Short Communication

Biochar-supported zerovalent iron reclaims silver from aqueous solution to form antimicrobial nanocomposite

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HIGHLIGHTS

- Biochar-supported ZVI quickly and efficiently removed silver irons.
- Sorbed silver was reduced and formed silver nanoparticles on biochar.
- Spent sorbent laden with silver nanoparticles showed strong antimicrobial ability.

ARTICLE INFO

ABSTRACT

In this work, zerovalent iron (ZVI)-biochar composite (BBCF) was used to remove and reclaim silver ions from aqueous solution. Sorption experimental data showed that BBCF quickly and efficiently removed Ag^+ from aqueous solutions with a capacity greater than 600 mg/g. The strong sorption of silver on BBCF was mainly controlled by a reduction mechanism between the ZVI and Ag^+, which was confirmed by the characterization of the post-sorption sorbent (BBCF-Ag). The characterization results also showed that the sorbed silver on biochar surfaces were nanoparticles with an average size of 28 nm. As a result, the BBCF-Ag showed strong antimicrobial ability and effectively inhibited the growth of *Escherichia coli* (*E. coli*), while the original BBCF without silver nanoparticle promoted their growth. These findings suggest that, not only can biochar-supported ZVI be used to remove silver ions from aqueous solutions, but the products formed represent a new value-added nanocomposite.

1. Introduction

Silver, a precious metal, has been used for many years to make fine jewelry, coins, utensils, and art (Purcell and Peters, 1998; Johnson et al., 2005; Eckelman and Graedel, 2007). Because of its excellent antimicrobial activities, silver is also extensively used as an antimicrobial agent for many applications in dentistry, clothing, and the food industry (Purcell and Peters, 1998; Sotiriou and Pratsinis, 2010). As a result, environmental occurrences of silver contamination have been reported, particularly in waste water effluents (Benn and Westerhoff, 2008; Kent et al., 2014; Lombi et al., 2014). When ingested by humans, silver ions may be metabolized and deposited in subcutaneous fat, thus posing health risks (Song et al., 2011). The World Health Organization (WHO) and the U.S. Environmental Protection Agency (EPA) have classified soluble silver ions as hazardous substances in water systems and limited the level of silver in drinking water to less than 100 ppb (USEPA, 2013; Zhang et al., 2014).

Several treatment methods, such as precipitation, ion-exchange, and adsorption, have been applied to remove silver and other heavy metals from aqueous solutions (Ghassabzadeh et al., 2010). Among them, adsorption is one of the most commonly used methods because of its high efficiency and low energy consumption (Dias et al., 2007; Zhang et al., 2012a). The application of low-cost sorbents to sorb heavy metals, particularly renewable ones derived from biomass, has attracted much attention recently (Crini, 2006; Gupta et al., 2009; Kailash et al., 2010). Biochar is pyrogenic carbon prepared from biomass through pyrolysis that can be used as a low-cost adsorbent for various environmental remediation applications (Beesley et al., 2011; Inyang et al., 2011; Zhang et al., 2012b; Mohana et al., 2014). Because of its highly porous structure, biochar

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has also been used as a host for functionalized composite materials that can remove various aqueous contaminants, including heavy metals (Zhang et al., 2013; Zhou et al., 2013; Ahmad et al., 2014). No previous study, however, has explored the application of biochar-based sorbents to remove or reclaim silver from aqueous solutions.

In a previous study, zero valent iron (ZVI)-biochar composites were synthesized and were shown to display excellent adsorptive property for various contaminants, including heavy metals (Zhou et al., 2014). As a follow up, the goal of this study was to determine whether the ZVI-biochar composites could be used as an effective sorbent to remove silver ions from aqueous solutions. Another important objective of this work was to explore the beneficial uses of the post-sorption biochar-ZVI composite loaded with reclaimed silver. A range of laboratory experiments were conducted to measure the sorptive properties of the composite sorbent to silver. In addition, the antimicrobial ability of the spent adsorbent was examined.

