Short Communication

Biochar-supported zerovalent iron for removal of various contaminants from aqueous solutions

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HIGHLIGHTS

- Chitosan attached fine ZVI particles onto biochar surfaces.
- Biochar-supported ZVI removed heavy metals, phosphate, and methylene blue.
- Exhausted adsorbent could be separated by magnetic attraction.

ARTICLE INFO

ABSTRACT

This work describes the synthesis and testing of a novel environmental sorbent that combines the advantages of biochar, chitosan, and zerovalent iron (ZVI). Chitosan was used as a dispersing and soldering reagent to attach fine ZVI particles onto bamboo biochar surfaces. Characterization of the resulted ZVI-biochar composites (BBCF) indicated that chitosan effectively soldered the iron particles onto carbonaceous surfaces within the biochar pore networks. The BBCF showed enhanced ability to sorb heavy metals (Pb(II), Cr(VI), and As(V)), phosphate (P), and methylene blue (MB) from aqueous solutions. The removal of Pb(II), Cr(VI), and MB by the biochar-supported ZVI was mainly controlled by both the reduction and surface adsorption mechanisms. Removal of anionic contaminants (As(V) and P) was likely controlled by electrostatic attraction with the iron particles on the BBCF surfaces. An additional benefit is that the contaminant-laden BBCF could be removed from aqueous solution easily by magnetic attraction.

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1. Introduction

Zerovalent iron (ZVI) particles are inexpensive and environmentally friendly reducing agents that can be used to remediate many environmental contaminants (Chatterjee et al., 2010). Introduction of ZVI to treat wastewater and contaminated soils has become a prominent environmental technology in recent years (Liu et al., 2012). Due to their relatively large surface area and high reactivity, however, fine sized ZVI particles are unstable in aqueous solutions, which may present challenges to their environmental application (Zhang, 2003). Thus, several stabilization methods have been developed to facilitate the use of fine ZVI in various environmental remediation scenarios (Shu et al., 2010). Recent studies have showed that ZVI particles can be supported by porous materials including clays, resins, and carbon materials, to enhance their dispersion and stability (Shu et al., 2010; Sunkara et al., 2010).

Biochar is pyrogenic carbon produced by combusting biomass under low oxygen conditions (pyrolysis). Possessing, in some cases, large surface area, good ion exchange capacity, and a range in chemical compositions, biochar is emerging as a low-cost sorbent that can be used to remove both organic and inorganic contaminants from the environment (Inyang et al., 2010). Because of its porous structure, biochar has recently also been used as a mechanical support to disperse and stabilize engineered nanoparticles to facilitate their environmental application (Yao et al., 2013; Zhang and Gao, 2013). Nanocomposite sorbents with nano-sized metal oxyhydroxides attached onto carbonaceous surfaces within the biochar matrix have been successfully synthesized, through both chemical precipitation and direct pyrolysis, and demonstrated to have excellent abilities to remove a range of contaminants from aqueous solutions (Yao et al., 2011; Zhang et al., 2013). Because biochar can be easily obtained from many kinds of waste biomass and produced at relatively low-cost (e.g., compared to activated carbon), using biochar to support ZVI particles for environmental

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application is a potentially environmentally and economically beneficial but, as yet, unexplored remediation strategy.

In this work, a simple method was developed to synthesize ZVI-biochar composites using chitosan as a dispersing and stabilizing reagent. Chitosan is a renewable transformed polysaccharide that can be obtained from natural chitin, the second most abundant polysaccharide in the world. It has been used in many environmental applications to treat contaminants because of its surface functionalities, biodegradability, nontoxicity, and its useful tendency to dissolve in acid solution and precipitate from basic solution (Geng et al., 2009). In a previous study, chitosan has been coated onto biochar surfaces and the modified biochars show enhanced ability to remove heavy metals from water (Zhou et al., 2013). Here, chitosan was used as an 'organic glue' to attach fine ZVI particles onto biochar. The objectives of this study were to: (1) develop a method to synthesize ZVI-biochar composites, (2) characterize the resulting composites, and (3) evaluate the sorptive properties of the composites in regards to various contaminants in aqueous solutions.

