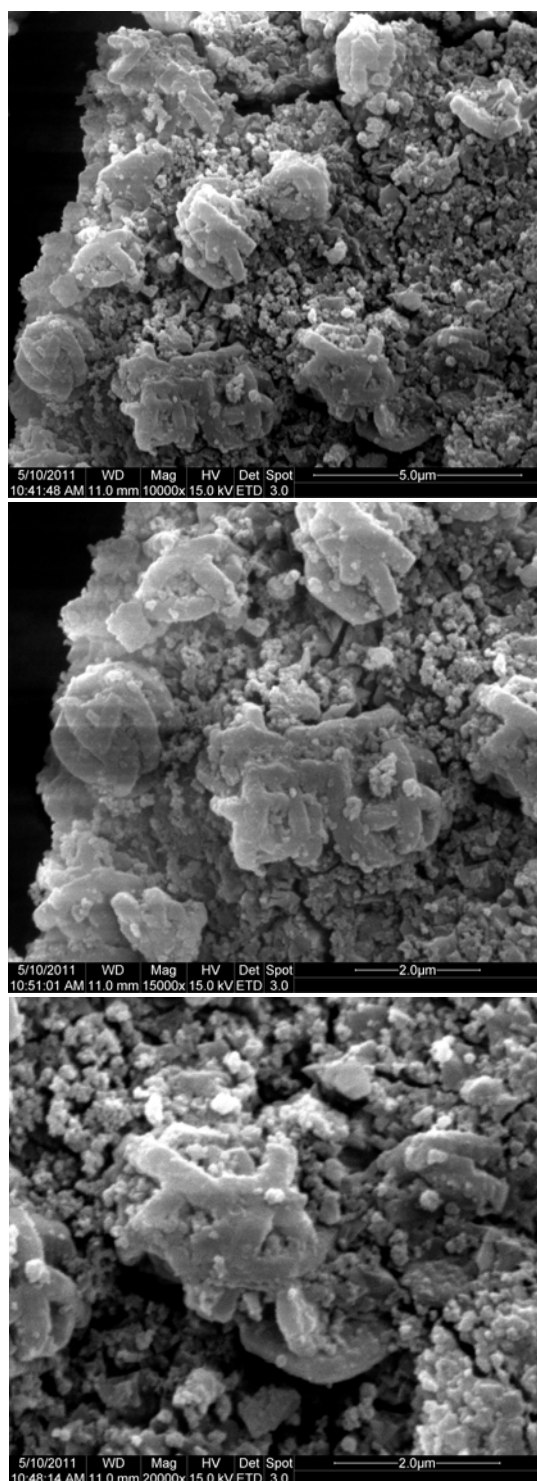


FIGURE 2 - SEM images of synthetic zeolite obtained from coal fly-ash.

3.2 Performance of synthetic zeolite obtained from coal fly-ash

3.2.1 Effects of shaking time

In order to determine the shaking time required for the ammonium-zeolite system to reach equilibrium, a $50 \text{ mg}\cdot\text{L}^{-1}$ ammonium solution (500 mL) was shaken with 2.5 g of zeolite. The equilibrium studies were performed at time intervals in the range 0.5–150 min. Fig. 3 shows the am-

monium uptake by the synthetic zeolite as a function of shaking time at 298 K. As seen from Fig. 3, the ammonium-adsorption rate by the zeolite was rapid and the final ammonium uptake was almost complete within 10 min of starting the reaction. The uptake reached near equilibrium 10 min after the initial reaction, and the uptake of ammonium became almost stable. The change in the rate of NH_4^+ -ion removal may be explained as follows. Initially, all the adsorbent sites are vacant and the solute concentration gradient is high [15]. The NH_4^+ -ion uptake rate by the zeolite then decreases significantly as a result of the decrease in adsorption sites. Zhang et al. [14] also found that ammonium uptake by zeolites was a fast process, and uptake equilibrium is achieved within 10–15 min. As can be seen from the data, there is no significant difference between the removal efficiency after 30 min and that after 150 min. On the basis of these results, a 30-min shaking period was selected for the subsequent experiments.

