



Ammonium removal from aqueous solution by zeolites synthesized from low-calcium and high-calcium fly ashes

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ARTICLE INFO

Article history:

Received 7 February 2011

Received in revised form 28 March 2011

Accepted 31 March 2011

Available online 20 April 2011

Keywords:

Low-calcium fly ash

High-calcium fly ash

Synthesized zeolite

Ammonium removal

Select criteria of raw fly ash

ABSTRACT

In this study, zeolites are synthesized from low-calcium (LC-Z) and high-calcium (HC-Z) fly ashes, respectively. The changes of mineralogy, morphology, cation exchange capacity (CEC) and specific surface area (SSA) are investigated during the synthesis process. The equilibrium uptake of ammonium on the two synthesized zeolites is compared. The main crystals of LC-Z and HC-Z are identified as faujasite and gismondine, respectively. The CEC and SSA increase significantly following the conversion process. The kinetic studies showed that the adsorption process of ammonium on both LC-Z and HC-Z follows Ho's pseudo-second-order model. Langmuir model agrees better with the equilibrium data for LC-Z, while Freundlich model gives the better fit for HC-Z. The obtained maximum ammonium uptake capacities are 23.8 mg/g for LC-Z and 3.17 mg/g for HC-Z in the synthetic solution. LC-Z also exhibits much better performance in ammonium uptake in effluent from a sewage treatment plant than HC-Z. These results indicate that LC-Z is a promising material for ammonium removal whereas HC-Z is not. The Ca^{2+} leaching and the lower zeolite content in HC-Z account for its lower uptake capacity. Thus, the low-calcium fly ash should be chosen preferentially as the raw material of the zeolite synthesis for ammonium removal.

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1. Introduction

The increasing accumulation of nitrogen and phosphorus can lead to eutrophication in lakes, ponds and reservoirs. Eutrophication in turn deteriorates greatly the quality and function of a water body [1,2]. The nitrogen and phosphorus removal from wastewater prior to discharge is thus obligatory in many countries nowadays. Nitrogen compounds in aqueous environments are usually found in the form of ammonium [3]. Among various methods available for ammonium removal, ion exchange is proved more useful and economical with the development of low-cost and high-efficient ion exchangers, such as zeolite [4,5].

Fly ash is a waste material generated from an electric power plant. The current annual production of fly ash is about 500 million tonnes, and the world average utilization only amounts to 16% of the total ash. A substantial amount of fly ash is still disposed of in landfills and/or lagoons at a significant cost to the utilizing companies and thus to the consumers [6]. As a resource utilization approach, extensive research has been carried out to synthesize zeolite using fly ash [7]. The

synthesized zeolites are also used to remove the ammonium from wastewater, and the results showed that they are promising ion exchangers for ammonium removal [8,9].

Fly ashes are a complex inorganic and organic mixture, and their chemical properties are influenced to a great extent by the properties of the coal being burned and the techniques used for handling and storage [6]. Various approaches and characteristics have been used to specify fly ashes for their applications. For example, American Association for Testing Materials (ASTM C618) defines two classes of fly ash, Class F fly ash ($\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3 > 70\%$) and Class C fly ash ($50\% < \text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3 < 70\%$) [10]. Fly ash used for cement and concrete in China (GB/T 1596–2005) classifies fly ashes into three groups: low-calcium fly ash ($\text{CaO} < 5\%$), intermediate-calcium fly ash ($\text{CaO} \approx 15\%$), and high-calcium fly ash ($\text{CaO} > 15\%$). The previous studies also showed that the composition of used fly ash is a determining parameter in the property of the synthesized zeolites [7]. However, the effect of the chemical property of fly ashes on the ammonium removal performance of the synthesized zeolites has received little attention. To obtain the synthesized zeolite with high ammonium uptake capacity, how to select fly ash based on the widely known criterion is still poorly understood.

The present study synthesizes zeolites from two fly ashes with different mineralogical and chemical compositions using alkaline fusion

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followed by hydrothermal method, and investigates the effectiveness of the two synthesized zeolites in removing ammonium from aqueous solution. The mineralogy, morphology, special surface area (SSA) and cation exchange capacity (CEC) of fly ashes and their derived zeolites are analyzed. The adsorption kinetics and equilibrium of ammonium on the two synthesized zeolites are determined, and their performance in ammonium uptake in effluent from a sewage treatment plant is studied. The reason for the difference of the ammonium removal by the two synthesized zeolites is also investigated.

2. Materials and methods

2.1. Zeolite synthesis and characterization

Fly ashes used in this study were obtained from a power plant located in Yunnan Province, China. A fusion method described previously [8] was adopted for the synthesis of zeolite. The two synthesized zeolites were dried at 100 °C for 12 h and then sieved through a 100 mesh (<150 μm) for further work. The XRD, SEM, SSA and CEC of the fly ashes and synthesized zeolites were analyzed using the same methods and equipments described in a previous paper [8]. The chemical compositions of the fly ashes and synthesized zeolites were measured using X-ray fluorescence spectrometer (Philips PW2404, Philips Co. Holland), and the results are listed in Table 1.

2.2. Batch experiments

The effect of contact time on ammonium removal by the two synthesized zeolites was investigated under different contact times ranging from 0 to 360 min. 0.1 g of the zeolite sample was loaded in a 100 mL conical flask. Then 50 mL of the ammonium solution (100 mg NH₄⁺-N/L) prepared from anhydrous NH₄Cl (analytical grade) was added into the flask. The flask was capped and placed in a thermostatic shaker at 25 °C and 180 rpm. The kinetics of ammonium uptake was determined by analyzing the adsorptive uptake of ammonium from aqueous solutions on the synthesized zeolites at different time intervals.

