Bioresource Technology 206 (2016) 217–224

Contents lists available at ScienceDirect

Bioresource Technology

journal homepage: www.elsevier.com/locate/biortech

Effective removal of heavy metal by biochar colloids under different pyrolysis temperatures

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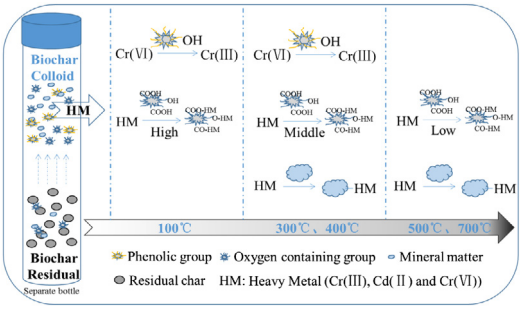
HIGHLIGHTS

- Biochar colloid contained numerous oxygen function group and mineral matters.
- Cr and Cd adsorption by biochar colloid was greater than that for biochar residue.
- RS400 was the most effective Cr(III) and Cd(II) adsorbent.
- RS300C was effective for Cr(VI) removal due to its reduction and adsorption.
- Dual reaction sites were responsible for effective removal of Cr and Cd by biochar.

GRAPHICAL ABSTRACT



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ARTICLE INFO

Article history:
Received 20 November 2015
Received in revised form 11 January 2016
Accepted 14 January 2016
Available online 25 January 2016

Keywords:
Biochar colloids
Cadmium
Chromium
Adsorption
Reduction

ABSTRACT

Biochar colloids' association with heavy metal needs be studied to precisely evaluate the effectiveness of biochar as sorbents. The structure of biochar colloids and their roles in heavy metal removal were investigated by Fourier-Transform Infrared Spectroscopy, X-ray Diffraction and batch adsorption experiments, respectively. Due to the numerous oxygen function groups and mineral matters contained in biochar colloids, the removal capacity of chromium (Cr) and cadmium (Cd) to biochar colloids was much greater than that of biochar residues. The highest adsorption capacities of Cr(III) and Cd(II) under initial pH 3.5 were obtained by RS400, which were mainly attributed to the presence of oxygen function groups and mineral matters simultaneously. The highest removal capacity of Cr(VI) was observed by RS300 due to the additional reduction by phenolic functional groups of RS300C. Therefore, the functions of biochar colloids for heavy metal removal should be considered.

1. Introduction

Biochar is often charred from biomass, and it is considered a novel and practical approach in the biowaste treatment and pollution remediation (Chen et al., 2008, 2012; Fang et al., 2015; Qian et al., 2013; Uchimiya et al., 2011; Yan et al., 2015). An increasing number of studies have shown that the organic components and inorganic ions of biochar played dominant roles in the immobilization of heavy metals (Cao and Harris, 2010; Qian and Chen, 2013, 2014; Qian et al., 2015; Uchimiya et al., 2011). Generally, the heavy metal immobilization by these constituents of biochar not only happens to biochar surfaces, but also reacts with the dissolved matters (Chen et al., 2015; Dong et al., 2014; Hsu et al., 2009). The oxygen-containing functional groups of the dissolved matter of biochar could lead to hexavalent chrome reduction and the dissolved phosphorus could co-precipitate with heavy metals (Shen et al., 2012; Zhang et al., 2013; Zheng et al., 2012). Typically, the most of these active components dissolved by biochar could be viewed as biochar colloids, which has been received increasing

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http://dx.doi.org/10.1016/j.biortech.2016.01.065
0960-8524/

focus on its association with heavy metals (Gao et al., 2011; Kumari et al., 2014; Wang et al., 2013b).

Colloids are generally considered as the suspended particles between 1 nm and 10 μm, which are highly reactive in the subsurface (Lead and Wilkinson, 2006; Manoharan, 2015). Colloids are also heterogeneous, including clay, metal oxides, silica, large organic molecules etc., making the association of heavy metals with colloids more complex (Gao et al., 2011; Sen and Khilar, 2006). Due to the heterogeneous nature, biochar exhibits mutable properties, which depend on the biomass and pyrolysis temperatures (Cantrell et al., 2012; Chen et al., 2008). Furthermore, as a series of biochar dissolving and break down would happen after biochar amendment to the environment, it is important to understand the interaction processes of such components with heavy metals. The effects of particles and pyrolysis temperatures on the transport and retention behaviors of biochar colloids were investigated (Wang et al., 2013a; Zhang et al., 2010). However, relatively less attention has been paid to the association of biochar colloids with heavy metals.

The main objective of this study was to evaluate the interaction of biochar colloids and heavy metals (trivalent chromium (Cr(III)), hexavalent chrome (Cr(VI)) and Cadmium (Cd(II))). The different biochar colloids were obtained from rice straw pyrolyzed at a series of temperatures (100, 300, 400, 500 and 700 °C). Then the structures of biochar colloids and biochar residues were analyzed by Elemental Analyses, Fourier-Transform Infrared Spectroscopy (FTIR) and X-ray Diffraction (XRD). The interaction of biochar colloids with heavy metals was observed by batch adsorption experiments with pH ranging from 1.5 to 4.5. Finally, the mechanism of biochar colloids for the adsorption of heavy metals was interpreted and implications for risk assessment were discussed.

