Effect of competing ions and causticization on the ammonia adsorption by a novel poly ligand exchanger (PLE) ammonia adsorption reagent
Quanzhou Chen, Kanggen Zhou, Yuanjuan Hu, Fang Liu and Aihe Wang

ABSTRACT
In this paper, a poly ligand exchanger, Cu(II)-loaded chelating resin named ammonia adsorption reagent (AMAR), bearing the functional group of weak iminodiacetate acid, was prepared to efficiently remove ammonia from solutions. Batch adsorption equilibrium experiments were conducted under a range of conditions. The effects of pH on the removal of ammonia by AMAR were investigated at 25°C. The copper loaded on the resin forms a complex with NH₃ in solution under alkaline condition. The effect of alkaline dosage (AD) on the ammonia adsorption was investigated. The maximum breakthrough bed volumes were obtained when the AD was set as 0.75 mmol OH⁻/C₀/mL. The higher AD did not guarantee the better ammonia removal efficiency due to the forming of Cu(OH)₂ precipitate between OH⁻/C₀ in solutions and Cu(II) on the resin. The effect of competing ions on the adsorption breakthrough curve of virgin AMAR and causticized AMAR was also investigated. The results demonstrated that the existence of competing ions had a negative impact on the adsorption capacity for both virgin AMAR and causticized AMAR. After causticization, the AMAR was more resistant to the competing ions comparing with virgin AMAR. The bivalent Ca²⁺ affects the ammonia adsorption more than does the monovalent Na⁺.

Key words | adsorption, ammonia removal, causticization, competing ion, ligand exchange

INTRODUCTION
Ammonia nitrogen (NH₃-N) is considered as a major pollutant in municipal wastewater as well as industrial wastewater and has got lots of attention in recent years (Zhang et al. 2015; Nosratinia et al. 2014; Yuan et al. 2016). Ammonia nitrogen, as an important chemical reagent and nutrient, is commonly present in municipal and industrial wastewater from sources such as meat-processing facilities, coke plants, pharmaceutical plants, glass production plants, cellulose manufacturers and paper manufacturing plants (Huang et al. 2000; Huang et al. 2008; Miladinovic & Weatherley 2008; Hasanoglu et al. 2010; Goncalves et al. 2011; Li et al. 2011). NH₃-N is an important nutrient for aquatic plants and algae, but excess levels of NH₃-N in water can result in the decline of dissolved oxygen and water quality. Water eutrophication, which mainly results from excessive emissions of ammonia, is currently the most widely recognized environmental problem. Moreover, wastewater containing ammonia is often toxic: it can be fatal to fish and other aquatic animals at concentrations ranging of 0.2–0.5 mg/L (Thurston et al. 1981; Wiesmann 1994; Park et al. 2010). The non-biodegradable nature of ammonia-containing wastewater can lead to highly inefficient treatment. In such instances, the removal of ammonia from aqueous solution is necessary to maintain proper water quality.

According to previous studies, conventionally used methods include biological and physico-chemical treatment, such as biological nitrification and denitrification, air stripping, precipitation, break-point chlorination, ion exchange using fixed or fluidized-bed biological reactors, and activated carbon adsorption in conjunction with suspended solids removal by sedimentation. Biological nitrification and denitrification are commonly used to treat ammonia-containing wastewater for economic reasons (Liao & Mayo 1974; Dudas 1981; Loucks et al. 1981; Abdelrazig & Sharp 1988; Wang et al. 2006; Bashir et al. 2010; Yoshikawa 2017). The non-biodegradable nature of ammonia-containing wastewater can lead to highly inefficient treatment. In such instances, the removal of ammonia from aqueous solution is necessary to maintain proper water quality.

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et al. 2012; Barbosa et al. 2013). However, this form of treatment is not effective when the ammonia concentration exceeds 100 mg/L, which inhibits the growth of microorganisms due to the lack of adequate carbon sources. Moreover, biological methods do not respond well to shock loads of ammonia (Carrera et al. 2004; Zhang et al. 2009; Hasanoglu et al. 2010). The ammonia removal rate achieved by air-stripping processes is surprisingly high at high concentrations, but the efficiency is significantly impaired by low temperature and pH (Liao & Mayo 1974). Reactions between CO₂ and some metal ions can also contribute to scaling and fouling in packed towers. Additionally, air stripping is a time-consuming process when traditional equipment is used (Wang et al. 2006; Basakciardan-Kabakci et al. 2007). The other methods have their insuperable disadvantages when applied in industry, too (Takaç et al. 1998; Onyango et al. 2004; Gunay et al. 2008; Diaz et al. 2011).