2. Methods

2.1. Materials

Bamboo biochar (BB) of 0.5–1 mm particle size was produced according procedures reported previously (Yao et al., 2012). Chitosan (C) with 100,000–300,000 g mol^{-1} molecular weight was purchased from Fisher Scientific. Fine sized ZVI of <850 μm particle size was obtained from Connelly-GPM, Inc. (Chicago, IL) and used as received.

To make the composite sample, chitosan powder was first dissolved in a 90 mL 2% acetic acid solution. The ZVI particles were then dispersed in the solution followed by the addition of the BB. The mixture was then stirred for 30 min to form a homogenous solution which was then added drop-wise into a 450 mL 1.2% NaOH solution and kept undisturbed in the solution for 12 h at room temperature. The solid products were then separated by decantation and washed with deionized (DI) water to remove the excess NaOH and oven-dried for 24 h at 70 °C. Eight types of ZVI-biochar composites were prepared by varying the mass (weight) ratio of each components producing BB:C:Fe composites (referred to as BBCF) with ratios of 1:1:0.3, 1:1:1, 1:1:2, 1:1:3, 1:2:0.3, 1:2:1, 1:2:2, and 1:2:3, respectively. For comparison, biochar coated with chitosan with no added ZVI (i.e., BB:C = 1:1) was also prepared and is labeled as BBC.

Lead nitrate (Pb(NO$_3$)$_2$), potassium dichromate (K$_2$Cr$_2$O$_7$), sodium arsenate (Na$_2$HAsO$_4$·7H$_2$O), potassium dihydrogen phosphate (KH$_2$PO4), and methylene blue (MB) were used for preparing the stock solutions of the heavy metals (i.e., Pb(II), Cr(VI), As(V)), nutrient (i.e., P), and organic dye (i.e., MB), respectively. All working solutions were freshly prepared before use by diluting the stock solution with DI water. All the chemical reagents used in this work were of analytical grades from Fisher Scientific.

2.2. Characterizations

Scanning electron microscope (SEM) imaging analysis of the samples was conducted using a JEOL JSM-6400 Scanning Microscope and X-ray photoelectron spectroscopy (XPS) measurements were carried out with a PHI 5100 series ESCA spectrometer (Perkin Elmer) to determine surface elemental compositions of the samples. Thermogravimetric analysis (TGA) was carried out at a heating rate of 10 °C/min using a Mettler's TGA/DSC thermogravimetric analyzer. Possible sample crystalinity was examined using X-ray diffraction (XRD) analysis with a computer-controlled X-ray diffractometer (Philips Electronic Instruments) and equipped with a stepping motor and graphite crystal monochromator.

