Sorption of heavy metals on chitosan-modified biochars and its biological effects

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HIGHLIGHTS

- Chitosan-modified biochars were synthesized for heavy metal remediation.
- Chitosan-modified biochars showed enhanced heavy metal removal ability.
- Chitosan-modified biochars reduced toxicity of lead.

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ABSTRACT

In this work, chitosan-modified biochars were synthesized in efforts to produce a low-cost adsorbent for heavy metal environmental remediation. Characterization results showed that the coating of chitosan on biochar surfaces could improve its performance as a soil amendment or an adsorbent. Batch sorption experiments showed that, compared to the unmodified biochars, almost all the chitosan-modified biochars showed enhanced removal of three metals (i.e., Pb^{2+}, Cu^{2+}, and Cd^{2+}) from solution. Further investigations of lead sorption on chitosan-modified bamboo biochar (i.e., BB-C) indicated that, although sorption kinetics were slow, BB-C had a relatively high Langmuir lead sorption capacity of 14.3 mg/g biochar (71.5 mg/g chitosan). Sorption of lead on the chitosan-modified biochar greatly reduced its metal toxicity. Both seed germination rate and seedling growth of the Pb-laden BB-C were similar to that of control groups without lead. In addition, uptake of lead by plants was reduced about 60% when lead was sorbed onto the chitosan-modified biochar. This work suggests that chitosan-modified biochars may be used as an effective, low-cost, and environmental-friendly adsorbent to remediate heavy metal contamination in the environment.

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1. Introduction

Biochar, the carbonaceous product of the pyrolysis of organic matter, has attracted much research attention recently because of its potential applications in many environmental areas. When applied to soils, biochar may not only serve as a carbon sink, but also improve soil fertility by increasing nutrient and water holding capacity [1–3]. Recent studies have also shown that biochar has potential as an environmental sorbent to remove various contaminants from soil and water systems [4–6]. Because of the relatively low cost and the abundance of feedstock materials including agricultural and forestry wastes, biochar is becoming a practical alternative remediation agent for various contaminants in the environment, including heavy metals, organic pollutants, and possibly nutrients [7–9].

The effectiveness of biochars in immobilizing heavy metals from the environment, however, varies greatly among different types of biochars and could be controlled by several factors including feedstock type, production methods and processing conditions [4,6]. In general, 'as-is' biochars prepared directly from biomass feedstock without pre- or post-treatments have relatively low heavy metal sorption capacity. Thus, various modification/activation methods, such as surface oxidization, exploration, and functionalization, have been applied to improve their performance in environmental remediation [9–11]. These modifications may increase the surface sorption sites, particularly, add surface functional groups, which can be the dominant control on sorption of heavy metal ions by biochars [6,12]. For example, Xue et al. [10] found that the H_2O_2 oxidization increased functional groups on biochar surfaces and

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the modified biochar showed enhanced lead sorption capacity, more than 20 times of the as-is biochar. Several other methods have also been developed to create functional groups on biochar surfaces and thus, to improve their contaminant sorption ability [11].

Chitosan is an inexpensive, plentiful, renewable, and non-toxic product of the shellfish processing industry and is among the most abundant natural polysaccharide in the world [13]. As a result, chitosan has been used in many industrial and environmental applications, including as a remediation agent to remove heavy metal ions from aqueous solutions [14]. Chitosan powders, flakes, or beads thus have been used as alternative sorbents and showed excellent aqueous heavy metals removal ability [15]. Chitosan has also been used as a surface modification agent impregnated onto supporting surfaces as adsorption sites because its amine functional groups have strong bonding ability to various heavy metal ions [14–16]. As yet, no previous study has explored the use of chitosan to modify the surfaces of biochars to enhance their affinity to heavy metal. This combination is an attractive one because both chitosan and biochar are low-cost and 'green' materials with large availability. Chitosan-modified biochars would combine the advantages of biochar's relatively large surface area and porous network with chitosan's high chemical affinity.

Because of their strong affiliation to heavy metal ions, biochar-based adsorbents have also been suggested as an effective remediation agent to immobilize heavy metals in contaminated soils [4,17]. On the other hand, however, the biochar-based adsorbents could also potentially concentrate toxic heavy metals in soils due to their extremely high sorption capacities. Although previous studies have suggested that biochar, when applied to soils, could reduce the leaching of heavy metals in soils and reduce their uptake by earthworms [17,18], the biological effects of heavy-metal-laden biochars to plants are still unclear.

In this work, chitosan-modified biochars were synthesized and tested for their heavy metal sorption ability. Biochars were produced from various biomass feedstocks in a N_2 environment at 600 °C without activation. Chitosan was then used to modify them to prepare the chitosan-modified biochars. Batch sorption experiments were used to examine the sorption behaviors of heavy metals on these adsorbents under various conditions. The biological effects of the heavy-metal-laden biochars on seed germination and early growth were also evaluated. The objectives of this research were to: (1) synthesize and characterize chitosan-modified biochars from various biomass feedstocks; (2) determine the sorption characteristics and mechanisms of heavy metals on chitosan-modified biochars; (3) evaluate the effects of lead-laden biochar on seeds germination and early growth; and (4) determine the effects of biochar on the bioaccumulation of lead in plants.