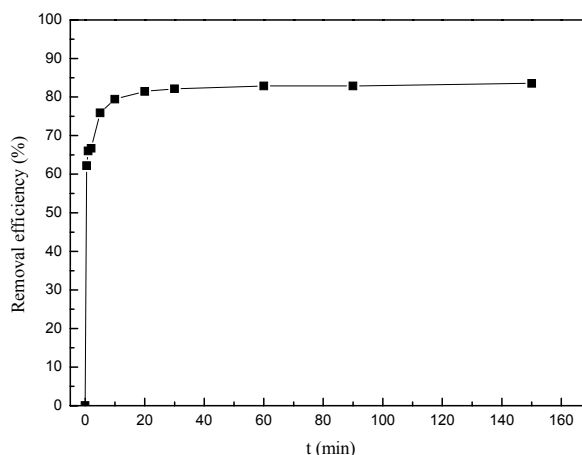


FIGURE 3 - Effects of contact time at 298 K for ammonium adsorption on synthetic zeolite obtained from coal fly-ash

3.2.2 Effects of pH

The pH is an important factor in the exchange of ammonium by zeolites. The pH can affect the characteristics of the ammonium and of the zeolite. The effects of initial pH values in the range 2–10 were investigated. The pH values were adjusted using $0.2 \text{ mol}\cdot\text{L}^{-1}$ HCl and $0.2 \text{ mol}\cdot\text{L}^{-1}$ NaOH solutions. 200 mL of $50 \text{ mg}\cdot\text{L}^{-1}$ ammonium solution were agitated with 1.0 g of zeolite at 298 K. The experimental results are shown in Fig. 4. As seen from Fig. 4, the pH has an obvious impact on ammonium removal by the zeolite. The removal efficiency increased slowly as the pH was increased from 2 to 6, reached a maximum value at pH 6, and then decreased at pH 7. At pH values below 6, the decrease in the ammonium-removal efficiency may be the result of two factors [12, 15]:

(1) At lower pH values, the ammonium ions have to compete with hydrogen ions for the adsorption sites, so the efficiency is lower.

(2) The zeolite crystals begin to collapse or dissolve with decreasing pH in aqueous solutions. However, when

the pH is higher than 7, the ionized ammonium is gradually transformed to non-ionized forms of NH_3 ; this is unfavorable for adsorption on the zeolite surface [18]. Partial dissolution of the zeolite in alkaline solutions may be another reason [19]. As the optimum pH of the ammonium solution was near 6, the solution pH was not adjusted in the following experiments.

