Controllable Fabrication of a Hierarchical CuO-Al₂O₃/C Composite from Green Algae for Removal of Ammonia Nitrogen

Xiangjun Zhang

Xiamen institute of architectural sciences co. LTD., Xiamen 361004, Fujian Province, China
Email: moyiboy@126.com; minwang9308@163.com

Abstract. In this work, a hierarchical composite with copper-alumina loaded on biochar from green algae (H-CuAl/BC) was prepared and removal process of ammonia nitrogen from simulation wastewater was developed. The composites were characterized by using SEM, XRD, BET and FTIR to investigate their morphologies and structures. The effects of temperature, dosage, initial ammonia concentration were investigated. The BET surface area of H-CuAl/BC was 302.3 m²/g. The adsorption isotherm and kinetic model of the adsorption of AN onto H-CuAl/BC from the simulated solution were investigated and the adsorption mechanism was discussed. In addition, the maximum adsorption capacity was achieved 52.89 mg/g. The mechanism of AN adsorption include the micropore adsorption by Van der Waals forces, electrostatic attraction of hierarchical Al₂O₃ and complexation by copper-based.

1. Introduction
With the rapidly development of economic and industry, environment was suffered a great destroy result from emissions of various pollutants increased dramatically, especially for AN increased year by year. Many technologies have been applied for removal AN from wastewater, including air stripping, biological processes, electrochemical oxidation technology, ion exchange, breakpoint chlorination and so on [1-5]. In recent years, adsorption method attracted remarkable attention owing to its high removal rate and low-cost, simple operation and stabilization, no secondary pollution, renewable and sustainable. Meanwhile, biomass-based materials as precursor to prepare adsorbents become more attractive for environmental treatment [6, 7].

In this study, hierarchical Cu-Al₂O₃/biomass carbon (H-CuAl/BC) has been fabricated from green algae through in situ growth method and applied to removal of AN in wastewater. The relative preparation methods of the former have been studied [8, 9]. Hierarchical CuO-Al₂O₃ have not only micro-nano coupling effects but also both effects between copper and aluminum due to germinates nanoscale structure units and microns overall shapes. Moreover, it could avoid liquid phase reunion as well as improve separate, recycle in production and application. Moreover, this work using algae as the precursor to preparation of adsorbent not only make waste profitable but also gives an excellent adsorbent for removal of AN.
2. Experimental

2.1. Materials and Characterization

Materials: Sodium hydroxide (NaOH), sodium hypochlorite (NaClO₂), acetic acid (CH₃COOH), aluminium nitrate (Al(NO₃)₃·9H₂O), ammonium hydroxide (NH₃·H₂O), ethyl alcohol (CH₃CH₂OH), copper nitrate (Cu(NO₃)₂·3H₂O), ammonium chloride (NH₄Cl), seignette salt (KNaC₄H₄O₆·4H₂O) and potassium iodide (KI) were obtained from Sinopharm Chemical Reagent Co., Ltd, which were all of analytical grade. All the solutions were prepared with deionized water (DW).

Characterization: SEM, XRD, BET and FTIR.

2.2. Preparation of H-CuAl/BC

At the first stage, biomass material was prepared as follows: the dried green algae were soaked in NaOH, 5% at 70 ℃ for 3 h. Then, a certain amount of white biomass material was added into alumina sol (100 mL) for 10 h at 60℃. Then, the sample was calcined at 500 ℃ for 2 h to obtain the Al₂O₃/BC. After that, hexamethylenetetramine (0.56 g) and Al₂O₃/BC (0.408 g) were dissolved in DW, then the mixture was put into autoclave Teflon vessel with a hydrothermal reaction at 120 ℃ for 10 h. The product was filtered. The as-prepared AlOOH/BC was calcined at 450 ℃ for 2 h and the product of hierarchical H-Al/BC was obtained. H-Al/BC (0.4 g) was soaked in Cu(NO₃)₂·3H₂O solution for 5 h. After being dried at 65 ℃ for 8 h, the product was calcined at a rate of 5 ℃/min and heated at 450 ℃ for 2 h. Finally, cooling to room temperature, the H-CuAl/BC was obtained.