2. Materials and methods

2.1. Materials

Bamboo biochar (BB) were produced from bamboo biomass through slow pyrolysis. Bamboo biomass was dried, chopped into small pieces (around 1 mm), and then pyrolyzed in a tube furnace (MTI, Richmond, CA) under flowing N_2 for 2 h at 600 °C. The resulting biochar was washed with tap and deionized (DI) water several times and then dried at 70 °C. Chitosan of 100 000–300 000 g/mol molecular weight was purchased from Fisher Scientific and was dissolved in 2% acetic acid solution prior to use. Commercial iron powder with particle size around 850 μm obtained from Connelly-GPM, Inc. (Chicago, IL) was used as the experimental ZVI. Analytical grade silver nitrate ($AgNO_3$) was purchased from Fisher Scientific and was used for preparing the stock solutions of Ag^+. All working solutions were freshly prepared before use by dilution from a stock solution with DI water. The ZVI-biochar composites (referred to as BBCF) were synthesized following the methods reported previously (Zhou et al., 2014), whereby chitosan was used as a 'glue' to distribute and stabilize fine ZVI particles on biochar surfaces within the pores. The mass (weight) ratio of biochar:chitosan:ZVI used to synthesize the BBCF was 1:1:1.

2.2. Characterizations

Scanning electron microscope (SEM) imaging analyses were conducted using a JEOL JSM-6400 Scanning Microscope to compare the structure and surface characteristics of the samples. X-ray photoelectron spectroscopy (XPS) measurements were carried out with a PHI 5100 series ESCA spectrometer (Perkin Elmer) to determine the elemental composition on sample surfaces. X-ray diffraction (XRD) analyses were also conducted to identify crystalline structures on the Ag-loaded sorbents using a computer-controlled X-ray diffractometer (Philips Electronic Instruments) equipped with a stepping motor and graphite crystal monochromator.

2.3. Sorption experiments

The sorption ability of the BB and BBCF to Ag^+ was examined initially by adding 0.05 g of each sorbent to 25 mL 100 ppm Ag^+ aqueous solutions in 68 mL digestion vessels (Environmental Express) at room temperature for 24 h (22 ± 0.5 °C). The characteristics and mechanisms of silver sorption onto BBCF were then studied using sorption kinetic and isotherm experiments. For each experiment, 0.05 g of the sorbent was mixed with 25 mL silver solution in the digestion vessel. The mixture was then shaken at 55 rpm on a horizontal shaker at room temperature. To measure the sorption kinetics, 1200 ppm silver solutions were used at a range contact time intervals. To obtain sorption isotherms, different concentrations of silver solution (i.e., 0, 40, 100, 200, 400, 600, 1000, 1200, 2400 and 3000 ppm) were mixed with the 0.05 g of the BBCF sorbent and shaken for 24 h. At the end of each experiment, the mixtures were immediately filtered through 0.22 μm pore size nylon membranes (GE cellulose nylon membranes). Control experiments showed no removal of silver by the membranes. Silver concentrations in the filtrates were determined using inductively-coupled plasma atomic emission spectroscopy (ICP-AES, Perkin Elmer Plasma 3200RL). The quantity of silver sorbed was calculated as the difference between the initial and final Ag^+ concentrations in the supernatant.