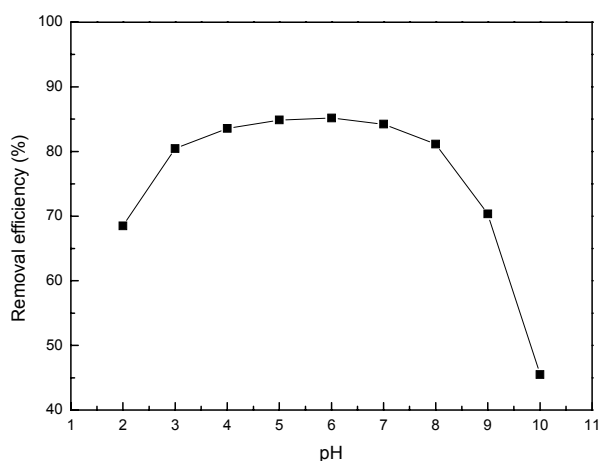


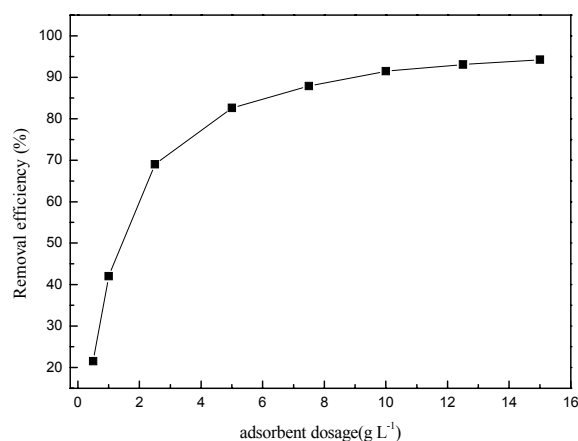
FIGURE 4 - Effects of pH at 298 K on ammonium adsorption on synthetic zeolite obtained from coal fly-ash

3.2.3 Effects of adsorbent dosage

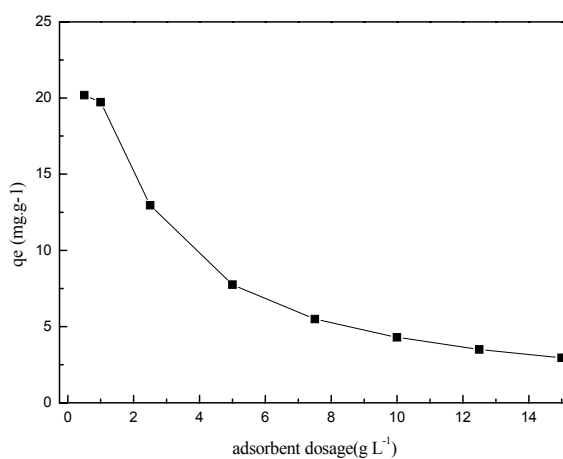
To determine the balance between the ammonium-adsorption capacity and removal efficiency needed to achieve the optimum adsorbent dosage, the effects of varying the synthetic zeolite dosage on the NH_4^+ -ion removal efficiency were studied. In the experiments, 200mL of $50 \text{ mg}\cdot\text{L}^{-1}$ ammonium solution of were agitated with different amounts of adsorbent at 298 K. The zeolite dosage was varied from $0.5 \text{ g}\cdot\text{L}^{-1}$ to $15.0 \text{ g}\cdot\text{L}^{-1}$; the results are shown in Fig. 5. As seen from Fig. 5(a), the NH_4^+ -ion removal efficiency increased from 21.52% to 94.24% as the zeolite dosage increased from $0.5 \text{ g}\cdot\text{L}^{-1}$ to $15.0 \text{ g}\cdot\text{L}^{-1}$. A plateau occurred at $10.0 \text{ g}\cdot\text{L}^{-1}$ of adsorbent. This can be explained as follows. First the surface area and number of exchange sites increased as the adsorbent dosage increased, so the NH_4^+ -ion removal efficiency increased rapidly. With further increases in adsorbent dosage, higher solid/liquid ratios resulted in the formation of aggregates or precipitation of particles, resulting in a plateau at a concentration of $10.0 \text{ g}\cdot\text{L}^{-1}$ of adsorbent. From Fig. 5(b), it can also be seen that the ammonium-adsorption capacity decreased with increasing synthetic zeolite dosage. The decrease in the ammonium-adsorption capacity with increasing zeolite dosage may be the result of two factors [14]:

(1) A decrease in the ammonium concentration gradient per unit mass of adsorbent with increasing synthetic zeolite dosage;

(2) A decrease in the total surface area of the synthetic zeolite as a result of particle interactions such as aggregation.