2. Methods

2.1. Preparation of biochars and biochar colloids

A crop residue (rice straw (RS)) was collected from the Changshu Agroecological Experiment Station of Institute of Soil Science, Chinese Academy of Sciences. The biochars were prepared by charring rice straw under anaerobic conditions under varying temperatures. The procedure of preparing the biochars is in accordance with a modified method (Qian and Chen, 2013). Briefly, the rice straw was air-dried for 2 days before being oven-dried overnight at 70–80 °C. Then the biomass sample was grounded and passed through a 0.154 mm sieve. The powdered biomass was tightly packed into a ceramic pot and covered with a fitted lid before being pyrolyzed for 6 h at different temperatures (100, 300, 400, 500 and 700 °C) in a muffle furnace under an oxygen-limited atmosphere. The heating rate was controlled at 5 °C/min for slow pyrolysis. Biochars produced at 100, 300, 400, 500 and 700 °C are here labeled respectively as RS100, RS300, RS400, RS500 and RS700. The biochars were passed through a 0.154 mm sieve prior to prepare biochar colloids. The procedure of preparing the biochar colloids was modified from a previous method (Wang et al., 2013a). Briefly, 6.0 g of biochars was added to 500 mL of distilled water, gently stirred for 1 min, and then sonicated (100 W, 45 kHz, KQ-600VDB sonicator, Kunshan, China) in a water bath for 30 min to disperse the suspension. After settling for a fixed time based on Stokes Law, the suspension particle size was less than 2 μm, and was designated as biochar colloids (Wang et al., 2013a). Then the solid and liquid was separated, the liquid suspension of biochar samples were named biochar colloids, marked as RS100C, RS300C, RS400C, RS500C and RS700C, and the solids of biochar samples were named as biochar residues, marked as RS100R, RS300R, RS400R, RS500R and RS700R. The biochar colloids and residues were dried and passed through a 0.154 mm sieve before use.

2.2. Sample characterization

The samples of biochar colloids and biochar residues were characterized by Elemental Analyses (Vario Macro CHNS-O-CL, Elementar, Germany) and Fourier-Transform Infrared Spectroscopy (FTIR, Thermo Scientific 7600, USA), X-ray Diffraction (XRD, RIGAKU D/MAX 2550/PC, Japan). The elemental (Carbon (C), Hydrogen (H), Oxygen (O) and Nitrogen (N)) analyses of biochar colloids and residues were conducted with the Elemental Analyses. For FTIR analyses, biochar samples were treated by KBr wafers with a 1/100 mass ratio, grounded and pressed into lamellar forms. The samples were recorded between 4000 and 400 cm^{-1} by the FTIR spectrophotometer at a resolution of 4.0 cm^{-1} and 64 interferograms to investigate the structural characteristics of organic matter in biochar residues and colloids. XRD data were obtained with a XRD equipped with a Cu Kα radiation source at a diffraction angle region of 2–70° to observe the crystalline substances in biochar residues and colloids.

2.3. Batch adsorption experiments

The pH dependent adsorption experiments were undertaken in 8 mL vials with sample-to-water ratios being 1.00 and 2.00 mg per 8 mL for biochar colloids and biochar residues. The initial $CrCl_3$, $K_2Cr_2O_7$ and $CdCl_2$ concentrations were 100 μmol/L (with 0.01 mol/L NaCl as a background electrolyte), and the initial pH ranged from 1.5 to 4.5. The initial pH of heavy metal solution was adjusted using 0.1 mol/L HCl or NaOH. The adsorption experiments including the blank and calibration control were performed in duplicate. The mixture was subsequently agitated on a reciprocating shaker at 150 rpm and 25 ± 1 °C for 24 h. Then the solution was filtered through a 0.22 μm millipore filter. The filtrate was acidified immediately with 0.2% (v/v) HCl for total Cr and Cd analysis. The total Cr and Cd concentrations in the supernatant fluid were determined by a Varian Spectra AA220 atomic adsorption spectrometer (Varian, USA). The total Cr and Cd were determined at wavelength of 357.9 nm and 228.8 nm, respectively, the Cr(III) was taken as the difference between total Cr and Cr(VI) values. The Cr(VI) concentration was determinated by an UV–vis Spectrophotometer (Shanghai Puyuan Alpha-1506) with diphenylcarbazide at 540 nm.

3. Results and discussion

3.1. Structural characterization of biochar colloids and biochar residues

As illustrated in Table 1, the element contents of biochar colloids and biochar residues were different as the pyrolysis temperature is increased. When the pyrolysis temperature was at 100 °C, Carbon (C), Hydrogen (H), Oxygen (O) contents were relatively

Table 1
Elemental compositions and atomic ratios of the biochar colloid and residue samples produced under different temperatures. The "C" and "R" represent "Colloid" and "Residue", respectively.

Samples	N (%)	C (%)	H (%)	O (%)	H/C
RS100C	1.10	34.48	5.38	45.39	1.87
RS300C	0.61	33.33	3.06	28.01	1.10
RS400C	0.59	25.79	2.03	23.77	0.94
RS500C	0.45	23.52	1.81	30.72	0.92
RS700C	0.01	24.65	1.15	27.04	0.56
RS100R	0.34	40.81	5.94	50.91	1.75
RS300R	0.69	50.21	4.45	28.91	1.06
RS400R	0.65	50.02	3.63	25.55	0.87
RS500R	0.52	50.84	3.28	19.21	0.77
RS700R	0.70	49.01	2.14	21.62	0.52