Manuscript Details

Manuscript number	JES_2018_1483_R1
Title	Assessing the capacity of biochar to stabilize copper and lead in contaminated sediments using chemical and extraction methods
Article type	Research Paper

Abstract

Because of its high adsorption capacity, biochar has been used to stabilize heavy metals when remediating contaminated soils; to date, however, it has seldom been used to remediate contaminated sediment. In this study, a biochar was used as a stabilization agent to remediate Cu- and Pb-contaminated sediments, collected from three locations in or close to Beijing. The sediments were mixed with a palm sawdust gasified biochar at a range of weight ratios (2.5%, 5%, and 10%) and incubated for 10, 30, or 60 days. The performance of the different treatments and the heavy metal fractions in the sediments were assessed using four extraction methods, including diffusive gradients in thin films, the porewater concentration, a sequential extraction, and the toxicity characteristic leaching procedure. The results showed that biochar could enhance the stability of heavy metals in contaminated sediments. The degree of stability increased as both the dose of biochar and the incubation time increased. The sediment pH and the morphology of the metal crystals adsorbed onto the biochar changed as the contact time increased. Our results showed that adsorption, metal crystallization, and the pH were the main controls on the stabilization of metals in contaminated sediment by biochar.

Keywords	biochar; sediment; heavy metal; stabilization assessing
Taxonomy	Environmental Remediation, Soil Science
Manuscript region of origin	Asia Pacific
Corresponding Author	Aizhong Ding
Corresponding Author's Institution	Beijing Normal University
Order of Authors	Mingming Wang, Liangsuo Ren, Dayang Wang, Zuansi Cai, Xuefeng Xia, Aizhong Ding
Suggested reviewers	Huixia Chen, Bruce Anderson, Yunzhe Cao

Submission Files Included in this PDF

File Name [File Type]

Cover letter.docx [Cover Letter]

Response to reviewer.docx [Response to Reviewers]

Abstract graphic.pptx [Graphical Abstract]

Title page.docx [Title Page (with Author Details)]

Manuscript.docx [Manuscript File]

Figures.docx [Figure]

Table.docx [Table]

author Agreement.jpg [Author Agreement]

Supplementary file.docx [e-Component]

Dear Editor,

We would like to submit the enclosed manuscript entitled “Assessing heavy metal stability enhanced by biochar in sediment using chemical and extraction methods” to be considered for publication as an original paper in *Journal of environmental sciences.*

The article is original, is not under consideration by another journal, and has not been published previously. All authors read and approved the final manuscript. The work undertaken is not owned by nor has it been conducted for any for-profit entity. The authors have no financial interest in this work.

In this paper, we use bioachr as a treatment for metal stabilization in contaminated sediment, which has been widely investigated and used in soil remediation but seldom in sediment management. Besides, we employed four extraction methods, diffusive gradients in thin-films technique (DGT), porewater concentration， sequential extraction (BCR) and toxicity characteristic leaching procedure (TCLP), to analyze stabilization efficiency. During incubation sediment slurry mixed with biochar, metal’s stability, bioavailability and geochemistry fraction have been altered and form a more stable speciation in sediment-biochar system. It is definite that the biochar can promote metals’ stability in sediment, but the adsorption is not the only stabilization mechanism. The pH value, total carbon content and so on affected by biochar directly or indirectly also contribute to the process of stabilization.

This biochar treatment process could be used for ex-situ remediation of dredged sediment from aquatic benthic before further disposal, as landfill disposal, confined aquatic disposal and dumping at sea are still the most applied sediment management strategies in China. Although this study was based on laboratory investigations, the information and data from these experiments could pave the way for further engineering application.

Thank you very much for your consideration.
Sincerely yours,

Aizhong Ding

College of Water Sciences,

Beijing Normal University,

No.19, Waida Jie, Xinjie Kou, Haiding District, Beijing 100875, China

Tel: +86-10-58805051, Fax: +86-10-58805051

Email: ading@bnu.edu.cn

Dear editor,
Thank you for arranging a timely review for our manuscript. We have carefully evaluated the reviewers' and editor's critical comments and thoughtful suggestions, responded to these suggestions point-by-point, and revised the manuscript accordingly. Moreover, according to our evaluate again this paper title have been modified from "Assessing biochar stabilization trace metal in contaminated sediment using chemical and extraction methods" to "Assessing the capacity of biochar to stabilize copper and lead in contaminated sediments using chemical and extraction methods".
The relevant reviewers's comments (in bold) and our response (in italics) are presented below. We hope that the revised version of the manuscript can be acceptable for publication in your journal.
I look forward to hearing from you soon.
With all my best regards!
Sincerely yours,
Corresponding author: Aizhong Ding
Point-by-point responses to the reviewers' comments: Mingming Wang

First of all, we thank all the reviewers for their positive and constructive comments and suggestions.