(a)



(b)

FIGURE 5 - Effects of adsorbent dosage on ammonium adsorption on synthetic zeolite at 298K: (a) shows the effects of adsorbent dosage on ammonium adsorption on the zeolite, and (b) shows adsorption capacities at different adsorbent dosages

3.2.4 Effects of initial ammonium concentration

The effects of the initial ammonium concentration were studied using initial concentrations in the range $5\text{--}100 \text{ mg}\cdot\text{L}^{-1}$. The zeolite dosage was kept at 1.0 g and the temperature was kept at 298 K. The results, in Fig. 6, show that the initial ammonium concentration had an obvious effect on both the ammonium uptake and the ammonium-removal efficiency. The ammonium-adsorption capacity increased with increasing initial ammonium concentration, reaching a maximum value of $14.63 \text{ mg}\cdot\text{g}^{-1}$ when the initial ammonium concentration was $100 \text{ mg}\cdot\text{L}^{-1}$. 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. 6 also shows that there was an obvious decrease in the ammonium-removal efficiency when the ammonium concentration in solution increased; this 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 100 mg·L⁻¹, the ammonium-removal efficiency decreased from 98.63% to 73.14%.

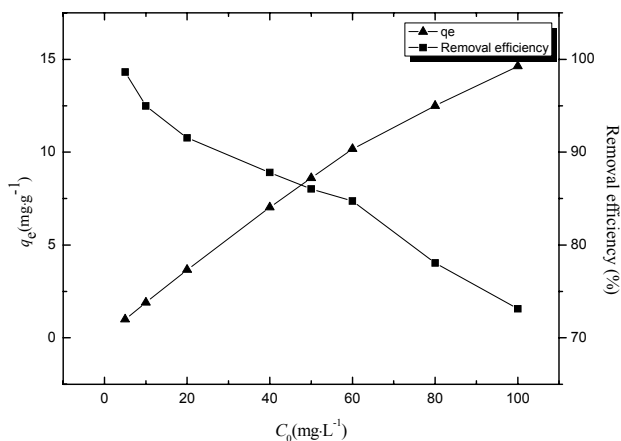


FIGURE 6 - Effects of ammonium initial concentration on adsorption on synthetic zeolite at 298 K

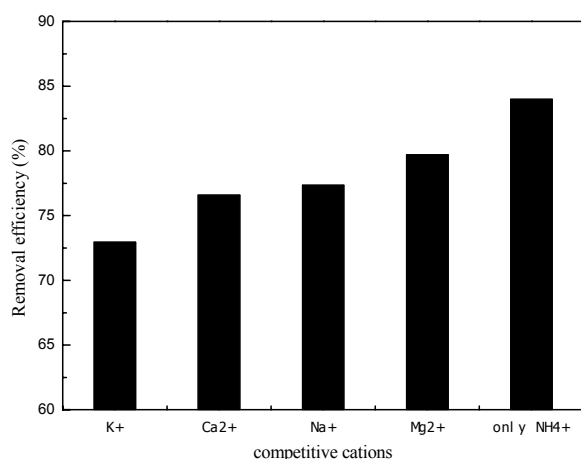


FIGURE 7 - Effects of competitive cations on adsorption on synthetic zeolite at 298 K

3.2.5 Effects of competitive cations

Actual wastewater such as municipal and industrial wastewaters is always contaminated with various additives such as inorganic salts, so it is necessary to investigate the influence of other cations on ammonium removal by the synthetic zeolite. The adsorption of ammonium at 298 K in the presence of various salts was therefore carried out at the same initial molar cation concentrations of sodium (Na⁺), potassium (K⁺), calcium (Ca²⁺), and magnesium (Mg²⁺), respectively. The amount of adsorbent is 1.0 g, and the constant initial ammonium concentration is 50 mg·L⁻¹. From the results shown in Fig. 7, it can be seen that the individual presence of other metal ions significantly reduced the ammonium-removal efficiency. The adsorption of ammonium on a zeolite is the result of ion-exchange between ammonium from the aqueous solu-

