Enhanced removal of Cr(VI) by biochar with Fe as electron shuttles

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ABSTRACT

Biochar is extensively used as an effective soil amendment for environmental remediation. In addition to its strong contaminant sorption capability, biochar also plays an important role in chemical transformation of contaminant due to its inherent redox-active moieties. However, the transformation efficiency of inorganic contaminants is generally very limited when the direct adsorption of contaminants on biochar is inefficient. The present study demonstrates the role of Fe ion as an electron shuttle to enhance Cr(VI) reduction by biochars. Batch experiments were conducted to examine the effects of Fe(III) levels, pyrolysis temperature of biochar, initial solution pH, and biochar dosage on the efficiency of Cr(VI) removal. Results showed a significant enhancement in Cr(VI) reduction with an increase in Fe(III) concentration and a decrease of initial pH. Biochar produced at higher pyrolysis temperatures (e.g., 700°C) favored Cr(VI) removal, especially in the presence of Fe(III), while a higher biochar dosage proved unfavorable likely due to the agglomeration or precipitation of biochar. Speciation analysis of Fe and Cr elements on the surface of biochar and in the solution further confirmed the role of Fe ion as an electron shuttle between biochar and Cr(VI). The present findings provide a potential strategy for the advanced treatment of Cr(VI) at low concentrations as well as an insight into the environmental fate of Cr(VI) and other micro-pollutants in soil or aqueous compartments containing Fe and natural or engineered carbonaceous materials.

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Introduction

Over the past decades, biochar has attracted widespread attention in terms of soil amendment, carbon sequestration, climate change mitigation, and environmental remediation (Lehmann, 2007; Liu et al., 2015; Godlewksa et al., 2017; Ahmad et al., 2014). Biochar is a carbonaceous solid material produced through the pyrolysis of low-cost biomass under minimum oxygen and at relatively low temperatures (e.g., <700°C) in a closed system (Hale et al., 2012; Lehmann and Joseph, 2009; Liu et al., 2015). The pyrolysis temperature determines the properties of biochar, wherein higher temperatures usually lead to a reduction in hydrogen and oxygen content and an increase in carbon content (Godlewksa et al., 2017). Generally,
moderate pyrolysis temperatures (e.g., 400–700°C) are selected to prepare biochars with a high content of organic carbon, a large specific surface area, and optimum pore volume (Tripathi et al., 2016). In addition to the specific physical structure aforementioned, biochar typically contains various surface functional groups (e.g., hydroxyl, carboxyl), making it an efficient adsorbent for pollutants from soil and aqueous solution (Lian and Xing, 2017). Given the highly aromatic and hydrophobic nature of biochar, it has been excessively used for the sorption of organic contaminants through hydrophobic interactions, π-π bond, and H-bond interactions (Sun et al., 2011; Lattao et al., 2014; Nguyen et al., 2007; Chen et al., 2008). Further, the high affinity of biochar to inorganic contaminants, including heavy metals (e.g., Pb²⁺, Cd²⁺) and anionic pollutants (e.g., F⁻), is mainly ascribed to electrostatic interactions or ion exchange (Wang et al., 2015; Trakal et al., 2014; Papari et al., 2017; Zhao et al., 2017).

Recently, some novel materials (e.g., magnetic active carbon and nanocomposites) were synthesized on a relatively large scale for enhanced removal of heavy metals (Huang et al., 2017; Gong et al., 2018; Wang et al., 2018) and efficient degradation of organic pollutants (Zhang et al., 2017a, 2017b; Song et al., 2017). Compared with carbon based materials and newly developed nanocomposites (Ma et al., 2017; Gu et al., 2018; Zhang et al., 2017a, 2017b), the biomass source is diverse and low-cost (Ahmad et al., 2014). More importantly, the versatile biochar could not only remove inorganic and organic contaminants (Tan et al., 2014), but also has the potential for improving the soil fertility and carbon sequestration (Ahmad et al., 2014).

