Preparation and characterization of amino modified eucalyptus biochar

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Abstract. Amino modified eucalyptus biochar (ABC) was prepared from eucalyptus biochar by amino amendment with ammonia, concentrated nitric acid, concentrated sulfuric acid and sodium dithionite. The preparation parameters of ABC were optimized by orthogonal experiment. It was found that the optimal preparation process of ABC was: carbonization temperature was 300 °C, volume ratio of nitric acid to sulfuric acid was 2:1 and the consumption of ammonia water was 15 ml. The results of characterization indicated that the morphological structure of ABC changed, and the amino functional group was successfully loaded on the surface of the biochar.

1. Introduction
Biochar is a kind of porous carbonaceous solid produced by the pyrolysis of biomass under hypoxic or anaerobic conditions and a lower temperature (<700 °C) [1]. Biochar is composed of aromatic hydrocarbons carbon or carbon with graphite structure. However, due to the single surface functional group and poor selective adsorption, the adsorption efficiency and capacity of biochar for specific metal elements are reduced [2]. In order to develop the adsorption potential of biochar, many scholars have carried out research on the modification of biochar surface functional groups to enhance the adsorption activity and capacity to metal ions. Amino modification is one of the important methods. WANG used ammonium citrate amino modified biochar to remove La (III) from water, and found that modified biochar had rich amino and carboxyl functional groups [3]. MA used polyethyleneimine amino modified biochar as adsorbent to remove Cr³⁺ from water. It was found that the modified biochar surface was rich in amino functional groups and the adsorption capacity was about 200% of the original biochar [4].

Eucalyptus is an economic tree with a short growth cycle. However, eucalyptus produces a lot of waste after utilization. Eucalyptus waste can be converted into biochar and amended by amino groups, which leads to a new way for the utilization of eucalyptus waste.

Orthogonal experimental design is an efficient, fast and economical experimental design method to study multi-factors and multi-levels based on the orthogonality to select some representative points from the comprehensive experiment to carry out the experiment. For many affecting factors of the preparation of amino-modified eucalyptus biochar, the orthogonal design method can be introduced to optimize the preparation conditions with the index of the adsorption amount of Cr (VI) of amino modified eucalyptus biochar.

2. Materials and methods
2.1. Material and equipment
- Source of biomass raw materials: eucalyptus branches collected from Huixian Wetland were washed, dried, crushed and reserved.
- The reagents used in the experiment were hydrochloric acid, sodium hydroxide, potassium dichromate, diphenylcarbazide, acetone, concentrated sulfuric acid, phosphoric acid, ammonia water, concentrated nitric acid and sodium dithionite. The solution was prepared with deionized water.
- Instruments used in the experiment: water bath thermostat (SHZ-B, Shanghai Boxun Industrial Co., Ltd.), scanning electron microscope (JSM-6380LV, Japan), elemental analyzer (EA240 II, Perkin-Elmer, USA), XRD diffractometer (X'Pert PRO, PANalytical, Netherlands), muffle furnace (SX2-5-12, Shanghai Huyue Experimental Instrument Co., Ltd.), specific surface and porosity analyzer (NOVAe1000, Quantachrome, USA), electric blower (GZX)-9240MBE, Shanghai Boxun Industrial Co., Ltd.), infrared absorption spectrometer (470 FTIR, American Thermoelectric Nico)

2.2. Preparation of amino modified eucalyptus biochar
- Pretreatment
  Eucalyptus branches collected from Huixian Wetland were washed with clean water and dried in an oven at 120°C for 24 hours. The dried eucalyptus branches were crushed into powder by a crusher before sifting through 30 meshes, and then were reserved in a sealed plastic bag.
- Preparation of amino modified eucalyptus biochar
  The powdered eucalyptus wood obtained from first step packed in a 200 mL crucible was carbonized in a muffle furnace. The carbonized products were washed with dilute hydrochloric acid and water and dried in an oven after filtering. The dried eucalyptus biochar was added into a mixture of concentrated sulfuric acid and nitric acid and then was stirred at 400 rpm for 4 hours in a water bath before filtering. The filtered residue was washed and dried to get nitrified biochar. The dried nitrified biochar was added to a mixture of 50 mL of water, ammonia water and sodium dithionite to be stirred at 400 rpm for 4 h. The mixture was filtered, and the residue was washed and dried to obtain an amino biochar (indicated by ABC) sealed for use.