tion and cations from the zeolite. When Na⁺, K⁺, Ca²⁺, or Mg²⁺ were present in the solution, the ammonium-adsorption capacity decreased as a result of competition with other cations for adsorption sites on the zeolite. Given identical concentrations of metal cations, the reduction in ammonium-adsorption capacity followed the order K⁺ > Ca²⁺ > Na⁺ > Mg²⁺, indicating that the order of selectivity over ammonium of other cations on the synthetic zeolite was K⁺ > Ca²⁺ > Na⁺ > Mg²⁺. Similar results have previously been reported by Zhang et al. [14]. However, different results for the selectivity of natural and synthetic zeolites toward Na⁺, K⁺, Ca²⁺, and Mg²⁺ have been found in other studies [6,20,21]. This is because different zeolites have different chemical compositions and structures, and thus different cation selectivities [14].

3.3 Ammonium adsorption isotherms study

Adsorption isotherms are important for describing how ammonium interacts with the synthetic zeolite, and are useful in investigating the use of the zeolite as an adsorbent. The Freundlich and Langmuir models are usually used to describe the equilibrium data [22,23]. In this study, both the Freundlich and Langmuir models are used to describe the equilibrium isotherm data.

The linear form of the Langmuir model is expressed as:

$$\frac{C_e}{q_e} = \frac{1}{q_{\max} k} + \frac{1}{q_{\max}} C_e$$

where q_e (mg·g⁻¹) is the equilibrium amount of ammonium adsorbed (mg) per unit mass of adsorbent (g), C_e (mg·L⁻¹) is the concentration of ammonium in the equilibrium solution, and q_{\max} (mg·g⁻¹) and k (L·mg⁻¹) are the maximum adsorption capacity of the adsorbent and the adsorption energy coefficient, respectively.

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

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

where C_0 (mg·L⁻¹) is the initial concentration of ammonium and k is the Langmuir constant (L·mg⁻¹). 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, $R_L = 0$ [24].

The Langmuir plots for ammonium adsorption on the synthetic zeolite obtained from coal fly-ash are shown in Fig. 8. The parameters are given in Table 1. The experimental data fit the Langmuir model well, with a correlation coefficient of 0.9644. The maximum adsorption capacity and Langmuir constant (k) deduced from the Langmuir isotherm are 16.36 mg·g⁻¹ and 0.2164 L·mg⁻¹, respectively. So the parameter R_L lies between 0 and 1, which shows that the conditions for removal of ammonium are

favorable. In addition, the values of R_L prove that the synthetic zeolite obtained from coal fly-ash is a potential adsorbent for ammonium removal from aqueous solutions. Saltali et al. [25] and Sarioglu et al. [26] reported that the maximum amounts of ammonium exchanged using a natural Turkish zeolite were 9.64 mg g^{-1} at 21°C and 12.83 mg g^{-1} at 20°C . Zheng et al. [4] found that the maximum adsorption capacity of zeolite 13X was 8.61 mg g^{-1} at 298 K. Juan et al. [16] found that the maximum adsorption capacity of a zeolite synthesized from fly-ash using a hydrothermal method was 7.02 mg g^{-1} at 298 K. This kind of synthetic zeolite obtained from coal fly-ash showed relatively high ammonium adsorption compared to other zeolites.

The linear form of the Freundlich model is as follows:

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

where K_f is the Freundlich constant (mg g^{-1}), the measure of the adsorption capacity of the adsorbent, and $1/n$ is the heterogeneity factor, a constant related to adsorption intensity or surface heterogeneity. High values of K_f indicate high affinities for ammonium, and the value of the empirical parameter $1/n$ lies in the range $0.1 < 1/n < 1$, indicating favorable conditions for adsorption [27]. Freundlich constants were calculated from the slopes and intercepts in Fig. 8b, and are given in Table 1. The correlation coefficient of 0.9836 showed that the experimental data agree well with the Freundlich model. The value of $1/n$ is less than 1 (0.4814 at 298 K) and therefore represents favorable removal conditions. The K_f in the Freundlich model is 3.179, which indicates high affinities for ammonium. Sarioglu et al. [26] and Weatherley [28] determined K_f as 2.23 and 2.27 for the adsorption of ammonium.