2.3. Sorption experiments

The aqueous sorptive ability of the samples was evaluated with a simple batch sorption method. About 0.05 g of each sorbent was place in homopolymer polypropylene digestion vessels (Environmental Express) with 25 mL solutions of each sorbate, separately, at room temperature. The initial concentrations of the sorbates were 40, 53, 21, 12, and 20 ppm for Pb(II), Cr(VI), As(V), P, and MB, respectively. After agitating in a reciprocating shaker for 24 h, the solutions were filtered immediately through 0.22 μm pore size nylon membranes (GE cellulose nylon membranes). The filtrate concentrations of Pb(II), Cr(VI), As(V), and P were determined using an inductively-coupled plasma atomic emission spectroscopic (ICP-AES, Perkin Elmer Plasma 3200RL) and that of MB with a dual beam UV/vis spectrophotometer (Thermo Scientific, EVO 60) at a wavelength of 665 nm. The sorbed concentrations (solid phase amounts) were calculated as the difference between the initial and final sorbate concentrations in the supernatants. All sorption experiments were performed in triplicate and the average values are reported. Additional analyses were conducted whenever two measurements showed a difference larger than 5%.
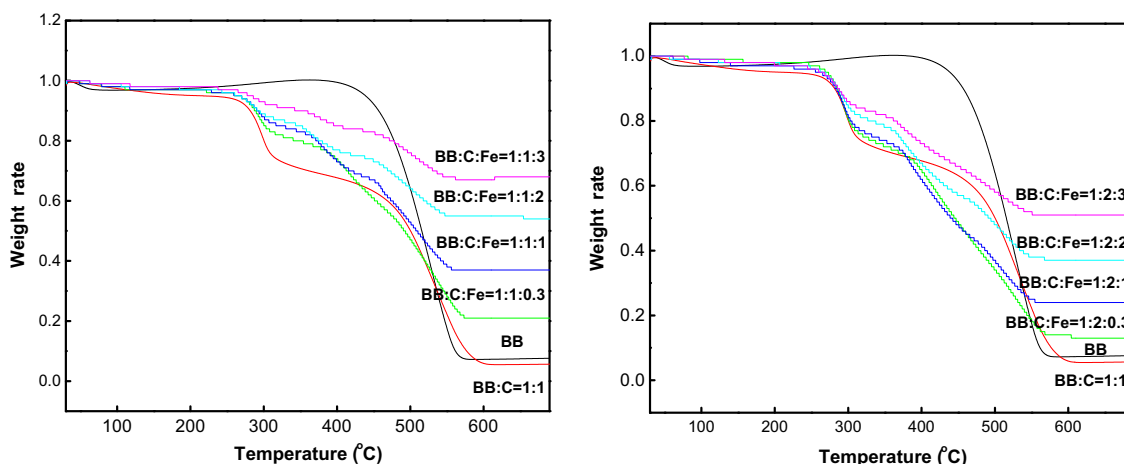

Fig. 1. Thermal decomposition (TGA) curves for BB, BBC, and eight BBCF samples.