2.4. Antimicrobial ability

Microbial growth inhibition tests were conducted on the BBCF and silver-laden BBCF made by mixing about 0.4 g of the BBCF with 200 mL Ag^+ solution (13 000 ppm) and shaking for 24 h. After filtration, the silver-laden BBCF samples were collected, rinsed with DI water several times, and dried at 70 °C (referred to as BBCF-Ag). The concentration of the adsorbed Ag in the BBCF-Ag samples was 640.1 ± 14.8 mg/g. Growth inhibition tests of the BBCF and BBCF-Ag were conducted with *E. coli* DH5α. The bacteria were cultured overnight at 35 °C by constant agitation in a biochemical incubator (SenxinGRP-9160, Shanghai, China). About 40 mg sterile (autoclaved at 121 °C for 15 min) BBCF or BBCF-Ag was added to 5 mL of newly made nutrient broth medium (each group contained 10^5 cfu/mL *E. coli*) and the mixtures were incubated at 35 °C for 18 h. Previous studies have shown that the sterile process should not have effect on the biochar and Ag during autoclaving (Kora et al., 2012; Kora and Arunachalam, 2012; Venkatesham et al., 2012; Yao et al., 2012). Blank controls with no biochar sample addition were also tested. The pour-plate method was used to compare *E. coli* growth in the presence or absence of these sorbents (APHA, 1995; Yao et al., 2012). Briefly, about 0.5 mL of the diluted *E. coli*-sorbent mixtures were placed in the center of a sterile petri dish (100 mm diameter) using a sterile pipette. Sterile molten agar (45–50 °C) was added to each plate and then mixed gently by swirling. The mixtures were allowed to cool until solidified and then were incubated at 35 °C in the dark for 18 h. Colonies on the medium were counted to determine bacterial abundance following APHA standard procedures (APHA, 1995). The growth experiments were repeated nine times for each treatment and results were statistically analyzed using the *t*-test and one-way ANOVA with a significance level set to 0.05 ($p < 0.05$).

3. Results and discussion

3.1. Silver sorption

The initial evaluation showed that both BB and BBCF removed Ag^+ from aqueous solution. While BB removed about 37% of the silver, BBCF removed 100%, indicating that the presence of ZVI greatly improved the silver sorption efficiency of biochar. In a previous study (Zhou et al., 2014), the ZVI-biochar composites demonstrated strong sorption ability for various contaminants, including other heavy metals. The enhanced sorption of heavy metals by the ZVI-biochar composites has been attributed to both reduction and surface adsorption mechanisms (Zhou et al., 2014). In this work, the ZVI modification increased the silver sorption on the biochar for about two times, which also suggests the predominance of these two sorption mechanisms because of the similarity of silver ions to other heavy metal ions tested in the previous study.

Batch sorption experiments were conducted to better understand the sorption mechanisms of the silver on the ZVI-biochar composites. The kinetics of the sorption of the silver were relatively fast, reaching equilibrium within 5 h (Fig. 1a). In addition, more than 90% of the silver was removed from the solution by the BBCF within 1 h. While both pseudo-first-order and pseudo-second-order models described the Ag sorption kinetics data well (Fig. 1a), the second-order model fitted the data better with a R^2 of 0.988 (Table 1), suggesting that the sorption of silver by BBCF was not a constant rate process and may have involved multiple processes.