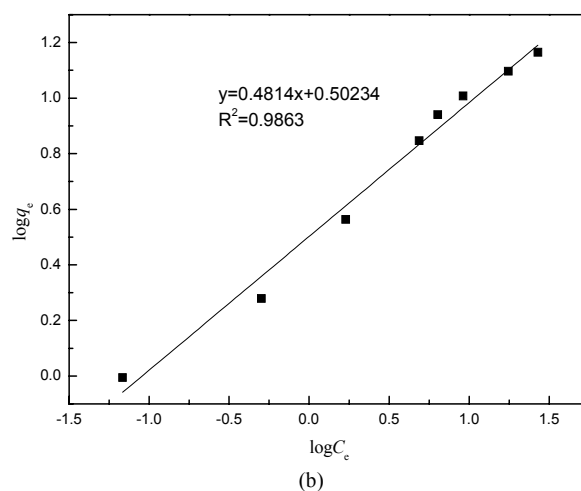
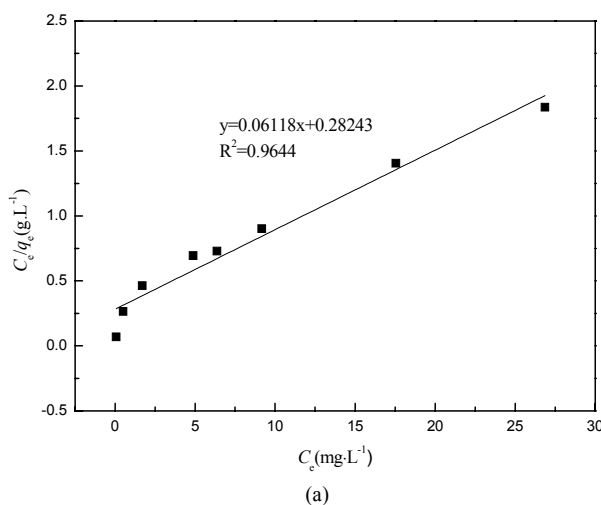


FIGURE 8 - Isotherm models at 298 K for ammonium adsorption on synthetic zeolite obtained from coal fly-ash: (a) Langmuir model and (b) Freundlich model

TABLE 1 - Isotherm constants for ammonium adsorption on synthetic zeolite at 298 K

Isotherm models	equation	Parameters	R^2
Langmuir	$C_e/q_e = 0.28234 + 0.061118 C_e$	$k (\text{L mg}^{-1}): 0.2164$ $q_{\max} (\text{mg g}^{-1}): 16.36$	0.9644
Freundlich	$\log q_e = 0.50234 + 0.4814 \log C_e$	$K_f (\text{mg g}^{-1}): 3.179$ $1/n: 0.4814$	0.9863

4. CONCLUSIONS

The novel zeolite adsorbent was characterized and its adsorption behavior with respect to removal of ammonium from aqueous solutions was investigated. SEM and XRD images showed that most of the synthetic zeolite obtained from coal fly-ash was crystalline, and zeolite Na-P₁ was the major component. Experimental parameters such as adsorbent dosage, pH, shaking time, initial ammonium concentration, and competitive cations influenced on NH_4^+ -ion removal from aqueous systems by the synthetic

zeolite. The zeolite exhibited a fast adsorption rate and high adsorption capacity for ammonium. A maximum adsorption capacity of 16.36 mg L^{-1} of ammonium was achieved. Langmuir and Freundlich models both fit well with the experimental data. This synthetic zeolite obtained from coal fly-ash has potential applications in the removal of ammonium pollutants from wastewaters. It can be used as a low-cost and relatively effective adsorbent for the removal of ammonium.