2. Materials and methods

2.1. Materials

Biochar samples were produced from four commonly used feedstock materials: bamboo, sugarcane bagasse, hickory wood, and peanut hull. The biomass materials were dried, chopped into small pieces (around 1 mm), and pyrolyzed in a tube furnace (MTI, Richmond, CA) under a N_2 flow condition for 2 h at 600 °C. The biochars were then crushed and sieved to a uniform 0.5–1 mm size fraction. After washing with deionized (DI) water several times to remove impurities such as ash, the biochar samples were oven-dried (80 °C). The resulting as-is biochar samples produced from bamboo, sugarcane bagasse, hickory wood, and peanut hull are hereafter referred to as BB, BG, HC, and PN, respectively.

Analytical grade chitosan with 100,000–300,000 g mol^{-1} viscosity molecular weight was purchased from Fisher Scientific (Suwanee, Georgia To modify biochars, 3 g of chitosan was first dissolved in 180 mL acetic acid (2%) and 3 g of the as-is biochar was then added to the solution. The mixtures were stirred for 30 min. Then the biochar-chitosan homogenous suspension was added drop wise into a 900 mL NaOH (1.2%) solution and kept in the solution for 12 h. The chitosan-modified biochars were then washed with deionized (DI) water to remove the excess of NaOH and oven-dried for 24 h at 70 °C. The resulting chitosan-modified biochar samples are hereafter referred to as BB-C, BG-C, HC-C, and PN-C, respectively.

Stock aqueous solutions of 1000 ppm Pb^{2+}, Cu^{2+} and Cd^{2+}, were prepared by dissolving appropriate amounts of lead (II) nitrate, copper (II) nitrate trihydrate, and cadmium (II) nitrate tetrahydrate in DI water without adjusting the pH. All the chemical reagents used in this work were of analytical grades from Fisher Scientific.

2.2. Characterizations

Elemental C, N, and H contents of the samples were determined using a CHN Elemental Analyzer (Carlo-Erba NA-1500) via high-temperature catalyzed combustion followed by infrared detection of the resulting CO_2, H_2 and NO_2 gases, respectively. The specific surface area of all the samples was determined using N_2 sorption isotherms run on a NOVA 1200 and using the Brunauer-Emmett-Teller (BET) method to determine mesopore-enclosed surface areas.

To measure the pH, samples were added into DI water at a mass ratio of 1:20. The mixture was then shaken and allowed to stand for 5 min before measurement with a pH meter (Fisher Scientific Accumet Basic AB15). The surface charge of the samples was determined by measuring the zeta potential (ζ) of colloidal biochar using a Brookhaven Zeta Plus (Brookhaven Instruments, Holtsville, NY) following procedures reported previously [5,19].

Scanning electron microscope (SEM) images were collected using a JEOL JSM-6400 Scanning Microscope. Varying magnifications were used to compare the structure and surface characteristics of the samples. Fourier Transform Infrared (FTIR) analysis of the samples was carried out to characterize the surface organic functional groups present on the samples. To obtain the observable FTIR spectra, the samples were ground and mixed with KBr to 0.1 wt.% and then pressed into pellets. The spectra of the samples were measured using a Bruker Vector 22 FTIR spectrometer (OPUS 2.0 software). Elemental composition on the sample surfaces were examined using X-ray photoelectron spectroscopy (XPS) on a PHI 5100 series ESCA spectrometer (Perkin Elmer). Thermogravimetric analysis (TGA) was carried out at a heating rate of 10 °C/min for both BB and BB-C using a Mettler's TGA/DSC thermogravimetric analyzer.

2.3. Sorption experiments

An initial evaluation of the sorption ability of the as-is and chitosan-modified biochars was investigated with batch sorption experiments. About 0.05 g of each adsorbent was added into 68 mL digestion vessels (Environmental Express) and mixed with 25 mL of each heavy metal solution at room temperature (22 ± 0.5 °C). Aqueous concentrations of Pb^{2+}, Cu^{2+} and Cd^{2+} were 50, 30, and 30 ppm, respectively. After shaking in a reciprocating shaker for 24 h, the vessels were withdrawn and filtered immediately through 0.1 μm pore size nylon membranes (GE cellulose nylon membranes). Concentrations of Pb^{2+}, Cu^{2+} and Cd^{2+} in the filtrates were determined using an inductively-coupled plasma atomic emission spectroscopic (ICP-AES, Perkin Elmer Plasma 3200RL) and the sorbed heavy metal amounts were calculated

based on the difference between the initial and final metal concentrations in the supernatant.

Adsorption kinetic and isotherm experiments were conducted to examine the characteristics and mechanisms of lead sorption on the BB-C biochar. For each treatment, 0.05 g of the adsorbent was mixed with 25 mL lead solution in the digestion vessel. The mixture was then shaken in a mechanical shaker at room temperature. To measure the sorption kinetics, 50 ppm lead solutions were used and sorption was measured at time intervals ranging from 0.5 to 32 h. To obtain sorption isotherms, BB-C in a range of lead concentrations (i.e., 2, 5, 10, 30, 50, 70, and 100 ppm) were shaken for 32 h. At the end of each experiment, the mixtures were immediately filtered and lead concentrations in the filtrate were determined by ICP-AES. At the end of the sorption experiments, the post-adsorption BB-C samples were collected, rinsed with deionized water, and dried at 70 °C for later examination.

