NaA zeolite derived from blast furnace slag: its application for ammonium removal
Hongwei Guo, Lizhen Tang, Bingji Yan, Kang Wan and Peng Li

ABSTRACT
In this paper, high value added NaA zeolite material was prepared from blast furnace (BF) slag by hydrothermal method and its adsorption behavior on the removal of ammonium ion was investigated. It was found out that the synthetic NaA cubic zeolite with smaller crystal size obtained at $n_{\text{SiO}_2}/n_{\text{Al}_2\text{O}_3} = 2$ and $n_{\text{H}_2\text{O}}/n_{\text{NaOH}} = 20$ showed better adsorption performance. The kinetics of the adsorption of ammonium ion by synthesized NaA zeolite was fitted by the pseudo-second-order kinetic model. The intra-particle diffusion modeling reveals that two mixed rate-controlling mechanisms were involved in the adsorption process. The relatively high value of activation energy of 92.3 kJ·mol$^{-1}$ indicates a high impact of temperature on the adsorption rate, and the nature of ammonium adsorption is chemical reaction rather than physisorption. Based on the thermodynamics calculations, the adsorption of ammonium was found to be an endothermic, spontaneous process. The adsorption isothermal analysis showed that the Langmuir model could be well fitted and a maximum adsorption capacity of 83.3 mg·g$^{-1}$ of NH$_4^{+}$ was obtained. Thus, it was demonstrated that by forming low cost NaA zeolite and using it for environmental remediation, the synchronous minimization of BF slag and ammonia nitrogen contamination could be achieved.

Key words | adsorption, ammonium removal, blast furnace slag, zeolite

INTRODUCTION
In the iron-making process, the iron oxides are reduced to molten Fe by coke with the presence of flux such as limestone or dolomite (Piatak et al. 2015). The blast furnace (BF) slag is one of the major solid wastes produced during this process. In 2015, around 803 million tons of crude steel had been produced in China, whereas the production of BF slag was around 274 million tons. The main composition of BF slag depends on the iron ore and the added flux, normally with a typical composition of calcium oxide (28–35 mass%) and silica (30–35 mass%), with the rest being Al$_2$O$_3$ and MgO. Interest in using BF slag has arisen because it is readily available, cheap, and most often produced and stored with environmental concerns. Due to the low iron content, BF slag has been used as a supplementary cementitious material in Portland cement concrete for many years (Oss 2003; Piatak et al. 2015). However, the traditional cement industry is compelled to reduce its production scale due to the severe environmental regulations and economic contraction in recent years. As a consequence, the use of BF slag as cementitious material has been limited and most is disposed of in landfills.

The solution for this problem lies in the exploitation of BF slag for producing high value added materials. Many researchers have attempted to develop new processes based on its physical and chemical properties. Mostafa et al. (2010) have prepared ceramics from the BF slag and kaolin. Also low cost glass–ceramics have been produced by using BF slag as raw material (Zhao et al. 2012). Beyond that, the utilization of alkali oxides (CaO, MgO) in BF slag provided an alternative way for reducing CO$_2$ emission by carbonation (Eloneva et al. 2008). Kuwahara & Yamashita (2015) have studied the catalytic application of synthesized Ca-based hydrotalcite-like compounds (HTlcs) from BF slag using acid-leaching. However, the silicon oxide remains in the acid-leaching residue without further utilization. As shown in Figure 1, the present authors offer an approach for the total utilization of BF slag, where the Ca, Al and Mg elements are recovered by acid leaching and subsequently subjected to HTlcs synthesis, and the silica gel residue yielded could be further utilized as silica source for zeolite formation.
Ammonium discharged together with municipal or industrial effluents is responsible for harmful effects such as eutrophication, toxicity to aquatic life and increased corrosion towards soil (Lei et al. 2009). The ammonia nitrogen in water can be in the form of ammonia and ammonium ion, and depends on the pH and temperature according to the equilibrium reaction (Equation (1)). A number of methods are capable of removing the ammonia nitrogen from aquatic environments, and among them, the adsorption process is widely used. Zeolites can provide adsorption sites with exchangeable cations, which makes it an efficient adsorbent for ammonium removal (Kithome et al. 1998; Lei et al. 2009; Moussavi et al. 2011). Different kinds of zeolites, like natural zeolites with or without modification, and artificial zeolites have been used to remove the ammonium ( Yusof et al. 2010; Moussavi et al. 2011; Soetardji et al. 2015). The utilization of BF slag for zeolite synthesis would provide a low cost solution for ammonium removal. In addition, it would be interesting to investigate the ammonium removal performance of BF slag-derived zeolite and compare it with the literature values.