In addition to immobilization via adsorption, biochar plays an important role in the transformation or degradation of contaminants through a redox reaction involving the quinone and aromatic groups in its structure. For example, biochar was found to stimulate H₂O₂ to produce hydroxyl radicals, which led to degradation of 2-chlorobiphenyl (Fang et al., 2014). Further, biochar can also efficiently degrade diethyl phthalate and redox-active metals, have been reported to act as electron shuttles in liquid solutions between electron donor and acceptor (Ko et al., 2004; Cervantes et al., 2013; Chen et al., 2017a, 2017b). However, to the best of our knowledge, the impact of electron shuttle on the transformation of inorganic contaminants mediated by biochar has not yet been reported. Iron (Fe), the most abundant redox-active metal and widely present in aquatic and soil environments (Fuller et al., 2014), has been shown to act as an electron shuttle to enhance redox reaction in the environment (Yin et al., 2017). Herein, the role of Fe as an electron shuttle in the presence of biochar was assessed through its effect on the removal of Cr(VI). Cr(VI) was selected as the model inorganic contaminant due to its great threat to public health and the high redox potential of the Cr (VI)/Cr(III) couple (He et al., 2013; Hu et al., 2016). The relevant parameters, such as Fe(III) concentration, biochar pyrolysis temperature, pH, and biochar dosage for effectiveCr(VI) removal, were also investigated, elucidating the catalytic mechanism of Fe as an electron shuttle. The results obtained herein present an alternative method for the treatment of Cr (VI) pollution as well as a method to evaluate the environmental fate of Cr(VI) at environmentally relevant concentrations in the presence of both Fe and natural or engineered carbonaceous materials in aquatic environments.

1. Materials and methods

1.1. Chemical reagents and materials

All chemicals used in the study were at least of analytical reagent grade and used as received without further purification. The certified standard stock Cr(III) and Cr(VI) solutions (both 100 mg/L) were purchased from the National Institute of Metrology of China. All other reagents used (such as Fe(ClO₄)₃, ethylenediaminetetraacetic acid (EDTA), inorganic acids, etc.) were obtained from Sinopharm Chemical Reagent Co. (Shanghai, China). A stock solution of 100 mg/L Fe(III) was freshly prepared by dissolving Fe(ClO₄)₃ in ultrapure water just prior to the batch Cr(VI) removal experiment. The ultrapure water (18.3 MΩ) was produced by a Milli-Q Gradient system (Millipore, Bedford, USA) and used throughout this work.

Walnut shell biochar was obtained from Zhejiang Biochar Engineering Technology Research Center, Hangzhou, China. The biochar was produced by pyrolyzing walnut shells at 300, 400, 500, 600, and 700°C under a continuous flow of N₂, and was labeled as BC300, BC400, BC500, BC600, and BC700, respectively. To eliminate the DOM induced reduction (Dong et al., 2014), the biochar used was washed with ultrapure water, dried and stored under vacuum condition. Prior to its use, the biochar was slightly ground in an Agata mortar, and passed through a 100-mesh nylon sieve.

