Removal of ammonia nitrogen from copper-loaded resin based on ligand adsorption

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Abstract. A ligand adsorbent with strong selectivity towards ammonia nitrogen in solution was prepared by loading Cu onto the chelating resin of iminodiacetic acid. The static adsorption results showed that the removal rate of ammonia nitrogen reached the maximum when the equilibrium pH of solution was 9.5-10. The presence of competing cations, such as Na⁺ and Ca²⁺, had no obvious effect on the optimal equilibrium pH, but had a certain inhibitory effect on the adsorption of ammonia nitrogen and Ca²⁺ > Na⁺. The adsorption of ammonia nitrogen by copper-loaded resin was in line with the Langmuir isothermal equation, and the maximum adsorption capacity of ammonia nitrogen was 44mg/g(dried copper-loaded resin).

1. INTRODUCTION
Ammonia nitrogen (NH₃-N), as the main form of nitrogen pollutants, is widely derived from human life and production processes [1]. Ammonia nitrogen pollution is the main pollutant of eutrophication and causes fatal harm to aquatic organisms[2]. The treatment of ammonia nitrogen wastewater has been a difficult problem and has attracted worldwide attention. Traditional ammonia nitrogen treatment technologies, such as biological nitrification and denitrification, physical and chemical methods, such as stripping, precipitation, ion exchange, have been relatively mature [3-5], and the treatment of ammonia nitrogen urgently needs technical innovation.

The complex structure of metal and ligand can effectively eliminate the interference of non-ligand and choose adsorption ligand. Due to its unique advantages, the ligand exchange technology has attracted much attention applied in wastewater treatment. At present, the ligand exchange technology is mainly used in water body anion (F⁻, the As (III), the As (V), ClO⁻) removal and organic molecules (phenol, amine, amino acid, etc.) [6-8]. It shows a strong competitive advantage and broad prospects in wastewater treatment.

Chelating resins have been extensively studied because of its good mechanical and chemical properties. It is often used as a metal adsorption material. Although chelating resins and carboxylic acid resins reduce metal coordination sites and to some extent weaken the binding force between ligands and metals in solution due to the coordination between metals and resins, and meanwhile, reduce the leakage of metal ions.

In this article, batch experiments was conducted to investigate possible influences of various factors such as contact time, competition ions (such as Na⁺ and Ca²⁺) concentration. Through static adsorption
experiment and kinetic experiment, the mechanism of ammonia nitrogen adsorption of copper-supported resin was explained.

2 EXPERIMENTAL SECTION

2.1 Preparation of adsorbent
The resin was provided by Shanghai Huizhu Co.LTD. The resin is yellow to beige spherical particles. Its maximum tolerance temperature is 120°C and working pH is 1-14. The resin was fully washed with pure water to be neutral, and then loaded into the ion exchange column, so that the saturation analysis pure CuSO₄ solution passed through the resin to the effluent copper ion concentration was the same as the inlet water, and then the resin was rinsed with pure water until the effluent could not detect copper ion, and then the copper loaded resin was prepared by drying at a constant temperature at 48°C for 48 hours. The copper on the resin was completely exchanged by soaking 1g dried copper-loaded resin with concentrated hydrochloric acid. The copper load of the resin was calculated as 2.32mmol/g (dried original resin) by measuring the concentration of copper ions in the solution by ICP-AES.

2.2 Batch Experiment
1g dried copper-loaded resin and 100ml of NH₄Cl solution at a certain concentration were added into a 250mL conical flask. The solution was placed in a constant temperature oscillating chamber and oscillated at 120r/min. Samples were taken at different time intervals to determine the concentration of residual ammonia nitrogen in the solution. The remaining conditions were consistent. NaOH and HCl were used to adjust the equilibrium pH value of the solution to 4-11. Meanwhile, by adding a certain amount of NaCl and CaCl₂ to change the concentration of competing cations in the solution, the influence of coexistence cations on ammonia nitrogen adsorption was investigated. The isothermal adsorption line experiment was carried out under the condition of different initial ammonia concentration.