\[
\text{NH}_3 + \text{H}_2\text{O} \leftrightarrow \text{NH}_4^+ + \text{OH}^-
\]  

Equation (1)

Investigations have been carried out to study the synthesis, characterization and ammonium adsorption on BF slag-derived zeolite. Zeolite was synthesized with acid leaching residue of BF slag through a conventional hydrothermal method. The efficiency of ammonium adsorption on zeolite was studied regarding the synthetic parameters, initial ammonium ion concentration, contact time and temperature. The mechanism of ammonium adsorption is discussed according to the adsorption isotherms, kinetics and thermodynamics models.

**METHODS**

**Raw material**

The BF slag was received from Sha Steel Company (JiangSu Province, China). Its chemical composition (as oxides) as determined by X-ray fluorescence (XRF) is shown in Table 1. The dominant components are SiO_2, CaO, MgO and Al_2O_3, which account for 95% of total mass. The X-ray diffraction (XRD) result in Figure 2 shows the presence of a small amount of hydrated silicates, along with a vitreous structure indicated by an amorphous hump, owning to a water quenching procedure adopted (Piatak et al. 2015). The raw materials were crushed, ground and finally powdered through 200 mesh sieve before further use. All the chemical reagents employed were analytical grade (Sinopharm Chemical Reagent Co. Ltd) and distilled water was used throughout the experiment.

**Synthesis of zeolite from BF slag**

Ten grams of BF slag was dissolved in 3 mol·L\(^{-1}\) of HCl solution (200 mL) in a Teflon beaker. After 2 hrs of stirring at 90°C, the slurry was filtered, and the separated filter liquor containing Ca\(^{2+}\), Mg\(^{2+}\), Al\(^{3+}\) can be used as precursor for HTlcs synthesis. The XRF result in Table 2 shows that the resulting solid residue from acid leaching consists of around 89.7 wt% of silica and 7.3 wt% of alumina and can be used as raw material for zeolite preparation.

**Table 1** | Chemical composition of the BF slag

<table>
<thead>
<tr>
<th>Composition</th>
<th>SiO_2</th>
<th>CaO</th>
<th>Al_2O_3</th>
<th>MgO</th>
<th>SO_2</th>
<th>MnO</th>
<th>TiO_2</th>
<th>Fe_2O_3</th>
</tr>
</thead>
<tbody>
<tr>
<td>wt%</td>
<td>36.172</td>
<td>35.532</td>
<td>14.081</td>
<td>8.869</td>
<td>2.125</td>
<td>0.973</td>
<td>0.688</td>
<td>0.493</td>
</tr>
</tbody>
</table>
The synthesis of zeolite was carried out by the conventional hydrothermal method. NaAlO\(_2\) and NaOH were used to adjust the synthetic parameters as presented in Table 3, i.e. SiO\(_2\)/Al\(_2\)O\(_3\) molar ratio and H\(_2\)O/NaOH molar ratio, respectively. For instance, for nSiO\(_2\)/nAl\(_2\)O\(_3\)/nNaOH/nH\(_2\)O \(= 2:1:12:240\), NaOH and NaAlO\(_2\) solutions were prepared with 4.8 gram of solid NaOH and 1.64 gram of solid NaAlO\(_2\) dissolving in 21.6 gram of water, respectively. Then 1.2 gram of solid residue obtained from HCl leaching was dissolved in NaOH solution with continuous stirring at 80\(^\circ\)C for 2 hrs. After that, NaAlO\(_2\) solution (to balance the SiO\(_2\)/Al\(_2\)O\(_3\) molar ratio) was added drop-wise to the resulting solution and was stirred for 4 hrs. The obtained gel precursor was transferred into a high pressure Teflon-lined autoclave and kept for 5 hrs at 100\(^\circ\)C. Finally, the solid products were separated by filtration, washed with distilled water and dried in air at 80\(^\circ\)C for 24 h.