The silver ion sorption isotherm showed that BBCF had excellent ability to remove silver from aqueous solution with a capacity above 600 mg/g (Fig. 1b). The ZVI-biochar composite almost completely removed all the silver ions in the solutions when their initial concentrations were lower than 1000 ppm. This suggests that silver removal by the BBCF could be dominated by a chemical reduction mechanism, despite the finding that BBCF can sorb other metals through both reduction and surface adsorption (Zhou et al., 2014). This governing sorption mechanism was further suggested by the modeling results showing the Langmuir model to describe the sorption isotherm much better than the Freundlich model (Table 1). Although the Langmuir was originally developed to simulate physical adsorption processes, studies have shown that it also simulates sorption processes controlled by chemical reactions,
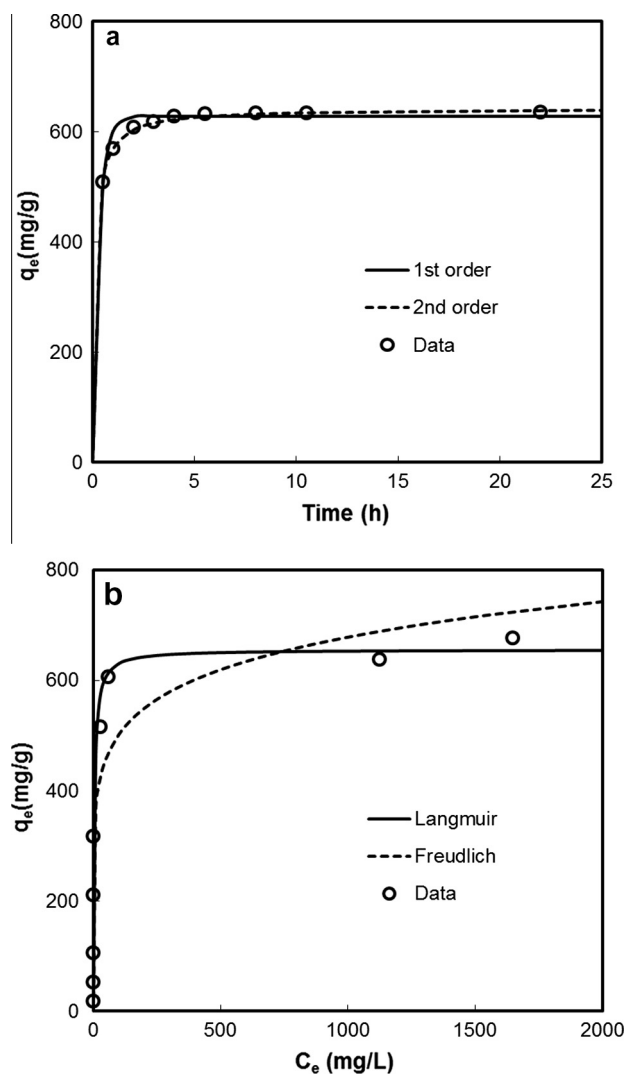
Table 1
Best-fit model parameters for silver sorption onto BBCF.

	Governing equation[*]	Parameter 1	Parameter 2	R^2
First-order	$q_t = q_e(1 - e^{-k_1 t})$	$k_1 = 3.12$	$q_e = 627.6$	0.889
Second-order	$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t}$	$k_2 = 0.012$	$q_e = 641.6$	0.988
Langmuir	$q_e = \frac{K S_{max} C_e}{1 + K C_e}$	$K = 0.25$	$S_{max} = 655.4$	0.938
Freundlich	$q_e = K_f C_e^n$	$K_f = 274.35$	$n = 0.131$	0.873

[*] q_t and q_e are the amount of sorbate removed at time t and at equilibrium, respectively (mg g^{-1}), k_1 (h^{-1}) and k_2 (g mg^{-1} h^{-1}) are the first-order and second-order sorption rate constants, respectively, K and K_f are the Langmuir bonding terms related to interaction energies (L mg^{-1}) and the Freundlich affinity coefficient (mg$^{(1-n)}$ L^n g^{-1}), respectively, S_{max} is the Langmuir maximum capacity (mg g^{-1}), C_e is the equilibrium solution concentration (mg L^{-1}) of the sorbate, and n is the Freundlich linearity constant.

such as precipitation (Cao et al., 2009; Inyang et al., 2011, 2012). In contrast, the Freundlich isotherm model assumes a sorption mechanism with heterogeneous energetic distribution of active sites, as well as interactions between adsorbed molecules. Based on these findings, the removal of the silver from aqueous solution by the BBCF was most likely through the reduction of silver ions by the ZVI on the biochar surfaces, which can be expressed as:

$$BS - Fe^0 + 3(2)Ag^+ \rightarrow BS - 3(2)Ag^0 + Fe^{3(2)+} \tag{1}$$
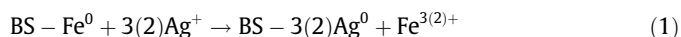
where *BS* represents the biochar surface.