Among current technologies, ion exchange has received considerable interest due to its high efficiency and the exchange substrate can easily be recovered and reused by regeneration for the removal of ammonia (Lee et al. 2007; Alyüz & Veli 2009). Standard ion exchange methods are increasingly being applied in wastewater treatment, especially in the removal of ammonia nitrogen, heavy metals and other contaminants that cannot be efficiently or commercially eliminated using traditional methods (Vilensky et al. 2002; Jodra & Mijangos 2003; Diniz et al. 2005; Hsu-Kim & Sedlak 2005; Wolowicz & Hubicki 2012). Nevertheless, ion exchange technology is still being developed at the laboratory scale, and research has concentrated on the effect of ammonia adsorption onto various types of zeolite (e.g., clinoptilolite, mordenite, chabasite, carphostilbite) and ion exchange resins (Wang et al. 2006; Mohan & Pittman 2007; Wang et al. 2007; Halim et al. 2010; Li et al. 2010; Fu & Wang 2011; Zhou & Boyd 2014; Ding & Sartaj 2015; Mochizuki et al. 2016; Seredych et al. 2016). Despite its advantages over traditional methods, ion exchange is limited in real wastewater applications because of the presence of competitive ions in solution and the unstable exchange capacity of ammonium ions (Farkaš et al. 2005).

Organic ion exchange resins have gained the attention of researchers for their mechanical stability, high exchange capacity, and ion exchange rate (Mustafa et al. 1998). The concept of ligand-exchange-based separation was first suggested by Helfferich. Transition metal ions (e.g., Cu²⁺, Ni²⁺, Zn²⁺, Co²⁺, Co³⁺) are immobilized onto the functional groups of a hosting resin to create a polymeric ligand resin. The potential ligands such as NH₃ were adsorbed through the formation of complexes with metals in the cation exchanger. The coordination number between the ligands and transition metal ions was usually very high, which means the restricted adsorption sites were used more efficiently by the formation of complexes that can achieve high capacities and selectivity compared with traditional ion exchange methods (Helfferich 1962). Separation processes based on ion exchange have also been applied in various other ways. Recently, the use of poly ligand exchangers (PLEs) to remove anions (F⁻, HAsO₄²⁻, PO₄³⁻, and ClO₄⁻) and organic neutral ligands has received extensive attention, and this method has demonstrated great potential in the treatment of wastewater. Literature discussing the use of ligand exchange to remove ammonia, however, is rare (An et al. 2005; Xiong et al. 2006; Viswanathan & Meenakshi 2008).

Mustafa et al. (1998) observed that Amberlite IRC-50 loaded with Cu²⁺, Ni²⁺, and Zn²⁺ served as a ligand exchanger. However, the adsorption properties and other operating conditions of the Amberlite IRC-50 were not described. Typical ‘ligand exchange’ reactions can be described as follows:

$$\text{(R)}_2\text{[Cu(H₂O)₄]²⁺} + 4\text{NH}_3 ⇌ \text{(R)}_2\text{[Cu(NH₃)₄]²⁺} + 4\text{H₂O}$$

(1)

where R is the organic part in the resin.

In this paper, Cu was loaded on a chelating resin with the functional group of iminodiacetate to form a new PLE with high affinity and adsorption capacity for ammonia nitrogen. Copper was fixed onto the resin in ionic bond form or in covalent bond form, which strengthened the connection between copper and the resin and weakened the competitive effect of ammonia adsorption reagent (AMAR) for ammonia adsorption in the presence of competing ions Na⁺ and Ca²⁺. Moreover, the copper loaded onto the resin was also a good ligand exchanger for NH₃ as the neutral ligand. The purpose of this study is to investigate the sorption property of ammonia on AMAR and find out the optimum adsorption conditions for ammonia removal. The use of causticization as a pretreatment process for the enhancement of ammonia adsorption on AMAR was investigated using a laboratory scale fixed bed column. The effect of alkaline dosage (AD) on the ammonia adsorption on the AMAR was investigated. Effects of competing ions Na⁺ and Ca²⁺ on the adsorption of both virgin AMAR and causticized AMAR were investigated through breakthrough curve experiments.
EXPERIMENTAL

Materials and apparatus

A macroporous styrene type chelating ion exchange resin with weak iminodiacetate acid functional groups was purchased from Shanghai Huizhu Resin Co., Ltd, China. The physical properties and specifications reported by the supplier are shown in Table 1. Analytical reagent grade copper sulfate pentahydrate (CuSO₄·5H₂O) loaded on the resin was applied as the modifier without further purification. The other chemical reagents used in this study, including ammonium chloride, concentrated hydrochloric acid, sodium hydroxide, sodium chloride, calcium chloride and ammonium chloride, were all analytical reagent grade and were used as received. Metal standard solutions were prepared by diluting 1,000 mg/L (Merck) solutions. Ammonia-simulated wastewaters with various ammonia concentrations were prepared by diluting the ammonium chloride solutions.

The pH of the solutions was measured using a Mettler Toledo 320 pH meter. The resin was dried in a 101 electric blast-drying oven. The ammonia and Cu²⁺ concentrations were determined by using Nessler reagent and copper reagent (diethylenediaminotetraacetic acid) with a VIS-7220 spectrophotometer. The detection limits for ammonia and copper using the spectrophotometric method were 0.2–2 mg/L. The resins that were immersed in different solutions were all shaken in an SHZ-82A constant-temperature water-bath oscillator.