### Sample characterization

Chemical composition of the BF slag and acid leaching residue was determined by XRF. The phase analysis of the sample was investigated by a Rigaku Ultima-IV X-ray diffractometer using Cu K\(\alpha\) radiation (\(\lambda = 0.154,056\) nm). The spectrum was recorded with the 2\(\theta\) range of 10–90\(^\circ\) and a step size of 0.02\(^\circ\). The microstructure of the prepared samples was examined by a field emission scanning electron microscope (SEM, Hitachi, SU5000).

### Adsorption performance tests

Analytical grade ammonium chloride salt (NH\(_4\)Cl) was used in the preparation of the stock NH\(_4^+\) solution. The initial pH value was adjusted by adding NaOH or HCl to the designed value of 7. Under such circumstance, the dominant form for ammonia nitrogen is NH\(_4^+\). The experimental conditions of the adsorption tests performed are summarized in Table 3.

The synthetic parameters, temperature, contact time and initial ammonium concentration were selected as adsorption parameters for study. For example, adsorption kinetics

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**Table 2 | Chemical composition of the residue obtained from acid leaching of BF slag**

<table>
<thead>
<tr>
<th>Composition</th>
<th>SiO(_2)</th>
<th>Al(_2)O(_3)</th>
<th>Fe(_2)O(_3)</th>
<th>MgO</th>
<th>TiO(_2)</th>
<th>CaO</th>
<th>K(_2)O</th>
<th>MnO</th>
</tr>
</thead>
<tbody>
<tr>
<td>wt%</td>
<td>89.68</td>
<td>7.34</td>
<td>1.61</td>
<td>0.43</td>
<td>0.38</td>
<td>0.27</td>
<td>0.04</td>
<td>0.01</td>
</tr>
</tbody>
</table>

**Table 3 | Adsorption tests at varied conditions**

<table>
<thead>
<tr>
<th>No.</th>
<th>Adsorption tests</th>
<th>Conditions</th>
<th>(\text{SiO}_2/\text{Al}_2\text{O}_3/\text{NaOH}/\text{H}_2\text{O})</th>
<th>(\text{NH}_4^+)/mg L(^{-1})</th>
<th>Zeolite/g</th>
<th>Duration/ min</th>
<th>Temperature/ (^\circ)C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Effect of synthesis parameters</td>
<td>2:1:12:240</td>
<td>50</td>
<td>0.1</td>
<td>120</td>
<td>32</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>3:1:12:240</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>6:1:12:240</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>2:1:12:240</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>2:1:12:360</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>2:1:12:480</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Adsorption thermodynamic</td>
<td>2:1:12:240</td>
<td>50</td>
<td>0.1</td>
<td>120</td>
<td>32, 40, 45, 50</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Adsorption kinetic</td>
<td>2:1:12:240</td>
<td>50</td>
<td>0.1</td>
<td>10, 15, 20, 30, 60, 80, 120</td>
<td>32, 40, 45, 50</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Adsorption isothermal</td>
<td>2:1:12:240</td>
<td>30, 50, 80, 100, 120</td>
<td>0.1</td>
<td>120</td>
<td>32</td>
<td></td>
</tr>
</tbody>
</table>
experiments were carried out in the thermostatic shakers at different temperatures of 32, 40, 45 and 50 °C by adding 0.1 gram of zeolite into 50 mg·L⁻¹ NH₄⁺ solution. Meanwhile, a high agitation rate of 350 rpm was applied to minimize the volume subsurface layer and increase transport rate of adsorbate in the solute. The adsorbent was separated at predetermined time interval by centrifugation at 3,500 rpm. The residual NH₄⁺ concentration after the adsorption process was analyzed using a UV spectrophotometer (Beijing Purkinje General Instrument Co., Ltd, TU-1810) by monitoring the absorbance changes at a wavelength of maximum absorbance (420 nm). The amount of ammonium adsorbed at time \( t \) (\( q_t \), mg·g⁻¹) and removal efficiency (\( R\% \)) were calculated by Equations (2) and (3).

\[
q_t = \frac{C_i - C_t}{W} \times V \tag{2}
\]

\[
R(\%) = \frac{C_i - C_t}{C_i} \times 100\% \tag{3}
\]

where \( C_i \) and \( C_t \) are the initial NH₄⁺ concentration and the remaining concentration of NH₄⁺ after predetermined duration (\( t \)) of adsorption, respectively, and \( V \) is the volume (mL) of the solution.