Solutions without either the sorbent or the sorbate were included in all sorption experiments under the same conditions (concentration, duration, pH, etc.) as controls. All sorption experiments were performed in duplicate and the average values are reported here. Additional analyses were conducted whenever two measurements showed a difference of larger than 5%.

2.4. Seed germination, early growth, and bioaccumulation

Seed germination assays were carried out by spreading the same number of grass (Brown Top Millot) seeds on a layer of filter paper moistened with DI water in containers with BB-C or Pb-laden BB-C (added at the rate of 0.1 g/container, Pb content 13.57 mg/g). Controls with 1 mL lead solution of 1.357 mg/mL (i.e. containing same amount of Pb^{2+} as the Pb-laden biochar) and blanks (1 mL DI water) were included in experiments. Each treatment, which was carried out in triplicate, was covered and incubated in the dark at room temperature. Germination percentage was assessed after 72 h and germinal length was measured on the fourth day. The early stage (first 7 days) seedling growth was recorded. Differences between the numbers of seeds germinated and seedling lengths were statistically analyzed with a t-test and one-way ANOVA with a significance level of 95% ($p < 0.05$).

After 12 days growth, all of the plants were harvested, washed thoroughly with water, and dried at 105 °C for 30 min. The Pb contents in the dried plants were determined using a method similar to that of Buss et al. [20]. Briefly, after recorded the plant dry weights, the samples were heated in a muffle furnace at 550 °C for 10 h. The ashes were digested with a HNO_3-HCl (4:1, v/v) solution. The Pb contents in the samples were then measured by ICP-AES and calculated on a dry weight basis.

3. Results and discussion

3.1. Physiochemical properties

All the as-is biochars contained more than 75% of carbon (Table 1), which is among the typical reported values of other biochars produced at this temperature [21]. After the modification, the biochars showed a lower percentage of carbon and higher nitrogen, hydrogen, and oxygen contents, suggesting the presence of chitosan ($C_6H_{11}NO_4$) on biochar surfaces (Table 1). In particular, the nitrogen content of the modified biochars is about 3–17 times higher than that of the as-is biochars. The C/N ratios of the as-is biochars in this study are between 97 and 539 whereas a good soil amendment should have a C/N ratio lower than 20; otherwise, it may cause N deficiency of plants [22]. Although it is still unclear whether the C/N ratio criterion is directly applicable to biochars, which do not decompose at the same rate as other amendment,

Table 1
Properties of the studied as-is and chitosan (-C) modified biochars.

Samples	pH	Surface area (m²/g)	N	C	H	O[a]	C/N ratio
BB	7.9	470.4	0.15	80.89	2.43	16.54	539.3
BB-C	8.2	166.9	2.64	71.60	4.22	21.54	27.1
BG	7.5	557.4	0.79	76.45	2.93	19.81	96.8
BG-C	8.1	123.7	3.03	69.61	4.58	22.78	23.0
HC	8.4	401.0	0.73	81.81	2.16	15.3	112.1
HC-C	8.6	2.6	3.28	66.69	4.54	26.49	20.3
PN	6.9	27.1	0.94	86.39	1.36	11.26	91.9
PN-C	7.3	0.2	4.23	65.40	4.26	26.11	15.5

[a] Determined by weight difference assumed that the total weight of the samples was made up of the tested elements only.

applications of biochars with higher C/N ratios may lead to lower N uptake [22]. Here, the chitosan modification greatly lowered the C/N ratios of the biochars (15.5–27.1), which may make them better soil amendments.

Almost all the as-is and modified biochars (except PN) were alkaline (Table 1). The presence of chitosan on the biochar surfaces increased the alkalinity, probably because the amine functional groups are weak bases. Thus, when applied to soils as an amendment, these biochars could be also used to mitigate soil acidity. Because high temperature (600 °C) pyrolysis was used, the as-is biochars, except for that made from peanut hulls, had relatively large surface areas (401–557 m²/g, Table 1) as has been shown previously (Zimmerman, 2010). After the modification, the surface area of the biochars decreased dramatically, due either to partial infilling of the pores or pore opening blockage by the chitosan or alteration of the chemistry of biochar's surface so that N_2 has less affinity for surface adsorption. For example, many biochars with sorbed organic matter have been shown to register very low surface areas [23].

Comparison of the thermogravimetric analysis (TGA) curves of BB and BB-C also suggested the presence of chitosan on the biochar surface (Fig. 1). The BB was thermally stable up to a temperature of about 420 °C and lost about 92% weight in the range 420–560 °C due to decomposition of the carbon. Because the chitosan is more thermally labile than the biochar, the TGA curve of BB-C showed obvious weight loss at 260–300 °C and 450–560 °C, which could be attributed to chitosan volatilization off the biochar and decomposition of biochar, respectively. The TGA results thus indicated that the chitosan accounts for about 20% of the weight of the BB-C. The SEM imaging of the BB-C were not visibly different from that of many pristine biochars as reported in the literature [5,19] and showed the highly porous networks (Fig. 2).
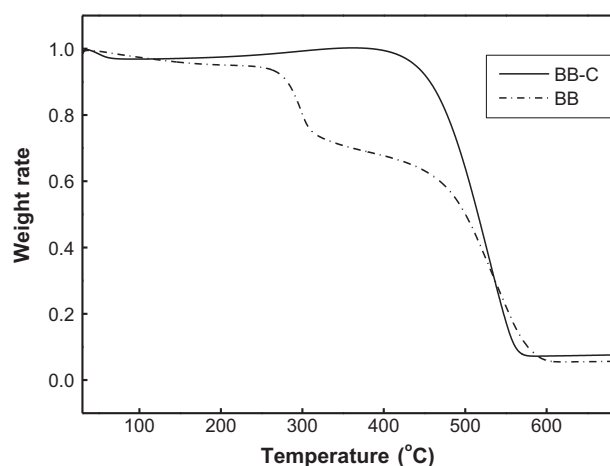