3. Results and discussion

3.1. Properties of biochar-supported ZVI

Even after loaded with large amount of the chitosan and ZVI, the biochar composites showed similar structure and surface morphology to typical biochars as reported in the literature (Inyang et al., 2010; Yao et al., 2011). For example, SEM analysis shows the BBCF samples to be highly porous (Fig. S1, Supplementary data), similar to the structure of the biochar and chitosan-modified biochars reported previously (Zhou et al., 2013). In addition, at higher resolution, the SEM images also show clusters of fine iron particles with size ranged from several to hundreds of micrometers associated with the carbon surfaces within the biochar matrix (Fig. S1b). The presence of ZVI on biochar surfaces was further confirmed by both the XPS and the XRD analyses (Fig. S2, Supplementary data). The XPS spectra of the BBCF show the Fe peaks, corresponding to the immobilized ZVI particles on the biochar surfaces, which are not shown on the BBC sample (Fig. S2a). Similarly, the XRD patterns show that the BBCF had additional diffraction peaks at 45.0° and 63.0° (corresponding to ZVI) and 30.2°, 35.7°, and 57.1° (corresponding to maghemite or magnetite) (Geng et al., 2009; Schwickardi et al., 2006). The presence of iron oxides on the ZVI particle surfaces is unsurprising given their high reactivity when in contact with oxygen (Kanel et al., 2006).
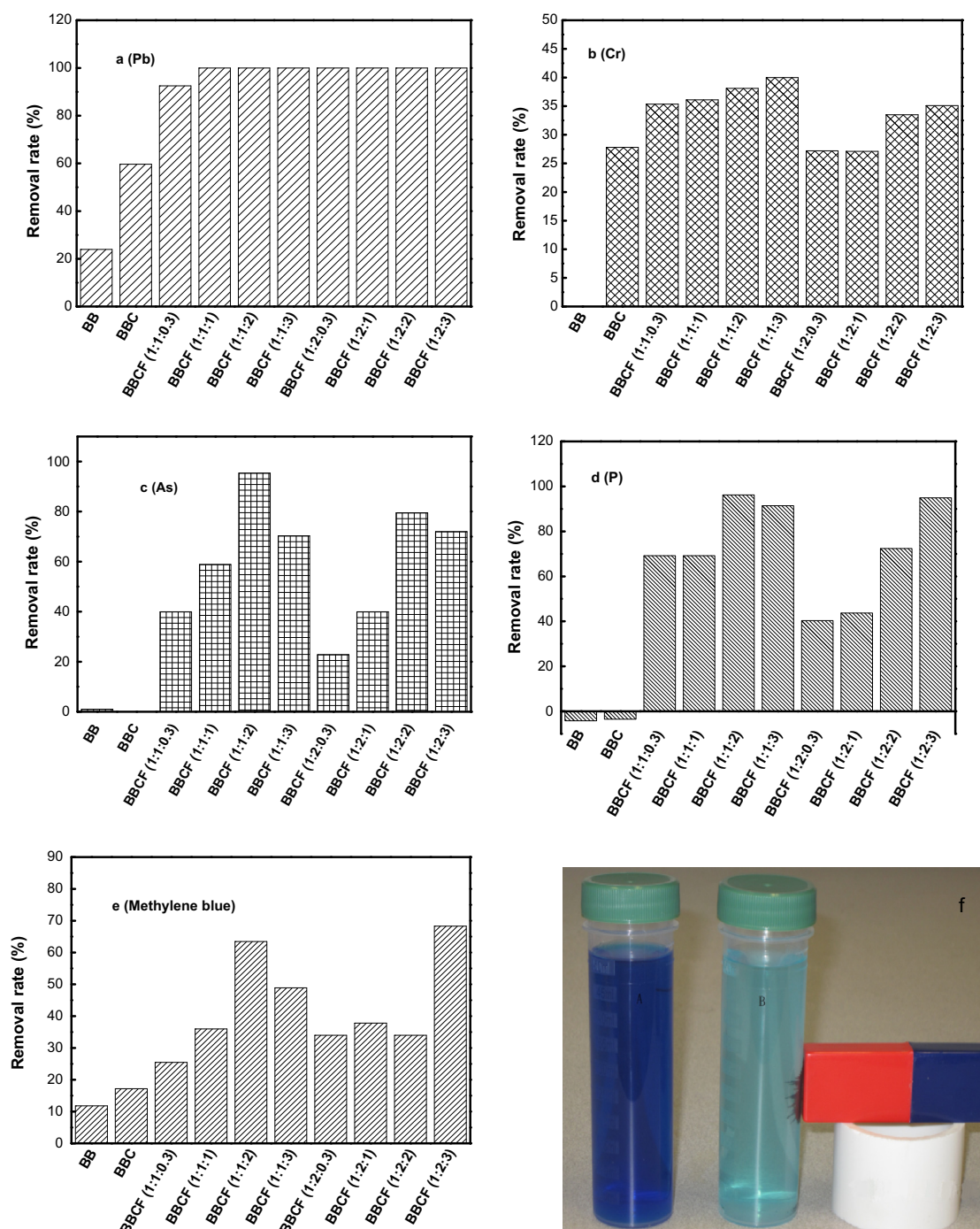

Fig. 2. Removal of heavy metals (a–c), P (d), and MB (e) from aqueous solution by the biochar sorbents and (f) separation of MB-laden BBCF using a magnet (at right).

Comparisons between the TGA curves of the samples show that all the biochar composites were less stability than the pristine biochar (Fig. 1), which is consistent with the previous findings showing that chitosan decomposes at much lower temperature than the pyrogenic carbon (Hong et al., 2007; Zhou et al., 2013). Hong et al. (2007) conducted a TG analysis of the pure chitosan and found that chitosan degrades at around 300–400 °C. Compared with the BB and BBC, the BBCF samples had much higher residual mass at 700 °C and thermal stability increased with the amount of ZVI used in the synthesis (Fig. 1). This result further confirmed association of the iron particles with biochar surfaces.