**RESULTS AND DISCUSSION**

**The effect of SiO₂/Al₂O₃ molar ratio**

Figure 3 shows the XRD patterns of synthesized zeolites with different SiO₂/Al₂O₃ molar ratios. It is seen that when SiO₂/Al₂O₃ molar ratio is fixed at 2, the synthetic products are consisting of NaA zeolite and small amount of NaX zeolite. With the increasing of SiO₂/Al₂O₃ molar ratio, the intensity of diffraction peaks assigned to NaX zeolite is increased; further increasing the SiO₂/Al₂O₃ molar ratio to 6, the NaX zeolite becomes the dominant phase. It indicates that the formation of particular zeolite strongly depends on the SiO₂/Al₂O₃ molar ratio. According to earlier studies (Chang & Shih 2000; Tanaka et al. 2002), the preferred crystallization of either NaA zeolite (Na₉₆[(AlO₂)₉₆(SiO₂)₉₆]·216H₂O) or NaX zeolite (Na₈₈[(AlO₂)₈₈(SiO₂)₁₀₄]·220H₂O) is correlated with its initial inorganic framework composition and anions in the precursor, especially when the reaction system becomes close to its equilibrium state.

The morphologies of obtained zeolites with different SiO₂/Al₂O₃ molar ratios are shown in Figure 4. In Figure 4(a), the microscopic observations reveal that the crystal grains with a size of 3–4 μm are typical cubic morphology of NaA-type zeolite when SiO₂/Al₂O₃ molar ratio is 2. With the increasing of SiO₂/Al₂O₃ molar ratios from 2 (Figure 4(a)) to 3 (Figure 4(b)), crystals with octahedral morphology of NaX zeolite grains appear with sizes around 1 μm. The amount of cubic particles is decreased obviously at SiO₂/Al₂O₃ molar ratio of 6. The SEM observations are in accordance with the XRD phase analysis, suggesting that higher SiO₂/Al₂O₃ molar ratio is beneficial to the crystallization of NaX zeolites.

The zeolite products prepared with different SiO₂/Al₂O₃ molar ratios were used as adsorbents for ammonium removal. The adsorption tests were conducted at set conditions (zeolite dosage of 0.1 gram, temperature of 32 °C, contact time of 120 min) with initial NH₄⁺ concentration of 50 mg·L⁻¹. Based on the results presented in Table 4, the adsorption performance of zeolite slightly decreases with the increase of SiO₂/Al₂O₃ molar ratio. It suggests that the NaA-type zeolite has a better adsorption performance towards ammonium removal. This possibly could be due to the smaller Si/Al molar ratio in the NaA zeolite framework. This will generate more charge deficiency resulting from the substitution of Si by Al atoms and consequently the framework needs more Na⁺ to compensate for the excess negative charge (Wang et al. 2005; Izidoro et al. 2013) during the synthesis. Thus NaA zeolite exhibits higher cation exchange capacity and more Na⁺ ions could be exchanged by NH₄⁺.

**The effect of H₂O/NaOH molar ratio**

In order to investigate the influence of alkalinity, the products were obtained at different H₂O/NaOH molar ratios of 20, 30 and 40. According to the XRD analysis in Figure 5, the main synthetic product is NaA zeolite. Hydroxysodalite (Na₈[(Al₆Si₆O₂₄)(OH)₂H₂O]) as minor phase coexisted at
H2O/NaOH molar ratio of 20 and 30. Due to their same molar ratio of SiO2/Al2O3 and similar structure, the crystalization of NaA zeolite is often accompanied by the formation of hydroxysodalite (Ma et al. 2017). The SEM images of synthetic products obtained at different alkalinities are shown in Figure 6. It is noted that the crystal size of cubic NaA zeolite increases with the increasing of H2O/NaOH molar ratio. When H2O/NaOH molar ratio increased to 40, the synthesized products had much larger crystal size of around 5 \( \mu \)m (Figure 6(c)). Meanwhile, the zeolite crystals synthesized at H2O/NaOH = 20 have a much smaller size range of 0.5–2 \( \mu \)m (Figure 6(a)). Similar results were also observed in a previous study; the morphology of NaA zeolite strongly depends on the alkalinity of the synthetic system (Liu et al. 2015).

The zeolite products prepared from different H2O/NaOH molar ratios were subjected to ammonium removal tests. From Table 5, it is seen that the zeolite products obtained at higher synthetic alkalinity exhibit better adsorption towards ammonium ion. Based on the SEM observations in Figure 6, it is reasonable to believe that the NaA zeolite products produced at higher alkalinity with small crystal size possess higher surface area which enhances the adsorption kinetics.