3.2. Characterization of BBCF–Ag

Characterization of the biochar surfaces loaded with silver (BBCF-Ag) also showed silver to have likely been removed from solution by a reduction mechanism. The SEM micrographs (Fig. 2) showed clusters of small particles on the post-sorption biochar surfaces, which were not found on original BBCF samples. The XPS
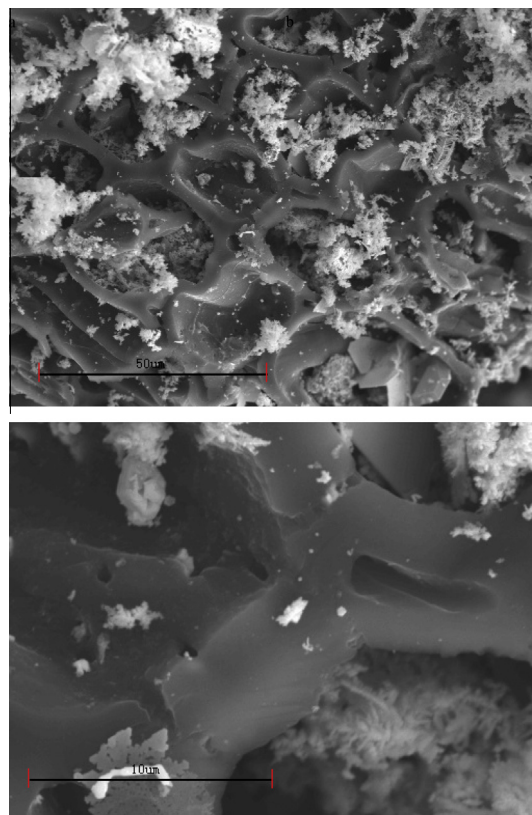

Fig. 1. Sorption kinetics (a) and isotherm (b) of silver onto BBCF.

Fig. 2. SEM images of BBCF-Ag: (a) 1000× and (b) 5000×.
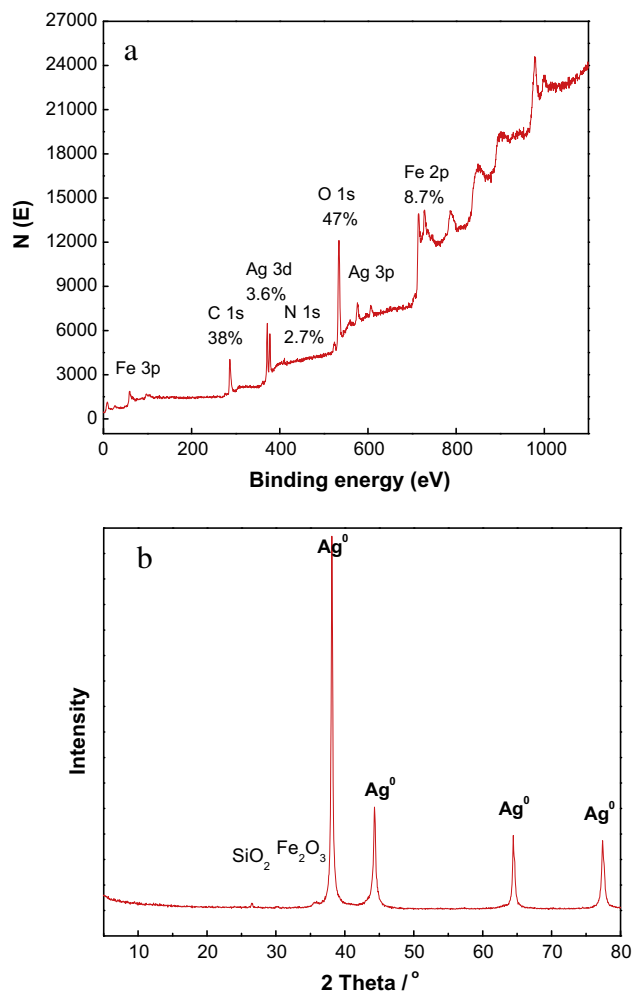
Fig. 3. XPS (a) and XRD spectra of BBCF–Ag.

