Controlled Synthesis of Fly Ash-Based Zeolite X/A for Ammonia- Nitrogen Removal

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Research Article

Keywords: fly ash, zeolite, ammonia nitrogen adsorption, wastewater treatment

Posted Date: April 22nd, 2024

DOI: https://doi.org/10.21203/rs.3.rs-4113345/v1

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Abstract

Fly ash is a kind of industrial solid waste, which mainly comes from thermal power plants using coal as power fuel. The lack of effective disposal and utilization of fly ash has led to its not only destroying and polluting the ecological environment but also seriously endangering human health. In addition, the treatment of ammonia nitrogen wastewater is an important issue in environmental pollution control, so the study of efficient and low-cost separation materials has become a challenging topic. This study utilizes the hydrothermal method to convert fly ash into fly ash-based zeolite, which is capable of treating ammonia nitrogen wastewater. The successful synthesis of Zeolite X, zeolite A and zeolite A-X are confirmed through various characterisation techniques, including XRD, TG-DSC, TEM, BET, and FT-IR. Simultaneously, the synthesized zeolite is tested for its capacity to adsorb and regenerate ammonia nitrogen wastewater. The pure zeolite with the largest adsorption capacity, simpler preparation process, good stability, and high regeneration capacity is selected.

Introduction

With the continuous expansion of industrial fields, ammonia nitrogen wastewater is continuously discharged, which makes the ecological environment seriously damaged [1, 2]. In recent years, many technological advances have been made in the treatment of ammonia nitrogen wastewater. The current means of treating ammonia wastewater mainly include chemical, biological, and physical methods [3, 4], which generally have the disadvantages of long treatment cycle, poor separation efficiency, and poor recycling performance [5–8]. In contrast, the adsorption method based on porous materials has become a current research hotspot due to its good adsorption efficiency. Therefore, the use of efficient and feasible adsorption materials to realize the treatment of ammonia nitrogen wastewater is an important aspect to protect the environment and achieve sustainable development [9, 10]. Most of the ammonia nitrogen adsorbent materials have the following advantages, such as a wide source of raw materials, lower price, safe to use, can absorb ammonia nitrogen quickly, avoid the waste of resources, and will not cause secondary pollution to the environment [11–16]. Therefore, ammonia nitrogen adsorbent materials have become the hotspot and focus of research on the treatment of ammonia nitrogen wastewater, which has received increasing attention. Many adsorbent materials such as activated carbon materials and zeolite materials have been used in the research of ammonia nitrogen treatment and water purification, showing attractive application prospects [17–19]. Meanwhile, to achieve efficient and rapid adsorption of ammonia nitrogen, the adsorbent materials for ammonia nitrogen wastewater should have some important performance: (1) a uniform pore structure; (2) a large specific surface area and a large specific pore volume; (3) good hydrothermal stability; (4) a high rate and multiplicity of adsorption of ammonia nitrogen; and (5) some regeneration capacity.

Zeolite is a typical porous adsorbent material [20–22], which have uniform pore structure, large specific surface area and specific pore volume, and good hydrothermal stability. In addition, with the development of power industry, especially the development of coal-burning power plants, the emission of fly ash increases year by year. Therefore, the treatment and utilization of fly ash is also one of the hotspots of widespread concern. Fly ash contains a variety of elements such as silicon and aluminum required for the synthesis of zeolite, if the use of fly ash to prepare zeolite, not only can save chemical raw materials, there are
advantages such as low preparation costs. In summary, the preparation of zeolite adsorbent materials using fly ash, so that it can be applied to reduce the ammonia nitrogen content of wastewater, is a highly efficient, inexpensive and environmentally friendly method, but also for the treatment of fly ash provides a new way of thinking, so that it achieves the purpose of "waste for waste, green chemistry" [23].

In this paper, we have successfully synthesized zeolite X/A and series of zeolite A-X by hydrothermal method using fly ash as raw material, which has been pre-treated with impurity removal through grinding, acid treatment, and calcination pathways, and screened out the optimal preparation process by combining with a series of characterizations to obtain the purified zeolite X with higher adsorption efficiencies. Finally, the adsorption and regeneration capacities of zeolite X are tested on ammonia nitrogen wastewater. The results further confirms that the purified zeolite have a large adsorption capacity, high removal rate, and good regeneration capacity.