Table 1 | Physical properties and specifications of the virgin resin

<table>
<thead>
<tr>
<th>Matrix</th>
<th>Styrene-divinylbenzene</th>
</tr>
</thead>
<tbody>
<tr>
<td>Functional group</td>
<td>Iminodiacetate</td>
</tr>
<tr>
<td>Structure</td>
<td>Macroporous</td>
</tr>
<tr>
<td>pH range</td>
<td>0–14</td>
</tr>
<tr>
<td>Ion type</td>
<td>Na⁺ form</td>
</tr>
<tr>
<td>Particle size (0.4–1.25 mm)</td>
<td>≥95%</td>
</tr>
<tr>
<td>Loading density</td>
<td>760 kg/m³</td>
</tr>
<tr>
<td>Coefficient of uniformity</td>
<td>≤1.6</td>
</tr>
<tr>
<td>Wet superficial density</td>
<td>0.72–0.76 g/mL</td>
</tr>
<tr>
<td>Wet density</td>
<td>1.10–1.16 g/mL</td>
</tr>
<tr>
<td>Loading density (wet)</td>
<td>0.6 mL/mL</td>
</tr>
<tr>
<td>Volume total exchange capacity</td>
<td>≥1.8 mmol/mL</td>
</tr>
</tbody>
</table>

AMAR fabrication

The macroporous styrene type chelating ion exchange resin AMAR was sufficiently washed with deionized water, before adding to the ion exchange column, to remove the possible dissolved salts or other contaminants (Naddafi et al. 2015). Saturated copper sulfate solution was passed slowly through the ion exchange column until the effluent reached a copper concentration that was identical to that of the initial solution to create a saturated Cu(II)-loaded resin. Next, the resin was washed repeatedly with deionized water until the effluent copper concentration was less than 0.5 mg/L and the Cu(II)-loaded resin was dried in a drying oven at 48 °C for 48 h. The amount of Cu(II) ions loaded onto the resin was determined by washing off the copper from the resin with concentrated hydrochloric acid and deionized water.

Batch adsorption equilibrium

The R-Cu resin was fixed to 1 g when it was added into conical flask and the flasks were completely sealed. Batch adsorption equilibrium experiments of R-Cu were conducted in an SHZ-82A constant-temperature water-bath oscillator for 10 h at 25 °C. Then, the ammonia concentration and solution pH at equilibrium were determined to illustrate the relationships between them. The pH of the solutions were adjusted to constant values ranging from 3.5 to 11 by drop-wise addition of 0.1 mol/L HCl or 0.1 mol/L NaOH solutions. The initial pH in the batch experiments were 3.5, 4.05, 4.89, 5.74, 6.37, 7.04, 7.56, 8.01, 8.53, 8.85, 9.31, 10.06, 10.54 and 11.1. The initial ammonia concentration was set as 200 mg/L in view of the convenience of the calculation of ammonia adsorption capacity. Samples were withdrawn from these solutions and the solution ammonia concentrations were determined over a comparatively long time to reach the equilibrium. All other procedures were conducted as previously described.

Causticization

A designated amount of AMAR (50 mL) was added to each flask. Then 1 mol/L NaOH was added into the flasks. The AD was 25, 37.5 and 50 mmol by adding 1 mol/L NaOH solution to each flask. The final solution volume was 200 mL by adding the corresponding volume of deionized water. The mixtures were shaken for 2 h in a constant-temperature water-bath oscillator at 25 °C. After causticization, the mixtures of AMAR and solutions were filtered.
and washed sufficiently with deionized water. The alkaline concentration was determined by acid–base titration. The AD (mmol/mL) was calculated by using the following equation:

\[
AD = \frac{C_{OH} - C_{eqOH}}{V_{resin}} \times V_{OH}
\]  

(2)

where \(C_{OH}\) and \(C_{eqOH}\) are the initial and final equilibrium alkaline concentrations in solution (mg/L), respectively. \(V_{OH}\) is the alkaline solution volume. \(V_{resin}\) represents the moist resin volume.

Then the different causticization ADs of 0.5, 0.75 and 1 mmol/mL AMAR were obtained.

**Column experiments**

Column experiments were performed in a glass tubular reactor. A certain amount of AMAR R-Cu was used to fill a miniature ion exchange column (diameter of 15.6 mm, 700 mm in length). In the following breakthrough curve experiments, the resin dosage was fixed to 1 g. The initial solution pH was 5.4 and the initial concentration of the simulated ammonia wastewater was 980 mg/L. The simulated wastewater was prepared by diluting the ammonium chloride solution to an appropriate concentration and passing the resulting solution through the ion exchange column at a constant flow of 1 mL per minute. The effluent was fractionated into 100 mL portions, and the ammonia concentrations, pH and copper concentrations in each fraction were determined. The breakthrough bed volume (BV) was calculated for the breakthrough curve to demonstrate the adsorption properties. BV refers to the volume of water passed through the bed expressed in terms of the total volume of the packed bed. BV is defined as:

\[
BV = \frac{\text{Volume of treated solution}}{\text{Volume of resin}}
\]  

(3)

The saturation point of ammonia was set as 15 mg/L based on the Class A of the Integrated Wastewater Discharge Standard (GB8978-1996). The removal efficiency (%) was calculated by using the following equation (Soetardji et al. 2015):

\[
\text{Removal efficiency} (\%) = \frac{C_0 - C_e}{C_0}
\]  

(4)

where \(C_0\) (mg/L) and \(C_e\) (mg/L) are the initial and final equilibrium ammonia concentrations in solution (mg/L), respectively.

