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Preparation of rice straw-derived biochar for efficient cadmium removal by modification of oxygen-containing functional groups

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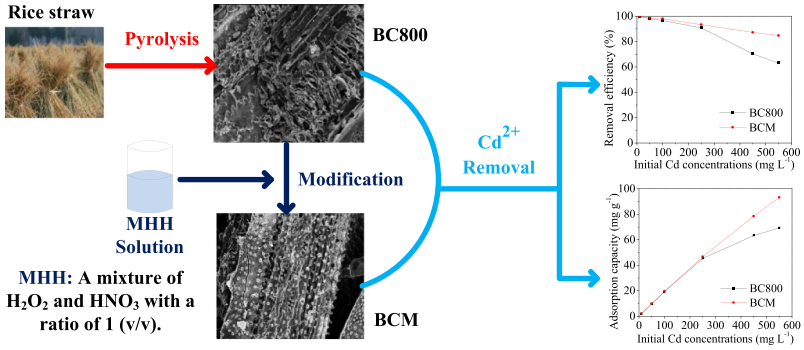
HIGHLIGHTS

- Biochar was modified by a mixture of H_2O_2 and HNO_3 (MHH) with equal volume.
- The carboxyl and phenol group on biochar surface were doubled after MHH modification.
- Cd^{2+} adsorption on modified biochars was mainly controlled by chemisorptions.
- MHH modification enhanced biochar's adsorption capacity for high Cd^{2+} concentration.

GRAPHICAL ABSTRACT



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ABSTRACT

In order to enhance the adsorption capacity of cadmium (Cd) ion from aqueous solution, the rice straw-derived biochar (BC800) was modified by a mixture of HNO_3 and H_2O_2 (MHH) with equal volume. Several elemental, chemical and structural characterization methods were used to determine the characteristics of biochars. Batch adsorption experiments were carried out concerning the influences of contact time, initial pH value, and initial concentration. The results indicated that the modified biochar (BCM) was more effective in removing Cd^{2+} from water than BC800. For 550 mg L^{-1} Cd^{2+} concentration solution, the adsorption capacity of 93.2 mg g^{-1} was observed for BCM, which was much higher than that of BC800 (69.3 mg g^{-1}). The BCM had a significant increase of acidic functional groups with a rate of 101.6% and the component carboxyl, lacton and phenol groups increased by 124.1%, 29.3% and 111.3% respectively, while the specific surface area increased about 22.0%, compared with BC800. The pseudo-second-order model provided high correlation coefficients for BCM, speculating chemisorption of the Cd^{2+} onto biochars. Therefore, the rice straw-based biochar treated by MHH is considered to be an efficient adsorbent for Cd^{2+} removal from aqueous solution, especially for high concentrations of cadmium solution.

1. Introduction

With the extensive exploitation and utilization of fossil fuels, and the rapid development of metal smelting, battery manufacturing and chemical production, heavy metals have been discharged into the environment, resulting in heavy metal pollution (Barakat, 2011). Toxic heavy metals of particular concern in treatment of industrial wastewaters include zinc, copper, nickel, mercury, cadmium, lead and chromium (Fu and Wang, 2011). Cadmium is easy to endanger human health by the enrichment of the food chain (Loganathan et al., 2012), and has been considered as one of the most toxic elements to humans (Mohan

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and Singh, 2002). Therefore, there is a pressing need to solve the cadmium pollution problem.

Various physical, chemical, and biological removal techniques have been widely used for the decontamination of heavy metals in wastewater before releasing into the environment (Annadurai et al., 2002; Feng et al., 2000). Although all this techniques can be employed to remove heavy metals, they have their inherent advantages and limitations (Fu and Wang, 2011). Chemical precipitation is effective and by far the most widely used process in industry (Ku and Jung, 2001) for its simplicity process and inexpensive capital cost. However, it is ineffective for low metal ion concentration and can produce large amount of sludge treated with great difficulties. Ion-exchange processes have been widely used to remove heavy metals from wastewater due to its high treatment capacity, high removal efficiency and fast kinetics (Kang et al., 2004). However, ion-exchange resins are expensive and its regeneration can cause serious secondary pollution. Adsorption is considered one of the most effective and economical technology for heavy metal removal from contaminated effluents (Inyang et al., 2012; Sun et al., 2013). Besides, the adsorption efficiency depends on the performance of the adsorbent.

Activated carbon (AC) has been recognized as the most commonly used adsorbent for its large micropore and mesopore volumes with high surface area. A lot of studies focused on using AC to remove heavy metals (Jusoh et al., 2007; Kang et al., 2008). However, these materials tend to be more expensive than other adsorbents because of their high production costs (Dias et al., 2007), which limits its use in adsorption. More and more researchers focused on the developments of low-cost adsorbents to remove heavy metal ions, and one of attempt was the pyrolysis of agricultural straw (Wang et al., 2015). Compared with activated carbon, biochars have higher adsorption capacities for heavy metals from aqueous solutions (Xu et al., 2013). Many literatures have suggested biochars are a promising alternative agent for the treatment of heavy metals considering both preparation and running costs (Demirbas, 2008; Zhou et al., 2014). It can be used as a multifunctional material to agricultural soils and an effective sorbent for the heavy metal stabilization like Cd^{2+} (Ahmad et al., 2014). However, the applications of original biochars are restricted by its limited removal ability to a certain extent.