1.2. Characterization of biochar

The specific surface area and pore volume of biochar were obtained using (Brunauer-Emmett-Teller) BET method with the N₂ adsorption and desorption isotherms at 77 K by a surface analyzer (ASAP 2460, Micromeritics, USA). The morphology of biochar samples was examined using a field emission scanning electron microscope (SU8020, Hitachi, Japan). The functional groups on the surface of biochar were identified by Fourier transform infrared spectroscopy (FT-IR) (VERTEX 70, Bruker, Germany) in the range from 400 to 4000 cm⁻¹ with a resolution of 4.0 cm⁻¹. The valence states of Cr and Fe species adsorbed onto the biochar surface were analyzed by X-ray photoelectron spectroscopy (XPS) (ESCALAB 250Xi, Thermo Fisher, USA), and XPS spectra were analyzed using XPS Avantage software. The surface charge
achieved using an Agilent Bio WAX column (4.6 mm × 50 mm, 0.6 mmol/L of EDTA. The separation of Cr(VI) and Cr(III) was
justified to pH 8.0 with NaOH), the Fe(II) concentration in the
4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid buffer ad-
according to the ferrozine method (Lovley and Phillips, 1987).
Further, Fe(II) ions were determined
concentrations in solution. Further, Fe(II) ions were determined
by chelating with
1 by chelating with
μm) in a column oven at 25°C. The mobile phase was
μm
μm
μm
μm
μm
2. The separation of Cr(III) and Cr(VI) in the collected filtrate was
analyzed using high performance liquid chromatography (HPLC) (1200, Agilent, USA) coupled with inductively
3, 5, 8, 10, 12 hr). At different time intervals, suspension aliquots were removed
with a 2-mL disposable syringe and filtered through 0.22 μm polytetrafluoroethylene (PTFE) syringe filters. The filtrates
were collected to the anion [Cr(III)-EDTA]
NIR) (UV-3600, Shimadzu, Japan).
2. Results and discussion
2.1. Characterization of biochar
The morphologic and structural properties of biochar were
firstly characterized by BET and scanning electron microscopy (SEM). As shown in Table 1, the specific surface area and pore
volume of biochar increased with increasing pyrolysis temperature. Specially, specific surface area and pore volume increased significantly from 300°C to 500°C, and then presented slow increase from 500°C to 700°C. The specific surface area of these biochars from walnut shell (427.12 m²/g) is generally higher than that from rice hull (10.66 m²/g)(Khorram et al., 2017) and peanut hull (144.60 m²/g) (Han et al., 2016) produced at similar pyrolysis temperature (i.e., 600°C), suggesting that walnut shell biochars have great potential for pollution remediation due to the abundant interaction site. SEM images of BC500 showed a rough and heterogeneous surface, whereas the cross-sectional view showed a high internal porosity, leading to a large surface area, consistent with BET results.
FT-IR was performed to probe the functional groups on the
walnut shell biochar (Fig. 1a). The broad bands detected on biochar samples at 3000–3400 cm⁻¹ were assigned to the stretching vibrations of −OH and C–H bond, whereas the bands at 1573 and 1600 cm⁻¹ corresponded to the C=O stretching vibration and aromatic ring symmetrical stretching vibrations. Further, the peak near 1430 cm⁻¹ was related to the −OH bending vibration (Chia et al., 2012; Dong et al., 2014; Guo et al., 2014). Thus, the surface of BC500 showed abundant hydroxyl and carboxyl groups helpful for the adsorption of heavy metals (Guo et al., 2014). An abundance of aromatic carbon confers the potential redox activity of biochar to donate electrons (Yuan et al., 2017).
Compared with BC500, BC600, and BC700, the peak intensity of BC300 and BC400 at 1430 cm⁻¹ (−OH bending vibration) and 1573 and 1600 cm⁻¹ (C=O and aromatic ring stretching vibrations) was weaker, while a strong peak appeared near 1213 cm⁻¹ (−C−O stretching vibration). Thus, biochars produced under high pyrolysis temperatures have a greater number of functional groups, including −OH, −CHO, C=O, −COO− and aromatic groups, than that of BC300 and BC400 under oxygen-limiting conditions.
XPS was employed to obtain surface chemical composition information for BC500. Given the inapplicability of XPS for hydrogen, the two dominating elements were found to be C and O, and other elements were not obviously observed mainly due to their extremely low contents. The C 1s XPS spectrum of BC500 was curve-fitted into the three peak components at approximately 284.8 eV (C−C), 286.2 eV (C−O), and 287.2 eV (C=O) (Fig. 1b). Thus, XPS data also indicates the existence of oxygen-containing functional groups on the surface of biochar.
The zeta potential of BC500 was evaluated at a pH range of
2.2–8.0. The point of zero charge was found to be at pH 2.5. Therefore, at the pH range studied in further experiments (4.0–8.0), the surface of BC500 was always negatively charged.
2.2. Enhancement of Cr(VI) removal by Fe in the presence of biochar