The calculation of adsorption breakthrough curves in the fixed bed was a complex issue. Researchers have done lots of work on the adsorption calculation and model-building to calculate the adsorption parameters in a fixed bed (Grubner & Burgess 1979; Brosillon et al. 2001; Liu et al. 2007; El-Sayed et al. 2016). To simplify the calculation, the adsorption capacity \(q_e\) was calculated using the following equation:

\[
q_e = \int_0^V (C_i - C_V) dV
\]  

(5)

where \(C_i\) is the initial ammonia concentration in solution. \(C_V\) is the effluent ammonia concentration when the total volume of treated wastewater is \(V\) (mL).

**Effect of competing ions on the adsorption of virgin AMAR**

The virgin Cu(II)-loaded resin was used as an adsorbent for this experiment. The initial ammonia concentration in solution was 980 mg/L when diluted by high concentrations of ammonium chloride solution, and the effects of other competing ions, such as \(Na^+\) and \(Ca^{2+}\), on the Cu(II)-loaded ammonia adsorbent were also considered. The concentration of competing ions such as \(Na^+\) (1,000, 5,000 and 10,000 mg/L) and \(Ca^{2+}\) (100, 200 and 500 mg/L) was adjusted by different amounts of NaCl and CaCl\(_2\), respectively. All the experiments were conducted at room temperature 25°C. The S-shape and the appearance of the breakthrough point describe the typical behavior of the ion exchange resins inside the fixed bed column systems.

**Effect of competing ions on the adsorption of causticized AMAR**

The causticized AMAR (0.75 mmol/mL) was chosen as the ammonia adsorbent. Sodium chloride and calcium chloride were used to adjust the \(Na^+\) and \(Ca^{2+}\) concentrations in simulated wastewater. Effect of causticization on the breakthrough curve of AMAR for ammonia removal in presence of competing ions was investigated. All the adsorption breakthrough curve experiments were conducted at room temperature, 25°C.
RESULTS AND DISCUSSION

Effect of pH

Figure 1 shows the batch adsorption equilibrium of R-Cu for ammonia removal without Na\(^+\) and Ca\(^{2+}\) as the competing ions in various pH conditions. Synthetic water containing ammonia at an initial concentration of 200 mg/L was used.

As demonstrated in Figure 1, the solution pH had an important influence on the equilibrium ammonia concentration and the ammonia removal efficiency. At a pH lower than 7, the equilibrium ammonia concentration decreased at an increasing rate. The ammonia removal efficiency increased with the increasing of solution pH but was lower than 10%. As the solution pH increased from 7 to 9.5, the equilibrium ammonia concentrations decreased sharply with the increasing of pH. The ammonia removal efficiency significantly increased from 19.4% (pH = 7) to 91.6% (pH = 9.31). When the solution pH was higher than 9.5, the removal efficiency decreased as the pH increased. There existed two forms of ammonia, un-ionized (NH\(_3\)) and ionized (NH\(_4^+\)), in the aqueous solutions (Emerson et al. 1975). The ratio of the two forms of ammonia changes with the changing of solution pH and temperature (Lin & Wu 1996). The two forms of ammonia follow the equation (Udert et al. 2003):

\[
\text{NH}_4^+ + \text{OH}^- \leftrightarrow \text{NH}_3 + \text{H}_2\text{O} \quad K_b = 1.8 \times 10^{-5} \quad (6)
\]

1. At a pH lower than 7, ammonia exists as stable ionized NH\(_4^+\).
2. As the solution pH increases to 7–9.5, NH\(_4^+\) is gradually converted to NH\(_3\) and the NH\(_3\) concentration rapidly increases, which results in good conditions for the adsorption of ammonia onto the Cu(II)-loaded resin. As shown in Equation (1), the ammonia could be removed more easily as NH\(_3\) than as NH\(_4^+\). This difference explains how the ammonia removal efficiency changes with the solution pH. F. Helfferich (Helfferich 1962) studied using Amberlite IRC-50 resin as a ligand exchanger for removing ammonia and arrived at a similar conclusion.
3. In addition, Doury-Berthod et al. (1977) studied the distribution equilibrium of NH\(_3\) between solutions and a copper iminodiacetic resin over a pH range of 9–12. The reactions in these solutions can be described by the following equation:

\[
\text{RCu} + \text{A}^- + \text{iNH}_3 + \text{NH}_4^+ \leftrightarrow \text{RCuA(NH}_3\text{)i} + \text{NH}_4^+ \quad (7)
\]

It is clear that NH\(_3\) is the predominant species above pH 9.5 according to Equation (6). Simultaneously, a sharp increase in the OH\(^-\) concentration would result in forming the unexpected precipitate Cu(OH)\(_2\) and lead to the decrease of Cu(II) loaded on the resin. The drop-off of Cu(II) on the resin restricted the forming of copper complex with the neutral
ligand NH$_3$ and caused the reduction in ammonia adsorption.

**Effect of AD on the ammonia adsorption breakthrough curve of AMAR**

The causticized AMAR resin with different AD was used as the ammonia adsorbent. All the experiments were conducted at room temperature of 25°C by passing the simulated ammonia wastewater through a packed bed column in a down-flow mode.