2.3. Amino-modified eucalyptus biochar performance test
The adsorption capacity of amino-modified eucalyptus biochar was determined by the adsorption capacity of Cr (VI). The content of Cr (VI) in the solution was determined by diphenylcarbazide spectrophotometry.

3. Orthogonal experimental design
According to the rules of orthogonal experiment, the carbonization temperature of eucalyptus biochar (A), ammonia water consumption (B), the volume ratio of concentrated nitric acid and concentrated sulfuric acid (C) were selected as factors. Each factor was set at two levels for orthogonal experiment. The orthogonal experimental factors and the level table are shown in table 1.

| Level | Factor | A / °C | B /mL | C     |
|-------|--------|--------|-------|-------|
| 1     |        | 300    | 15    | 2:1   |
| 2     |        | 400    | 20    | 1:2   |

4. Results and discussion
4.1. Experimental results and analysis of optimization of preparation conditions
The ABC orthogonal results are shown in table 2.
According to Table 2, the order of influencing factors is A>B>C. The optimum preparation conditions are as follows: carbonization temperature 300°C, volume ratio of nitric acid to sulfuric acid 2:1, ammonia water consumption 15 ml.

4.2. Analysis of pore size distribution, element and specific surface area
The pore size is less than 2 nm for micropores, the mesopores in the range of 2 to 50 nm, and the macropores greater than 50 nm. It can be seen from Table 3 that the amino-modified eucalyptus biochar is a mesoporous-based hierarchical porous material.

Table 3. Analysis of specific surface area and pore size.

| Material       | Specific surface area (m²/g) | Total pore volume (m³/g) | Average pore size (nm) |
|----------------|------------------------------|--------------------------|------------------------|
| Eucalyptus biochar | 67.99                        | 4.32                     | 1.69                   |
| ABC            | 65.18                        | 3.77                     | 1.48                   |

Adsorption performance of adsorbent is related to specific surface area and internal pore structure. The results showed that the specific surface area of eucalyptus biochar is 0.854 m²/g and that of amino modified eucalyptus biochar was 0.767 m²/g.

The results of elemental analysis showed in Table 4 that the carbon, hydrogen and oxygen contents of amino modified eucalyptus biochar decreased slightly, while the nitrogen content had a significant rise. It can be inferred that amino modified eucalyptus biochar contains a large number of N functional groups, possibly amino functional groups.

Table 4. Element analysis of eucalyptus biochar and ABC.

| Material       | C(%) | H(%) | N(%) | S(%) |
|----------------|------|------|------|------|
| Eucalyptus biochar | 67.99 | 4.32 | 1.54 | 1.69 |
| ABC            | 65.18 | 3.77 | 1.54 | 1.48 |

4.3. SEM
It can be observed by electron microscopy at 5000 times that eucalyptus biochar had a plate-shaped biochar crystal structure with obvious morphological features, mainly attributing to high lignin content in eucalyptus. For the strong etching of concentrated sulfuric acid and nitric acid to eucalyptus biochar during the process of modification, the surface of ABC sample became rough and loose as shown in figure 1.
4.4. FT-IR
The peak at 3423 cm\(^{-1}\) and 2924 cm\(^{-1}\) in the infrared spectrum of ABC is the phenolic hydroxyl O-H stretching vibration absorption peak in biochar \([5]\) as shown in figure 2. 1318 cm\(^{-1}\) is the C-N stretching vibration absorption peak, and 1623 cm\(^{-1}\) is the N-H denaturation vibration peak \([6]\). It can be concluded that the amino functional groups were successfully loaded on the surface of biochar, and functional groups of the modified were much more abundant than that of the unmodified.

4.5. XRD
The diffraction peak of ABC at 2θ=26° can be attributed to the characteristic peak of element C according to the PDF index card 26-1076, indicating its structure is amorphous, which is shown in figure 3.
Figure 3. XRD pattern of ABC.

5. Conclusion

- The order of the main influencing factors is: A>B>C. The optimal preparation process of eucalyptus biochar is that carbonization temperature is 300°C, volume ratio of nitric acid to sulfuric acid is 2:1 and amount of ammonia water is 15mL.
- The surface morphology of eucalyptus biochar modified by amino group was rough and loose and its morphology and structure changed. Meanwhile, the amorphous degree of amino modified eucalyptus biochar increased and the amino functional groups were loaded on the ABC surface successfully with the increase of nitrogen content.

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