**Experimental section**

**1.1 Reagents**

Fly Ash; NaAlO₂ (chemically pure, Sinopharm Chemical Reagent Co., Ltd.); NaOH, Na₂SiO₃·9H₂O, KCl, NH₄Cl (analytically pure, Sinopharm Chemical Reagent Co., Ltd.); MgCl₂ (analytically pure, Fuchsun (Tianjin) Chemical Reagent Co., Ltd.); CaCl₂ (analytically pure, Jiangsu Qiangsheng Functional Co., Ltd.); NaCl (analytically pure, Sahn Chemical Technology (Shanghai) Co., Ltd.); HCl (analytically pure, Fujian Xusheng Chemical Co., Ltd.).

**1.2 Instrument**

X-ray Diffractometer XD-3 (Beijing Pulse Analytical General Instrument Co., Ltd.); Scanning Electron Microscope SU-4800 (Hitachi, Japan); FTIR spectrometer SF-61/FTIR (TgK Scientific, UK); Thermogravimetric Analyzer SC-TGA1150 (Fujian Sanchuang Keji Company); High Performance Multi-Pass Automatic Specific Area and Pore Analyzer (N₂ Adsorption) TriStar ® 3020 Series (Mack, Inc., USA); Muffle Furnace KSL-1200X (Hefei Kejing Material Technology Co., Ltd.); Vacuum drying oven DZF type (Shanghai Jinghong Experimental Equipment Co., Ltd.); XOM-0.4L Frequency Conversion Planetary Ball Mill(Nanjing Keranalytical Experimental Instrument Research Institute); pH meter ST3100 (OHAUS USA, Inc.).

**1.3 Preparation of zeolites**

**1.3.1 Pre-treatment of fly ash**

Fly ash directly excluded from coal-fired power plants has large particles, uneven particle size distribution and complex composition (Table 1). Therefore, we need to pre-treat the raw material of fly ash accordingly to enhance the surface activity for subsequent research.
Table 1
Chemical composition of fly ash

<table>
<thead>
<tr>
<th>Composition</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>CaO</th>
<th>TiO₂</th>
<th>MgO</th>
<th>Na₂O</th>
<th>K₂O</th>
<th>SO₃</th>
<th>LOI</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Content</td>
<td>48.21</td>
<td>33.18</td>
<td>4.80</td>
<td>5.68</td>
<td>1.61</td>
<td>0.75</td>
<td>0.45</td>
<td>0.29</td>
<td>0.26</td>
<td>1.20</td>
<td>96.44</td>
</tr>
</tbody>
</table>

(1) Abrasiveness

We adopted mechanical ball milling of fly ash in a ball mill at 2400 r/h for 2 h to achieve the effect of primary activation of fly ash.

(2) Pickling

Weigh 5 g of fly ash after ball milling, add 100 mL of hydrochloric acid with a mass fraction of 5%, and react at 85 °C for 2 h. Then the fly ash was washed to make its pH value neutral and dried. After pickling, the content of Fe²⁺, Fe³⁺ and Ca²⁺ of raw fly ash is reduced, while some organic impurities are removed, the content of silica and alumina is increased, and the activity of fly ash is enhanced.

(3) Alkali fusion and calcination

Fly ash and sodium hydroxide were mixed at a mass ratio of 1:1.2 and calcined at 800°C for 2 h. Alkali controls the polymerization degree of silicate ions and participates in the condensation reaction of silicate ions and aluminate ions in the process of zeolite crystallization, speeding up the crystallization speed and shortening the crystallization reaction time.

