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

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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.

Keywords: Biochar colloids; Cadmium; Chromium; Adsorption; Reduction.

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., 2012; Chen et al., 2008; 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 & Harris, 2010; Qian & Chen, 2013; Qian & Chen, 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 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 & 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 & 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 pyrolysed 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 Materials and 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 & 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 $K\alpha$ 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 , $\text{K}_2\text{Cr}_2\text{O}_7$ and CdCl_2 concentrations were 100 $\mu\text{mol/L}$ (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 determined by an UV-vis Spectrophotometer (Shanghai Puyuan Alpha-1506) with diphenyl-carbazide 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 similar between biochar colloids and biochar residues, indicating the organic matters were easily dissolved at 100 °C. The Nitrogen (N) content in the biochar colloids was significantly higher than that in the biochar residues, which illustrated that N was easily dissolved from biochar at 100 °C. As the charring temperature was increased to 700°C, the C, H, O, N contents of biochar colloids were decreased from

34.48% to 24.65%, 5.38% to 1.15%, 45.39% to 27.04 and 1.10% to 0.01, respectively. Therefore, the dissolved organic constituents were reduced as the charring temperature was increased, indicating that the biomass pyrolysis to biochar could promote the carbon and nitrogen fixation. The phenomenon was affirmed by the C and N contents increased with pyrolysis temperature increasing in biochar residue. Furthermore, the H/C ratio of biochar colloids and residues were decreased with the increase of pyrolysis temperature. As the H/C ratio is the molar ratio, it is the representative of the degree of carbonization, indicated the thermal alteration of lignocellulose to more condensed aromatic structures (Chen et al., 2008).

The evolution of FTIR spectra of biochar colloids and residues with the increasing pyrolysis temperatures are illustrated in Fig. S1 (Supplementary data). For biochar residues, RS100R was rich in organic and inorganic functional groups, as occurred at 3405 cm^{-1} (-OH), 1732 cm^{-1} and 1162 cm^{-1} (ester C=O), 1651 cm^{-1} (aromatic C=C) and between 1200 and 1060 cm^{-1} (C-O), 1100-1000 cm^{-1} , 880-780 cm^{-1} and 470 cm^{-1} (Si-O-Si). When the pyrolytic temperature of the biochar was increased further, the functional group were decreased or eliminated. A previous study compared the FTIR spectra of original biochar with washed biochars confirmed that the matters released from biochar could not change its functional group (Xiao et al., 2014). However, the FTIR spectra performance of biochar colloids showed different variation from that of biochar residues. For RS100C, the bands at 3400-3420 cm^{-1} , 3000-2800 cm^{-1} represent the stretching of -OH, -CH₃ and -CH₂, respectively, which indicated that fatty alcohol

compounds existed in the biochar colloids. The RS100C exhibits stronger peak intensity at 1384 cm^{-1} , 1632 cm^{-1} and 3405 cm^{-1} than that of RS100R, which are attributed to C-H deformation of aliphatic groups, aromatic C=C stretching vibration and O-H stretching from the presence of phenols, respectively (Li et al., 2014). A much higher absorption intensity was occurred at the 1632 cm^{-1} , 1113 cm^{-1} and 619 cm^{-1} bands indicated the presence of the aromatic and polysaccharide contents in biochar colloids (Zhu et al., 2014). Similar to RS100C, such characteristic bands were also identified by the FTIR spectra of dissolved organic matter of biochars derived from rice straws (Matilainen et al., 2011). As the charred temperature was increased to 300 °C, the stronger peak intensity of C-H deformation of aliphatic groups (1378 cm^{-1}), aromatic C=C stretching vibration (1620 cm^{-1}) and O-H stretching (3428 cm^{-1}) were still observed, indicating that the phenol functional groups were remained on the RS300C. As the charred temperatures were further increased in case of RS400C, RS500C and RS700C, the organic functional groups were also decreased or eliminated, and the band of Si-O-Si occurred in biochar colloid indicated high Si dissolution. Remarkably, new bands were found in RS500C and RS700C, such as 1586 cm^{-1} for RS500C and 1460 cm^{-1} , 1116 cm^{-1} , 849 cm^{-1} for RS700C, indicating the appearance of a C=C aromatic stretch (Eusterhues et al., 2011; Oren & Chefetz, 2012).

