Green synthesis of fly ash-based zeolite Y by mixed alkali fusion method

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A solvent-free process was used to synthesize high-purity zeolite Y from fly ash. Different from the traditional two-step method, fly ash was activated efficiently by mixed alkali of NaOH and Na₂CO₃ at 750 °C for 2 h. For prepared zeolite Y, the composition, phase structure, morphology, specific surface areas and ammonium adsorption were evaluated comprehensively. The results show that a single phase zeolite Y with octahedral structure and an average diameter of 2.5 µm is obtained. The Brunauer–Emmett–Teller surface area is as high as 503.34 m²/g. Ammonium adsorption isotherm model on obtained zeolite Y was more consistent with the Langmuir model ($R^2 > 0.99$). And the maximum adsorption capacity is 18.6 mg/g. It can be concluded that the study provides an economic process to utilize fly ash for the synthesis of zeolite Y, which is an excellent adsorbent to remove ammonium. In addition, this study provides an eco-friendly approach to synthesize low-cost zeolite Y from solid waste, which is of excellent adsorption for ammonium removal.

1 | INTRODUCTION

The development of green synthetic method is a hot research topic in recent years [1]. Zeolites are a kind of inorganic material with excellent adsorption properties which was used for separation [2]. However, in traditional synthesis process, plenty of water is needed, meanwhile, a great deal of alkaline wastewater was generated, causing environmental pollution and resources waste. Hence, green synthesis of zeolites is of great significance [3], and a lot of studies have already been carried out.

In 1990s, Xu et al. put forward the vapour phase method [4]. Firstly, aluminium oxide gel is prepared and then it is dried or evaporated into dry powder. Then, transfers the powder into a container filled with vapour and crystallizes for a certain period, then zeolite is obtained. This method improves the quality of zeolite greatly, but the operation is complicated and special preparation instruments are needed. Xiao et al. proposed a solvent-free route for green synthesis of zeolites [5, 6]. In this process, all the reactants are solid, and directly put into the reactor for crystallization after mixing evenly. Compared with the traditional synthesis methods, solvent-free synthesis zeolites has significant advantages, such as high yield, environmental friendly, reduced energy consumption, simple and easy operation. Up to now, MFI, ZSM-39, SOD, MOR, Beta and FAU were successfully synthesized by solvent-free method [7, 8].

To achieve green production and improve the economic benefit, industrial waste has been used to synthesize zeolites. Among them, fly ash is a suitable material for zeolite synthesis because of its high silicon and aluminium content. Thus, preparing zeolite by solvent-free method using fly ash is a promising green technology. Liu et al. has successfully synthesized zeolite P1 from fly ash under solvent-free conditions which is of great ammonium adsorption capacity [9]. Yang et al. adopted a green method to prepare high-purity zeolite 4A using fly ash, before crystallization, mixture alkali (NaOH and Na₂CO₃) was used to activate fly ash by calcination [10]. However, synthesis of zeolite Y by similar method has not been conducted.

The objective of this work is to synthesize low-cost zeolite Y with high adsorption capacity from fly ash using a solvent-free method. For the prepared zeolite Y, physical and chemical properties were fully characterized. Then, adsorption property...
of ammonium on obtained zeolite Y was discussed. The work supplied a green and efficient method to prepare an excellent adsorbent for ammonium removal. What is more, changing waste into valuables is of great significance in both economic and social benefits [11].

2 | EXPERIMENTAL SECTION

2.1 | Materials

The fly ash (FA) used in the experiment comes from Shaanxi, China. The main compositions of fly ash are shown in Table 1. The Si/Al of used fly ash is 1.47, to prepare zeolite Y, extra silicon source is needed. Besides, loss on ignition (LOI) is as high as 13.72%, which means the content of unburned carbon is too high, and a calcination process prior to synthesis is necessary. The phase and morphology results are shown in Figure 1. The crystalline minerals are mainly anatase, mullite and quartz. SEM images show that the sample is irregular particles with porous structure instead of regular spherical particles.