**Adsorption kinetics and thermodynamics modeling**

Based on the above results, the adsorbent used here was prepared at optimal conditions, i.e. \( n_{\text{SiO}2}/n_{\text{Al}2O3}/n_{\text{NaOH}}/n_{\text{H}2O} = 2:1:12:240 \), crystallization time of 5 hrs at 100 °C. The variation of ammonium adsorption onto zeolite in terms of time and temperature is shown in Figure 7. The initial
uptake of ammonium ion occurs fast during the first 60 min of contact and is followed by a slower process until a plateau is reached. At 32°C, near equilibrium situation is established within 90 min. When the temperature increases, it is found that the time required for equilibrium state becomes shorter and adsorption capacity of NH₄⁺ onto NaA zeolite is increased, thereby indicating the process is endothermic. At higher temperature, the ammonium diffusion process may be promoted by lower solution viscosity (Motin 2004) and more energetic adsorption sites on the zeolite.

**Pseudo-first- and pseudo-second-order kinetic models**

In order to understand the factors that influence the adsorption rates, the kinetics of ammonium adsorption is studied by modeling based on fitting the time-course experimental results with two of the most applied models: the pseudo-first and pseudo-second-order kinetic reactions. Linear forms of these models are shown in Equations (4) and (5) for the boundary conditions of \( t = 0, q_t = 0 \) and \( t = t, q_t = q_e \):

\[
\ln(q_e - q_t) = \ln q_e - k_1 t \\
t/q_e = 1/k_2 q_e^2 + t/q_e, \quad h = k_2 q_e^2
\]

where \( k_1 \) and \( k_2 \) are the pseudo-first-order rate constant (min⁻¹) and pseudo-second-order rate constant (g·mg⁻¹·min⁻¹), respectively; \( q_t \) (mg·g⁻¹) is amount of ammonium adsorbed at time \( t \) (min), \( q_e \) is adsorption capacity at equilibrium state (mg·g⁻¹), and \( h \) gives the initial adsorption rate (mg·g⁻¹·min⁻¹).

The \( k_1, k_2, \) and \( q_e \) values along with linear correlation coefficient \( R^2 \) for the pseudo-first-order model and pseudo-second-order model are presented in Table 6. It is confirmed that the adsorption of NH₄⁺ on zeolite derived from BF slag could be well fitted by the pseudo-second-order kinetic model, according to its higher value of \( R^2 \). This suggests that the rate-controlling step is likely to involve chemical interactions. The experimental amount of ammonium adsorbed at 90 min is 35, 38.9, 39.8 and 40.9 mg·g⁻¹ at 305, 313, 318 and 323 K, respectively, close to the values of \( q_e \), calculated from the pseudo-second-order kinetic model. Thus, the contact time of 90 min is required for adsorption capacity to reach its equilibrium state. It is seen that the initial adsorption rate, \( h \), increased as the temperature increased. The value of \( h \) increased from 7.162 to 69.56 (mg·g⁻¹·min⁻¹) when temperature increased from 305 K to 323 K, which indicated a fast initial adsorption rate towards ammonium removal at higher temperature.

**The intra-particle diffusion modeling**

Adsorption is often a process integrated with several steps, i.e. the external diffusion (which can be accelerated by
mechanical stirring), the migration of adsorbate through liquid film to adsorbent surface, and the interactions with active surface sites of adsorbent. Although adsorption of ammonium on zeolite followed second-order kinetics, considering zeolite as a highly porous adsorbent, the intraparticle diffusion is likely to play a significant role in the adsorption process. Weber & Morris (1963) introduced a simple expression as shown in Equation (6).

$$q_t = k_i t^{1/2}$$

(6)

where \(k_i\) is the intraparticle diffusion rate constant (mg·g\(^{-1}\)·min\(^{-1/2}\)).