The X-ray diffraction spectra of the biochar colloids and residues are shown in Fig. S2. The diffraction peaks (2θ) between $2\theta= 15$ and 30 in the RS100R were attributed to amorphous organic components (Cao & Harris, 2010). These components were

gradually disappeared as the pyrolysis temperature was increased. No crystalline substances were observed in the XRD spectra of RS100R. Previous studies have confirmed this observation (Qian & Chen, 2013). Unlike the original biochar where the great amount crystalline substances were appeared with increasing pyrolysis temperatures, the crystalline substances of biochar residues were decreased or eliminated. A few crystalline substances, such as calcium oxalate (CaC_2O_4), calcite (CaCO_3), sylvite (KCl), quartz (SiO_2), were appeared in RS300R, RS400R, RS500R and RS700R, respectively. This phenomenon indicated that many crystalline substances were mainly dissolved into the solution to form biochar colloids. The diffraction spectra confirmed the presence of many crystalline substances in biochar colloids. The calcium oxalate (CaC_2O_4) and sylvite (KCl) were appeared in RS100C. As the pyrolysis temperature was increased, new diffraction peaks for magnesia calcite (MgCO_3), calcite (CaCO_3), dolomite ($\text{CaMg}(\text{CO}_3)_2$) were appeared in RS500C and RS700C. The presence of quartz and calcite indicated that the rice straw was rich in silicon and the alkaline elements.

3.2 The heavy metal removal properties by biochar colloids and residues

The effect of pH on Cr(III) adsorption by biochar colloids and residues are given in Fig. 1. The Cr(III) adsorption by biochar residues was gradually increased when the pH values were increased from 2.5 to 4.5. The Cr(III) adsorption by RS100R was increased from 2.4 to 3.1 mg/g when initial pH 3.0 was raised to pH 4.5. Similarly, the Cr(III) adsorption by RS300R, RS400R, RS500R and RS700R were also increased with the

increase of the pyrolysis temperature and reached to the highest amount of 5.2, 6.5, 3.5 and 3.5 mg/g at initial pH 4.5, pH3.9, pH3.3 and pH3.5, respectively. It is apparent that the Cr(III) adsorption capacity was not efficient. This was mainly attributed to the alkaline elements and inorganic ion being released from biochar (Fig. S2). The final pH of RS100R, RS300R, RS400R, RS500R, RS700R were around 3.5, 3.7, 3.8, 4.0, 4.4 with initial pH 3.5 (Fig. 2), indicating that the pH increased by biochar residue amendment was limited. In addition, the results of FTIR and XRD spectra confirmed that the dissolved organic matters and inorganic ions were released into the solution as biochar colloids (Fig. S1 and Fig. S2). These components released from biochar mainly affected the adsorption performance of biochar. The Cr(III) adsorption by biochar colloids is provided on Fig. 1. Surprisingly, the Cr(III) adsorption by biochar colloids was higher than that by biochar residues. For RS100C, the adsorption capacity between RS100C and RS100R were more or less the same at the initial pH3.0. As the pH was increased, the adsorption capacity for Cr(III) by RS100C was higher than that of RS100R, reaching 3.8 mg/g by RS100C. The Cr(III) adsorption by biochar colloids was hastened with the increase of the pyrolysis temperature. The highest Cr(III) adsorption capacity by RS300C, RS400C, RS500C and RS700C reached 13.3, 14.1, 10.4 and 10.5 mg/g at initial pH 4.5, 3.9, 3.5 and 3.5, respectively. The Cr(III) adsorption by biochar colloids was significantly greater than that by biochar residues (Fig. 1). The highest Cr(III) adsorption capacity of RS300C, RS400C, RS500C and RS700C was around two to three times greater than those of RS300R, RS400R, RS500R and RS700R. These