ACKNOWLEDGEMENTS

The authors are grateful to the National Natural Science Funds (51108436), the National Key Technology R&D Program (2012BAJ21B04), the China Postdoctoral Science Foundation (20110490468), the National Hi-Tech Project (2009ZX07106) and the R&D Special Fund for Public Welfare Industry (201109024) for support.

REFERENCES

- [1] Sprynskyy, M., Lebedynets, M., Zbytniewski, R., Namieśnik, J. and Buszewski, B. (2005) Ammonium removal from aqueous solution by natural zeolite, Transcarpathian mordenite, kinetics, equilibrium and column tests. *Separation and Purification Technology* 46 (3), 155 - 160.
- [2] Manipura, A., Barbosa, V.L. and Burgess, J.E. (2007) Comparison of biological ammonium removal from synthetic metal refinery wastewater using three different types of reactor. *Minerals Engineering* 20 (6), 617 - 620.
- [3] Vázquez, I., Rodríguez, J., Marañón, E., Castrillón, L. and Fernández, Y. (2006) Simultaneous removal of phenol, ammonium and thiocyanate from coke wastewater by aerobic biodegradation. *Journal of Hazardous Materials B* 137 (3), 1773 - 1780.
- [4] Zheng, H., Han, L.J., Ma, H.W., Zheng, Y., Zhang, H.M., Liu, D.H. and Liang, S.P. (2008) Adsorption characteristics of ammonium ion by zeolite 13X. *Journal of Hazardous Materials* 158 (2-3), 577 - 584.
- [5] Zaitsev, G., Mettänen, T. and Langwaldt, J. (2008) Removal of ammonium and nitrate from cold inorganic mine water by fixed-bed biofilm reactors. *Minerals Engineering* 21 (1), 10 - 15.
- [6] Lei, L.C., Li, X.J. and Zhang, X.W. (2008) Ammonium removal from aqueous solutions using microwave-treated natural Chinese zeolite. *Separation and Purification Technology* 58 (3), 359 - 366.
- [7] Leaković, S., Mijatović, I., Cerjan-stefanović, Š. and Hodšić, E. (2000) Nitrogen removal from fertilizer wastewater by ion exchange. *Water Research* 34 (1), 185 - 190.
- [8] Karadag, D., Koc, Y., Turan, M. and Armagan, B. (2006) Removal of ammonium ion from aqueous solution using natural Turkish clinoptilolite. *Journal of Hazardous Materials* 136 (3), 604 - 609.
- [9] Kuleyin, A. and Ergun, O.N. (2007) Studies on removal of ammonium ions from synthetic aqueous solutions and field leachate samples using clinoptilolite. *Fresenius Environmental Bulletin* 16 (2), 169 - 175.
- [10] Zhao, Y.F., Zhang, B., Zhang, X., Wang, J.H., Liu, J.D. and Chen, R.F. (2010) Preparation of highly ordered cubic NaA zeolite from halloysite mineral for adsorption of ammonium ions. *Journal of Hazardous Materials* 178 (1-3), 658 - 664.
- [11] Yusofa A.M., Keata L.K., Ibrahim Z., Majida Z.A. and Nizamb N.A. (2010) 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. *Journal of Hazardous Materials* 174 (1-3), 380 - 385.
- [12] Wang, Y., Liu, S., Xu, Z., Han, T., Chuan, S. and Zhu, T. (2006) Ammonia removal from leachate solution using natural Chinese clinoptilolite. *Journal of Hazardous Materials* 136 (3), 735 - 740.
- [13] Franus, W. and Wdowin, M. (2010) Removal of ammonium ions by selected natural and synthetic zeolites. *Mineral Resources Management* 26 (4), 133 - 148.
- [14] Zhang, M.L., Zhang, H.Y., Xu, D., Han, L., Niu, D.X., Tian, B.H., Zhang, J., Zhang, L.Y. and Wu, W.S. (2011) Removal of ammonium from aqueous solutions using zeolite synthesized from fly ash by a fusion method. *Desalination* 271 (1-3), 111 - 121.