-Reviewer 1

Thanks for your positive and constructive comments.

-Reviewer 2

1. The manuscript suffers severely from poor grammar, awkward writing, spelling mistakes, and other stylistic faults. For example, Line 1 "bioichar", Line 37 "poses", Line 46 "involve", Line 130 "were", Line 280 "fig. 4", and etc. The authors are suggested to polish English by a native English speaker (Please give the polishing company or expert's name and email).

Answer:

We appreciate you for your valuable suggestion. This manuscript have already been polished by a professional company (Liwen Bianji, Edanz Editing China).

2. Page 12 line 230, the authors introduced several abbreviation (ORP) without any descriptions. It really confuses me.

Answer:

All abbreviations have been descripted at their first time exist in the paper. The ORP was descripted at line 41.

3. Page 17 line 337-340, "Furthermore, there is a study point out that the particle size of biochar has no significant relationship with or effect on the fraction re-distribution, whereas finer size particulate treatment results in higher efficiency in reducing porewater concentration than coarse biochar (Lu et al., 2017)". This sentence is contradictory.

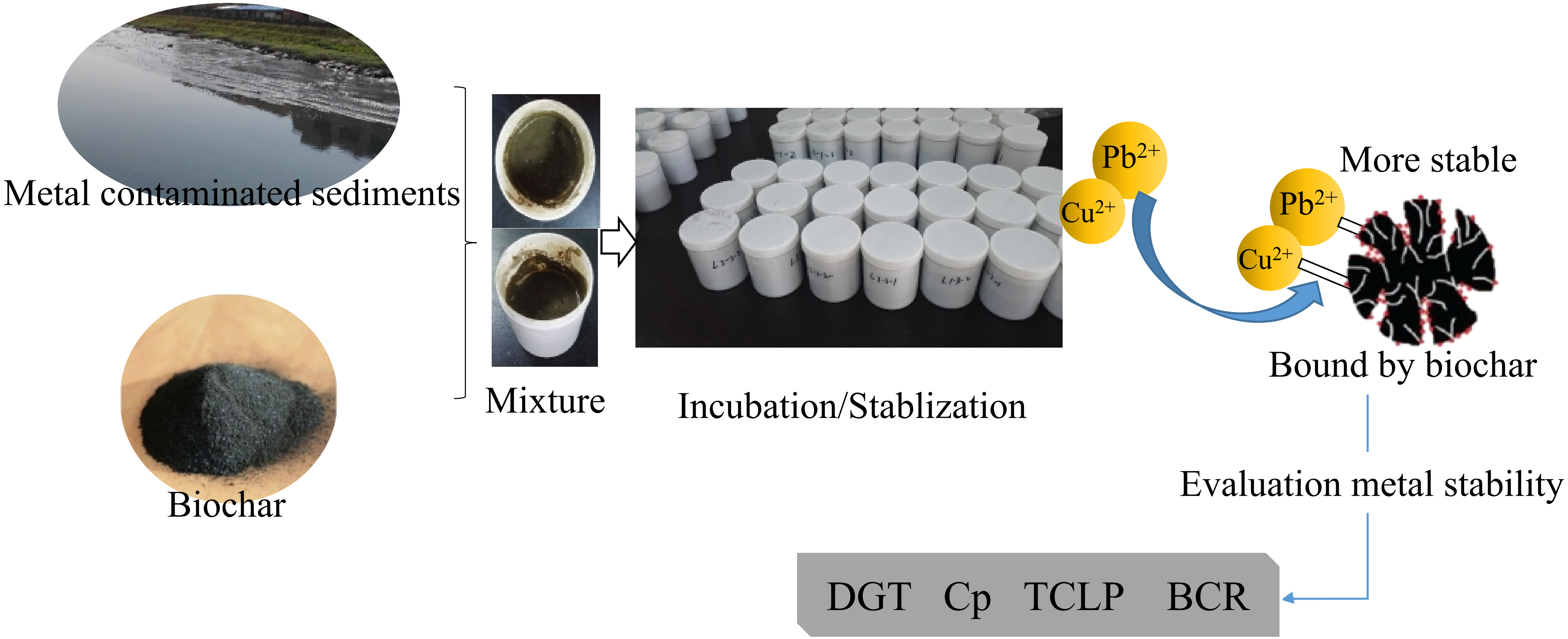
Answer:

We carefully evaluate this reference again and we think its result is inapposite to be quoted in this place, so we deiced to delete it.

4. Page 17-18 line 341-344, "However, we must acknowledge that metal stabilization efficiency by biochar is not sensitive enough when compared with phosphate or iron-bearing materials (Chen et al., 2016), which have been observed both in this and other studies (Igalavithana et al., 2017; Lu et al., 2017; Zhang et al., 2017)". However, I cannot find any studies on the metal stabilization by phosphate and iron-bearing materials in the manuscript.

Answer:

We appreciate you for your valuable suggestion. We supplement some content about the metal stabilization by phosphate and iron-bearing materials from line 339 to 344.



Metal contaminated sediments

Biochar

Mixture

Incubation/Stablization

More stable

Bound by biochar

Evaluation metal stability

DGT Cp TCLP BCR

Assessing bioichar stabilization trace metal in contaminated sediment using chemical and extraction methods

Mingming Wang[1], Liangsuo Ren[1], Dayang Wang[1], Cai Zuansi[2], Xuefeng Xia[1], Aizhong Ding[1]*

[1]: College of Water Sciences, Beijing Normal University, Beijing 100875, PR China

[2]: School of Engineering and the Built Environment, Edinburgh Napier University, Edinburgh, EH10 5DT, UK

*Corresponding author

Address: No.19, Waida Jie, Xinjie Kou, Haiding District, Beijing 100875, China

E-mail: ading@bnu.edu.cn

Tel: +86-10-58805051, Fax: +86-10-58805051

Assessing the capacity of biochar to stabilize copper and lead in contaminated sediments using chemical and extraction methods

Mingming Wang[1], Liangsuo Ren[1], Dayang Wang[1], Cai Zuansi[2], Xuefeng Xia[1], Aizhong Ding[1]*

[1]: College of Water Sciences, Beijing Normal University, Beijing 100875, PR China

[2]: School of Engineering and the Built Environment, Edinburgh Napier University, Edinburgh, EH10 5DT, UK

*Corresponding author

Address: No.19, Waida Jie, Xinjie Kou, Haiding District, Beijing 100875, China

E-mail: ading@bnu.edu.cn

Tel: +86-10-58805051, Fax: +86-10-58805051

Abstract: Because of its high adsorption capacity, biochar has been used to stabilize heavy metals when remediating contaminated soils; to date, however, it has seldom been used to remediate contaminated sediment. In this study, a biochar was used as a stabilization agent to remediate Cu- and Pb-contaminated sediments, collected from three locations in or close to Beijing. The sediments were mixed with a palm sawdust gasified biochar at a range of weight ratios (2.5%, 5%, and 10%) and incubated for 10, 30, or 60 days. The performance of the different treatments and the heavy metal fractions in the sediments were assessed using four extraction methods, including diffusive gradients in thin films, the porewater concentration, a sequential extraction, and the toxicity characteristic leaching procedure. The results showed that biochar could enhance the stability of heavy metals in contaminated sediments. The degree of stability increased as both the dose of biochar and the incubation time increased. The sediment pH and the morphology of the metal crystals adsorbed onto the biochar changed as the contact time increased. Our results showed that adsorption, metal crystallization, and the pH were the main controls on the stabilization of metals in contaminated sediment by biochar.