results were potentially caused by the colloidal effect and the pH increased by biochar colloids (Fig. 2). As colloids have higher specific surface areas and strong affinity, which results in biochar colloids being highly reactive (Gao et al., 2011). The biochar colloids contained numerous oxygen function groups and mineral matters, which could be served as the adsorption sites of Cr(III). Furthermore, the increasing pH may lead to transformation of Cr form to insoluble species, and also could activate the adsorption site (such as silicate particles) of biochar colloids. The highest Cr(III) adsorption was observed at RS400, which is consistent with the previous report about the Al adsorption by biochar (Qian & Chen, 2013). The study found that the organic components and silicate particles within the biochars were served as dual adsorptive sites for Al, as RS400 owned both of them, thus had the highest Al adsorption capacity.

The Cd(II) adsorption by biochar colloids confirmed the phenomenon obtained in Cr(III) adsorption by biochar colloids and residues (Fig. 3). The Cd(II) adsorption capacity by biochar colloids was higher than that of the correspondent biochar residue. When the initial pH was lower than 3.5, similar to Cr(III), the highest Cd (II) adsorption capacity by RS100C, RS300C, RS400C, RS500C and RS700C were obtained at 2.75, 9.00, 14.56, 13.54 and 10.80 mg/g at initial pH 3.5, respectively. These compared with the highest Cd adsorption capacity by RS100R, RS300R, RS400R, RS500R and RS700R achieved at 1.13, 3.28, 6.68, 7.54 and 5.83 mg/g at initial pH 3.5, respectively. When the initial pH was higher above 3.5, the highest adsorption capacity for both biochar colloids and residues were reached at initial pH 4.5. The highest adsorption

capacity of RS500C (39.0 mg/g) and RS700C (45.8 mg/g) were two orders of magnitudes greater than those of RS500R (19.0 mg/g) and RS700R (20.4 mg/g), respectively, which was potentially caused by their high content of alkaline and mineral elements (Fig. S1 and Fig. S3). As the final pH of RS500 and RS700 were higher above 7.0 in case of the initial pH 4.5 (Fig. S3), the precipitation of Cd was one of reasons for the high Cd(II) removal by RS500 and RS700.

The effect of pH on Cr(VI) removed by biochar colloids and residues are presented in Fig. 4. For biochars pyrolysed at low temperatures (RS100, RS300 and RS400), the Cr(VI) removal capacity of biochar colloids was higher than that of correspondence biochar residues. Unlike the adsorption behavior of the cationic heavy metals by biochar, the removal capacity of Cr(VI) by biochar colloids and residues was decreased significantly with increasing solution pH, but the removal capacity between them has significant differences. At the initial pH1.5, the adsorption capacity of Cr(VI) by RS100C was reached 11.15 mg/g, which is about 3 times higher than that of RS100R (3.76 mg/g). This was mainly attributed to the adsorption and reduction processes of the Cr(VI) removed by RS100. Due to its high redox potential, Cr(VI) is easily reduced to Cr(III) under acid conditions in the presence of oxygen-containing organic components. Previous studies have shown that the biomaterials present in nature could lead to the Cr(VI) reduction (Park et al., 2007). Then as the initial pH was increased, the removal capacity of Cr(VI) by both the biochar colloids and residues have been declined significantly. When the initial pH was raised to 4.0, the adsorption capacity of Cr(VI) by

