



Investigation of the adsorption–reduction mechanisms of hexavalent chromium by ramie biochars of different pyrolytic temperatures



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HIGHLIGHTS

- Ramie residue can be converted into biochar as an effective sorbent for Cr(VI) removal.
- Cr(VI) sorption on the biochars was dependent on their physiochemical properties resulting from pyrolysis temperature.
- Both electrostatic and ionic interactions were responsible for Cr(VI) adsorption and reduction.
- The low-temperature biochar had better adsorption capability due to its abundant carboxyl and hydroxyl groups.

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ABSTRACT

To investigate the relationship between Cr(VI) adsorption mechanisms and physio-chemical properties of biochar, ramie residues were oxygen-limited pyrolyzed under temperature varying from 300 to 600 °C. Batch adsorption experiments indicated that higher pyrolysis temperature limits Cr(VI) sorption in terms of capacity and affinity due to a higher aromatic structure and fewer polar functional groups in biochar. Both electrostatic (physical) and ionic (chemical) interactions were involved in the Cr(VI) removal. For low-temperature biochar, the simple physical adsorption was limited and the significant improvement in Cr(VI) sorption was attributed to abundant carboxyl and hydroxyl groups. The adsorption–reduction mechanisms could be concluded that Cr(VI) ions were electrostatically attracted by the positively charged biochar surface and reduced to Cr(III), and then the converted Cr(III) was retained or discharged into the solution. The study demonstrates ramie residues can be converted into biochar as a low-cost and effective sorbent for Cr(VI) removal.

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1. Introduction

Chromium (Cr), a common contaminant in surface water and groundwater, is mainly derived from industrial processes such as leather tannery, electroplating, mining, metallurgy, steel manufacturing, textile, etc (Bayazit and Kerkez, 2014). In general, Cr occurs in aqueous media as two major valence states, the trivalent [Cr(III)] and hexavalent [Cr(VI)] states. Cr(III) is an essential bioelement to mammals at low concentration and is rather immobile in natural environment. Cr(VI) is five hundred times more poisonous than Cr(III) and may cause carcinogenesis, mutation or teratogenesis

to living creatures (Chen et al., 2015; Suksabye and Thiravetyan, 2012). Depending on the pH levels, Cr(VI) primarily exists in the form of chromate (CrO_4^{2-} and HCrO_4^-) and dichromate ($\text{Cr}_2\text{O}_7^{2-}$), which are highly toxic and water-soluble (Zelmanov and Semiat, 2011). Thus, Cr(VI) has been identified as a top-priority hazardous pollutant by the U.S. Environmental Protection Agency (EPA) (Ma et al., 2014). The Ministry of Environmental Protection in China has set the maximum permissible limit of Cr(VI) discharged in surface water to be below 0.05 mg L^{-1} according to the international standards (Zelmanov and Semiat, 2011). It is therefore of great significance to develop a cost-effective and reliable technique to eliminate Cr(VI) from industrial wastewater before being discharged into aquatic system. A variety of treatment technologies to remediate Cr(VI)-contaminated wastewater including chemical precipitation, membrane separation, oxidation/reduction, ion

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exchange, adsorption, ultrafiltration and reverse osmosis have been proposed (Albadarin et al., 2012). Among them, adsorption process has evolved as the frontline for Cr(VI) disposal because of its high selectivity, economic efficiency and operation simplicity. However, the selection of low-cost and environmental-friendly adsorbent is a matter of concern (Albadarin et al., 2012; Chen et al., 2015).

Biochar, a carbon-rich product similar to activated carbon, is obtained by pyrolysis of biomass under relatively low temperature (<700 °C) and oxygen-limited environment (Tytlak et al., 2015). The conversion of waste biomass into biochar has received considerable interests due to its potential in soil amendment, crop fertilization, carbon sequestration and environmental remediation of heavy metals and organic pollutant (Chen et al., 2014; Tan et al., 2016). In comparison with activated carbon, the specific surface area and micropore volume of biochars are much smaller (Chen et al., 2014). However, the adsorption capacity of biochars in regard to hazardous cations and anions is comparable with that of activated carbon. Due to its abundant functional groups and lower cost, biochar is a best replacement of commercial activated carbon (Chen et al., 2015; Tytlak et al., 2015). Generally, there are different kinds of mechanisms for Cr(VI) removal by biochars: (i) electrostatic interaction, where Cr(VI) ions are adsorbed on the positively charged surface of sorbent without any Cr(VI) reduction; (ii) complete reduction, where Cr(VI) ions are adsorbed and entirely reduced by sorbent to Cr(III) form; (iii) cationic adsorption, where Cr(VI) ions are entirely reduced by sorbent to Cr(III) form and then adsorbed onto the sorbent; (iv) adsorption coupled with reduction, where Cr(VI) ions are partly adsorbed onto the sorbent and the remainder are reduced to Cr(III) form (Tytlak et al., 2015). These different mechanisms responsible for Cr(VI) sorption by biochar are probably attributed to the chemical composition and properties of biochar, which largely depend on the characteristics of feedstock source and the pyrolysis conditions. Among pyrolysis conditions, temperature plays a key role in the pyrolysis process of feedstock and it greatly influences the physicochemical properties of biochar as well as the toxic ions' fate in the biochar body (Chen et al., 2014). It is well known that the chemical compositions of biochar are oxygen-containing functional groups, carbon fractions with aromatic structure and mineral constituents, which are greatly controlled by the pyrolysis temperature (Wang et al., 2015). A number of researches have been reported to determine how pyrolysis temperature as a critical factor of structural transformation translates into the function of biochar as a soil amendment, nature fertilizer, carbon sequestration agent or environmental sorbent (Mendez et al., 2013; Uchimiya et al., 2011; Yuan et al., 2014). However, very limited studies have been performed to elaborate the relationship between Cr(VI) adsorption and biochar properties based on different pyrolysis temperature. Thus, probing the exact mechanisms underlying Cr(VI) sorption by biochars produced from various temperatures is indispensable.