As can be seen in Figure 8, it was found that the plot of \(q_t\) versus \(t^{1/2}\) exhibited an initial linear portion followed by a plateau occurring after 60 min. The linear plots did not pass through the origin clearly, and the value of non-zero intercepts is becoming bigger when the temperature is increasing. Also the correlation coefficients of the intraparticle diffusion plots is low at higher temperatures as shown in Table 7. These observations imply that the effect of the intraparticle diffusion on the adsorption process is lower at higher temperature, and the adsorption process is governed by a mixed controlling mechanism (Sen Gupta & Bhattacharyya 2011). The values of \(k_i\) can be calculated from the slope of curves at different temperatures from intraparticle diffusion plots (Figure 8) and are given in Table 7. The results show that the intraparticle diffusion rate constant decreases with increasing temperatures. Similar behavior was encountered in previous studies (Al-Ghouti et al. 2005; Srivastava et al. 2011). This phenomenon may be attributed to: (i) the strong ionic interaction between the ammonium ions and the zeolite surface enhanced by increased temperature slowing the rate of intraparticle diffusion; and (ii) the decreased ammonium concentration gradient between the inner pores and external surface caused by surface adsorption.

The adsorption thermodynamics evaluation

The adsorption thermodynamic properties in terms of standard Gibbs free energy change (\(\Delta G^o\)), standard enthalpy change (\(\Delta H^o\)), standard entropy change (\(\Delta S^o\)) and activation energy (\(E_a\)) were evaluated. The adsorption \(\Delta G^o\) can be calculated from Equation (7):

$$\Delta G^o = -RT \ln K_c = C_{ae}/C_{se}$$

(7)

where \(K_c\) is the equilibrium constant, \(R\) is the gas constant and is equal to 8.314 J·mol\(^{-1}\)·K\(^{-1}\), \(T\) is the solution temperature, and \(C_{ae}\) and \(C_{se}\) are the amount of NH\(_4^+\) adsorbed on the adsorbent and remaining in the solution at equilibrium state (mg·L\(^{-1}\)), respectively. The standard enthalpy change \(\Delta H^o\) can be determined from the van’t Hoff equation (Equation (8)),

$$\ln K_c(T_3) - \ln K_c(T_1) = -\frac{\Delta H^o}{R} \left( \frac{1}{T_3} - \frac{1}{T_1} \right)$$

(8)

where \(T_3\) and \(T_1\) are different temperatures. The standard entropy change \(\Delta S^o\) is given by

$$\Delta S^o = \frac{\Delta G^o - \Delta H^o}{T}$$

(9)

The pseudo-second-order rate constant of adsorption, \(k_i\), is expressed as a function of temperature by the
The change of thermodynamic parameters $\Delta G$, $\Delta H$, $\Delta S$

<table>
<thead>
<tr>
<th>T (K)</th>
<th>$K_c$</th>
<th>$\Delta G$ (kJ·mol$^{-1}$)</th>
<th>$\Delta H$ (kJ·mol$^{-1}$)</th>
<th>$\Delta S$ (kJ·K$^{-1}$·mol$^{-1}$)</th>
<th>$E_a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>305</td>
<td>2.27</td>
<td>--2.09</td>
<td>30.51</td>
<td>0.107</td>
<td>92.3</td>
</tr>
<tr>
<td>313</td>
<td>3.55</td>
<td>--3.08</td>
<td></td>
<td></td>
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<tr>
<td>318</td>
<td>3.90</td>
<td>--3.60</td>
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<td></td>
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<tr>
<td>323</td>
<td>4.49</td>
<td>--4.06</td>
<td></td>
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</tr>
</tbody>
</table>

Arrhenius-type relationship shown in Equation (10).

$$\ln k = \ln A - \frac{E_a}{RT}$$

(10)

where $E_a$ is the Arrhenius activation energy of adsorption, representing the minimum energy that reactants must have for the reaction to proceed, and $A$ is the Arrhenius factor.

As shown in Table 8, a positive standard enthalpy change of 30.51 kJ·mol$^{-1}$ obtained in this study indicates that the adsorption of NH$_4^+$ by the zeolite adsorbent is endothermic, which is further supported by the increase in the adsorption of NH$_4^+$ with temperature. A negative change in adsorption standard Gibbs free energy reveals that the adsorption reaction is a spontaneous process. The standard Gibbs free energy becomes more negative when temperature is increased from 305 K to 323 K, suggesting the adsorption process is more favored at high temperatures. The activation energy of 92.3 kJ·mol$^{-1}$ can be calculated based on the pseudo-second-order rate constant variation. The relatively high value of activation energy shows a high impact of temperature on the adsorption rate and further provides evidence that the adsorption of ammonium ion onto zeolite is mainly a chemical reaction rather than physisorption (Al-Ghouti et al. 2005) and this can be related to the fact that the adsorption process is activated by the ion-exchange reaction as shown in Equation (11).