Figure 2 shows effect of AD on the breakthrough curve of AMAR for ammonia adsorption. It is demonstrated that the ammonia adsorption capacity and breakthrough BV were significantly increased with the increasing of causticization AD. The breakthrough BV of AMAR for ammonia adsorption was 10.83, 11.90, 14.84 and 14.81, while the corresponding causticization ADs were 0, 0.5, 0.75 and 1 mmol/mL. The higher the breakthrough BV, the more wastewater could be treated. When the AD increased from 0.75 mmol/mL to 1 mmol/mL, the breakthrough BV slightly changed from 14.84 to 14.81. Considering that the main technical index in application is the amount of treated wastewater per unit volume, the causticization AD was suggested to be 0.75 mmol/mL. Table 2 shows the calculation results for the breakthrough curve of AMAR for ammonia adsorption under various causticization conditions.

**Effect of competing ions on the breakthrough curve of R-Cu**

In the industrial application of any sort of absorbents, there may exist competing adsorption between the target waste and the competing ions in solutions, such as ions (Na$^+$, Ca$^{2+}$, K$^+$, Mg$^{2+}$, etc.), anions (PO$_4^{3-}$, Cl$^-$, SO$_4^{2-}$, etc.) or other micro-molecular organic pollutants. The existence of competing ions may have negative effect on the adsorption of ammonia by AMAR due to the limited prime adsorption sites in resins. The effect of competing ions Na$^+$ and Ca$^{2+}$ on the adsorption process was studied to illustrate the adsorption property of AMAR under complex and changeable wastewater conditions.

**Effect of competing ions on the breakthrough curve of virgin R-Cu**

The effect of Na$^+$ concentration on the breakthrough curve of virgin AMAR for ammonia adsorption is presented in Figure 3 and the calculation results are listed in Table 3. As shown in Figure 3 and Table 3, the breakthrough point can be measured to determine the adsorption properties of the column. The effluent ammonia concentration was less than 10 mg/L when the BV was less than 10 in the solution without competing ions. The breakthrough BV of the virgin AMAR decreased sharply with the increasing concentration.

![Figure 2](https://iwaponline.com/wst/article-pdf/75/6/1294/454633/wst075061294.pdf)
of Na\(^+\) in solutions. The ammonia adsorption BVs of virgin AMAR decreased dramatically from 10.83 (0 mg/L Na\(^+\)) to 2.32, 1.83 and 0.72 when the Na\(^+\) concentrations were 1,000, 5,000 and 10,000 mg/L, respectively. Meanwhile, the ammonia adsorption capacity of virgin AMAR decreased from 14.24 mg/mL (0 mg/L Na\(^+\)) to 7.7, 6.32 and 4.91 mg/mL under the corresponding Na\(^+\) concentrations. The results inferred that the virgin AMAR without causticization with NaOH was sensitive to the existence of competing ions in solutions. The existence of competing Na\(^+\) ions had a negative effect on the ammonia adsorption.

Effect of competing Ca\(^{2+}\) ions on the breakthrough curve of virgin AMAR for ammonia adsorption is illustrated in Figure 4 and the calculation results are listed in Table 4. It is inferred that the ammonia adsorption breakthrough BV decreased dramatically with the increasing of Ca\(^{2+}\) concentration. The ammonia adsorption BVs of virgin AMAR decreased dramatically from 10.83 (0 mg/L Ca\(^{2+}\)) to 1.91, 0.92 and 0.41 when the Ca\(^{2+}\) concentrations were 100, 500 and 1,000 mg/L, respectively. The ammonia adsorption capacity of virgin AMAR decreased from 14.24 mg/mL (0 mg/L Ca\(^{2+}\)) to 7.64, 6.94 and 5.55 mg/mL. Ca\(^{2+}\) resulted in the reduction of adsorption capacity as well as the breakthrough BV even at lower concentrations. Analysis shows that the weakening effect of Ca\(^{2+}\) is more than the effect of Na\(^+\) in the adsorption process of virgin AMAR.

The elution pH values versus the BVs in the presence of competing ions in the column adsorption experiment are shown in Figure 5. The elution pH decreased with the increasing concentration of competing ions. The elution pH reached the maximum value in no competing condition. The former experiments showed that the breakthrough BV of virgin AMAR decreased with the increasing of competing ions concentration and the optimum adsorption pH was 9.5 according to Figure 1, whereas the elution pH of virgin AMAR was about 3 to 5 according to Figure 5 and not in the optimum pH range. The increasing elution pH demonstrated that the adsorption mechanism of virgin AMAR is mainly ion exchange but not ligand exchange. The NH\(_4^+\) concentration in solutions increased with the increasing concentration of H\(^+\) in AMAR resin. The leaking of H\(^+\) in solutions by ligand sorption leads to the reduction of solution pH in elution. Ions in solutions are able to compete with ammonia for the limited

<table>
<thead>
<tr>
<th>Causticization AD mmol/mL</th>
<th>Breakthrough BV</th>
<th>Breakthrough AC mg/mL</th>
<th>Ammonia AC mg/mL</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>10.83</td>
<td>10.58</td>
<td>14.24</td>
</tr>
<tr>
<td>0.5</td>
<td>11.90</td>
<td>11.53</td>
<td>15.52</td>
</tr>
<tr>
<td>0.75</td>
<td>14.84</td>
<td>14.44</td>
<td>17.14</td>
</tr>
<tr>
<td>1</td>
<td>14.81</td>
<td>14.86</td>
<td>18.32</td>
</tr>
</tbody>
</table>