2.3. Removal of Ammonia Nitrogen Experiments

In order to test the adsorption performance of H-CuAl/BC, the adsorption experiment of ammonia nitrogen on H-CuAl/BC was carried out 0.01g-0.08g H-CuAl/BC was added in 100 mL of 20, 50 and 100 mg/L ammonia solution at 30 ℃ for 4 h to triplicate, respectively. The removal efficiency (%) of ammonia was calculated by the equation (1):

\[ R(\%) = \frac{(C_0 - C_\infty)}{C_0} \times 100\% \]  

The equilibrium adsorption capacity (qe) of adsorbed ammonia on H-CuAl/BC (mg/g) was calculated by the equation (2):

\[ q_e = \frac{(C_0 - C_\infty)V}{M} \]

3. Results and Discussion

3.1. Characterization

The samples morphologies were analyzed by SEM and the images were shown in figure 1. The surface of BC exhibited fish scale-like (figures 1a-1b). Meanwhile, the surface of AlOOH/BC exhibited comparatively rougher surface. Especially, AlOOH sheets appeared and dispersed regularly embossments on the surface of AlOOH/BC. The low-magnification (figures 1c, 1e and 1g) SEM images show that the samples are composed well-homogeneous fully of embossing which consist of micro-nano hierarchical structure. After calcination at 450 ℃ for 2 h, the flower-like Al₂O₃ needles were well transformation and with the length of 100 nm~1 µm (figure 1f). The high-magnification SEM photograph showed the three-dimensional flower-like and well-aligned alumina oxide nano-needles. Furthermore, it can improve the speed of electronic transmission between Al and Cu [10]. Consequently, the AN can be removal faster with the Al-Cu coupling effect.
The XRD was used to identify the crystallinities and components of the samples and the results are shown in figure 2A. The typical XRD pattern of carbon precursor in nether curve, which has a diffraction peaks at 2θ=24º [11]. It is obvious that AlOOH are highly crystalline because of the sharp and strong reflection peaks at 2θ=14.4º, 28.2º, 38.4º and 48.9º [12]. After calcined formation H-Al/BC, the peaks at 2θ=29.3º, 45.4º, 66.32º (JCPDS no. 04-0878) are consistent with Al2O3 [13]. The functional groups of H-CuAl/BC while before and after AN adsorption was detected by FTIR analysis (figure 2B). The band at about 1551.87 cm⁻¹ was the N–H bending vibration, 1386.23 cm⁻¹ attributed the peak of C–N valence stretching vibration [14, 15]. The spectrum of all showed peaks at about 3442.59 cm⁻¹ is attributed to the overlapping peak of -OH and -NH₂ stretching vibration of hydroxyl groups [16, 17], and the peak of C is more intense than A and B indicated that -OH and -NH₂ may be involved in the process and to form complexation with copper.

The relevant nitrogen adsorption–desorption isotherm curves, including BC, H-Al/BC and H-CuAl/BC are depicted in figure 3A, which exhibited type IV with a H2 hysteresis loop on the basis of the IUPAC classification [18]. Simultaneously, the pore characteristics and specific surface areas of the H-CuAl/BC, H-Al/BC composite and pure BC samples are showed in table 1, and BET corresponding 302.3, 226.7, 175.4 m²/g, respectively. Obviously, the BET of the H-CuAl/BC composite is higher than H-Al/BC composite, which could be improved the adsorption capacity of H-CuAl/BC composites. As a result, the pore size of the adsorbents is large enough which could not impede the inward diffusion to adsorb the AN [19].

Figure 1. (A) (a, b) SEM of AlOOH/BC, (c, d) H-Al/BC and (e, f) H-CuAl/BC; (B) EDS of H-CuAl/BC.

Figure 2. (A) XRD of BC, AlOOH/BC, H-Al/BC and H-CuAl/BC; (B) (a) The FT-IR spectra of H-CuAl/BC before adsorption, (b) adsorption once and (c) adsorption twice.
Table 1. BET and pore characteristics of the H-Al/BC, H-CuAl/BC composite and BC samples.

| Sample       | Surface area (m²/g) | Average pore size (nm) | Pore Volume (cm³/g) |
|--------------|---------------------|------------------------|---------------------|
| H-CuAl/BC    | 302.3               | 3.94                   | 0.24                |
| H-Al/BC      | 226.7               | 4.74                   | 0.27                |
| BC           | 175.4               | 5.04                   | 0.15                |

Figure 3. (A) Nitrogen sorption/desorption isotherms of BC, H-Al/BC and H-CuAl/BC; (B) Compare the adsorption capacity of BC, H-Al/BC and H-CuAl/BC.