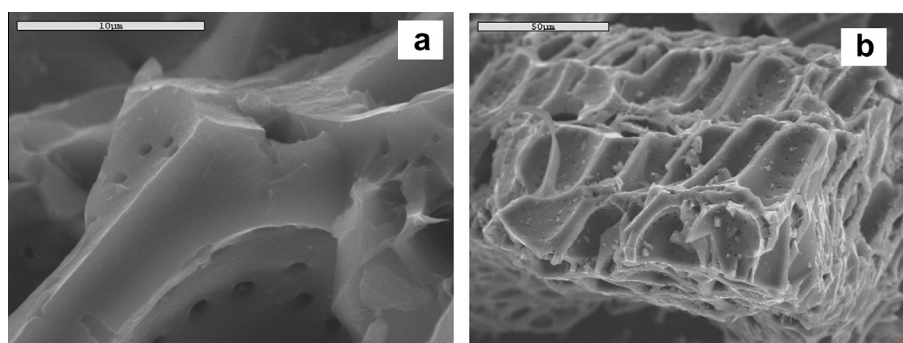**Fig. 1.** Thermogravimetric curves for as-is bamboo (BB) and chitosan-modified bamboo (BB-C) biochars.

Fig. 2. SEM images of BB-C biochar: (a) 5000× and (b) 700×.

3.2. Removal of heavy metals

All the biochar samples showed ability to remove the three heavy metals from aqueous solution (Fig. 3). In general, most of the chitosan-modified biochars (except PN-C) removed more of heavy metals from aqueous solutions than their unmodified forms. For example, BB-C biochar removed 150% more Pb, 316% more Cd and 233% more Cu than BB biochar. BB-C removed more Pb and Cd than any other biochar whereas BG-C moved the most Cu (58%). These data suggest that feedstocks may be chosen to produce chitosan-modified biochar tuned to sorb specific metals with the greatest efficiency. It should be noted that the chitosan modification reduced the sorption of Pb to BG, and Pb and Cd to PN, probably because the modification reduced the surface area of the as-is biochars. Further investigations thus are needed to optimize the coating of chitosan on biochar surfaces. Among all the adsorbents, the BB-C showed relatively good sorption ability for all three heavy metals with removal rates higher 45%, and was thus used in the Pb sorption studies to determine the sorption characteristics and mechanisms.

3.3. Sorption of lead on BB-C biochar

The adsorption of lead on the chitosan-modified biochar reached equilibrium after about 30 h (Fig. 4a), which is much longer than some pure chitosan adsorbents [24,25]. Previous studies have suggested that the adsorption of metal ions on chitosan could be controlled by diffusion-controlled mechanisms [14]. Similarly,
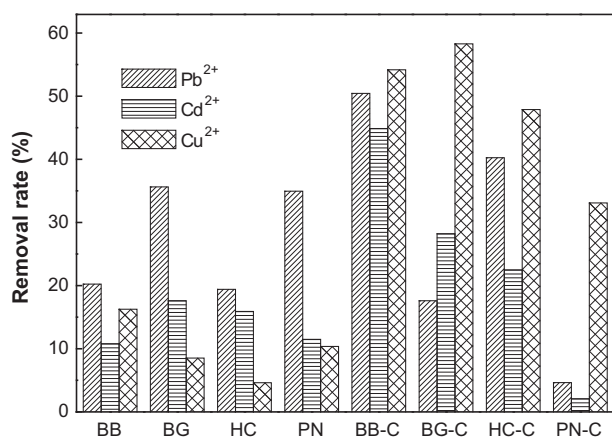

Fig. 3. Aqueous sorption of heavy metals by the as-is (BB, BG, HC, and PN) and chitosan-modified (BB-C, BG-C, HC-C, and PN-C) biochars. BB, BG, HC, and PN represent biochars made from bamboo, sugarcane bagasse, hickory wood, and peanut hull, respectively. BB-C, BG-C, HC-C, and PN-C are chitosan-modified samples from the corresponding biochars.

the pore-networks of the biochar could impede the intraparticle mass transfer of metals and thus prolong the sorption equilibrium time. Pseudo-first-order, pseudo-second-order, and Elovich models were tested for their ability to simulate the sorption kinetics data (Table 2). All models described the kinetics data equally well with coefficients of correlation (R^2) all above 0.94. Thus, control by diffusion could not be ruled out nor could control by the chitosan on biochar surfaces because the adsorption kinetics of metal ions on chitosan are well-described by the three models [14].