Fe(III) ions are ubiquitous in the environment and play crucial roles in the transformation and degradation of inorganic and organic pollutants (Lindsay and Schwab, 1982). The effect of Fe(III) (200 μg/L) on Cr(VI) removal by biochar (100 μg/L Cr(VI), 100 mg/L biochar, and pH 5.0) was investigated firstly. The Cr(VI) removal efficiency in the presence of Fe(III) reached nearly 30%, while that of biochar alone was less than 5% over 2 hr (Fig. 2a). Moreover, the removal efficiency of Cr(VI) in the presence of both biochar and Fe(III) was always higher than that of biochar alone over 12 hr, indicating that Fe(III) significantly enhanced Cr(VI) removal in the presence of biochar. Considering the repulsive interaction between the negatively charged BC500 and the Cr(VI) anion, Cr(VI) removal in the absence of Fe(III) could be ascribed to the reduction of Cr(VI) (Dong et al., 2014). To elucidate the role of Fe(III), we further evaluated the effect of Fe(III) concentration on the efficiency of Cr(VI) removal in the presence of biochar over 12 hr. The efficiency of Cr(VI) removal was shown to increase with increasing Fe(III) concentration (Fig. 2b). Notably, the efficiency of Cr(VI) removal dramatically increased within 2 hr for all the Fe(III) concentrations selected. In a recent study (Zhou et al., 2017), biochars containing quinones and aromatic structures were proven to expedite the reduction rates of ferrihydrite. Therefore, we supposed that, herein, Fe(II) ions generated through Fe(III) reduction by BC500 may be responsible for the enhancement of Cr(VI) removal, as discussed later.

2.3. Effect of biochar pyrolysis temperature

The pyrolysis temperature is an important factor in biochar production, influencing the surface characteristics of biochar, including the functional groups and specific surface area, and thus has a major effect on the behavior of Cr(VI) removal (Fig. 3). The removal capability of the high-temperature
biochar was better than that of the low-temperature biochar in both the absence or presence of Fe(III). The removal of Cr (VI) by biochars in the absence of Fe(III) increased with pyrolysis temperature of biochars, mainly ascribed to the increase in adsorption between Cr(VI) and biochars with higher specific surface area (as summarized in Table 1), which was consistent with previous studies (Han et al., 2016; Zhang et al., 2017a, 2017b). Further, the efficiency of Cr (VI) removal of the high-temperature biochar (BC500, BC600, BC700) was over 17% higher than that of the low-temperature biochar (BC300, BC400) without Fe(III), and over 27% higher in the presence of Fe(III). Thus, the efficiency of Cr(VI) removal of biochars in the presence of Fe(III) was always higher than that in the absence of Fe(III), while the increase of the removal efficiency was at least 5% (by BC300), and at best 17% (by BC500). Therefore, Fe(III) can improve the efficiency of Cr(VI) removal by all biochars prepared at different pyrolysis temperature. Moreover, the abundance of functional groups, including $\text{-OH}$, $\text{-CHO}$, $\text{C=O}$, $\text{-COO}$ – and aromatic groups, increased with pyrolysis temperatures, which facilitates the adsorption and reduction of Fe(III). The enhanced removal by the BC700 was approximately 10% higher than that of BC300 in the presence of Fe(III). The highest efficiency of Cr(VI) removal (17%) in the presence of Fe(III) was achieved with BC500.

### 2.4. Effect of initial pH

The solution pH is a key factor controlling the species of metal ions (Lindsay and Schwab, 1982; Martin et al., 1998) as well as the surface charge and functional group dissociation of biochar (Lian and Xing, 2017). Taking into consideration the general pH of a surface waters (Valenti et al., 2009), the effect of initial pH on the enhancement of efficiency of Cr(VI) removal was studied within the range 4.0–8.0. The efficiency of Cr(VI) removal increased with the decrease in pH (Fig. 4). At pH 4.0, the removal efficiency was greatly improved, reaching approximately 50% within 3 hr, demonstrating that an acidic condition is more favorable for Cr(VI) removal. At pH 4.0–8.0, HCrO$_4^-$ and CrO$_4^{2-}$ were the dominating species of Cr(VI) (Dong et al., 2014), while BC500 was negatively charged, implying that an electrostatic attraction between BC500 and Cr(VI) should be negligible. Fe(III) can be readily hydrolyzed in aqueous solutions (e.g., as Fe(OH)$_2^+$, Fe(OH)$_3$, Fe(OH)$_4^{2-}$) in a pH-dependent manner (Martin et al., 1998). Under acidic conditions (e.g., pH 4.0–6.0), the Fe(OH)$_3^-$ cation is the dominant specie of Fe(III), which could be favorably absorbed by negatively charged BC500. With the increase in pH, the fraction of neutral and negatively charged Fe(III) (e.g., Fe(OH)$_3^-$ and Fe(OH)$_4^{2-}$) (Martin et al., 1998) should correspondingly increase, leading to decrease in the electrostatic attraction between Fe(III) and biochar and thus the adsorption and reduction of Fe(III) by biochar. Remarkably, with increasing pH, the adsorption of Cr(VI) by Fe(OH)$_3^-$ colloid becomes more plausible, which may also cause Cr(VI) removal with time. Meanwhile, the Fe(II) concentration also varied as a function of time, confirming the redox reaction of Fe(III) played a role in Cr(VI) reduction. Therefore, we presumed that under the neutral or alkaline conditions the Cr(VI) removal may be attributed to the reduction mediated by Fe(III) as an electron shutter as well as adsorption by Fe(OH)$_3^-$ colloid formed. Detailed studies on the contribution of these two process for Cr(VI) removal are beyond the scope of study, but deserved further research in future work.