Figure 3 | Effect of Na\(^+\) concentration on the adsorption breakthrough curve of virgin AMAR for ammonia.
adsorptive sites, resulting in a decrease in the amount of ammonia adsorbed. The basic ligand chemistry theory suggests that a copper and ammonia complex would form under the weak alkaline condition and the optimum pH would be approximately 9. Zhang et al. (2012) had also investigated the recovery of ammonia–copper complexes from wastewater and found that the ammonia–copper complex formed when the solution pH > 8.83 in the presence of excessive ammonia. An assumption was proposed that the improving of solution pH may promote the adsorption of ammonia.

**Effect of competing ions on the breakthrough curve of causticized R-Cu**

Figure 6 shows the effect of Na\(^+\) concentrations as the competing ion on the adsorption breakthrough curve of AMAR. Table 5 shows the calculation results of effect of Na\(^+\) concentration on the adsorption breakthrough process. The initial inflow pH of simulated wastewater was 7.8 and the ammonia concentration was determined as 980 mg/L.

It is illustrated from Figure 6 and Table 5 that the adsorption breakthrough BV of AMAR for ammonia adsorption decreased with the increasing of Na\(^+\) concentration. The ammonia adsorption BV decreased from 14.84 (no competing ions) to 14.16, 10.35 and 6.29 when the Ca\(^{2+}\) concentrations were 100, 500 and 1,000 mg/L, respectively. The corresponding ammonia adsorption capacity decreased from 17.14 mg/mL (no competing ions) to 16.16, 15.32 and 9.48 mg/mL, respectively.

The effect of Ca\(^{2+}\) as the competing ion on the ammonia adsorption breakthrough curve of causticized AMAR and the calculation results are shown in Figure 7 and Table 6. It was inferred that the adsorption breakthrough BV decreased with the increasing of Ca\(^{2+}\) concentration. The ammonia adsorption BV decreased from 14.84 (no competing ions) to 11.38, 6.33 and 5.12 when the Ca\(^{2+}\) concentrations were 100, 500 and 1,000 mg/L, respectively. The corresponding ammonia adsorption capacity decreased from 17.14 mg/mL (no competing ions) to 14.88, 10.35 and 8.7 mg/mL, respectively.

<table>
<thead>
<tr>
<th>Na(^+) concentration mg/L</th>
<th>BV</th>
<th>Ammonia adsorption capacity mg/mL</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>10.83</td>
<td>14.24</td>
</tr>
<tr>
<td>1,000</td>
<td>2.32</td>
<td>7.7</td>
</tr>
<tr>
<td>5,000</td>
<td>1.83</td>
<td>6.32</td>
</tr>
<tr>
<td>10,000</td>
<td>0.72</td>
<td>4.91</td>
</tr>
</tbody>
</table>

**Figure 4** | Effect of Ca\(^{2+}\) concentration on the adsorption breakthrough curve of virgin AMAR for ammonia.
Similarly, the competing ions dramatically affected the adsorption capacity of AMAR for ammonia, while the weakening effect was much less effective comparing the causticized AMAR to the virgin AMAR. It was confirmed that the causticization process did have an enhancement effect on AMAR for ammonia adsorption. To further confirm our assumption, the elution pH versus the BV of causticized AMAR is shown in Figure 8. As shown in Figure 8, the elution pH reduced with the increasing of BV. The solution pH reduced to some extent with the increasing of competing ions in solutions, but it did not drop below 8.2. The existence of two forms of ammonia, un-ionized (NH₃) and ionized (NH₄⁺), and their changing from one to another under different conditions contribute a lot to the adsorption efficiency. When the solution pH in solution or the resin is relatively low (pH < 7), the ammonia in solutions mainly exists in ionized form (NH₄⁺). The main reaction in solution is ion exchange. The NH₄⁺ in solutions exchanges with H⁺ in AMAR. The more the NH₄⁺ adsorbed onto the resin by ion exchange, the lower solution pH is, which explains the rapid pH decrease when the BV is relatively low (BV < 10). The elution pH of the breakthrough curve of virgin AMAR was 3 to 5 at the beginning of adsorption, which demonstrated that the ion exchange reaction played a leading role and released mounts of H⁺ into solutions. Nevertheless, the optimum adsorption pH was about 9 to 9.5, which was confirmed by former experiments. The acidic solution condition had a negative effect on the adsorption by AMAR.