Biochar can be generated from various raw materials such as wood materials, switch grass, agricultural residues (cereal straw, nutshells and rice hulls), chicken litter, dairy manure and sewage sludge (Ahmad et al., 2012). To our knowledge, there is few research to date on the preparation and characterization of biochar produced from ramie residue via different pyrolysis temperature. Ramie (*Boehmeria nivea*) is a crop that extensively grown in Asian countries such as China, Philippines, India and Thailand. The coat of ramie stem is used for textile industry, whereas the decorticated stem is normally treated as solid waste. In China, the annual production of ramie residue is estimated to be approximately 450,000 tons (Wang and Wang, 2013). Additionally, ramie is mainly composed of cellulose (68.6–76.2%) (Liu et al., 2008), which is a linear macromolecule formed by anhydroglucose. Byproducts of cellulose pyrolysis include unsaturated anhydrosugars, catechol,

diols and other compounds those can act as reducing and chelating agents toward metal ions (Mohan et al., 2011). Therefore, it is environmentally and financially viable to regard ramie residue as a good feedstock to make biochar.

In this study, oxygen-limited pyrolysis was used to prepare a series of ramie biochars using a laboratory-scale reactor at 300–600 °C, and then their physio-chemical properties were characterized. The main aims of this study were to: (i) investigate the effect of pyrolysis temperature on the characteristics and chemical composition of ramie biochar; (ii) determine Cr(VI) adsorption properties on the ramie biochars; (iii) probe the relationship between Cr(VI) sorption mechanisms and the properties of ramie biochar by using various instrumental analysis.

2. Materials and methods

2.1. Chemicals

All chemicals including HCl, NaOH, H₂SO₄, HNO₃, H₃PO₄, CH₃COCH₃, C₁₃H₁₄N₄O, and K₂Cr₂O₇ were analytical reagent grades. A stock solution (1000 mg L⁻¹) of Cr(VI) was prepared by dissolving K₂Cr₂O₇ in ultrapure water (Milli-Q Millipore, conductivity of 18.25 MΩ cm⁻¹). The working solutions of desired Cr(VI) concentrations were prepared daily by appropriately diluting the stock solutions.

2.2. Biochar preparation

Ramie residues, mainly the decorticated stems of ramies, were supplied by the farms in Changsha City, Hunan Province, China. The samples were air-dried at room temperature and then smashed to pass through a 100 mesh sieve (0.147 mm). The ground ramies were pyrolyzed at 300, 450, and 600 °C under 50 mL min⁻¹ nitrogen flow rate using a muffle furnace with tubular reactor. The furnace was programmed to heat with a rate of 5 °C min⁻¹ until it reached at a specified temperature and maintained the temperature for 2 h. The resulting biochars were allowed to cool down under nitrogen flow. Then the biochars were washed with deionized water for several times, dried at 60 °C for 24 h and sieved to a size ≤0.147 mm. The dried biochars were stored in an airtight desiccator prior to use and were abbreviated as RB300, RB450 and RB600 respectively, according to the pyrolysis temperature.

2.3. Biochar characterization

Biochar yield was calculated as the ratio of the weight of biochar samples to that of dried ramie biomass. The pH value of biochar samples was determined by mixing biochar to deionized water at a ratio of 1:10 (w/v). The zeta potential of biochar was determined by using Electroacoustic Spectrometer (ZEN3600 Zetasizer UK) at varying solution pH from 2.0 to 8.0. The elemental composition of biochar was performed by an elemental analyzer (Vario EL III, Elementar, Germany). The surface area, pore size and pore volume were measured by the N₂ adsorption-desorption isotherm at 77.3 K using a Micromeritics TriStar II 3020. The surface morphology of biochar was observed by Quanta FEG 250 environmental scanning electron microscopy (SEM). The surface functional groups of biochar involved in the Cr(VI) removal were determined by Fourier transform infrared spectrophotometer (FTIR) (Nicolet 5700 Spectrometer, USA).

2.4. Adsorption experiments

Batch adsorption experiments of Cr(VI) were performed in triplicate in 100 mL sealed conical flasks on a thermostat water-wash

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