The adsorption isotherm tests were conducted to investigate the ammonium adsorption capacities of the two synthesized zeolites. 25 mL of solutions in the range of 10–300 mg NH₄⁺-N/L was agitated with 0.1 g of the zeolite sample. The pH of the solution was adjusted to 8.0 (optimal pH for the ammonium removal by the synthesized zeolites according to the pre-experiments) by adding 1 mol/L of HCl or NaOH. The pH of the solution was monitored by a pH meter (DELTA 320). The solutions were shaken in the thermostatic shaker at 25 °C and 180 rpm for 1.25 h (sufficient time to reach equilibrium according to the above experiments).

Table 1
Chemical compositions of fly ashes and synthesized zeolites (wt.%).

Component	Content (%)			
	Low-calcium fly ash (LC-F)	High-calcium fly ash (HC-F)	Zeolite synthesized from LC-F (LC-Z)	Zeolite synthesized from HC-F (HC-Z)
SiO ₂	75.69	30.76	50.76	23.75
Al ₂ O ₃	6.43	14.31	15.18	9.06
Fe ₂ O ₃	5.45	10.27	5.41	9.37
MgO	0.12	3.03	0.072	2.62
CaO	3.31	37.55	2.09	32.51
Na ₂ O	0.51	0.15	16.24	1.02
K ₂ O	0.07	1.27	0.016	0.037
MnO	0.41	0.042	0.38	0.033
TiO ₂	1.36	0.76	0.91	0.64
P ₂ O ₅	0.44	0.27	0.10	0.14
FeO	1.3	2.15	0.25	0.45

To evaluate their ammonium removal capacity in real wastewater, 0.05–0.5 g of the zeolite sample was added into 25 mL of the effluent from Tengzhou Sewage Treatment Plant in Shandong Province, China in 100 mL stoppered conical flask. The mixture was then agitated in the thermostatic shaker at 25 °C and 180 rpm for 1.25 h. During this process, the pH of the solutions was kept at 8.0 by adding 1 mol/L of HCl or NaOH.

To reflect the effect of co-existing cations in real wastewater on the ammonium removal capacities of the synthesized zeolites, the ammonium concentrations in the real wastewater from Tengzhou Sewage Treatment Plant and distilled water were adjusted to 100 mg/L using anhydrous NH₄Cl (analytical grade), respectively. The two obtained solutions (25 mL) were mixed with LC-Z and LC-Z at adsorbent dosage of 2–20 g/L, respectively. The mixtures were then shaken in the thermostatic shaker at 25 °C and 180 rpm for 1.25 h, and the pH of the solutions was kept at 8.0.

To investigate whether there was Ca²⁺-ion leaching from Ca-component in HC-Z or not, 0.1 g of HC-Z was added into 25 mL of distilled water in 100 mL stoppered conical flasks. The mixture was then stirred in the thermostatic shaker at 25 °C and 180 rpm for 1.25 h with equilibrium pH of 8.0.

To improve its ammonium uptake capacity, HC-Z was washed with distilled water and NaCl solution, respectively. About 0.5 g of HC-Z was added into 100 mL of distilled water and 100 mL NaCl solution (1 mol/L) in 250 mL stoppered conical flasks, respectively. The pH of the solutions was adjusted to 8.0. After they were stirred in the thermostatic shaker at 25 °C and 180 rpm for 1.25 h, the mixtures were then centrifuged. The obtained solid residues were dried at 100 °C for 12 h, and then sieved through a 100 mesh (<150 μm) for further work. To examine their ammonium removal capacity of the two materials obtained, 0.1 g of the zeolite sample was added into 25 mL of ammonium solution (50 mg NH₄⁺-N/L) in a 100 mL stoppered conical flask. The solution was stirred in the thermostatic shaker at 25 °C and 180 rpm for 1.25 h. During the period, the pH of the solutions was maintained at a defined value (8.0).

After shaking, the suspensions of the abovementioned batch experiments were filtered using 0.45 μm cellulose acetate membrane. The concentrations of the ammonium in the resulting supernatants were determined using the Nesslerization method with a unico spectrophotometer (US-2102 PCS). The concentrations of other metal cations (Na⁺, K⁺, Ca²⁺, and Mg²⁺) in the supernatants were measured using inductively coupled plasma optical emission spectrometer (ICP-OES, Optima 2000, PerkinElmer Co. USA). The amounts of ammonium exchanged by the synthesized zeolites (q_e (mg/g)) and the ammonium removal percentage were calculated by Eqs. (1) and (2).

$$\text{Amounts of ammonium exchanged} = \frac{C_o - C_e}{W} \times V \quad (1)$$

$$\text{Ammonium removal percentage(\%)} = \frac{C_o - C_e}{C_o} \times 100 \quad (2)$$

where C_o and C_e are the initial and equilibrium ammonium concentrations of the test solution (mg/L), respectively, V is the test solution volume (L), and W is the amount of adsorbent (g).

All the above experiments were duplicated and the average values were used for analysis.

3. Results and discussion

3.1. Fly ashes

As it is shown in Table 1, LC-F was characterized by a low CaO content (3.31%), while HC-F was much higher in abundance in Ca (37.55%). On the other hand, the content of SiO₂ and Al₂O₃ in LC-F was 82.12%, which was higher than that of HC-F (45.07%). The content of

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