$$(\text{Zeolite} - \text{Na}^+) + \text{NH}_4^+ \rightarrow (\text{Zeolite} - \text{NH}_4^+) + \text{Na}^+$$

(11)

The effect of initial ammonium concentration and adsorption isotherms

The effect of initial NH$_4^+$ concentration was investigated using synthetic solution containing 30, 50, 80, 100, and 150 mg·L$^{-1}$ of ammonium ion at 32 °C with 0.1 gram of zeolite and 120 min of contact time. As shown in Table 9, the NH$_4^+$ adsorption capacity increases with the increasing of initial ammonium concentration. Meanwhile, a decrease in removal efficiency when NH$_4^+$ concentration increases is observed.

The adsorption equilibrium data of ammonium on to the zeolite is analyzed in terms of Langmuir and Freundlich isothermal models. The Langmuir isotherm is applied to describe the formation of a monolayer on the surface of adsorbent, assuming that the finite number of energetic adsorption sites are homogeneous and can be saturated (Aksu 2005). The corresponding model is shown in Equation (12).

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m}$$

(12)

where $C_e$ (mg·L$^{-1}$) and $q_e$ (mg·g$^{-1}$) are the concentrations of ammonium in the solution and adsorbed at equilibrium state, respectively; $q_m$ (mg·g$^{-1}$) and $K_L$ (g$^{-1}$) are the terms related to maximum monolayer coverage capacity and Langmuir adsorption constant, respectively.

The Freundlich isotherm assumes the adsorbent has a heterogeneous surface with non-uniform distribution of adsorption sites. Freundlich parameters can be determined by the following Equation (13).

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

(13)

where $K_F$ (mg·g$^{-1}$) is the multilayer adsorption capacity, while $1/n$ is a function of the strength of adsorption.

The linear plots of the Langmuir isotherm and Freundlich isotherm are shown in Figure 9. The Langmuir model yields a better fit ($R^2 = 0.973$) to the data compared with that of the Freundlich model ($R^2 = 0.93$), which suggests the adsorption of NH$_4^+$ on the zeolite is a monolayer adsorption. The maximum amount of NH$_4^+$ adsorbed by the zeolite at equilibrium was calculated from the slop of the Langmuir linear plot.
To give an illustration of the potential of BF slag-derived zeolite in ammonium removal, the maximum adsorption capacities of natural or artificial zeolites reported in the literature are compared. As shown in Table 10, the maximum ammonium adsorption capacity for zeolite derived from BF slag is 83.3 mg·g⁻¹, and that is much higher than zeolites synthesized from other raw materials, except for the zeolite from coal fly ash, where a maximum ammonium adsorption capacity of 109.53 mg·g⁻¹ is reported. Therefore, by comparing the results of the present work with those reported in literature, it is found that the BF slag could be an alternative precursor for zeolite production and further used as an efficient adsorbent for ammonium removal.

**CONCLUSION**

In the present paper, NaA zeolite was synthesized successfully using acid leaching residue of BF slag. The effects of SiO₂/Al₂O₃ and H₂O/NaOH molar ratio on the crystal phase and microstructure of prepared zeolites were investigated. The results indicated that well crystallized cubic NaA zeolite with small crystal size could be obtained with SiO₂/Al₂O₃ and H₂O/NaOH molar ratio fixed at 2.0 and 20.

The synthesized NaA zeolite shows an effective removal capacity for ammonium. Ammonium adsorption kinetics could be well-described by the pseudo-second-order model. The intra-particle diffusion model analysis reveals the adsorption is governed by a mixed controlling mechanism consisting of the ion-exchange and intra-particle diffusion process. Thermodynamic properties evaluation shows that the ammonium adsorption onto zeolite is a spontaneous and endothermic natural process. The activation energy of 92.3 kJ·mol⁻¹ is obtained based on the pseudo-second-order rate constant, which implies that the ammonium adsorption is a chemical reaction rather than physisorption. The adsorption isotherms of ammonium fit well with the Langmuir isotherm model, and the maximum adsorption capacity is 83.3 mg·g⁻¹ at 32 °C. It demonstrated that the low cost NaA zeolite can be derived from BF slag waste and used for environmental remediation; the synchronous minimization of BF slag and ammonia nitrogen contamination could be achieved.
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