1.3.2 Exploring optimal process parameters for zeolite preparation

Reviewing the literature, we found that the preparation of purified zeolite from alkali-melted fly ash is related to its solid-liquid ratio (the ratio of fly ash to water), hydrothermal time, Si/Al ratio, hydrothermal temperature, and whether to add crystal seeds. Therefore, we adopted control variables to explore the optimal process parameters for the preparation and purification of zeolite. The specific experimental scheme is as follows:

(1) Exploration of hydrothermal temperatures

Weigh 3 g of alkali-melted fly ash, 4.25 g of Na₂SiO₃·9H₂O and 27 mL of H₂O into four 50 ml polytetrafluoroethylene-lined reactors, stir them for 20 min, and put them in a hydrothermal reaction for 18 h at 70 °C, 80 °C, 90 °C, and 100 °C, respectively, recorded as X-1, X-2, X-3, and X-4. Then they were taken out to a centrifuge tube, washed with deionized water, and the pH adjusted to 9–10, filtered and dried to obtain zeolite samples.

(2) Exploration of hydrothermal time

The experimental procedure is the same as (1), only the hydrothermal reaction time is changed, and four 50 ml reactors are reacted at 80 °C for 6 h, 12 h, 18 h, and 24 h, denoted as X-5, X-6, X-2 and X-7, respectively.

(3) Exploration of solid-liquid ratio
The experimental procedure is the same as (1), only the amount of solvent added is changed, and 21 mL, 27 mL and 33 mL of water (the ratio of fly ash to water is 1:7, 1:9 and 1:11 in sequence) are added in the three 50 ml reactors successively. The hydrothermal reactants 18 h at 80°C are denoted as X-10, X-11, X-2, and X-12.

(4) Exploration of Si/Al ratio

The experimental procedure is the same as (1), only the Si-Al ratio is changed, and 0.3467 g NaAlO\(_2\), 3.19 g, 4.25 g and 4.80 g Na\(_2\)SiO\(_3\)·9H\(_2\)O are added to four 50 ml reactors successively (Si/Al ratio is 1:1, 2:1, 2.5:1 and 2.8:1 in sequence). Hydrothermal reactions at 80°C for 18 h are denoted as X-10, X-11, X-2 and X-12.

(5) Exploration of crystal seed

The experimental procedure is the same as (1), the addition of crystal seed is controlled, three 50 ml reactors are recorded as X-2, X-6 and X-13, and only a small amount of crystal seed is added to X-13, and X-2 and X-13 are reacted at 80 °C for 12h, while X-2 is reacted at 80 °C for 18 h.

1.4 Adsorption experiments with zeolite

1.4.1 Study of adsorption conditions

The zeolite obtained from the above preparation is tested in adsorption experiments to compare the adsorption effect, and according to the preliminary adsorption effect, the experimental procedure is adjusted appropriately to screen out the optimal zeolite and adsorption condition parameters [24]. In this experiment, ammonium chloride aqueous solution was used as a model pollutant, and ammonia nitrogen concentration was measured by UV spectrophotometry to calculate the adsorption amount and removal rate of ammonia nitrogen, which is measured in parallel for three times, and the average value was taken.

(1) Determination of adsorption capacity of different zeolites

Weighing 150 mg of different types of zeolites are added into pH = 7, 50 mL of 50 mg/L ammonia nitrogen solution, respectively, and adsorbed at 300 r/min for 60 min at room temperature.

(2) Effect of adsorption time on adsorption properties

Weighing 150 mg of purified zeolite X is added into pH = 7, 50 mL of 50 mg/L ammonia nitrogen solution, respectively, and adsorbed at 300 r/min for 5, 10, 20, 30, 40, 50, 60, 70, 80, and 90 min at room temperature.

(3) Effect of temperature on adsorption properties

Weighing 150 mg of purified zeolite X is added into pH = 7, 50 mL of 50 mg/L ammonia nitrogen solution, put into 30, 40, 50, 60, 70 and 80 °C water bath heating, respectively, and adsorbed at 300 r/min for 60 min at room temperature.

(4) Effect of pH on adsorption properties

Weighing 150 mg of purified zeolite X is added into 50 mL of 50 mg/L ammonia nitrogen solution at pH = 3, 5, 6, 7, 8, 9 and 11, respectively, and adsorbed at 300 r/min for 60 min at room temperature.
(5) Effect of initial concentration on adsorption properties

Weighing 150 mg of purified zeolite X is added into pH = 7, 50 mL of ammonia nitrogen solution with concentrations of 25, 50, 75, 100, 150, 200, and 250 mg/L, respectively, and adsorbed at 300 r/min for 60 min at room temperature.