2.2 | Synthesis of zeolite Y

It is known that alkalinity and Na\(^+\) has a great importance on the nucleation and crystallization of the zeolite synthesis process. Therefore, mixed alkali was used to synthesize zeolite Y and the synthesis process was as follows [10]. Firstly, 10 g fly ash, 12.6 g NaOH and 4.5 g Na\(_2\)CO\(_3\) were mixed evenly. Secondly, the mixture was calcined at 750 °C for 2 h. After natural cooling, the pretreatment product was mixed with a certain amount of Na\(_2\)SiO\(_3\)·9H\(_2\)O and grinded for 10 min. Then transferring the mixture into autoclave and heating in an oven at 120 °C for 24 h. After washing and drying at 80 °C, zeolite Y product was obtained which was named synthesized zeolite Y (SZY). The detailed flow chart is shown in Figure 2.

2.3 | Characterization of samples

Composition of raw ore and zeolite Y were analysed by AXIOS\(^\text{Max}\) (PANalytical, Holland) X-ray fluorescence spectrometer. The phase structure of the samples were analysed by D8-FOCUS (Bruker, Germany) X-ray diffractometer (XRD). Textural characteristics of the samples were performed using a SU8010 (HITACHI, Japan) scanning electron microscope (SEM). The Brunauer–Emmett–Teller (BET) surface area, pore

| TABLE 1 | Main compositions of fly ash (mass fraction, %) |
|---|---|---|---|---|---|
| Composition | SiO\(_2\) | Al\(_2\)O\(_3\) | TFe | CaO | MgO |
| wt% | 50.85 | 29.35 | 1.71 | 0.22 | 0.10 |
| Composition | Na\(_2\)O | K\(_2\)O | MnO | TiO\(_2\) | LOI |
| wt% | 0.07 | 0.11 | 0.02 | 2.32 | 13.72 |

FIGURE 1 | The XRD patterns of fly ash; and insert (a,b) are SEM images
volume and pore size distribution were performed by N\textsubscript{2} adsorption at 77 K with an ASAP2020 (TSI, US) automatic volumetric sorption analyzer. The concentration of ammonium is measured by UV–vis spectrophotometer (UV-1800 PC, Shanghai Mapada Instrument Co., Ltd).

### RESULTS AND DISCUSSION

The mineral compositions and morphology are shown in Figure 3. Obviously, zeolite Y (JCPDS card No. 43–0168) with high crystallinity is prepared. And the morphology of zeolite Y is of regular octahedron and uniform particle size (about 2.5 μm). The chemical composition result of SZY is shown in Table 2, and the Si/Al ratio of SZY was 2.12, which is consistent with the XRD result (Figure 3(a)).

The pore structure of SZY was evaluated by nitrogen adsorption–desorption measurement, and the results is shown in Figure 4. According to the IUPAC classification, the sample isotherm is of classical type IV with H3 hysteresis loop, at higher relative pressures, between the adsorption and the desorption curves, indicating the presence of micropores in the sample [12]. The BET surface area is 503.34 m\textsuperscript{2}/g, and the specific surface area of the micropores fitted by t-plot method was 475.31 m\textsuperscript{2}/g, both are higher than some other works [13,14].

The ammonium adsorption behaviour on SZY was comprehensively studied. Generally, the pH of solution plays an outstanding role in adsorption process, because the H\textsuperscript{+} in solution not only determines the surface charge of the adsorbent, but also results in competitive adsorption with other cations among adsorption sites [15–17]. So pH is an essential factor for the study of NH\textsubscript{4}\textsuperscript{+} adsorption, and the related result is demonstrated in Figure 5. When pH is 2, the adsorption is rather low. Because the excess H\textsuperscript{+} ions in the system strongly competed with the NH\textsubscript{4}\textsuperscript{+} ions for the active adsorption sites, and repulsion occurs between the positively charged surface of SZY and the NH\textsubscript{4}\textsuperscript{+} simultaneously [18,19]. With pH rising, competitive adsorption behaviour weakens, adsorption capacity of NH\textsubscript{4}\textsuperscript{+} increases significantly. However, when the pH is higher than 6, the NH\textsubscript{4}\textsuperscript{+} will convert into NH\textsubscript{3}, which cannot be adsorbed by ion exchange. Therefore, 6 is the optimal pH for NH\textsubscript{4}\textsuperscript{+} adsorption, and the adsorption capacity is 19.5 mg/g.