### 2.5. Effects of biochar dosage

Biochar dosage has been observed to largely influence the absorption sites and collision efficiencies of adsorbents and targets in sorption processes (Tabaraki et al., 2013; Pan et al., 2014). Herein, the amount of BC500 determined the capacity of electron donor, which significantly influence Fe(III) reduction. The effect of BC500 dosage in the range of 0–200 mg/L on the efficiency of Cr(VI) (100 μg/L) removal was assessed. As expected, the efficiency increased from 4.2% to 33.0% with increasing BC500 concentration from 0 to 100 mg/L (Fig. 5), again supporting that biochar serves as an electron donor in...
Cr(VI) reduction. However, when the concentration of biochar reached 200 mg/L, the efficiency of Cr(VI) removal decreased to 20.1%, possibly due to the reduced interaction between BC500 and Fe(III) due to biochar aggregation. Indeed, black biochar agglomerates were observed at the bottom of vials with 200 mg/L BC500.

2.6. Mechanisms on enhancement of Cr(VI) removal by Fe(III) as an electron shuttle

The enhanced efficiency of Cr(VI) removal was assumed to arise from the role of Fe as electron shuttle to enhance the electron transfer from biochar to Cr(VI) ions. Given that both BC500 and Cr(VI) ions are negatively charged in acidic solutions (pH 4.0–6.0), Cr(VI) removal as a result of electrostatic adsorption should be negligible. The efficiency of Cr(VI) removal in the presence of both biochar and Fe(III) reached nearly 30% (Fig. 2a), while that by biochar alone was less than 5% within 2 hr. The removal of Cr(VI) significantly increased with increasing Fe(III) concentration, implying that Fe(III) played a key role in Cr(VI) removal. The speciation analysis of Cr in the aqueous solution by HPLC-ICPMS (Fig. 6a) showed that the Cr(VI) concentration decreased steadily, while the Cr(III) concentration showed minimal change, leading to a decrease of total Cr concentration within 10 hr. Moreover, no precipitation was observed at the bottom of the vials. Therefore, biochar adsorption is

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**Fig. 5** – Effect of biochar dosage on Cr(VI) removal (initial Cr(VI) concentration = 100 μg/L; Fe(III) concentration = 200 μg/L; pH = 5.0; time = 2 hr).

**Fig. 6** – (a) Speciation analysis of Cr in an aqueous solution by high performance liquid chromatography online coupled with inductively coupled plasma mass spectrometry; (b) HR-XPS Cr 2p spectra of the biochar after batch experiment incubated with Cr(VI); (c) HR-XPS Fe 2p spectra of the biochar in the batch experiment; (d) Effect of initial Fe(III) concentration on concentration of Fe(II) newly generated. HR-XPS: high-resolution X-ray photoelectron.
responsible for the decrease in total Cr concentration in the solution. To assess this, XPS was used to characterize the Cr species adsorbed onto the BC500 surface. The high resolution XPS spectra obtained by deconvoluting the Cr 2p spectrum (Fig. 6b) showed two peaks centered at approximately 577.4 eV and 579.2 eV, respectively attributed to Cr(III) and Cr(VI) (Chen et al., 2017a, 2017b). Cr(III) and Cr(VI) accounted for approximately 81.5% and 18.5% of the total Cr, respectively. This result suggests that the positively charged Cr(III) ion from Cr(VI) reduction was adsorbed on the BC500 surface, which is consistent with the constant concentration of dissolved Cr(III) in the filtrate (Fig. 5a). FT-IR results (Fig. 1a) showed that BC500 contains plenty of aromatic carbon groups that can serve as electron donors (Saquing et al., 2016; Yuan et al., 2017; Dong et al., 2014; Chen et al., 2017a, 2017b) for Fe(III) reduction. Therefore, we hypothesized that the mechanism of enhanced Cr(VI) removal may involve electron shuttles between an electron donor (aromatic functional groups on the surface BC500) and an electron acceptor (Cr(VI)).