For the adsorption breakthrough of causticized AMAR, the H⁺ released at the beginning of the adsorption may react with the OH⁻ adsorbed onto the AMAR. And that was why the solution pH of the causticized AMAR did not react intensely but decreased at a certain speed and still remained above 8. The alkaline condition was also beneficial to the ammonia adsorption. The two mechanisms of ligand exchange and ion exchange are given by Equations (8) and (9) (Mustafa et al. 1998).

\[
R_nCu^{2+} + xNH_4^+ \leftrightarrow R_nCu^{2+}(NH_3)_x + xH^+ \tag{8}
\]

<table>
<thead>
<tr>
<th>Ca²⁺ concentration mg/L</th>
<th>BV</th>
<th>Ammonia adsorption capacity mg/mL</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>10.83</td>
<td>14.24</td>
</tr>
<tr>
<td>100</td>
<td>1.91</td>
<td>7.64</td>
</tr>
<tr>
<td>500</td>
<td>0.92</td>
<td>6.94</td>
</tr>
<tr>
<td>1,000</td>
<td>0.41</td>
<td>5.55</td>
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</tbody>
</table>

Similarly, the competing ions dramatically affected the adsorption capacity of AMAR for ammonia, while the weakening effect was much less effective comparing the causticized AMAR to the virgin AMAR. It was confirmed that the causticization process did have an enhancement effect on AMAR for ammonia adsorption. To further confirm our assumption, the elution pH versus the BV of causticized AMAR is shown in Figure 8. As shown in Figure 8, the elution pH reduced with the increasing of BV. The solution pH reduced to some extent with the increasing of competing ions in solutions, but it did not drop below 8.2. The existence of two forms of ammonia, un-ionized (NH₃) and ionized (NH₄⁺), and their changing from one to another under different conditions contribute a lot to the adsorption efficiency. When the solution pH in solution or the resin is relatively low (pH < 7), the ammonia in solutions mainly exists in ionized form (NH₄⁺). The main reaction in solution is ion exchange. The NH₄⁺ in solutions exchanges with H⁺ in AMAR. The more the NH₄⁺ adsorbed onto the resin by ion exchange, the lower solution pH is, which explains the rapid pH decrease when the BV is relatively low (BV < 10). The elution pH of the breakthrough curve of virgin AMAR was 3 to 5 at the beginning of adsorption, which demonstrated that the ion exchange reaction played a leading role and released mounts of H⁺ into solutions. Nevertheless, the optimum adsorption pH was about 9 to 9.5, which was confirmed by former experiments. The acidic solution condition had a negative effect on the adsorption by AMAR.

For the adsorption breakthrough of causticized AMAR, the H⁺ released at the beginning of the adsorption may react with the OH⁻ adsorbed onto the AMAR. And that was why the solution pH of the causticized AMAR did not react intensely but decreased at a certain speed and still remained above 8. The alkaline condition was also beneficial to the ammonia adsorption. The two mechanisms of ligand exchange and ion exchange are given by Equations (8) and (9) (Mustafa et al. 1998).

\[
R_nCu^{2+} + xNH_4^+ \leftrightarrow R_nCu^{2+}(NH_3)_x + xH^+ \tag{8}
\]
\[ \text{R}_n \text{Cu}^{2+} + 2\text{NH}_4^+ \rightleftharpoons \text{R}_n(\text{NH}_4)_2 + \text{Cu}^{2+} \] (9)

For the virgin AMAR, when the solution pH was lower than 7, the main adsorption process would follow Equation (8), which increased the H\(^+\) concentration in solution and reduced the solution pH. When the AMAR was saturated and the solution pH was lower than 7, the adsorption reaction may follow Equation (9). Mustafa et al. (1998) had drawn the similar conclusions by using Amberlite IRC-50 with functional groups that are similar to those of AMAR resin. The two possible mechanisms of Cu-loaded resin are ligand exchange and ion exchange. The ion exchange reaction between the NH\(_4^+\) in solution and Cu\(^{2+}\) in AMAR might cause the dropping-off effect of Cu\(^{2+}\). The less Cu\(^{2+}\) in AMAR means the less ammonia adsorbed onto the resin and the lower adsorption capacity. Moreover, the elution Cu\(^{2+}\), as a secondary pollutant, cannot reach the emission standard. This conclusion was proved by the breakthrough curve experiments and the elution Cu\(^{2+}\) was about 7.8 mg/L, which was far beyond the national elution standard in China.

After causticization, OH\(^-\) was adsorbed onto the resin and the hypothetical reaction between the OH\(^-\) in solutions and the AMAR may follow Equation (10).

\[ \text{R}_n\text{Cu} + x\text{OH}^- + x\text{Na}^+ \rightarrow \text{R}_n\text{Cu(OH)Na}_x \] (10)

Equations (11) and (12) show the hypothetical way of how ammonia was adsorbed onto the causticized AMAR.

\[ \text{R}_n\text{Cu(OH)Na}_x + x\text{NH}_4^+ \rightarrow \text{R}_n\text{Cu(OH)Na}_x + x\text{H}_2\text{O} + x\text{Na}^+ \] (11)

\[ \text{R}_n\text{Cu} + x\text{NH}_3 \rightarrow \text{R}_n\text{Cu(NH)}_x \] (12)

The existence of the causticization process made the ammonia adsorption mechanism change from that of Equation (9) to that of Equations (11) and (12), from ion exchange to ligand exchange. When ligand exchange reaction Equation (8) occurred, no desorption metals...
were detected in elution. After causticization, the adsorption equilibrium pH was increased from 3–5 (virgin AMAR) to 8–12 (causticized AMAR). And the alkaline condition contributes to a higher ammonia adsorption capacity of AMAR. As the concentrations of the competing ions in solution increased, the mechanism changed from ligand exchange to ion exchange.