The adsorption isotherm of lead on the BB-C showed a typical "L" shape with a maximum sorption capacity of around 15 mg/g (Fig. 4b), which is lower than that of most pure chitosan adsorbents [14], probably because the sorbent only contains about 20% chitosan. Both Langmuir and Freundlich models reproduced the isotherm data fairly well with R^2 larger than 0.95 (Table 2). It is well known that the adsorption of transition metals is primarily influenced by coordination with the amine group, which often follows a Langmuir process of uniform and single layer adsorption [14,26]. In contrast, several previous studies suggested that lead adsorption on non-modified biochar is a heterogeneous process and the Langmuir model did not perform well with the isotherm data [8,10]. In this work, the Langmuir model described the experimental data very well with correlation with R^2 exceeding 0.95, further suggesting that the adsorption of lead on BB-C could be mainly controlled by the chitosan on biochar surfaces. The Langmuir maximum sorption capacity of lead on the BB-C was 14.3 mg/g, equivalent to about 70 mg/g-chitosan, which is similar to previously reported values of lead sorption by chitosan [14,26]. Further investigations are required to optimize the modification method to optimize the sorption capacity of the modified biochars to aqueous heavy metals.

Solution pH showed a strong effect on the sorption of lead on the modified biochar (Fig. 4c). The increase in sorption with increasing pH is consistent with the characteristics of lead sorption by chitosan that has a pK_a value of ∼6.5 [27,28]. At low pH values, the BB-C biochar could be positively charged and the surface functional groups (amine groups) are closely associated with hydronium ions (H_3O^+), which may compete with Pb (II) ions for surface active sites. With increasing solution pH, the adsorption sites become deprotonated, and electrostatic attraction of Pb (II) ions for amine groups is likely to increase [29]. This result is consistent with the conclusion that chitosan on BB-C surfaces controlled lead sorption.

3.4. Sorption mechanisms

Previous studies have demonstrated that the amine functional groups of chitosan could immobilize various metal ions, including lead, from aqueous solution through chelation amine functional groups (likely two): $M^{n+} + nRNH_2 \leftrightarrow [M(RNH_2)]^{n+}$, where M^{n+} is a
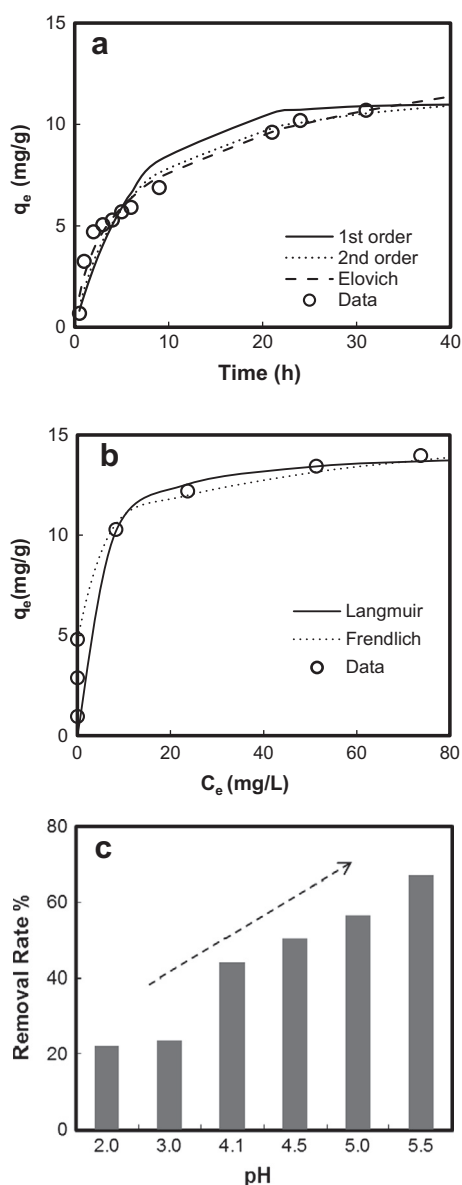
Fig. 4. Sorption of lead (50 ppm, pH 4.5) on chitosan-modified bamboo (BB-C) biochar dependency with: (a) time, (b) sorbate concentration, and (c) pH.

Table 2
Best-fit model parameters of lead adsorption on BB-C biochars.

	Governing equation[a]	Parameter 1	Parameter 2	R^2
First-order	$q_t = q_e(1 - e^{-k_1 t})$	$k_1 = 0.15$	$q_e = 11.0$	0.94
Second-order	$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e^2 t}$	$k_2 = 0.014$	$q_e = 12.5$	0.95
Elovich	$q_t = \frac{1}{\beta}\ln(\alpha\beta t + 1)$	$\alpha = 4.10$	$\beta = 0.36$	0.96
Langmuir	$q_e = \frac{KS_{max}C_e}{1 + KC_e}$	$K = 0.30$	$S_{max} = 14.3$	0.95
Freundlich	$q_e = K_f C_e^n$	$K_f = 8.20$	$n = 0.12$	0.98

[a] q_t and q_e are the amount of sorbate removed at time t and at equilibrium, respectively (mg g^{-1}), and k_1 and k_2 are the first-order and second-order sorption rate constants (h^{-1}), respectively, α is the initial sorption rate (mg g^{-1}) and β is the desorption constant (g mg^{-1}), K and K_f are the Langmuir bonding term 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 kg^{-1}), C_e is the equilibrium solution concentration (mg L^{-1}) of the sorbate, and n is the Freundlich linearity constant.