3.2. Compare the Adsorption Capacity of BC, H-Al/BC and H-CuAl/BC
The adsorption of the AN with three adsorbents after 4 h reaches equilibrium and the result as shown in figure 3B. The maximum adsorbed capacity of BC is 12.36 mg/g, but the H-Al/BC is substantial increase to 37.72 mg/g, and the H-CuAl/BC can achieve 52.89 mg/g, which is five times more than the initial biomass carbon and H-Al/BC. The results due to the hierarchical alumina oxide not only have adsorptive property as a kind of adsorbent but also increase the specific surface area of composite. As for the H-CuAl/BC highest adsorption capacity of, both of two reasons can be enhance the adsorption capacity: copper oxide as the additional adsorption sites enhancing the adsorption probability of AN [20].

3.3. Adsorption Isotherm
The adsorption isotherms of ammonia onto H-CuAl/BC composites were investigated and different temperature effect the adsorption capacity is shown in figure 4A. It can be seen clearly that with the increase of ammonia concentration, the adsorption capacity of ammonia increases gradually. Of course, this can be attributed to the adsorption rate and molecular motion is faster in higher concentration [21]. As for the influence of temperature, the amount of adsorption increases with increasing of the temperature. The maximal adsorption capacity increased to 54.74 mg/g while the temperature increased to 45 °C, indicating that the AN adsorption process is endothermic.

The relevant isotherm parameters, including 1/n, KF, qmax, KL, AT, bT, and R² of ammonia adsorption are listed in table 2, Freundlich and Tempkin isotherm were shown vivid in figures 4B-4D. As showed in table 2, the Langmuir correlation coefficient (R²>0.99) is highest under 15 °C, 30 °C and 45 °C. In other words, The Langmuir isotherm model was fitting well more than Freundlich and Tempkin isotherm model through compare with the value of R².
Figure 4. (A) Effect of different temperature on the adsorption capacity; (B) Langmuir adsorption isotherms; (C) Freundlich adsorption isotherms; (D) Temkin adsorption isotherms.

Table 2. Parameter of Langmuir, Freundlich and Tempkin isotherm for AN adsorption.

| Temperature (°C) | Langmuir  | Freundlich | Tempkin  |
|-----------------|-----------|------------|----------|
|                 | $q_{\text{max}}$ | $K_L$ | $R^2$ | $1/n$ | $K_F$ | $R^2$ | $A_T$ | $b_T$ | $R^2$ |
| 15              | 36.1      | 0.034     | 0.9977  | 0.1831 | 10.56 | 0.9727 | 3.45  | 543.386 | 0.9932 |
| 30              | 45.25     | 0.031     | 0.9986  | 0.2342 | 9.72  | 0.9497 | 1.17  | 369.420 | 0.9904 |
| 45              | 56.82     | 0.028     | 0.9993  | 0.2888 | 8.79  | 0.939  | 0.57  | 260.914 | 0.9928 |

3.4. Effects of Competitive Cations

Investigating the effects of co-existing cations to remove ammonia, including $K^+$, $Ca^{2+}$, $Na^+$, $Al^{3+}$, $Mg^{2+}$ and natural water ($K^+$, $Ca^{2+}$, $Na^+$, $Al^{3+}$, $Mg^{2+}$ and humic acid). The adsorption capacity of ammonia was 49.02 mg/g, 47.50 mg/g, 47.70 mg/g, 48.53 mg/g, 48.73 mg/g, 41.33 mg/g and 20.35 mg/g with the existence of none competition cation, $K^+$, $Ca^{2+}$, $Na^+$, $Al^{3+}$, $Mg^{2+}$ and natural water, respectively. There were no significant influences on the ammonia adsorption with the existence of $K^+$, $Na^+$, $Ca^{2+}$ and $Mg^{2+}$. As for $Al^{3+}$, have a greater influence than other cations, $Al^{3+}$ in the solution would surrounded on H-CuAl/BC and electrostatic repulsion with ammonia result in ammonia nitrogen couldn’t be removed by H-CuAl/BC [22]. However, on the whole, the other cations have a litter threat for ammonia adsorption on H-CuAl/BC (figure 5).
3.5. The Adsorption Mechanism

The hierarchical composite possesses high-performance for removal of ammonia due to the cooperation between biomass carbon, alumina oxide and copper oxide, and the adsorption process is relatively complicated include physical absorption, chemisorption and so on. Firstly, biomass carbon is a unique kind of carbon material, including micropores, mesoporous and adsorption sites. Then, Al₂O₃ is a kind of unique amphoteric oxide which both exhibit acidity and alkalinity in different condition. Finally, CuO on the surface of Al₂O₃ increase not only the specific surface area but also the adsorption sites which as an important adsorbed site for AN, as previous reported [23]. In addition, CuO adsorption mechanism as analyze by FTIR, copper ammonia complex was formed between copper ion and AN. Simultaneously, the ammonia can be removed rapidly under the cooperation between copper and aluminum species. Table 3 shows the adsorption capacities of the H-CuAl/BC composite and some materials reported previously.