To verify the potential role of Fe(III) as an electron shuttle between BC500 and Cr(VI), XPS and UV–vis–NIR were employed to probe the iron species on the surface of the biochar or in the solution. We initially analyzed the speciation of Fe in the mixture of biochar and Fe(III) by XPS. The high resolution XPS spectrum obtained by deconvoluting the Fe 2p spectrum (Fig. 6c) showed peaks at 710.6 eV and 713.9 eV and representative contents of Fe(II) (61.0%) and Fe(III) (39.0%) respectively (Hu and Chen, 2005), demonstrating newly born Fe(II) resultant from reduction of Fe(III) by biochars. Considering the relatively high solubility of Fe(II) in the aqueous phase, most of the produced Fe(II) could dissolve after Fe(III) reduction. Indeed, the presence of Fe(II) in the aqueous phase was confirmed (Fig. 6d). Further, biochar can increase the Fe(II) concentration, thus having an important role in Fe(III) reduction. The concentration of Fe(II) in the solution increased with the increase in Fe(III), but decreased in the presence of Cr(VI), in agreement with the reduction of Cr(VI) by Fe(II) (Pan et al., 2014).

Thus, these above results firmly support the role of Fe as an electron shuttle between negatively charged BC500 and Cr(VI) ions. Therefore, the mechanism of Cr(VI) removal may take place through (1) the reduction of adsorbed Fe(III) (>Fe3+) to Fe(II) by biochar (Eq. (1)), (2) the dissolution of adsorbed Fe(II) (>Fe2+) into the aqueous phase (Eq. (1)), (3) the reduction of Cr(VI) to Cr(III) by Fe(II) in the solution (Eq. (3)), and (4) the adsorption of Cr(III) onto BC500 (Eq. (4)). The resulting Fe(III) can then re-adsorb onto biochar and serve as an electron shuttle again (Fig. 7).

\[
> \text{Fe}^{3+} + \text{biochar} \rightarrow > \text{Fe}^{2+} \quad \text{(1)}
\]

\[
> \text{Fe}^{2+} \rightarrow \text{Fe}^{2+} \quad \text{(2)}
\]

\[
\text{Cr}_2\text{O}_7^{2-} + 6\text{Fe}^{2+} + 14\text{H}^+ \rightarrow 2\text{Cr}^{3+} + 6\text{Fe}^{3+} + 7\text{H}_2\text{O} \quad \text{(3)}
\]

\[
\text{Cr}^{3+} \rightarrow > \text{Cr}^{3+} \quad \text{(4)}
\]

3. Conclusions

This study revealed the role of Fe as an electron shuttle between negatively charged biochar and Cr(VI) anions. The results showed that Fe(III) was adsorbed onto the biochar surface, being further reduced to Fe(II). Subsequently, the resulting Fe(II) directly reduced Cr(VI) into Cr(III). The enhancement effect of Fe(III) in Cr(VI) reduction was closely dependent on the acidity of the solution, Fe(III) concentration, and the temperature of biochar preparation. The results presented herein suggest that the combination of biochar with Fe(III) could be an effective strategy to treat Cr(VI) contamination, which provides a potentially novel strategy for field-scale remediation of Cr(VI) contaminated aquatic and terrestrial systems. Moreover, Fe(III) could be incorporated into the structure of functional composites to enhance their capacity for pollutant removal. In addition, given the ubiquitous presence of Fe and natural or engineered carbonaceous materials in the environment, the impact of Fe(III) as an electron shuttle on the redox of inorganic and organic pollutants by carbonaceous materials could be universal, and should be further investigated.

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