RS100C and RS100R was decreased to 2.13 and 0.48 mg/g, respectively. Remarkably,
 the removal capacity of Cr(VI) by biochar colloids pyrolysed at higher temperature was
 falling sharply. At an initial pH1.5, the removal capacity of Cr(VI) by RS300C, RS400C,
 RS500C and RS700C were 11.02, 7.91, 4.42 and 1.34 mg/g respectively. As greater
 mobility was observed for the smaller particle sizes of biochar (Wang et al., 2013a), this
 phenomenon indicated that the risk of Cr(VI) migrating to groundwater was reduced
 when biochar pyrolysed at higher temperatures. However, the removal capacity of Cr(VI)
 by biochar residues showed different trends compared to that of biochar colloids.
 Biochar residues derived from the middle and high pyrolysis temperatures had higher
 removal capacity of Cr(VI) than that of RS100 residues. At an initial pH1.5, the removal
 capacity of Cr(VI) by RS300R, RS400R, RS500R and RS700R were 6.52, 6.20, 5.70
 and 6.77 mg/g respectively, indicating a strong capacity by biochar residues to reduce
 groundwater contaminated by Cr(VI). The total removal capacity of Cr(VI) by biochar
 colloids and residues was also investigated with the decreasing order of significance:
 RS300>RS100>RS400>RS500>RS700. The highest removal capacity of Cr(VI) by
 RS300 at pH1.5 has reached 17.54 mg/g, about two times higher than that of RS700.
 This was mainly related to the strong adsorption and reduction of Cr(VI) by RS300, with
 the phenolic groups and hydroxyl groups responsible for Cr(VI) reduction and mineral
 matters and other oxygen functional groups for promoting the Cr(VI) adsorption by
 biochar (Fig.S1 and Fig. S2). Previous studies indicated that the phenolic groups of
 biochar are the dominant drivers of Cr(VI) reduction (Hsu et al., 2009). Therefore, from

the removal of high mobility of Cr(VI) by biochar, it was found that as the biochar pyrolysis temperatures were raised, the removal capacity of Cr(VI) by biochar colloids were decreasing, and that of Cr(VI) by biochar residues were firstly increasing then maintaining at a high level, thereby reducing the risk of groundwater contaminated by Cr(VI).

To better understand the removal characteristics of biochar, the total Cr removal by the biochar colloids and residues were also investigated (Fig.4). As illustrated in Fig. 4, total Cr removal capacity by biochar colloids were significantly higher than that of biochar residues. At initial pH1.5, total Cr removal capacities by biochar colloids were 28.32, 25.33, 22.52, 19.69 and 16.17 mg/g for RS300C, RS400C, RS500C, RS100C and RS700C respectively. At pH1.5, total Cr removal capacities by biochar residues were 11.62, 10.67, 9.74, 9.01 and 7.86 mg/g respectively for RS300C, RS400C, RS700C, RS500C and RS100C. The above results showed that the total Cr removal capacity by biochar colloids was about two times higher than those of the corresponding biochar residues. This phenomenon was mainly due to the biochar colloids rich of dissolved organic matters and inorganic minerals, these substances have a strong capability on chromium fixation with biochar colloids having very strong colloidal effects, thus a combination of these characteristics enhanced the Cr removal by biochar colloids (Dong et al., 2014; Gao et al., 2011; Kumari et al., 2014; Zhang et al., 2013). Among biochars pyrolysed at the different temperatures, total Cr removal capacity for RS300 ranked the highest, this may be related to biochar having large amounts of organic components,

such as the oxygen-containing functional groups and a certain amount of mineral components, and both of the two components contributed to the total Cr removal by RS300 (Dong et al., 2014; Hsu et al., 2009; Shen et al., 2012).