(6) Effect of zeolite dosage on adsorption properties

Weighing 50, 100, 150, 200, 250 and 300 mg of purified zeolite X is added into pH = 7, 50 mL of 50 mg/L ammonia nitrogen solution, respectively, and adsorbed at 300 r/min for 60 min at room temperature.

1.4.2 Regeneration properties tests

(1) Preparation of zeolite for saturated adsorption of ammonia nitrogen

Weighing 150 mg of purified zeolite X is added into 50 mg/L ammonia nitrogen wastewater, stirred for 2 h, and then the ammonia nitrogen concentration is measured by UV spectrophotometry to determine its saturation adsorption capacity.

(2) Preparation of regeneration solution

1000 mL NaCl solution with a concentration of 0.1 mol/L and 1000 ml NaOH solution with a concentration of 0.1 mol/L are mixed to obtain the regeneration solution [25].

(3) Regeneration

Weighing 150 mg of saturated ammonia nitrogen adsorption zeolite X is added into pH = 7, 50 mL of 50 mg/L ammonia nitrogen solution and adsorbed at 300 r/min for 60 min at room temperature. Then the concentration of ammonia nitrogen is measured and the adsorption and removal rate of ammonia nitrogen are calculated.

Results and Discussion

2.1 Exploration of zeolite preparation process

(1) Exploration of hydrothermal temperature

According to Fig. 2a, when the hydrothermal temperature is 70 °C, no obvious diffraction peaks appears, indicating that X-1 is an amorphous silica-aluminate. When the hydrothermal temperature is 80 °C, the characteristics of the impurity crystal phase disappear, and X-2 shows a relatively pure zeolite X; When the hydrothermal temperature is 90 °C, X-3 is composite zeolite A-X with weak zeolite A characteristic peak; When the hydrothermal temperature is 100°C, X-4 has a clearer characteristic peak of composite zeolite A-X. It can be seen that the hydrothermal temperature is too high, the order in the crystal arrangement process is
affected, and the crystal is no longer a single crystal. For comprehensive consideration, the hydrothermal temperature of 80 °C is more suitable for the synthesis of single crystal phase zeolite X.

(2) Exploration of hydrothermal time

According to Fig. 2b, when the hydrothermal time is 6 h, X-5 shows the mixed characteristic peaks of composite zeolite A-X, but the intensity of the diffraction peaks is weaker, which indicates that the relative crystallinity of the zeolite is lower under the shorter hydrothermal time. When the hydrothermal time is 12 h, the intensity of the characteristic diffraction peak of X-6 becomes higher, but it is still composite zeolite A-X. When the hydrothermal temperature is 24 h, X-7 has the characteristic diffraction peak of zeolite X like X-2. Considering the economy and efficiency of practical industrial application, the hydrothermal time of synthesizing single crystalline phase zeolite X is chosen to be 18 hours.

(3) Exploration of solid-liquid ratio

Figure 2c shows that when the solid-liquid ratio is 1:7, both zeolite A and zeolite X exist in X-8, and the peak strength is very weak. As the solid-liquid ratio increased to 1:9, the zeolite X peak increased significantly, and the characteristic peak of zeolite A disappears, forming a single zeolite X. When the solid-liquid ratio continued to increase to 1:11, the characteristic peak of zeolite A appears again, and the relative crystallinity also decreases relatively. The solid-liquid ratio of 1:9 is more suitable for the synthesis of single crystalline zeolite X.

(4) Exploration of the Si/Al ratio

According to Fig. 2d, when the Si/Al ratio is 1, X-10 is a single zeolite A with weak peak strength. When the Si/Al ratio increases to 2, X-11 has characteristic peaks of both zeolite A and zeolite X to form zeolite A-X. When the Si/Al ratio is 2.5 and 2.8, the diffraction characteristic peak of zeolite A almost disappears, and both X-2 and X-12 are relatively pure zeolite X. In summary, when synthesizing single crystalline zeolite X, the Si/Al ratio of 2.5 is more suitable.