3.2. Removal of contaminants from aqueous solutions

Compared to the modified sorbents, the pristine biochar had less sorption of the three heavy metals, P, and MB in from aqueous solutions (Fig. 2). The coating of chitosan on biochar (BBC) enhanced the removal of Pb(II) from 23.9% to 59.6% and Cr(VI) from 0% to 27.8% compared to the unmodified biochar because the amine functional groups of the chitosan have strong affiliations (chelation) to cationic metal ions in aqueous solutions (Fig. 2a and b) (Zhou et al., 2013). The presence of ZVI further increased the removal of the two heavy metals, particularly Pb(II), by most of the ZVI-biochar samples. More than 93% of the Pb was removed by all eight BBCF samples (Fig. 2a). The removal of Cr(VI) by the BBCF increased with the amount of ZVI in the samples when the mass ratios of the other components were the same. These results suggest that both the chitosan and the ZVI particles on the biochar surfaces played important role in the enhanced removal of the two cationic heavy metals. It has been reported in the literature that ZVI can remove cationic heavy metals from aqueous solutions through both adsorption and reduction processes (Xi et al., 2010).

Both the BB and BBC samples showed no/little ability to remove the anionic As(V) and P from solution (Fig. 2c and d), probably because their surfaces are net negatively charged (Zhou et al., 2013). The BB and BBC even released little amount of P into the solution, which is common for biochars converted from plant biomass (Yao et al., 2011, 2012). After ZVI particles were loaded, all the ZVI-biochar composites removed large amount of As(V) (23–95%) and P (40–96%). In general, the samples with the greater amounts of Fe (1:1:2, 1:1:3 and 1:2:3) removed the greater amounts of As(V) and P (70–95% and 91–96%, respectively). The strong removal of As(V) and P can be attributed to the electrosteric attractions between the anions and the ZVI particles on the composites' surface. The pH of the experiments, around 5.7, is much lower than the point of zero charge of the ZVI (around 7.7) (Almeelbi and Bezbaruah, 2012). So the positively charged ZVI could serve as the adsorption sites for the anionic As(V) and P. It should be noted that the greatest removal of As(V) and P (by BBCF (1:1:2)); however, was not by the composites with the greatest amount of Fe. Further investigations thus are still needed to optimize the synthesis and production of the BBCF with optimized proportion of Fe for contaminant removal.

While all the tested adsorbents showed some MB removal ability, those with iron modification had the greatest MB removal (Fig. 2e). Among all the iron-modified biochars, the BBCF of 1:2:3 removed the greatest amount of MB with a removal rate of 68%. The enhanced removal of MB by the biochar-supported ZVI particles could also be attributed to both surface adsorption and chemical reduction mechanisms (Miyajima and Noubactep, 2012; Noubactep, 2009).

Because the BBCF are loaded with iron minerals, they are attracted to a permanent magnet. As a visual demonstration, Fig. 2f shows that post-sorption MB-laden BBCF could be collected by a magnet. This property of the ZVI-biochar composites could be of use in removing contaminant-laden BBCF from solution after use.

4. Conclusion

For the first time, a novel synthesis was developed to prepare ZVI-biochar composite materials. Chitosan, a natural biopolymer, was found to be able to attach fine ZVI particles on biochar surfaces. The resulted iron modified biochar showed excellent ability to remove various contaminants, including heavy metals, phosphate, and MB from aqueous solutions. In addition, the modified biochars are ferromagnetic and could be easily collected by a magnet. Because the synthesis presented here is simple and environmentally friendly, it can be further optimized to prepare high-efficiency and low-cost biochar-supported ZVI for various environmental applications, including water treatment and soil remediation.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.biortech.2013.11.021.

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