**Comparison with other adsorbents**

The literature data on ammonia removal include various adsorbents, such as activated carbon, traditional ion exchanger (natural zeolite, zeolite clinoptilolite and other kinds of zeolites), bio-adsorbent (strawberry leaves, Boston ivy leaves, etc.), commercial ion exchange resins and other newly synthesized ammonia adsorbents (titanate nanotubes (TNT), titanosilicates, etc.). To justify the practicality of the presented materials as effective ammonia removal reagents, the adsorption capacities of ammonia were compared to those of potential ammonia adsorbents. Table 7 presents a comparison of the maximum adsorption capacity ($q_m$) of various ammonia adsorbents. The initial ammonia concentration ($C_i$) (mg/L) is also listed in Table 7 for comparison.

It is evident that the adsorption capacity of Cu(II)-loaded chelating resin AMAR (18.32 mg/g) is significantly higher than the traditional ammonia adsorbents, e.g., 15.2 mg/g for zeolite clinoptilolite and 11.6 mg/g for transcarpathian clinoptilolite. The maximum ammonia adsorption capacity was 45.66 mg/g through our previous equilibrium adsorption experiments. The newly synthesized adsorbent TNT had a relatively high adsorption capacity (29 mg/g), but the cost issue and the manufacturing process are the two obstacles in application.

Some researchers have also investigated the influence of competing ions Na$^+$, K$^+$, Ca$^{2+}$ and Mg$^{2+}$ on the adsorption (Farkaš et al. 2005; Thornton et al. 2007; Huang et al. 2010), but either the competing ion concentrations were very low (K$^+$ < 800 mg/L and Ca$^{2+}$ < 400 mg/L) and unlikely to occur in full application or the adsorption capacities were badly influenced by the co-existing ions.
CONCLUSIONS

A novel ligand exchanger was synthesized by loading a weak iminodiacetate acid chelating resin with Cu$^{2+}$. Batch adsorption experiments indicated that the synthesized R-Cu resin showed high affinity and selectivity towards ammonia. The maximum adsorption capacity was obtained at pH 9.0 at room temperature of 25°C. A series of breakthrough column experiments were conducted in the presence of Na$^+$ and Ca$^{2+}$ by using R-Cu resin as the adsorbent. The main conclusions are as follows. (1) The ammonia adsorption capacities were significantly influenced by the presence of competing ions. The elution pH decreased, which accelerated the breakthrough of the R-Cu resin. (2) Using causticization as a pretreatment process for R-Cu resin significantly enhanced the adsorption properties of the R-Cu resin, and the elution pH remained relatively stable. (3) The maximum adsorption capacity was obtained

Table 7  | Adsorption capacity of ammonia by various adsorbents

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>$C_i$, mg/L</th>
<th>$q_m$, mg/g</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>AMAR</td>
<td>980</td>
<td>18.32</td>
<td>This study</td>
</tr>
<tr>
<td>Natural Australian zeolite</td>
<td>25–50</td>
<td>4.5</td>
<td>Booker et al. (1996)</td>
</tr>
<tr>
<td>Activated carbon</td>
<td>600–2,400</td>
<td>0.6–1.8</td>
<td>Rodrigues et al. (2007)</td>
</tr>
<tr>
<td>Zeolite clinoptilolite</td>
<td>1,400</td>
<td>15.2</td>
<td>Bernal &amp; Lopez-Real (1993)</td>
</tr>
<tr>
<td>Strawberry leaf powder</td>
<td>1,000</td>
<td>7.66</td>
<td>Liu et al. (2010a)</td>
</tr>
<tr>
<td>Natural zeolite</td>
<td>10,000</td>
<td>49.7</td>
<td>Moussavi et al. (2011)</td>
</tr>
<tr>
<td>Boston ivy leaves</td>
<td>1,000</td>
<td>6.07</td>
<td>Liu et al. (2010b)</td>
</tr>
<tr>
<td>Natural New Zealand zeolites</td>
<td>750</td>
<td>8.28</td>
<td>Nguyen &amp; Tanner (1998)</td>
</tr>
<tr>
<td>Transcarpathian clinoptilolite</td>
<td>1,000</td>
<td>11.6</td>
<td>Lebedynets et al. (2004)</td>
</tr>
<tr>
<td>TNT</td>
<td>300</td>
<td>29</td>
<td>Lee et al. (2014)</td>
</tr>
<tr>
<td>Titanosilicates</td>
<td>60</td>
<td>7.647 mg</td>
<td>Luca et al. (2015)</td>
</tr>
</tbody>
</table>
when a causticization pH of approximately 9.5 was used. The effluent ammonia concentration was much lower than 15 mg/L, which corresponds with the Class A Integrated Wastewater Discharge Standard (GB8978-1996). (4) The adsorption by AMAR of ammonia was a combination of ligand exchange and ion exchange. When the solution pH was in alkaline condition, the adsorption mechanism was ligand exchange. When the solution pH was in acidic condition, the adsorption mechanism was ion exchange. Due to the incomparable advantage of ligand exchange, the causation, the adsorption mechanism was ion exchange. Due to the disadvantage of ligand exchange, the causation process was conducted as the pretreatment process and proved to be beneficial to the ammonia adsorption.

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REFERENCES