According to the mass conservation equation, the removal rate of ammonia nitrogen from the solution and the adsorption capacity of resin equilibrium ammonia nitrogen were calculated:

\[\text{Removal efficiency(\%) } = \frac{c_0 - c_e}{c_0} \times 100 \]  
\[q_e = \frac{(c_0 - c_e) \times V}{m} \]  

Where \(q_e\) is adsorption capacity of copper-loaded resin (mg/g), \(V\) is the volume of solution (ml), \(c_0\) and \(c_e\) are the initial concentration and equilibrium concentration of ammonia nitrogen in the solution respectively. \(M\) is the mass (g) of the copper-loaded resin. All experiments were carried out at room temperature 25°C except the temperature influence experiment.

The concentration of ammonia nitrogen was determined by national standard sodium reagent spectrophotometry.

2.3 Column Adsorption Experiment
The experimental device consists of an ion exchange column, a high inlet flume and a water outlet collector. Simulated ammonia nitrogen waste water containing different competitive cation concentrations(Na⁺ and Ca²⁺) containing 30g dried copper-loaded resin, and the ammonia nitrogen concentration of the effluent was measured by sampling at the same effluent volume.

The resin penetration point was taken as the ammonia nitrogen concentration of effluent reached 15mg/L, and the adsorption saturation point was reached when the ammonia nitrogen concentration of effluent approached the ammonia nitrogen concentration of inlet water.

3. Results And Discussion

3.1 Effect of contact time
Fig. 1 shows the effect of contact time on the adsorption of ammonia nitrogen by copper-loaded resin under the conditions of different concentrations of competing cations in the solution. It can be shown from the figure that the ammonia nitrogen adsorption capacity of resin increases rapidly within the initial 100 min of adsorption. Subsequently, the adsorption speed gradually slowed down and the adsorption capacity reached the top at 350 min, indicating that the adsorption reached equilibrium. At the same time, the presence of competing cations such as Na$^+$ and Ca$^{2+}$ in the solution had no significant effect on the equilibrium time of ammonia nitrogen adsorption. In order to ensure complete equilibrium of the reaction, the adsorption time was set as 10 hours in subsequent experiments.

![Adsorption Capacity vs Time](image1)

**Fig.1 Effect of contact time on static adsorption equilibrium of Cu-loaded adsorbent under different competitive ion conditions**

### 3.2 Effect of pH

![Removal Efficiency vs pH](image2)

**Fig.2 Effect of coexisting ions on removal of ammonia for copper-loaded resin at different pH conditions**

Fig. 2 shows the effect of coexisting ions on removal of ammonia for copper-loaded resin at different pH conditions. Simulated ammonia wastewater was used in this experiment. The removal rate of ammonia nitrogen rises linearly with the increase of pH. When the equilibrium pH is about 9.3, the maximum removal rate of ammonia nitrogen reaches up to 90.4%. The adsorption of ammonia nitrogen by copper-loaded resin was similar at different competitive conditions: the removal rate of ammonia nitrogen first increased and then decreased with the increase of solution equilibrium pH. The presence of competitive cations had no significant effect on the optimal equilibrium pH of the adsorption of ammonia nitrogen by copper-loaded resin. When the competitive ions concentration were Na$^+$...
1000mg/L, 2000mg/L and Ca 200mg/L, respectively, the removal rate of ammonia nitrogen reached the highest when the solution equilibrium pH was between 9.5-9.8, which was 69.6%, 63.8% and 54.2%, respectively. It can be seen that the presence of competing cations, especially calcium ions, has a negative effect on ammonia adsorption. The pH of solution can affect the adsorption of ammonia nitrogen from two aspects. The two existing forms of ammonia nitrogen (NH₄⁺ and NH₃) are mainly controlled by the pH of solution. With the increase of pH of the solution, the increasing OH⁻ in the solution will competition with NH₃ for the vacant orbital of transition metal on the resin. This effect is particularly prominent in the presence of competitive cations in the solution. Due to the special coordination between Cu and NH₃, as shown in equation (3), copper-loaded resin selectively adsorbs ammonia nitrogen instead of NH₄⁺. When pH<7, 99% of ammonia nitrogen in the solution exists in the form of NH₃, thus the removal rate of ammonia nitrogen is very low. With the increase of pH from 7 to 9.8, NH₄⁺ in the solution gradually changed to NH₃, and the concentration of NH₃ in the solution increased rapidly, which created favorable conditions for the adsorption of ammonia nitrogen by copper-loaded resin. When the solution pH exceeds 9.8, NH₃ is already the main form of ammonia nitrogen in the solution. While in the presence of competitive cations, the competition from OH⁻ becomes the main factor that prevents the further improvement of ammonia nitrogen removal rate. The equation (4) - (6) can be used for qualitative interpretation. As a Lewis acid, Cu(II) ion loaded on chelating resin can adsorb OH⁻ to the surface to occupy a limited coordination site, making the resin surface negatively charged. As described in equation (4), NH₄⁺ is then adsorbed to the resin by electrostatic equilibrium. However, in the solution with relatively high concentration of competitive cation Na⁺, Ca²⁺ may replace NH₄⁺. As described in equations (5) and (6). In this sense, under the joint action of competitive cation and OH, ammonia nitrogen adsorption is inhibited. Since Ca has a higher charge and can form Ca(NH₃)₆ with NH₃. The negative effect of calcium ion is more obvious.

