



Research article

Eucalyptus sawdust derived biochar generated by combining the hydrothermal carbonization and low concentration KOH modification for hexavalent chromium removal

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ABSTRACT

In this study, *Eucalyptus* sawdust was hydrothermally carbonized, and the resulting biochar was modified by a low concentration potassium hydroxide. The morphology and surface property was characterized by SEM-EDS, BET, FTIR and XPS techniques. A series of batch adsorption experiments were conducted to screen out the optimum conditions, and to investigate the isotherm, kinetics and thermodynamic behaviors. The results indicated that a high adsorption capacity of hexavalent chromium (q_e 45.88 mg/g) was achieved by the combining of hydrothermal carbonization at 220 °C and 0.05 N potassium hydroxide modification, and a high biochar yield (47.61%) was obtained. The isotherm, kinetics and thermodynamic studies suggested that the spontaneously and endothermically chemical adsorption was the main mechanism, which was partially supported by BET, FTIR and XPS results. This finding suggested that the combination of hydrothermal carbonization and a subsequent low alkali modification was an effective method to prepare a high-performance adsorbent for hexavalent chromium removal.

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1. Introduction

Cr(VI) is a highly toxic metal, causing carcinogenic, mutagenic and teratogenic effects on biological system (Kalidhasan et al., 2016). Cr(VI) is released to the environment through various industrial processes including leather tanning, electroplating, manufacturing of chromate and dye and petroleum refining (Zhang et al., 2015a). Low Cr(VI) levels for water environment (below 0.1 mg/L) and for drinking water (below 0.05 mg/L) were set by the US Environmental Protection Agency. Therefore, it is necessary to remove the excessive Cr(VI) from supply water or wastewater for drinking or discharging into water body.

Conventionally, the methods that have been utilized to remove the heavy metals include oxidation, precipitation, coagulation, ion exchange, membrane technology, adsorption, etc. (Ihsanullah et al., 2016). Among them, adsorption method is considered as a versatile and widely used technology for metal ion removal. It has the advantages of easy operation and high removal efficiency. For

adsorption process, a high-performance adsorbent is the key factor, determining pollutant removal efficiency and operating cost. Several adsorbents have been employed for the adsorption of heavy metals, which can be classified into organic type (including activated carbon, polymeric resins, chitosan, etc.) and inorganic type (including clay based adsorbents, etc.). Therefore, it is important to develop efficient adsorbents for Cr(VI) removal.

Activated carbon has been employed as an excellent adsorbent for the removals of heavy metals and organic pollutants. Typically, activated carbon is a carbonaceous material obtained from thermal degradation of coal or biomass, followed by activation step. Its adsorption capacity depends on the raw material and processing conditions for activated carbon production. In this field, pyrolysis is the most popular thermal conversion method for organic materials, because the resulting pyrolytic char has a well-developed pore structure. The subsequent activation process can further improve the pore structure and surface area for activated carbon production. Although activated carbon is effective for heavy metal removal like Cr(VI), some drawbacks relating to raw material and manufacturing process have to be taken account. For example, coal derived activated carbon is limited by the exhaustion risk of fossil fuel. The low yield and high cost of biomass derived activated carbon via

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pyrolysis and activation treatment are the barrier for widely application.

Biochar is the solid residue of thermal conversion of biomass. Due to the special surface characteristics, recently, biochar is directly used as a low-cost and environmentally friendly sorbent instead of activated carbon for the removal of heavy metals (Inyang et al., 2015). In general, biochar was produced from pyrolysis of biomass, called pyrochar, which contains rich aromatic functional groups. However, the biochar yield from pyrolysis was very low (slow pyrolysis yield 30%; fast pyrolysis yield 12–26%) (Cha et al., 2016). More recently, the attention of biochar production from high-temperature pyrolysis gradually shifted to hydrothermal carbonization, which is also an effective thermo-chemical conversion process for carbonaceous material production. Assisted by hydrothermal carbonization, various carbon materials with a large number of reactive oxygen functional groups were synthesized from waste biomass (Hu et al., 2010). Biochar produced from hydrothermal carbonization at a mild temperature possessed a high yield and abundant surface functional groups (Liu et al., 2013). Different from pyrochar mainly containing aromatic functional groups, the biochar from hydrothermal treatment was composed of more alkyl moieties (Kambo and Dutta, 2015). The researchers compared the copper adsorption capacity of hydrothermal biochar with that of pyrolytic biochar, and found that the adsorption capacity of hydrothermal biochar was much higher than pyrolytic biochar (Liu et al., 2010). Therefore, the hydrothermal biochar might be a better candidate for Cr(VI) removal.