Fig. 4. Effect of BBCF and BBCF–Ag on the growth of *E. coli*.

analysis of the BBCF-Ag confirmed that these new particles on the biochar surface were Ag^0 (Fig. 3a). The spectrum of Ag 3d showed that the $3d_{5/2}$ and $3d_{3/2}$ signals were located at 371.50 eV and 377.50 eV, respectively. The splitting of the 3d doublet is 6.0 eV, indicating that the deposited Ag mainly existed in the Ag^0 state on the biochar surface (Stathatos et al., 2000). The XRD diffraction peaks at 38.2°, 44.2°, 64.3° and 77.1° on the BBCF-Ag (Fig. 3b) can also be assigned to Ag^0 particles as they correspond to four indexed planes of zerovalent silver (1 1 1), (2 0 0), (2 2 0) and (3 1 1) (Zhang et al., 2011). The widths of the XRD peaks were used to calculate the average crystal size of Ag^0 particles using the Debye–Scherrer equation (Yao et al., 2013). These results showed that the Ag^0 particles on the post-sorption BBCF surfaces were nanosized (27.8 nm), suggesting that the sorption process not only removed silver ions from the solution, but formed another novel nanocomposite, i.e. stabilized silver nanoparticles on biochar surfaces.

3.3. Antimicrobial ability

Because of the strong antimicrobial ability of silver nanoparticles, the BBCF–Ag might be useful as a value-added antibacterial/antifungal agent. The bacterial growth study indicated that the BBCF-Ag strongly inhibited the growth of the *E. coli* (Fig. 4). In comparison to the control and the BBCF sample which showed abundant bacterial growth (4.1×10^8 cfu/mL and 7.4×10^8 cfu/mL, respectively), no *E. coli* growth was found in any of the samples
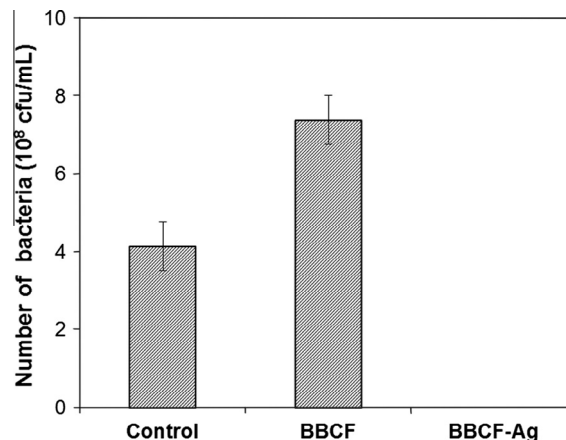
with added BBCF-Ag. This suggests that the post-sorption adsorbent loaded with reclaimed silver nanoparticles acted as an antimicrobial agent. One-way ANOVA analysis showed there was there was significantly greater bacterial growth in the sample treated with BBCF compared to the control ($p < 0.001$), suggesting that, without the reclaimed silver nanoparticles, the ZVI-biochar composite actually promoted the bacterial growth. This is in line with findings of previous studies that biochar amendment can benefit microorganisms by providing them with suitable habitats, and additional organic carbon and mineral nutrients (Lehmann et al., 2011; Yao et al., 2012).

4. Conclusions

In summary, BBCF not only effectively sorbed silver ions from aqueous solutions, but also reclaimed the silver to form a novel value-added nanocomposite (BBCF-Ag) with stabilized silver nanoparticles on biochar surfaces. The sorption of silver onto BBCF was mainly through a reduction mechanism by the ZVI on biochar surfaces. The biochar sorbent laden with silver nanoparticles showed strong antimicrobial ability and thus may be used as an antibacterial/antifungal agent in various applications, particularly environmental applications. Because the antimicrobial activities of silver nanoparticles are mainly from silver ion release (Sotiriou and Pratsinis, 2010; Radniecki et al., 2011), the BBCF-Ag should be used with caution to avoid secondary contamination.

Acknowledgements

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