Keywords: biochar; sediment; heavy metal; stabilization assessment

Introduction

Sediment is a major component of river ecosystems and has a fundamental influence on ecosystem health. As such, there is great concern about heavy metal contamination of river sediment (Akcil et al., 2015). The heavy metals commonly found in sediments usually originate from industrial waste discharges through direct emissions, such as dumping, or indirect emissions, such as rain runoff and atmospheric deposition. Approximately 90% of the heavy metals that enter rivers may be deposited onto the sediment surface and incorporated into the lattice structure of minerals via adsorption, precipitation, and flocculation (Du et al., 2009; Lin et al., 2013). The stability of metals in sediment depends, to some degree, on the environmental conditions. With changes in the environmental conditions, such as the pH, oxidation reduction potential (OPR), temperature and salinity, the bound metals may be released into water, from where they may be taken up and bioaccumulated in food webs, thereby presenting risks to river ecosystems. In addition, the mobility and bioavailability of sediment-bound metals in river ecosystems may increase during resuspension by natural processes, waste disposal, and dredging activities (Akcil et al., 2015). Therefore, sediments act as both a sink and a source of heavy metals in aquatic ecosystems and can switch between these roles under different conditions (Peng et al., 2009). Because, when released, metals are toxic to aquatic ecosystems, the stability of metals in sediment matrices should be enhanced to reduce their potential impacts on the aquatic environment.

Currently physical, chemical, and biological technologies are used to treat contaminated sediments, both *in-situ* and *ex-situ* (Wang et al., 2017). During *ex-situ* remediation, sediment is dredged from the riverbed and disposed of, disturbing aquatic benthic life; *in-situ* remediation, however, does not impact on natural hydrological conditions and methods are designed to prevent the desorption of pollutants from the sediment to the water column (Peng et al., 2009; Wang et al., 2017). In most case, *ex-situ* remediation is the first choice in many restoration projects because of the severity of the pollution and doubts that *in-situ* remediation methods can provide stable results over the long-term (Peng et al., 2009). The concentrations of toxic metals can increase dramatically during dredging operations because of the re-suspension of sediment and release of dissolved metal pollutants (Akcil et al., 2015). Sediment remediation methods are designed to either dislodge or extract contaminants from sediment or to enhance their stability in the sediment. Sorbent amendments and stabilization strategies that mimic biogeochemical processes are used to enhance the stability of heavy metals, and potentially reduce the ecological risks (Bolan et al., 2014). A wide range of materials such as zero-valent iron, hematite, ferrihydrite, apatite, clays, calcium-rich sepiolite, attapulgite, and activated carbon have already been used to remediate metal-contaminated sediments (Ghosh et al., 2011; Qian et al., 2009; Yin and Zhu, 2016). However, while biochar is well-known for its stability and high adsorption, it has been used infrequently in sediment management applications (Wang et al., 2017).

Biochar is a carbon-rich material obtained from the thermochemical conversion of biomass under oxygen-limited conditions (Keiluweit et al., 2010; Tong et al., 2011; Wang et al., 2017; Yuan et al., 2011). Because of its unique properties, it is increasingly used in soil remediation applications (Zhang et al., 2013). Studies to date have shown that biochar can enhance the matrix pH under most acid and neutral conditions, and hold moisture, thereby increasing the soil water content and retaining necessary nutrients for plant growth (Atkinson et al., 2010; Gunes et al., 2014; Jeffery et al., 2015; Major et al., 2010). In a recent study, biochar was used to improve and remediate several metal-contaminated rice fields in China. The results from a series of field trials showed that the bioavailability of metals in soil and the metal concentrations in rice grains decreased by between 20% ~ 70%, and 20% ~ 60%, respectively, in soils treated with biochar (Wang et al., 2017). In terms of sediment, studies have addressed the effects of biochar on (1) mercury-related processes such as methylation and demethylation (Liu et al., 2016), (2) the fractions of Fe and As (Chen et al., 2016), and (3) the basic physico-chemical properties of sediment such as water retention, CO_2 emissions, total organic carbon, pH, and electrical conductivity (Ojeda et al., 2016). Despite the fact that few studies have addressed how biochar can be used to treat metal-contaminated sediments, we speculate that the benefits already seen in soil management might also apply to sediment remediation.