(5) Exploration of the crystal seed

Figure 3 shows that compared with X-6 prepared without crystal seed under the same other conditions, X-13 has changed from the original composite zeolite A-X to A single crystal phase zeolite X. Compared with the X-2, its purity is higher, and the synthesis time is shortened by 6 h. It can be seen that the crystal seed plays an important role in guiding the crystallization direction and shortening the synthesis period in the process of preparing zeolite from fly ash. This may be related to the zeolite in the hydrothermal crystallization nucleation period in a substable state, crystallization without the need to first form metastable crystal nucleus, but directly on the basis of the existing crystal seed growth. Overall consideration, we choose to prepare X-13 process parameters as the best process parameters.

2.2 Characterization and analysis of zeolites
2.2.1 Characterization and analysis of X-ray diffraction spectroscopy (XRD)

The XRD comparison of zeolite X (X-13), zeolite A-X (X-4) and zeolite A (X-10) synthesized by different process parameters is shown in Fig. 4. It is obvious that the purification degree of zeolite X synthesized by the optimal process parameters is higher.

2.2.2 Characterization and analysis of infrared spectroscopy (FT-IR)

As shown in Fig. 5, the strong absorption peak at position 3439–3450 cm$^{-1}$ belongs to the stretching vibration characteristic peak of the -OH group adsorbing water on the surface, and the absorption peak at 1598–1634 cm$^{-1}$ belongs to the bending vibration characteristic peak of the water-adsorbing -OH group. The absorption peaks at 554–567 cm$^{-1}$ in zeolite is attributed to the double ring vibration characteristic peak connected to the outside of zeolite, indicating the formation of the double ring structure of zeolite crystal frame. The absorption peaks at 720–756 cm$^{-1}$ and 988–1199 cm$^{-1}$ are the symmetric and asymmetric stretching vibration characteristic peaks of Si-O tetrahedra, respectively. It can be seen that single crystalline phase zeolite X, zeolite A and composite zeolite A-X are successfully synthesized.

2.2.3 Characterization and Analysis of Scanning Electron Microscopy (SEM)

The surface morphology of zeolite X synthesized by optimal process parameters is shown in Fig. 6(a,d). It can be clearly seen from the SEM photos that the sample is composed of particles, and the crystal is an octahedral structure with regular shape and complete morphology. The morphology of the synthesized zeolite A is shown in Fig. 6(b,e), with an obvious cube structure, and the morphology rules are consistent with the standard crystal type of zeolite A. The synthesized zeolite A-X is shown in Fig. 6(c,f), from which it can be observed that there are not only cubic zeolite A but also octahedral zeolite X, with relatively rough crystal surface. The SEM results show that the synthesized single crystalline phase zeolite X has higher crystal purity and better quality, which is conducive to the adsorption of ammonia nitrogen in wastewater.

2.2.4 Characterization and Analysis of Transmission Electron Microscopy (TEM)

Figure 7 shows the transmission electron microscope (TEM) images of synthesized single crystalline phase zeolite X and zeolite A. From the images, it can be observed that the clumps of zeolite molecular sieves are formed by stacking multilayer two-dimensional sheet structures with smooth surfaces and clear sheet edges. Among them, it can be seen from Fig. 7b that zeolite X is in the form of polygonal flakes and has multiple fine and uniform pores distributed on its flake structure, which improves the adsorption performance of the zeolite. Figure 7e shows that zeolite A has a quadrilateral sheet structure, which is consistent with the above SEM image. Thus it can be confirmed that the zeolite X and zeolite A with single crystal form have been prepared.
2.2.5 Characterization and analysis of nitrogen adsorption-desorption

Table 2
Pore structure parameters of zeolite X and zeolite A

<table>
<thead>
<tr>
<th>Typology</th>
<th>specific surface area(m²/g)</th>
<th>pore volume(cc/g)</th>
<th>aperture(nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>zeolite X</td>
<td>23.092</td>
<td>0.060</td>
<td>3.794</td>
</tr>
<tr>
<td>zeolite A</td>
<td>20.698</td>
<td>0.116</td>
<td>13.377</td>
</tr>
</tbody>
</table>

According to Table 2, the specific surface area and pore volume of the prepared single pure phase zeolite X are 23.092 m²/g and 0.060 cc/g, respectively, while the specific surface area of the single pure phase zeolite A is only 20.698 m²/g. According to Fig. 8, in the desorption process of the prepared zeolites, hysteresis occurs in the desorption curve to different degrees when P/P₀ = 0.45-1.0, and hysteresis loop appears, indicating that the zeolite sample has a certain amount of mesopore, which belongs to the typical curve of solid with narrow porous pores, conforming to the pore characteristics of zeolite. The results show that the interaction between zeolite and ammonia nitrogen is not through the distribution mode.