3.3 Mechanisms of heavy metal removal by biochar colloid and biochar residue

The heavy metal removal by the biochar colloids and residues were investigated under different pyrolysis temperatures. For cationic heavy metal (Cr(III) and Cd(II), the representative cationic heavy metal), RS400 was the most effective adsorbent for Cr(III) and Cd(II) under initial pH 3.5. These results were potentially caused by it contains oxygen function groups and mineral matters simultaneously and the pH increasing. As the oxygen function groups and mineral matters could be served as the adsorption sites of Cr(III) and Cd(II). Furthermore, the increasing pH may lead to the transformation of Cr and Cd form to insoluble species, and could activate the adsorption sites (such as silicate particles) of biochar colloids. This was consistent with the Al adsorption behavior by biochar, indicating that both the organic components and mineral matter within the biochars contributed to heavy metal adsorption by biochar. For Cr(VI) (commonly existed as chromate (CrO_4^{2-} , HCrO_4^-) and dichromate ($\text{Cr}_2\text{O}_7^{2-}$), RS300 was the most effective for Cr(VI) removal. The primarily responsible for the Cr(VI) removal were the reduction and adsorption. The phenolic groups and hydroxyl groups in biochar are responsible for Cr(VI) reduction, and the mineral matter and other oxygen functional groups are contributed to the Cr(VI) adsorption by biochar (Dong et al., 2014; Hsu et al., 2009). As RS300 owned both of them, thus had the highest Cr(VI) removal amount.

The result of heavy metal removal by biochar colloid and biochar residue showed that the removal rate of heavy metal by biochar colloid was higher than that of corresponding biochar residue except the Cr(VI) removal by RS500 and RS700. The high removal rate of Cr(III) and Cd(II) could be attributed to the numerous content of oxygen function group (Fig. S1) and mineral matter (Fig. S2). And the phenolic functional groups contained in RS100 and RS300 mainly the reason of high removal of Cr(VI). However, when the pyrolysis temperature increased (RS500 and RS700), the Cr(VI) removal rate by biochar residue was higher than that of biochar colloid. It is well known that colloid can be mobilized and transported by water flow to a distance in soil and groundwater environments (Sen & Khilar, 2006). Colloid-facilitated transport has been considered to be one of the most important mechanisms making reactive heavy metals mobiles in soils and groundwater (Grolimund & Borkovec, 2005). The high removal rate of Cr(III) and Cd(II) by biochar colloid could induced the heavy metal mobility enhanced, thus increased the risk of cationic heavy metal contamination in groundwater. Remarkably, as pyrolysis temperature increased, the Cr(VI) removal by biochar colloid was decreased, indicating that the potential risk of anionic heavy metal contamination in groundwater was decreased.

4 Conclusions

The structures of biochar colloids were different from those of biochar residues. Biochar colloids contain numerous oxygen function groups and mineral matters obtained under low and high pyrolysis temperatures. The high contents of oxygen function groups and mineral matters in biochar colloids lead to the high removal of

Cr(III) and Cd(II). The phenolic functional groups contained in RS100 and RS300 resulted in the enhancement of Cr(VI) reduction, and the Cr(VI) removal by biochar residues was higher than that of biochar colloids when the pyrolysis temperature was increased (RS500 and RS700).

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Reference

- Cantrell, K., Hunt, P., Uchimiya, M., Novak, J., Ro, K., 2012. Impact of pyrolysis temperature and manure source on physicochemical characteristics of biochar. *Bioresour. Technol.* 107, 419-428.
- Cao, X., Harris, W., 2010. Properties of dairy-manure-derived biochar pertinent to its potential use in remediation. *Bioresour. Technol.* 101(14), 5222-5228.
- Chen, B., Yuan, M., Qian, L., 2012. Enhanced bioremediation of PAH-contaminated soil by immobilized bacteria with plant residue and biochar as carriers. *J. Soil.*

381 Sediment. 12(9), 1350-1359.

382 Chen, B., Zhou, D., Zhu, L., 2008. Transitional adsorption and partition of nonpolar and
 383 polar aromatic contaminants by biochars of pine needles with different pyrolytic
 384 temperatures. Environ. Sci. Technol. 42(14), 5137-5143.

385 Chen, Z., Xiao, X., Chen, B., Zhu, L., 2015. Quantification of chemical states,
 386 dissociation constants and contents of oxygen-containing groups on the surface
 387 of biochars produced at different temperatures. Environ. Sci. Technol. 49(1),
 388 309-317.

389 Dong, X., Ma, L.Q., Gress, J., Harris, W., Li, Y., 2014. Enhanced Cr(VI) reduction and
 390 As(III) oxidation in ice phase: Important role of dissolved organic matter from
 391 biochar. J. Hazard. Mater. 267, 62-70.