Influence of initial concentration and temperature on ammonium adsorption is shown in Figure 6. With the increase of initial NH\textsubscript{4}\textsuperscript{+} concentration, adsorption capacity first increased and then reached a plateau which represents the maximum sorption capacity of the adsorbent [20]. At low initial concentration (less than 75 mg/L), the adsorption is positively correlated to the NH\textsubscript{4}\textsuperscript{+} concentration. This is because the higher concentration gradient provides more powerful driving force to replace cations in the media framework. Further increasing NH\textsubscript{4}\textsuperscript{+} concentration, all the adsorption sites are occupied by NH\textsubscript{4}\textsuperscript{+}, hence the adsorption increases more and more slowly. When NH\textsubscript{4}\textsuperscript{+} concentration reaches more than 150 mg/L, the adsorption capacity reaches the maximum, and the adsorption values are 18.6, 18.1, and 16.8 mg/g at 25, 35 and 45 °C, respectively.

Langmuir isotherm and Freundlich isotherm are two common models for the study of adsorption mechanism [21, 22]. In this work, the fitting curves and the related isotherm parameters are shown in Figure 7 and Table 3, respectively. The Langmuir isotherm model is a most famous model describing...
adsorption with monolayer coverage [23]. In Figure 7(a), it was observed that the regularity of adsorption fits Langmuir isothermal adsorption model ($R^2 > 0.99$) rather than Freundlich model ($R^2 < 0.97$) at three temperatures. In addition, the $q_{\text{max}}$ (21.60, 21.05 and 19.72 mg/g at 25, 35 and 45°C) calculated by Langmuir equation are much closer to the experimental values. Besides, as $0 < K_L < 1$, the $K_L$ value approaches zero with the increase of $C_0$ which indicates that high concentration is unfavourable to the adsorption of NH$_4^+$ on zeolite Y [24, 25]. The straight line in Figure 7(a) indicated NH$_4^+$ adsorption
on SZY is predominantly governed by a monolayer adsorption process. This also implies that the synthesized products are of homogeneous particle size and surface [26–28]. For Freundlich model, to achieve better linearity, the initial concentration is controlled within 200 mg/L. In this case, the values of $N$ were found to be more than 1, indicating a favourable adsorption process at three temperatures [29, 30].

Overall, the results show that the fabricated zeolite Y is a rather promising eco-friendly material in NH$_4^+$ capturing from wastewater.

4 | CONCLUSIONS

A special solvent-free method was used to synthesize fly ash-based zeolite Y. Prior to crystallization reaction, a mixed alkali fusion process is adopted to convert the anatase, mullite, and quartz into glassy phase. In addition, combined use of NaOH and Na$_2$CO$_3$ is favourable for nucleation process. The composition and phase structure analysis show that zeolite Y (JCPDS card No. 43–0168) is obtained and the Si/Al is 2.12. The morphology analysis shows that the SZY is of octahedral structure and the average particle size is about 2.5 µm. The specific surface area is 503.34 m$^2$/g which is higher than some other works, indicating excellent adsorption performance.

Further experiments prove that ammonium adsorption on SZY was suitable for Langmuir isotherm model ($R^2 > 0.99$). And the maximum adsorption capacity is 18.6 mg/g. The study provides a green and potential approach to synthesize other zeolite products. What is more, some other solid wastes such as silicon slag and Kaolin tailings can also be converted into a useful one in a similar way.

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