metal ion, RNH$_2$ is amine functional group of chitosan [14]. Although dissolved chitosan can precipitate metal ions from solutions, the chitosan in this work was coated on the biochar surfaces

and thus could not remove lead through the precipitation mechanism. Post-sorption characterizations of the Pb-laden BB-C strongly suggested that sorption of lead on the biochar is mainly through the interactions with the amine functional groups, i.e. adsorption by the chitosan on biochar surfaces. Comparison of the FTIR spectra of the BB-C, and Pb-laden BB-C (i.e., BB-C + Pb) showed that the N-H band at around 3300 cm^{-1} shifted somewhat after Pb was adsorbed on the biochar (Fig. 5a), which could be caused by the interactions between Pb and the amine functional groups introduced to biochar by the chitosan modification. Compared with BB-C spectra, the XPS spectra of the BB-C + Pb showed the Pb peaks, indicating the immobilization of Pb on the biochar surfaces (Fig. 5b). While XPS peaks of C, O, and H of the two samples were almost identical, the N peak shifted from 398.25 to 399.45 eV after the Pb adsorption, which could also be caused by the binding of Pb ions with the amine fictional groups through chelation. This further suggests an adsorption mechanism involving amine functional groups on the chitosan-modified biochar.

3.5. Seed germination, early growth, and bioaccumulation

Lead in solution (i.e., dissolved Pb group) showed a statistically significant inhibitory effect on seedling growth (Fig. 6a), which is consistent with findings from several previous studies [30-32]. However, the BB-C and Pb-laden BB-C (i.e., BB-C + Pb group) had no statistically significant toxic effect on the plant. While the seedlings in dissolved Pb appeared small and unhealthy, the seedlings
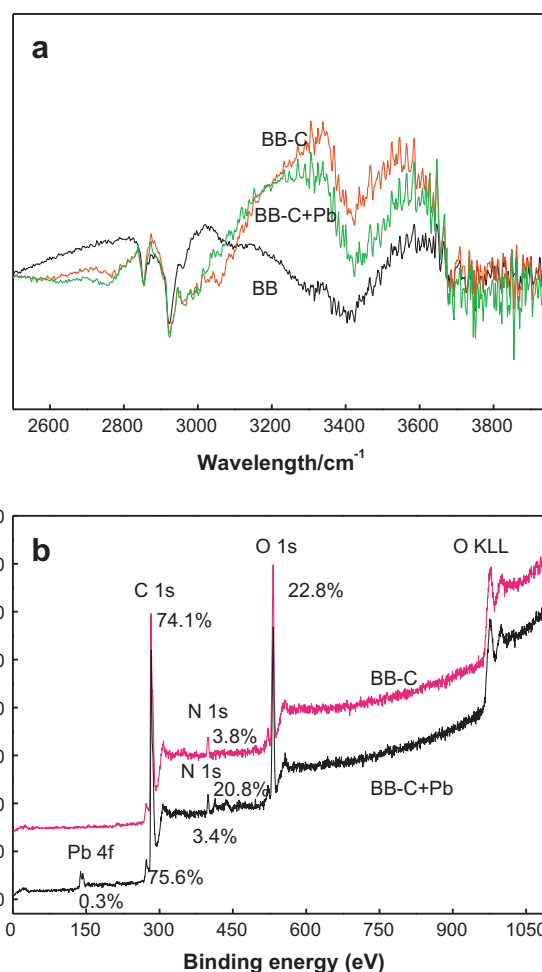

Fig. 5. Comparisons of chitosan-modified bamboo (BB-C) and lead-laden BB-C biochars: (a) FTIR and (b) XPS.
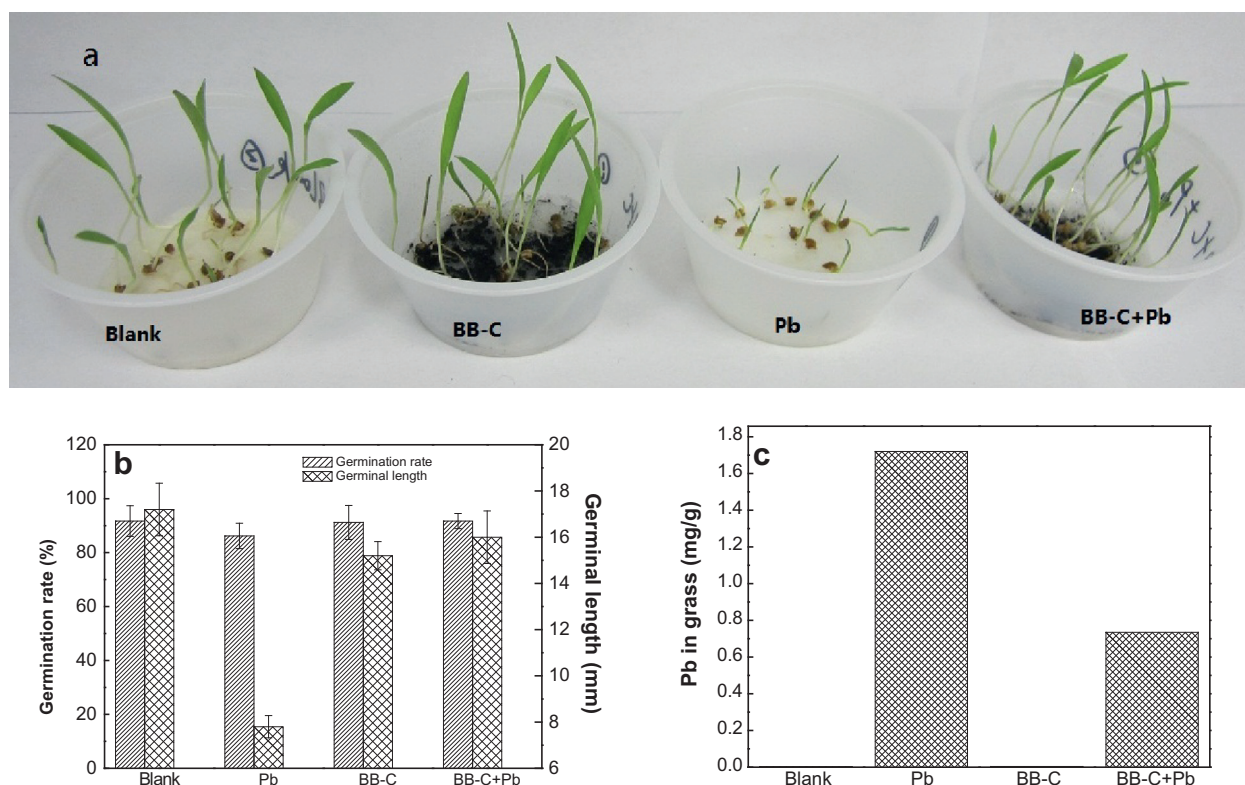
Fig. 6. Biological effects of dissolved lead (Pb), chitosan-modified biochar (BB-C), and lead-laden chitosan-modified biochar (BB-C + Pb) as indicated by: (a) photograph of seedlings on day 7, (b) seed germination rate and seedling growth, and (c) bioaccumulation of lead. Error bars represent standard deviations of multiple determinations.