2.2.6 Characterization and analysis of X-ray energy spectrometry (EDS)

The EDS analysis results of the synthesized zeolite X and zeolite A are shown in Fig. 9. It can be seen that the prepared samples contain silicon and aluminum, the necessary elements for zeolite synthesis. From the data in Table 3, it can be illustrated that the mass fractions of Si atom and Al atom of zeolite X are 14.74% and 11.04%. Through calculation, it can be seen that the Si/Al ratio at this time is 2.67, while the theoretical Si/Al ratio of zeolite X is 2.3–3.3, and the characterization results are consistent with the theoretical ratio [26]. The mass fractions of Si atom and Al atom of zeolite A are 7.64% and 6.87%. Through calculation, it can be seen that the Si/Al ratio at this time is 1.8, while the theoretical Si/Al ratio of zeolite A is 2, and the characterization results are similar to the theoretical data [26]. In summary, the characterization results can indicate the successful synthesis of zeolite X and zeolite A.

Table 3
EDS elemental analysis of zeolite X and zeolite A

<table>
<thead>
<tr>
<th>Typology</th>
<th>Mass fraction of Si%</th>
<th>Mass fraction of Al%</th>
</tr>
</thead>
<tbody>
<tr>
<td>zeolite X</td>
<td>14.74</td>
<td>11.04</td>
</tr>
<tr>
<td>zeolite A</td>
<td>7.64</td>
<td>6.87</td>
</tr>
</tbody>
</table>

2.2.7 Characterization and analysis of Thermogravimetric (TG-DSC)

We compared the TG-DSC of the zeolite X synthesized by the optimal process parameters with that of the standard zeolite X. As shown in Fig. 10, the two have almost identical curves, which indicates that the zeolite
X prepared by us is of high purity. The figure shows that zeolite X begin to lose weight rapidly after 50 °C, and has almost completely decomposed at about 450 °C. The synthesized zeolite does not release lattice energy by structural collapse before 800 °C, and the industrial zeolite use temperature is generally below 700 °C, which shows that the experimental synthesis of zeolite thermal stability is good, in line with industrial requirements.

2.3 Study on adsorption properties of zeolites

2.3.1 Study on adsorption properties of zeolites

(1) Determination of adsorption capacity of different zeolites

The synthesized zeolite X, zeolite A and zeolite A-X are subjected to ammonia nitrogen solution adsorption experiments under the same experimental conditions, and the results are shown in Fig. 12. The order of ammonia nitrogen adsorption of the three zeolites is zeolite X (14.33 mg/g) > zeolite A-X (10.00 mg/g) > zeolite A (9.33 mg/g), which is because the crystal type plays a role in promoting the synthesis of zeolites, thus improving the relative crystallinity of zeolite X and increasing the adsorption sites. At the same time, according to the above BET characterization, it can be seen that zeolite X is a polar adsorbent, and the ammonia nitrogen wastewater contains polar NH$_4^+$ ions, so it can strongly adsorb the surface of the zeolite. In summary, zeolite X prepared with the optimal technological parameters has a relatively good adsorption effect on ammonia nitrogen. In this section, zeolite X is selected as adsorbents to investigate the influence of different adsorption conditions on the adsorption of ammonia nitrogen by zeolites.