| Materials                     | Method                  | R (%) | qₑ (mg/g) | Ref. |
|-------------------------------|-------------------------|-------|-----------|------|
| Cu(II)-loaded chelating resin | Adsorb                  |       | 42.74     | 24   |
| Graphene-supported BiFeO₃     | Photocatalytic          | 91.2  |           | 25   |
| Zeolite tailings              | Biotechnology           | 90.5  |           | 26   |
| Mordenite                     | Adsorb                  | 90.0  |           | 27   |
| Struvite Microwave Radiation  | Decomposition           | 88.0  |           | 28   |
| Novel Silicate Material       | Adsorb                  | 83.9  |           | 29   |
| H-CuAl/BC                     | Adsorb                  | 92.5  | 60.33     | This work |

4. Conclusion

A novel low-cost hierarchically Cu-Al₂O₃ biomass carbon was successfully prepared using a typical hydrothermal method and serve as an effective adsorbent to remove the AN from aqueous solutions. The adsorption mechanism of the eco-friendly composite could be attributed to the strong consociation of the combination of biomass carbon, Al₂O₃ nano-needles and copper. The results indicate that the AN removal rate increased as increasing temperature. The results showed that the maximal adsorption capacity of AN was 52.89 mg/g, and the equilibrium data were best described by the Langmuir and the kinetics of adsorption process followed by the pseudo-second order model.

References
[1] Feng Z and Sun T 2015 Chem. Eng. J. 281 295.
[2] Silva J C M, Piasentin R M, Spinacé E V, Neto A O and Baranova E A 2016 Mater. Chem. Phys. 180 97.
[3] Bonmati A and Flotats X 2003 Waste Manage. 23 261.
[4] Huang H, Zhang D, Zhao Z, Zhang P and Gao F 2017 J. Clean Prod. 141 429.
[5] Xue R, Donovan A, Zhang H, Ma Y, Adams C, Yang J, Hua B, Inniss E, Eichholz T and Shi H 2017 J. Environ. Sci. 64 82.
[6] Zhu C, Yang W L, He H, Yang C, Yu J, Wu X, Zeng G, Tarrec S and Green M 2018 Chemosphere 200 380.
[7] He H, Xiang Z, Chen X, Chen H, Huang H, Wen M and Yang C 2018 Int. J Environ. Sci. Te. 15 1491.
[8] Yu J, He H, Yang W, Yang C, Zeng G and Wu X 2018 Bioresource Technol. 260 196.
[9] Wu S, He H, Intahapanya X, Yang C, Lu L, Zeng G and Han Z 2017 Environ. Sci. Pollut. R. 24 16560.
[10] da Silva T H and Nelson E B Appl. Surf. Sci. 439 910.
[11] Liu Y, Peng Y, Zhang T, Qiu F and Yuan D 2018 Cellulose 25 3067.
[12] Zhang Q, Sun S, Wang T, Liu F, Yang J and Cheng A 2018 Chem. Eng. Process. 132 169.
[13] Zhang J, Yang C, Chen Y and Wang C 2019 Ind. Eng. Chem. Res. 58 1495.
[14] Sha L, Guo X, Feng N and Tian Q 2010 J. Hazard. Mate. 174 756.
[15] Gaouar Yadi M, Benguella B, Gaouar-Benyelles N and Tizaoui K 2016 Desalin. Water Treat. 57 21444.
[16] Dinh C, Cho K Y and Oh W C 2019 Sep. Purif. Technol. 211 646.
[17] Tu Y, Feng P, Ren Y, Cao Z, Wang R and Xu Z 2019 Fuel 238 34.
[18] Liu Y, Hu X, Liu Z, Meng M, Pan J, Jiang Y and Ni L 2017 Chem. Eng. J. 328 11.
[19] Hwang K, Park J, Kim Y, Kim G, Choi C, Jin S, Kim N and Lee J W 2015 Sep. Sci. Technol. 50 1757.
[20] Ji Y, Bai J, Li J, Luo T, Qiao L, Zeng Q and Zhou B 2017 Water Res. 125 512.
[21] L Wang, H Zhang, C Lu, L Zhao 2014 J. Colloid Interf. Sci. 413 140.
[22] Bu I Y Y 2015 J. Ind. Eng. Chem. 28 91.
[23] Wang Z, Qu Z, Quan X, Li Z, Wang H and Fan R 2013 Appl. Catal. B-Environ. 135 153.