in the BB-C + Pb group were of similar length as those in the control groups (i.e., blank and BB-C groups), which also appeared deeper green in color (Fig. 6a). The average germination rate of the BB-C + Pb group was 91.7%, almost identical to that of the blank (91.7%) and the BB-C (91.2%) groups, but about 5% higher than that of the dissolved Pb group (Fig. 6b). The average seedling length of the dissolved Pb group was only about 7.8 mm, about half that of when Pb was adsorbed on BB-C biochar (16.0 mm), or of the control groups (17.2 and 15.2 for the blank and BB-C, respectively; Fig. 6b). Elemental analysis showed that, whereas high levels of Pb were found in the seedlings of the dissolved Pb group (1.72 mg/g), there was much less in the plants when Pb was present in the adsorbed state (BB-C + Pb = 0.72 mg/g) (Fig. 6c). It also showed that no detectable Pb (detection limit of the ICP-AES < 0.01 mg/L) in the control groups (i.e., blank and BB-C, Fig. 6c). Results from these germination, growth, and uptake experiments indicated that the chitosan-modified biochar could reduce the toxicity of heavy metals and may be applied to polluted soils as a remediation agent to improve soil quality and reduce the risks heavy metal contaminants.

4. Conclusions

This work demonstrated that that chitosan-modified biochar not only effectively removed heavy metals from aqueous solutions, but also greatly reduced the toxicity of heavy metals to plants. Because both chitosan and biochar are low-cost and environmental friendly materials that can be obtained from readily available natural waste materials, the chitosan-biochar composites have great advantage over many traditional adsorbents. The chitosan-modified biochars could be used as a low-cost, alternative adsorbent in various settings including soil remediation and the removal of heavy metal ions from wastewater.

References

[1] A.R. Zimmerman, B. Gao, M.Y. Ahn, Positive and negative carbon mineralization priming effects among a variety of biochar-amended soils, Soil Biol. Biochem. 43 (2011) 1169–1179.
[2] J. Lehmann, J. Gaunt, M. Rondon, Bio-char sequestration in terrestrial ecosystems – a review, Mitigation Adapt. Start. Global Change (2006) 403–427.
[3] S.P. Sohi, E. Krull, E. Lopez-Capel, R. Bol, A review of biochar and its use and function in soil, Adv. Agron. 105 (2010) 47–82.
[4] L. Beesley, E. Moreno-Jimenez, J.L. Gomez-Eyles, E. Harris, B. Robinson, T. Sizmur, A review of biochars' potential role in the remediation, revegetation and restoration of contaminated soils, Environ. Pollut. 159 (2011) 3269–3282.
[5] M. Inyang, B. Gao, P. Pullammanappallil, W. Ding, A.R. Zimmerman, Biochar from anaerobically digested sugarcane bagasse, Bioresour. Technol. 101 (2010) 8868–8872.
[6] M. Uchimiya, L.H. Wartelle, K.T. Klasson, C.A. Fortier, I.M. Lima, Influence of pyrolysis temperature on biochar property and function as a heavy metal sorbent in soil, J. Agr. Food Chem. 59 (2011) 2501–2510.
[7] Y. Yao, B. Gao, M. Inyang, A.R. Zimmerman, X.D. Cao, P. Pullammanappallil, L.Y. Yang, Removal of phosphate from aqueous solution by biochar derived from anaerobically digested sugar beet tailings, J. Hazard Mater. 190 (2011) 501–507.
[8] M.D. Inyang, B. Gao, W.C. Ding, P. Pullammanappallil, A.R. Zimmerman, X.D. Cao, Enhanced lead sorption by biochar derived from anaerobically digested sugarcane bagasse, Separ. Sci. Technol. 46 (2011) 1950–1956.
[9] M. Zhang, B. Gao, Y. Yao, Y.W. Xue, M. Inyang, Synthesis, characterization, and environmental implications of graphene-coated biochar, Sci. Total Environ. 435 (2012) 567–572.
[10] Y. Xue, B. Gao, Y. Yao, M. Inyang, M. Zhang, A.R. Zimmerman, K.S. Ro, Hydrogen peroxide modification enhances the ability of biochar (hydrochar) produced from hydrothermal carbonization of peanut hull to remove aqueous heavy metals: batch and column tests, Chem. Eng. J. 200 (2012) 673–680.
[11] W. Zhang, L. Wang, H.W. Sun, Modifications of black carbons and their influence on pyrene sorption, Chemosphere 85 (2011) 1306–1311.
[12] Y.P. Qiu, H.Y. Cheng, C. Xu, D. Sheng, Surface characteristics of crop-residue-derived black carbon and lead(II) adsorption, Water Res. 42 (2008) 567–574.