It has been shown that the chemical nature determined by the surface complexes has in general more influence than the surface area and the porosity of the adsorbent for the adsorption of inorganic compounds (Solar et al., 1990). It was concluded that the removal efficiency of biochar for heavy metals were closely related to the surface oxygenated complexes, such as hydroxyl, carbonyl and carboxyl groups (Smith et al., 2015). Furthermore, surface acidic functional groups were considered as the most important surface groups for its influence on catalytic, electrical, and chemical reactivity of carbon materials (Suliman et al., 2016). The effects of various preparation and modification methods on oxygen-containing functional groups have been investigated. Brewer et al. (2017) found that the addition of oxygen to the reaction environment could slightly increase the number of oxygenated surface functional groups, though this increase is unlikely to translate into a noticeable effect in practice compared to other post production surface oxidation methods. Besides, the surface oxygen complexes were formed on activated carbon when it was treated with oxidizing agents by different dry and wet methods (Pradhan and Sandle, 1999).

Most of oxidizing modifications of biochar reported in the literatures were conducted using aggressive reagents. Some results showed that the weak acid ester groups and the number of carboxylic acid of coconut fiber-based biochars modified with HNO_3 significantly increased (Wu et al., 2017). Pradhan and Sandle (1999) used two commercially available activated carbons oxidized with different oxidizing agents including HNO_3, H_2O_2 and $(NH4)_2S_2O_8$ to introduce surface oxygen complexes, and the results showed carboxylic groups were essentially fixed along with ketone and ether groups after the treatment of the oxidizing agents. Guo et al. (2013) conducted HNO_3 and H_2O_2 modifying carbon ball experiments and found that the strong oxidizing HNO_3 was conducive to the introduction of carboxyl and carbonyl. They also found that weak oxidizing H_2O_2 was beneficial to introduce hydroxyl, but the two kinds of oxidant mixture made the surface to introduce more oxygen containing functional groups. However, there are few reports about the use of mixed oxidation in biochar modification. Hence one can see that it is meaningful to study the mixed oxidation modification of biochar.

To enhance the adsorption capacity of original biochars, the rice straw-derived biochar with a mixture of HNO_3 and H_2O_2 with equal volume (MHH) was prepared for Cd^{2+} adsorption. The characteristics of the parental and modified biochars toward the removal of Cd^{2+} from aqueous solutions were systematically compared by elemental analysis, Fourier transform infrared spectroscopy (FTIR), Boehm titration, BET analysis and scanning electron microscopy (SEM). The objectives of this work were to: (1) prepare and characterize biochars modified by a novel modifier (MHH), and (2) comprehensively evaluate the function of MHH on adsorption capacity of biochar for Cd^{2+}.

2. Materials and methods

2.1. Materials

The rice straw used in this experiment was collected from the farmland in Yixing City, Jiangsu Province, China, and was washed with deionized water for several times and dried to constant weight at 60 °C. Dried rice straw was milled to obtain powders between 5 mm and 10 mm prior to use. Carbon dioxide and nitrogen (purity 99.999%) used for pyrolysis were purchased from Nanjing Shangyuan Gas Co., Ltd. (Nanjing, China). Hydrogen peroxide (H_2O_2) and Cadmium chloride hemipentahydrate ($CdCl_2 \cdot 2.5H_2O$) were purchased from Nanjing Chemical Reagent Co., Ltd. (Nanjing, China). Nitric acid (HNO_3) was purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). All chemicals and reagents in this work were of analytical grade.

2.2. Preparation of modified biochars

Fig. 1 showed the schematic diagram of the biomass pyrolysis to produce biochar system. The setup consisted of five main parts: pyrolysis reactor, gas supply and controlling unit, thermocouple and temperature controlling unit, circulating water and condenser unit, and gas purifying

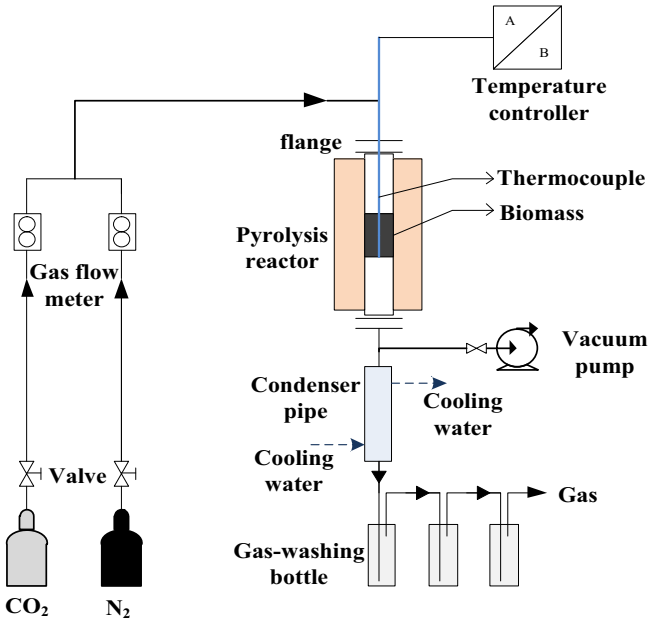

Fig. 1. Schematic diagram of the biomass pyrolysis to produce biochar system.