In sediment management strategies, sediment quality guidelines have traditionally been based on the total contaminant concentrations rather than the leachability or bioavailability (Qian et al., 2009). However, the total contaminant concentrations cannot adequately represent contaminant mobility, because the mobility, bioavailability and eco-toxicity of metals in sediments are generally controlled by different geochemical fractions and the binding relationships between contaminants and solid phases (Kazi et al., 2005), which can be more accurately explained by the metal fractions. It is well-known that, when incorporated into the lattice structures of minerals, heavy metals are stable and less bioavailable than weakly-bound labile metals. To date, a series of chemical methods, including porewater extraction, membrane extraction, and chemical reagent extraction, have been developed to facilitate rapid evaluation of the bioavailability of metals in soils or sediments (Chen et al., 2016; Yin et al., 2014; Yin and Zhu, 2016; Zhang et al., 2001). In these methods, speciation analysis and leaching tests are based on the different abilities of chemical reagents to extract and classify metal geochemical fractions and evaluate their mobility and bioavailability, and membrane extraction is based on the equilibrium between the solid and liquid to assess the dissolved pollutants concentration and their resupply ability from solid phase. These methods provide detailed information about metal species in sediment phases and helps to predict the potential future behavior of these pollutants (Hasan et al., 2018; Kazi et al., 2005; Song et al., 2017).

The objective of this study was to investigate if biochar could be used effectively to remediate sediments that were contaminated with heavy metals. Four extraction methods were employed to evaluate specific components of the performance of the biochar treatments, as follows: (1) diffusive gradients in thin films (DGT) were used to investigate the concentrations of labile metals (*in-situ* sample) (Zhang et al., 2001); 2) a centrifuge method was used to determine the concentrations of dissolved metals in porewater; 3) a multi-step sequential extraction method (the Community Bureau of Reference (BCR) method, Yin and Zhu (2016)) was used to evaluate the distribution of metal fractions, and 4) the toxicity characteristic leaching procedure (TCLP, USEPA (1984)), a one-step extraction method, was used to investigate the potential leachability of metals in sediments under strong or moderately acidic conditions. While this was a laboratory-based study, the information and data from these experiments could form the basis of further engineering applications.

1 Materials and methods

1.1 Sediment collection and biochar preparation

Three different sediments were collected from an inner-city river (CR), a standby reservoir (SR), and an artificial lake (AC) either close to or in Beijing, China. The sediments were collected by a grab sampler, packed into plastic bags and sealed, then transported to the laboratory, and stored at 4°C. The sediments were then amended with solutions of $Cu(NO)_2$ and $Pb(NO)_2$ to give medium-to-high concentrations of Cu(II) and Pb(II) (Gu and Hua, 2006; Zhu and Wang, 2012). The sediment slurries were hand-stirred several times to homogenize and then incubated in the dark for 40 days. The total concentrations of Cu and Pb in the sediments before and after the $Cu(NO)_2$ and $Pb(NO)_2$ solutions were added are presented in Table 1. A palm sawdust-based gasification biochar (SBIO), details of which are reported in an earlier study, was selected as the metal stabilization agent (supplementary file). Briefly, to prepare the biochar, the palm sawdust was air-dried and then pyrolyzed at approximately 550°C in a kiln in O_2-limited conditions for 2 hours.

1.2 Sediment and biochar properties

The physico-chemical properties of the biochar and air-dried sediments were characterized as follows. The pH was measured in a 1:1 suspension of solid and deionized water and shaken for 3 hours at 160 rpm. This test showed that all samples were alkaline (Table 1). The concentrations of total organic carbon (TOC) were determined with a TOC analyzer (Multi N/C 3100, Analytik Jena AG). The surface area was determined with the Brunauer–Emmett–Teller (BET) equation with multipoint adsorption isotherms of N_2 at 77 K. Solid samples of biochar and sediment were digested with HNO_3, HF, and $HClO_4$ (3 mL/2 mL/3 mL) in a Teflon bomb. The metal concentrations in the extract solution were measured by flame atomic absorption spectrometry (FAAS) or inductively coupled plasma mass spectrometry (ICP-MS), and the chemical compositions were characterized by X-ray fluorescence (XRF) spectrometry (Yin and Zhu, 2016)

The surface physical morphology of the SBIO was analyzed using scanning electron microscopy (SEM) (Chen et al., 2016). The functional groups were recorded using Fourier transform infrared spectra (Chen et al., 2016). There was a peak at 3438 cm^{-1} that corresponded to the hydroxyl group stretching vibration. Bonds at 1615 and 1440 cm^{-1} were caused by C=O deviational vibration and symmetrical stretching, and the stronger peak at 1038 cm^{-1} was assigned to the C-O stretching vibration (Keiluweit et al., 2010; Yuan et al., 2011) (Fig. S5). Analysis of the mineralogical composition of the related solid samples using powder X-ray diffraction (XRD) (Yin and Zhu, 2016) indicated that the solid samples were dominated by calcite and quartz (Figure S7a).