$$R_2 - Cu(H_2O)_x + NH_3 \rightarrow R_2 - Cu(H_2O)_{x-1}NH_3 + H_2O$$

$$R_2 - Cu(H_2O)_{x} + OH^- + NH_4^+ \rightarrow R_2 - Cu(H_2O)_{x-1}OH^-NH_4^+ + H_2O$$

$$R_2 - Cu(H_2O)_x + OH^- + Na^+ \rightarrow R_2 - Cu(H_2O)_{x-1}OH^-Na^+ + H_2O$$

$$\left[R_2 - Cu(H_2O)_x\right]_2 + 2OH^- + Ca^{2+} \rightarrow \left[R_2 - Cu(H_2O)_{x-1}OH^-\right]_2Ca^{2+} + H_2O$$

Controlling the pH of the solution, namely the existing form of ammonia nitrogen in the solution, is the key factor to ensure the adsorption effect of ammonia nitrogen of copper-loaded resin.

### 3.3 Kinetics Study

Langmuir and Freundlich equation were used to fit the isothermal adsorption lines of ammonia nitrogen in the presence of sodium ions, and the relevant parameters were obtained as shown in Table 2. Based on the regression data, it is concluded that the adsorption of ammonia nitrogen by copper-supported resin is in better accord with Langmuir adsorption, especially in the presence of competing cations.

$$\frac{C_e}{q_e} = \frac{C_e}{q_{max}} + \frac{1}{bq_{max}}$$

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

| Table 1. Langmuir and Freundlich isotherm parameters |
|-----------------------------------------------------|
| **Media** | **Langmuir parameters** | **Freundlich parameters** |
| | q₀(mg/g) | b(L/mg) | R² | n | K₀(mg/g) | R² |
| NH₃ only | 45.87 | 0.0104 | 0.997 | 4.8454 | 9.4532 | 0.988 |
| NH₃-Na⁺(1000mg/L) | 29.29 | 0.0121 | 0.998 | 3.2965 | 3.3219 | 0.951 |
| NH₃-Na²⁺(200mg/L) | 26.06 | 0.0107 | 0.999 | 2.942 | 2.245 | 0.944 |
4. Conclusion
To sum up, static and dynamic experiments in this paper have proved that by optimizing the pH of the system, the copper-loaded iminocarboxylic acid resin can efficiently and selectively remove ammonia nitrogen from the wastewater. While the complete regeneration of the resin is guaranteed. The equilibrium pH, namely the existing form of ammonia nitrogen in solution, is an important condition affecting the adsorption of ammonia nitrogen by copper supported resin. When pH=9.5-10, the removal effect of ammonia nitrogen reaches the best. Coexistence of cations in the solution (Na⁺, Ca²⁺) of ammonia nitrogen adsorption has certain inhibitory effect. Langmuir model can better fit the ammonia nitrogen adsorption process. The maximum adsorption capacity can reach 44 mg/g for copper-loaded resin copper at the optimal conditions.

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