(2) Effect of adsorption time, temperature and solution pH on adsorption performance

According to Fig. 13a, both the adsorption amount and removal rate of ammonia nitrogen increase with the increase of adsorption time. Within the first 40 min, the adsorption rate rises sharply, and the removal rate rapidly increases to 74%, reaching 12.53 mg/g adsorption capacity; when the adsorption time reaches 60 min, the removal rate is 82%, and the adsorption capacity is 13.67 mg/g; when the adsorption time is 120 min, the removal rate of ammonia nitrogen finally reaches 88%. This is because at the beginning of adsorption, the solution of ammonia nitrogen concentration is large, resulting in a large concentration difference between the solution and the surface of the zeolite, the driving force is large, and the adsorption sites of the initial zeolite are many, so the adsorption rate is fast and the adsorption amount is increased significantly. As time goes by, the adsorption rate and adsorption capacity increase with the trend of slowing down, and finally reach basically unchanged, which is because the adsorption of ammonia nitrogen is close to the saturation state, and the adsorption equilibrium and ion exchange equilibrium occur between zeolite and solution. In order to reduce the time cost and maximize the removal efficiency of ammonia nitrogen using zeolite X, the optimal adsorption time should be set to 60 min.

Figure 13b shows the adsorption effects of ammonia nitrogen at different temperatures. When the temperature is 30 °C, the ammonia nitrogen removal rate reaches the highest 86%, and the adsorption capacity is 14.33 mg/L. When the temperature is higher than 30 °C, the removal rate of ammonia nitrogen and the adsorption capacity shows a downward trend and then tends to be stable. From the point of view of
removal rate, the effect of temperature is not large, so the adsorption temperature can be selected at room temperature (30 °C).

Figure 13c shows the influence of solution pH on ammonia nitrogen adsorption properties. When the pH value is 6–8, the removal rate of ammonia nitrogen is significantly higher, especially when the pH value is 7, the removal rate climbs to the highest peak of about 78%. The reason is that when the pH value is low, the concentration of H\(^+\) in the solution is high, and ammonia nitrogen is mostly in the form of NH\(_4^+\), while the ionic radius of NH\(_4^+\) is much larger than that of H\(^+\), which is not easy to penetrate into the zeolite. When the pH value is high, the concentration of H\(^+\) in the solution decreases, ammonia nitrogen is mainly in the form of NH\(_3\)·H\(_2\)O, and the exchange ability of zeolite to NH\(_4^+\) is weakened, mainly through adsorption of NH\(_3\)·H\(_2\)O, resulting in poor overall adsorption efficiency. Therefore, the optimal pH value of ammonia nitrogen adsorption solution by zeolite should be controlled at 6–8.

(1) The effect of the initial concentration of ammonium chloride on the adsorption properties

Figure 14 demonstrates the effect of different initial concentrations of NH\(_4\)Cl solutions on the adsorption capacity of ammonia nitrogen. The NH\(_4\)Cl solution with high concentration forms a large concentration difference with the zeolite surface, which enhances the exchange and adsorption, and increases the adsorption capacity and removal rate of zeolite. When the initial concentration of NH\(_4\)Cl solution is 50 mg/L, the removal rate reaches a maximum value of 73.6%, and the adsorption capacity of zeolite is 12.27 mg/g. As the concentration continues to increase, although the adsorption capacity also increases, the removal rate decreases, resulting in poor removal effect.

(2) The effect of dosage of zeolite on adsorption properties

According to Fig. 15, the application amount of zeolite X has a significant effect on the adsorption properties of ammonia nitrogen. In the specific application range, the removal of ammonia nitrogen rises almost straight line, and the rising trend of removal rate slows down after reaching 150 mg. In contrast, the adsorption capacity of ammonia nitrogen decreases rapidly with the increase of the applied amount, and then becomes stable. The reason for this phenomenon is that the ammonia nitrogen concentration in the water body is high at the beginning, and the limiting factor is the amount of zeolite applied. However, as the solution concentration decreases and the amount of zeolite applied increases, the adsorption capacity of ammonia nitrogen per unit mass of zeolite encounters a bottleneck, resulting in no increase in the effective adsorption sites, and the adsorption of ammonia nitrogen is almost unchanged. Considering the economic cost and adsorption efficiency, the optimal application amount is estimated to be 150 mg.