[13] R.N. Tharanathan, F.S. Kittur, Chitin – the undisputed biomolecule of great potential, Crit. Rev. Food Sci. 43 (2003) 61–87.

[14] C. Gerente, V.K.C. Lee, P. Le Cloirec, G. McKay, Application of chitosan for the removal of metals from wastewaters by adsorption – mechanisms and models review, Crit. Rev. Environ. Sci. Technol. 37 (2007) 41–127.

[15] L. Pontoni, M. Fabbricino, Use of chitosan and chitosan-derivatives to remove arsenic from aqueous solutions – a mini review, Carbohyd. Res. 356 (2012) 86–92.

[16] A. Bhatnagar, M. Sillanpaa, Applications of chitin- and chitosan-derivatives for the detoxification of water and wastewater – a short review, Adv. Colloid Interface 152 (2009) 26–38.

[17] X. Cao, L.N. Ma, Y. Liang, B. Gao, W. Harris, Simultaneous immobilization of lead and atrazine in contaminated soils using dairy-manure biochar, Environ. Sci. Technol. 45 (2011) 4884–4889.

[18] M. Uchimiya, K.T. Klasson, L.H. Wartelle, I.M. Lima, Influence of soil properties on heavy metal sequestration by biochar amendment: 1. Copper sorption isotherms and the release of cations, Chemosphere 82 (2011) 1431–1437.

[19] Y. Yao, B. Gao, M. Inyang, A.R. Zimmerman, X. Cao, P. Pullammanappallil, L. Yang, Biochar derived from anaerobically digested sugar beet tailings: characterization and phosphate removal potential, Bioresour. Technol. 102 (2011) 6273–6278.

[20] W. Buss, C. Kammann, H.W. Koyro, Biochar reduces copper toxicity in chenopodium quinoa willd. in a sandy soil, J. Environ. Qual. 41 (2012) 1157–1165.

[21] K.A. Spokas, Review of the stability of biochar in soils: predictability of O:C molar ratios, Carbon Manage. 1 (2010) 289–303.

[22] J. Lehmann, S. Joseph, Biochar for environmental management: science and technology, Earthscan/James James (2009).

[23] G.N. Kasozi, A.R. Zimmerman, P. Nkedi-Kizza, B. Gao, Catechol and humic acid sorption onto a range of laboratory-produced black carbons (biochars), Environ Sci Technol 44 (2010) 6189–6195.

[24] S. Wang, D.M. Yu, Adsorption of Cd(II), Pb(II), and Ag(I) in aqueous solution on hollow chitosan microspheres, J. Appl. Polym. Sci. 118 (2010) 733–739.

[25] L.F. Qi, Z.R. Xu, Lead sorption from aqueous solutions on chitosan nanoparticles, Colloid Surf. A 251 (2004) 183–190.

[26] E. Onsoyen, O. Skaugrud, Metal recovery using chitosan, J. Chem. Technol. Biotechnol. 49 (1990) 395–404.

[27] L.L. Fan, C.N. Luo, M. Sun, X.J. Li, H.M. Qiu, Highly selective adsorption of lead ions by water-dispersible magnetic chitosan/graphene oxide composites, Colloid Surf. B 103 (2013) 523–529.

[28] M.W. Wan, C.C. Kan, B.D. Rogel, M.L.P. Dalida, Adsorption of copper (II) and lead (II) ions from aqueous solution on chitosan-coated sand, Carbohyd. Polym. 80 (2010) 891–899.

[29] L.V. Alves Gurgel, L.F. Gil, Adsorption of Cu(II), Cd(II) and Pb(II) from aqueous single metal solutions by succinylated twice-mercerized sugarcane bagasse functionalized with triethylenetetramine, Water Res. 43 (2009) 4479–4488.

[30] M. Wierzbicka, J. Obidzinska, The effect of lead on seed imbibition and germination in different plant species, Plant Sci. 137 (1998) 155–171.

[31] B. Bhushan, K. Gupta, Effect of lead on carbohydrate mobilization in oat seeds during germination, J. Appl. Sci. Environ. Manage. 12 (2008) 29–33.

[32] G. Madhu, R.S. Sengar, S.K. Garg, S. Kalpana, C. Reshu, Effect of lead on seed germination, seedling growth, chlorophyll content and nitrate reductase activity in mung bean (Vigna radiata), Res. J. Phytochem. 2 (2008) 61–68.