392 Eusterhues, K., Rennert, T., Knicker, H., Kogel-Knabner, I., Totsche, K., Schwertmann,
 393 U., 2011. Fractionation of organic matter due to reaction with ferrihydrite:
 394 coprecipitation versus adsorption. Environ. Sci. Technol. 45(2), 527-533.

395 Fang, G., Zhu, C., Dionysiou, D., Gao, J., Zhou, D., 2015. Mechanism of hydroxyl
 396 radical generation from biochar suspensions: Implications to diethyl phthalate
 397 degradation. Bioresour. Technol. 176, 210-217.

398 Gao, B., Cao, X., Dong, Y., Luo, Y., Ma, L.Q., 2011. Colloid deposition and release in
 399 soils and their association with heavy metals. Crit. Rev. Environ. Sci. Technol.
 400 41(4), 336-372.

401 Grolimund, D., Borkovec, M., 2005. Colloid-facilitated transport of strongly sorbing

contaminants in natural porous media: mathematical modeling and laboratory
column experiments. *Environ. Sci. Technol.* 39(17), 6378-6386.

Hsu, N., Wang, S., Lin, Y., Sheng, G., Lee, J., 2009. Reduction of Cr(VI) by
crop-residue-derived black carbon. *Environ. Sci. Technol.* 43(23), 8801-8806.

Kumari, K., Moldrup, P., Paradelo, M., Elsgaard, L., Hauggaard-Nielsen, H., de Jonge,
L., 2014. Effects of biochar on air and water permeability and colloid and
phosphorus leaching in soils from a natural calcium carbonate gradient. *J.*
Environ. Qual. 43(2), 647-657.

Lead, J., Wilkinson, K., 2006. Aquatic colloid and nanoparticles: current knowledge
and future trends. *Environ.Chem.* 3(3), 159-171.

Li, A., Zhao, X., Mao, R., Liu, H., Qu, J., 2014. Characterization of dissolved organic
matter from surface waters with low to high dissolved organic carbon and the
related disinfection byproduct formation potential. *J. Hazard. Mater.* 271,
228-235.

Manoharan, V., 2015. Colloidal matter: packing, geometry, and entropy. *Science*
349(6251), 1253751-1-1253751-7.

Matilainen, A., Gjessing, E., Lahtinen, T., Hed, L., Bhatnagar, A., Sillanpaa, M., 2011.
An overview of the methods used in the characterisation of natural organic
matter (NOM) in relation to drinking water treatment. *Chemosphere* 83(11),
1431-1442.

Oren, A., Chefetz, B., 2012. Sorptive and desorptive fractionation of dissolved organic

423 matter by mineral soil matrices. *J. Environ. Qual.* 41(2), 526-533.

424 Park, D., Lim, S., Yun, Y., Park, J., 2007. Reliable evidences that the removal
 425 mechanism of hexavalent chromium by natural biomaterials is
 426 adsorption-coupled reduction. *Chemosphere* 70(2), 298-305.

427 Qian, L., Chen, B., 2013. Dual role of biochars as adsorbents for aluminum: The effects
 428 of oxygen-containing organic components and the scattering of silicate particles.
 429 *Environ. Sci. Technol.* 47(15), 8759-8768.

430 Qian, L., Chen, B., 2014. Interactions of aluminum with biochars and oxidized biochars:
 431 Implications for the biochar aging process. *J. Agric. Food Chem.* 62(2),
 432 373-380.

433 Qian, L., Chen, B., Hu, D., 2013. Effective alleviation of aluminum phytotoxicity by
 434 manure-derived biochar. *Environ. Sci. Technol.* 47(6), 2737-45.

435 Qian, L., Chen, M., Chen, B., 2015. Competitive adsorption of cadmium and aluminum
 436 onto fresh and oxidized biochars during aging processes. *J. Soil. Sediment.* 15(5),
 437 1130-1138.