- [15] Murayama N., Yoshida S., Takami Y., Yamamoto H. and Shibata J. (2003) Simultaneous removal of NH_4^+ and PO_4^{3-} in aqueous solution and its mechanism by using zeolite synthesized from coal fly ash. *Separation Science and Technology* 38 (1), 113 - 129.
- [16] Juan, R., Hernández, S., Andrés, J.M. and Ruiz, C. (2009) Ion exchange uptake of ammonium in wastewater from a sewage treatment plant by zeolitic materials from fly ash. *Journal of Hazardous Materials* 161 (2-3), 781 - 786.
- [17] Wu, D.Y., Zhang, B.H., Li, C.J. Zhang, Z.J. and Kong, H.N. (2006) Simultaneous removal of ammonium and phosphate by zeolite synthesized from fly ash as influenced by salt treatment. *Journal of Colloid and Interface Science* 304 (2), 300 - 306.
- [18] Marañón, E., Ulmanu, M., Fernández, Y., Anger, I. and Castrillón, L. (2006) Removal of ammonium from aqueous solutions with volcanic tuff. *Journal of Hazardous Materials* 137 (3), 1402 - 1409.
- [19] Dikon, J.B. and Weed, S.B. (1989) *Mineral soil Environment*, SSSA Pub. Inc., Madison, WI, 874 - 911.
- [20] Huang H.M., Xiao X.M., Yan B. and Yang L.P. (2010) Ammonium removal from aqueous solutions by using natural Chinese (Chende) zeolite as adsorbent. *Journal of Hazardous Materials* 175 (1-3), 247 - 252.
- [21] Wang Y., Lin F.A. and Pang W. (2007) Removal of ammonium ions from wastewater using modified zeolites. *Fresenius Environmental Bulletin* 16 (1), 24 - 28.
- [22] Langmuir I. (1918) The adsorption of gases on plane surfaces of glass, mica and platinum. *Journal of America Chemistry Society* 40, 1361 - 1367.
- [23] Freundlich H.M.F. (1906) Uber die adsorption in losungen. *Zeitschrift fur Physikalische Chemie (Leipzig)* 57 A, 385 - 470.
- [24] Gupta, V.K., Mittal, A., Malviya, A. and Mittal, J. (2009) Adsorption of carmoisine A from wastewater using waste materials-bottom ash and deoiled soya. *Journal of Colloid and Interface Science* 335 (1), 24 - 33.
- [25] Saltali, K., Sarl, A. and Aydlm, M. (2007) Removal of ammonium ion from aqueous solution by natural Turkish (Yildizeli) zeolite for environmental quality. *Journal of Hazardous Materials* 141 (1), 258 - 263.
- [26] Sarioglu, M. (2005) Removal of ammonium from municipal wastewater using natural Turkish (Dogantepe) zeolite. *Separation and Purification Technology* 41 (1), 1 - 11.
- [27] Raji, C. and Anirudhan, T.S. (1998) Batch Cr(VI) removal by polyacrylamide-grafted sawdust: kinetics and thermodynamics. *Water Research* 32 (12), 3372 - 3780.

- [28] Weatherley, L.R. and Miladinovic, N.D. (2004) Comparison of the ion exchange uptake of ammonium ion onto New Zealand clinoptilolite and mordenite. *Water Research* 38 (20), 4305 - 4312.

Received: September 16, 2011

Revised: October 12, 2011; February 08, 2012

Accepted: March 26, 2012

CORRESPONDING AUTHORS

Ying Zhao and Beidou Xi

State Key Laboratory of Environmental Criteria and Risk Assessment

Chinese Research Academy of Environmental Sciences

8 Dayangfang BeiYuan Road

Chao yang District

Beijing 100012

P.R. CHINA

Phone: +86-10-51095628

Fax: +86-10-51095628

E-mail: zhao_ying005@yahoo.com.cn,
xibeidou@yeah.net