2.3.2 Research on regeneration properties

The regeneration experiment is carried out on the purified zeolite X with the regeneration solution, and the results are shown in Fig. 16a. The adsorption capacity decreases slightly from 14.00 mg/g in the first cycle to 13.33 mg/g in the fifth cycle, and the regeneration efficiency decreases from 84% in the first cycle to 80% in the fifth cycle. In summary, the adsorption properties of zeolite X can still maintain a high level after five
regeneration cycles, showing excellent stability and recycling, and can be repeated for a long time for the treatment of ammonia nitrogen wastewater.

The regenerated zeolite X is characterized by infrared and XRD. It can be seen from Fig. 16b,c that the structure of the regenerated zeolite X does not change significantly, which proves that the prepared zeolite X has good stability and regeneration ability while ensuring high adsorption efficiency.

Conclusions

In this paper, zeolites are successfully prepared using fly ash as raw material, and the structure and performance characteristics of different types of zeolites are deeply discussed and characterized in detail. The specific research summary is as follows:

1. Zeolite X, zeolite A and zeolite A-X are prepared by hydrothermal synthesis method by changing hydrothermal temperature, time, solid-liquid ratio and Si/Al ratio. Combined with XRD, TG-DSC, SEM, TEM, BET, EDS, FT-IR and other technologies, the optimal preparation parameters for the synthesis and purification of zeolite X is obtained: solid-liquid ratio 1:9, Si/Al ratio 2.5, supplemented by a few crystal seed, and reaction at 80°C for 12 h.

2. The adsorption and regeneration properties of purified zeolite X is studied. Taking 50 mg/L NH₄Cl aqueous solution as the model pollutant, the adsorption capacity of the three zeolites above is compared, and the results shows that the purified zeolite zeolites has better adsorption capacity of ammonia nitrogen. The adsorption performance of purified zeolite X is also investigated at different adsorption time, temperature, pH, initial concentration of NH₄Cl solution and dosage of zeolite. On this basis, the optimal parameters for adsorption of ammonia nitrogen wastewater by purified zeolite X is selected: 50 mg/L NH₄Cl solution, zeolite dosing of 150 mg, and adsorption at pH 6–8 and 30 °C for 60 min. Finally, its regeneration capacity is explored and tested, and the results shows that the purified zeolite X has good stability and regeneration capacity while ensuring high adsorption efficiency.

In this paper, fly ash is used as raw material, and purified zeolite with relatively simple process, better adsorption performance and higher regeneration capacity is successfully prepared. This study provides a good inspiration for the rational design of high-performance zeolite adsorption materials and the study of the interaction at the atomic level. At the same time, it also provides a new idea for the treatment of fly ash, so that it can achieve the purpose of "waste for waste, green chemistry".

References


Figures
Figure 1

Schematic diagram of preparation route
Figure 2

XRD patterns of samples prepared under different conditions: (a) hydrothermal temperature; (b) hydrothermal time; (c) solid-liquid ratio; (d) Si/Al ratio
Figure 3

XRD pattern of zeolites with or without crystal seed
Figure 4

XRD patterns of zeolite X, zeolite A and zeolite A-X
Figure 5

FT-IR of zeolite X, zeolite A and zeolite A-X
Figure 6

SEM images of (a,d) zeolite X; (b,e) zeolite A; (c,f) zeolite A-X
Figure 7

TEM images of (a,b,c) zeolite X; (d,e,f) zeolite A

Figure 8
Nitrogen adsorption-desorption of zeolite X and zeolite A

Figure 9

EDS spectra of (a) zeolite X; (b) zeolite A

Figure 10

TG-DSC images of standard zeolite X and prepared zeolite X
Figure 11

Schematic diagram of adsorption process of zeolites

Figure 12

Adsorption of ammonia nitrogen by different types of zeolites
Figure 13
(a) Adsorption time; (b) Adsorption temperature; (c) Effect of solution pH on ammonia nitrogen adsorption performance

Figure 14
Effect of initial concentration of ammonium chloride on adsorption properties of ammonia nitrogen
Figure 15
Effect of dosage of zeolite on adsorption properties of ammonia nitrogen

Figure 16
(a) The effect diagram of the number of cycles on ammonia nitrogen adsorption;
(b) XRD pattern of regenerated zeolite X; (c) Infrared image of regenerated zeolite X