438 Sen, T., Khilar, K., 2006. Review on subsurface colloid and colloid-associated
 439 contaminant transport in saturated porous media. *Adv. Colloid Interfac.* 119(2-3),
 440 71-96.

441 Shen, Y., Wang, S., Tzou, Y., Yan, Y., Kuan, W., 2012. Removal of hexavalent Cr by
 442 coconut coir and derived chars - the effect of surface functionality. *Bioresour.*
 443 *Technol.* 104, 165-172.

- Uchimiya, M., Chang, S., Klasson, K., 2011. Screening biochars for heavy metal retention in soil: role of oxygen functional groups. *J. Hazard. Mater.* 190(1-3), 432-441.
- Wang, D., Zhang, W., Hao, X., Zhou, D., 2013a. Transport of biochar particles in saturated granular media: effects of pyrolysis temperature and particle size. *Environ. Sci. Technol.* 47(2), 821-828.
- Wang, D., Zhang, W., Zhou, D., 2013b. Antagonistic effects of humic acid and iron oxyhydroxide grain-coating on biochar nanoparticle transport in saturated sand. *Environ. Sci. Technol.* 47(10), 5154-5161.
- Xiao, X., Chen, B., Zhu, L., 2014. Transformation, morphology, and dissolution of silicon and carbon in rice straw-derived biochars under different pyrolytic temperatures. *Environ. Sci. Technol.* 48(6), 3411-3419.
- Yan, J., Han, L., Gao, W., Xue, S., Chen, M., 2015. Biochar supported nanoscale zerovalent iron composite used as persulfate activator for removing trichloroethylene. *Bioresour. Technol.* 175, 269-274.
- Zhang, W., Mao, S., Chen, H., Huang, L., Qiu, R., 2013. Pb(II) and Cr(VI) sorption by biochars pyrolyzed from the municipal wastewater sludge under different heating conditions. *Bioresour. Technol.* 147, 545-552.
- Zhang, W., Niu, J., Morales, V.L., Chen, X., Hay, A., Lehmann, J., Steenhuis, T., 2010. Transport and retention of biochar particles in porous media: effect of pH, ionic strength, and particle size. *Ecohydrology* 3(4), 497-508.

465 Zheng, R., Cai, C., Liang, J., Huang, Q., Chen, Z., Huang, Y., Arp, H., Sun, G., 2012.

466 The effects of biochars from rice residue on the formation of iron plaque and the
467 accumulation of Cd, Zn, Pb, As in rice (*Oryza sativa* L.) seedlings.
468 Chemosphere 89(7), 856-862.

469 Zhu, W., Yao, W., Zhang, Z., Wu, Y., 2014. Heavy metal behavior and dissolved
470 organic matter (DOM) characterization of vermicomposted pig manure amended
471 with rice straw. Environ. Sci. Pollut. R. 21(22), 12684-12692.

Figure captions

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.

Fig. 1 Effect of pH on Cr(III) adsorption by the biochar colloid and residue samples produced under different temperatures. The “C” and “R” represent “Colloid” and “Residue” respectively.

Fig. 2. The pH changes during Cr adsorption by the biochar colloid and residue samples produced under different temperatures. The “C” and “R” represent “Colloid” and “Residue” respectively.

Fig. 3 Effect of pH on Cd adsorption by the biochar colloid and residue samples produced under different temperatures. The “C” and “R” represent “Colloid” and “Residue” respectively.

Fig. 4 Effect of pH on Cr(VI) removed by the biochar colloid and residue samples produced under different temperatures. The “C” and “R” represent “Colloid” and “Residue” respectively.

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

519 **Fig. 1** Effect of pH on Cr(III) adsorption by the biochar colloid and residue samples
 520 produced under different temperatures. The “C” and “R” represent “Colloid” and
 521 “Residue” respectively.

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534 **Fig. 4** Effect of pH on Cr(VI) removed by the biochar colloid and residue samples
 535 produced under different temperatures. The “C” and “R” represent “Colloid” and
 536 “Residue” respectively.

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Graphical Abstract

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