Although biochar is effective for pollutants removal, the indigenous inorganics, impurities, and organic debris in the raw biochar decreased the efficiency of adsorption. A post treatment is an effective way to improve the adsorption capacity. The activation step for activated carbon production is one kind of severe treatment. Physical activation and chemical activation are two typical methods to improve the specific surface area and pore size distribution of biochar. For example, switch grass was carbonized at 500 °C and 700 °C and the resulting biochar was subsequently steam activated at 800 °C for 45 min. The activated biochar (also called activated carbon) exhibited better adsorption performance than biochar for copper and phenol removal (Han et al., 2013). As mentioned above, biochar yield is very low, and the activation step will cause additional weight loss. In addition, high chemical cost and/or energy cost (steam supply) during the activation process will decrease the economic feasibility. This fact suggested that harsh activation treatment for biochar might not be the best approach to enhance its adsorption capacity.

Surface modification is a more attractive choice for biochar treatment to increase its adsorption capacity by a low-strength treatment than activation. The modified biochar by a simple post-processing showed a better adsorption performance for pollutants removal. For example, surface oxidation is a typical surface modification method using oxidizing agents such as air, HNO₃, H₂O₂, Fe(NO₃)₃ (Huang et al., 2009). Using H₂O₂ treatment on raw biochar increased the lead sorption ability from 1.04 mg/g to 22.82 mg/g (Xue et al., 2012). Alkali, acid or metal salt soaking is another modification method. A high-alkali concentration (2 N) to treat biochar for copper and cadmium removal, and high adsorption capacities for cadmium and copper removal (34 mg/g and 31 mg/g) were achieved (Regmi et al., 2012). However, it also has some disadvantages. The modification of biochar by strong oxidants or high concentrations of alkali/acid will inevitably lead to a great weight loss. The high dosage of chemicals is another main economic limitation. Therefore, it is important to develop a high-yield, low-cost, and high-performance biomass-based adsorbent.

The aim of this study is to develop a biochar based adsorbent from hydrothermal carbonization of wood sawdust with a high

yield and high performance. Firstly, a raw biochar was produced from hydrothermal carbonization of *Eucalyptus* sawdust at different hydrothermal temperatures. Then, an alkali or acid modification method was employed to clean up the raw biochar. A series of batch adsorption experiments were conducted to evaluate the effects of hydrothermal carbonization temperature and alkali concentration on Cr(VI) removal. In addition, the isotherms, kinetics and thermodynamics of Cr(VI) adsorption were performed, and by combining the different characterization methods, e.g. Brunauer-Emmett-Teller (BET), Fourier transform infrared spectroscopy (FTIR) and X-ray photoelectron spectrometer (XPS) (K-Alpha, Thermofisher Scientific Company, USA) analysis the mechanism of Cr(VI) removal by the modified biochar was tentatively elucidated.

2. Materials and methods

2.1. Biochar preparation

Eucalyptus sawdust was provided by the Guangxi Yulin Wood Manufacturing Factory, China. It was ground to pass through a 0.83 mm screen. Hydrothermal carbonization experiments were carried out in a 250-mL stirred batch reactor (Nickel alloy 625, GCF-type, Dalian Controlled Plant, China). For each run, 80 g of dry *Eucalyptus* sawdust and distilled water (biomass-to-water ratio 1:7) were weighed and transferred into the reactor. The reactor was purged with N₂ for 5 min and magnetically stirred at 100 rpm. Then it was heated to 160 °C, 190 °C, 220 °C, or 250 °C for 1 h. After the reaction, the reactor was cooled down with cooling water. The gas in the headspace of the reactor was released and the solid-liquid mixture was filtered with a 0.45 μm membrane filter. The solid residue, named as a biochar, was washed with deionized water until the pH was neutral. The biochar was dried in an oven at 105 °C for 24 h, and stored in an air-tight plastic tube.

2.2. Modification of raw material and biochar

The biochar (or raw material) and different concentrations of KOH (or HCl) solution with a ratio 1:50 (w/v) were mixed, and stirred for 1 h at 30 °C. The solution was transferred into a Buchner funnel, and filtered by a 0.45-μm membrane. Then the filtered biochar was washed with deionized water until the pH of filtrate remained neutral. Finally, the washed biochar was dried in an oven at 105 °C for 24 h, and named as a modified biochar. The yield of the modified biochar was calculated according to Equation (1):

$$\begin{aligned} \text{Yield} = & (\text{mass of solid residue} / \text{mass of dried feedstock}) \\ & \times (\text{mass of modified solid residue} / \text{mass of biochar}) \\ & \times 100\% \end{aligned} \quad (1)$$

2.3. Cr(VI) adsorption experiment

The biochar (or raw material) was used as an adsorbent for Cr(VI) removal from solution. A series of adsorption experiments were conducted to evaluate the adsorption capacity of different adsorbents. The typical adsorption parameters of pH, contact time, and adsorption temperature were examined. For comparison, two commercial activated carbons, commercial coconut activated carbon and coaly activated carbon, were tested as controls. The batch experiments were carried out in a 100-mL centrifuge tube with a sealing film. The Cr(VI) solutions with certain concentrations was obtained by diluting a stock solution of Cr(VI) (1000 mg/L). A mixture of 0.1 g biochar and 50 mL Cr(VI) solution was added into

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