Pure zeolite X synthesized from coal fly ash by pretreatment with solid alkali and using seed crystal

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Abstract. Coal fly ash was the main burning by-products in a coal-fired power station, which is a major global environmental problem and is threat to public health and environmental pollution. In this study, the optimum condition of synthesized zeolite from fly ash were investigated. The results showed that the optimum conditions were that the OH- concentration, the Si/Al ratio, the solid liquid ratio and aging time were 0.75 mol/L, 2.8, 9 ml/g and 0.5 h, respectively, for the synthesis of zeolites X. It is suggested that this method for synthesized zeolite X from coal fly ash is an efficient technology.

1. Introduction

Coal fly ash is generated from coal-fired power station as a waste product. It not only occupies a lot of territory but also pollutes water, air and soil, threatening environmental safety and human health [1]. How to reuse of fly ash is a hot topic. Comprehensive utilization of fly ash consists of the production of cement, ceramics, glass, concrete, soil conditioner, backfill materials, synthesized zeolite and mesoporous materials [2-3]. Synthesized zeolite is not only able to reuse of fly ash, but can also be used to remove water contaminants [4]. The zeolite X has the characteristics of microporous structure, high thermal stability and high cation exchange capacity and has good application prospect in environmental engineering [5]. Ammonia nitrogen (NH\(_4^+\)) is one of the main pollutants in urban sewage [6]. Using zeolite to treat ammonia nitrogen in sewage has advantages of simple process and high treatment efficiency [7]. This study focuses on synthesize zeolite X from coal fly ash by pretreatment with solid alkali with hydrothermal synthesis method. The optimum conditions of synthesized zeolite was studied by ammonium removal efficiency.

2. Materials and methods

2.1. Materials

Coal fly ash used in this study was collected directly from Hexi power plant, Inner Mongolia, China. The chemical analysis of raw coal fly ash is given in Table 1, where it can be seen that coal fly ash is primarily composed of Ca, Si, Fe, Ti and Al oxides.
Table 1. The composition of coal fly ash (wt. %).

|       | SiO$_2$ | Al$_2$O$_3$ | Fe$_2$O$_3$ | MgO | CaO | Na$_2$O | K$_2$O | MnO | TiO$_2$ | P$_2$O$_5$ | LOI |
|-------|---------|-------------|-------------|-----|-----|---------|-------|-----|---------|-----------|-----|
| Hexi fly ash | 57.45   | 20.56       | 7.51        | 1.14| 8.57| 1.21    | 2.05  | 0.1 | 0.88    | 0.092     | 0.438 |

All of the inorganic chemicals used in this study, i.e., Sodium metasilicate nonahydrate (Na$_2$SiO$_3$·9H$_2$O), ammonium chloride (NH$_4$Cl), sodium chloride (NaCl), sodium hydroxide (NaOH), and hydrochloric acid (HCl), were analytical grade reagents from the China National Pharmaceutical Group Chemical Reagent Co., Ltd.

2.2. Zeolite Preparation
Coal fly ash was initially mixed with a NaOH solid powder and grind by a planetary ball mill. The weight ratio of fly ash to NaOH powder was 0.6:1. After grinding, the powders were poured into the muffle furnace and heated at 660°C for 2h. Then a certain concentration of NaOH solution was added to the pretreated fly ash. A small amount of Na$_2$SiO$_3$·9H$_2$O and 13X zeolite zeolite were introduced into the reactor and mixed for 30 min. After this, the reactor was heated to 90°C and crystallized for 10 h. After cooling, distilled water was used to wash the samples until the pH value of the samples was about 9. Samples were dried at 100°C for 12 h.

2.3. NH$_4^+$ Adsorption experiments
Batch test for NH$_4^+$ adsorption were carried out. For each trial, 200ml NH$_4^+$ solution (50 mg/L) and 1.0 g zeolite were added into 250 ml conical flask. All the conical flasks were mixed at 200 rpm using an orbital agitator at room temperature (20 ± 3°C) for 60 min. After letting rest for about 30 minutes, the supernatant was sampled and filtered by 0.45 μm membrane for determination of NH$_4^+$. The applied solid/liquid ratio was 10 g/L. The adsorption capacity of the adsorbent per mass unit (qe) was calculated by Eq. (1).

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\text{Removal efficiency (\%) = } \left( \frac{C_0 - C_e}{C_0} \right) \times 100
\]

(1)

Where $C_0$ and $C_e$ (mg/L) are the initial and equilibrium concentrations, respectively. 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. Effect of OH$^-$ concentration
Figure 1(a) shows the effect of synthetic zeolite using Coal fly ash from different OH$^-$ concentration on the removal of ammonium. It was observed that the removal efficiency of ammonium increased as OH$^-$ concentration increased up to 0.75 mol/L, reached 53.45%, followed by a gradual decreased as the OH$^-$ concentration increased. This phenomenon could be explained by the XRD data (Figure 2), because there was the maximum amount of zeolite X synthesized when the OH$^-$ concentration was 0.75 mol/L. So, the optimization OH$^-$ concentration was 0.75 mol/L.
Figure 1. Effects of alkali concentration, Si/Al ratio, solid liquid ratio, aging time and crystallization time on ammonium removal efficiency of the synthesis zeolites from coal fly ash.

Figure 2. The effect of alkali concentrations on preparation of X zeolite obtained from coal fly ash.
3.2. Effect of Si/Al ratio
The removal effect of ammonium by zeolite synthesized from fly ash with different Si/Al ratio is shown in Figure 1(b). As seen from Figure 1(b), the removal efficiency of ammonium decreased with the Si/Al ratio increased. This could be explained by zeolite X was synthesized from coal fly ash with Si/Al ratio decreased. So, the optimum Si/Al ratio for removal ammonium was 2.8.

3.3. Effect of liquid-to-solid ratio
The liquid-to-solid ratio indicates the proportion of fly ash to solution volume. The results of synthesized zeolite X using coal fly ash from different liquid-to-solid ratio on the removal of ammonium as shown in Figure 1(c), indicate that the removal efficiency of ammonium increased as liquid/solid ratio increased up to 9 ml/g, reached 70.24%. When liquid-to-solid ratio was continuing to rise, the removal efficiency of ammonium decreased. So, the optimization liquid-to-solid ratio for synthetic zeolite from coal fly ash was 9 ml/g.

3.4. Effect of aging time
The effect of on the ammonium removal by zeolite synthesized from fly ash with different aging time of fly ash is shown in Figure 1(d). As seen from Figure 1(d), with the increased of the aging time, the trend of the removal efficiency of ammonium did not change significantly. The removal efficiency of ammonium was from 67.70% to 70.24%.

Figure 3. SEM images of coal (a) fly ash and (b) synthesized zeolite product.

SEM images of coal fly ash and the synthetic zeolite obtained from coal fly ash is shown in Figure 3. Figure 3 (a) show that there was no zeolite crystal clearly, but it had lots of armorphous phase. For the synthetic sample, zeolite crystal was present as shown in Figure 3 (b). Under different synthesis condition, it was clear to see the similar change, although the crystallization degree was different.

4. Conclusions
Zeolite X was synthesized from coal fly ash by the hydrothermal treatment with adding the two steps: pretreatment with solid alkali and introduction seed crystal. The optimization conditions of synthesized zeolite is that the OH\(^-\) concentration, the Si/Al ratio, the solid liquid ratio, aging time is 0.75 mol/L, 2.8, 9 ml/g and 0.5 h, respectively. The ammonium removal efficiency by the synthesized products ranged from 11.56% to 70.24%.

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