Table 1

1.3 Batch experiments to stabilize Cu and Pb with biochar

The biochar was mixed with approximately 200±10 g of each of the contaminated sediment slurries, which corresponded to 104.4, 85.0, and 90.2 g of dry sediment from SR, CR, and AC, respectively, at ratios of 0%, 2.5%, 5%, and 10%. The mixtures were placed into PVC cylinders that were covered with caps that measured 8×10 cm, and homogenized using a glass stirring rod. The containers were then incubated in the dark at room temperature for 15, 30, or 60 days. The sediment-biochar microcosms for each incubation time were grouped together and each cluster was kept separate from the others. The water content of each microcosm was maintained at the same level (60%) by adding deionized water. Each treatment was performed in triplicate.

1.4 Metal stabilization evaluation

The remediation ability of the biochar was assessed by various methods, namely the DGT technique, the porewater concentration, the BCR 4-step sequential extraction procedure and the TCLP. Analytical grade reagents, including HNO_3, HF, $HClO_4$, CH_3COOH, H_2O_2, $NH_2OH•HCl$, CH_3COONH_4, copper nitrate trihydrate, and lead nitrate, were used throughout.

1.4.1 DGT and porewater analysis

The DGT device used in this study was purchased directly from the manufacturer (Nanjing Weisheng Huangbao Keji Co. Ltd). The structure of this device is shown in Figure S3. After incubation, about 1/3 of the sediment slurry of each treatment was placed into a PVC box (Dimensions 2×3 cm) with a lid, and the DGT devices were carefully pressed onto the surface of the sediment slurry, and placed in an incubator at 25℃ for 24 h. The resin layer of DGT was then detached from the device and soaked in 1 mL of 1M HNO_3 to elute extracted metal by DGT for 10 h in a shaker (160 rpm) (160 rpm). The elution solution was diluted for a suitable time and stored at 4°C until analysis. The DGT extracted concentration (C_{DGT}) can be calculated from the analysis results, as in earlier study (See supplementary file). Porewater samples were collected by centrifuging the sediment slurry at 5,000 rpm for 20 min. The supernatant was filtered through a 0.45-μm membrane and stored at 4°C until analysis.

1.4.2 Sequential extraction (BCR)

The BCR method (Yin and Zhu, 2016), which involves four steps and four fractions, was used to evaluate the distribution of the metal fractions in sediments with or without biochar (Table 2). The sediment slurries were air-dried in an airing chamber and ground to pass through a 100-mesh sieve. Then 0.50 g of the dry weight solid sample was sequentially extracted by four reagents in 50-mL polyethylene centrifuge tubes. After each step, the supernatants of all the solutions were filtered with a 0.45-μm polytetrafluoroethylene syringe filter, and the filtrates were stored at 4°C until analysis. The average recoveries of the fractions extracted (F1+F2+F3+F4) ranged from 85% to 105% of the total concentrations.

Table 2

1.4.3 TCLP test

The leachability of Cu and Pb was estimated by the TCLP (USEPA, 1984). The TCLP reagents were prepared by diluting acetic acid until a pH of 2.88 was achieved. Then, 1.00 g of sediment (dry weight) and 20 mL of reagents were added into 50-ml polyethylene centrifuge tubes and shaken at 160 rpm for 18 h. Finally, the supernatant was filtered through a 0.45-μm polytetrafluoroethylene syringe filter, and the filtered extracts were stored at 4°C until analysis.

2 Results

2.1 Bioavailability of Cu and Pb reduced by biochar

The results from the tests with different amounts of biochar and for different incubation times with the C_{DGT} and porewater concentration (C_p) tests are shown in Figure 1. The bioavailabilities of Cu and Pb were much lower in AC than in the other sediments. For higher doses of SBIO, the C_{DGT} was considerably lower in the sediment microcosms than in the blank sample. The rates at which the bioavailabilities of Cu and Pb decreased were highest in CR with an amendment ratio of 10%; at the end of the incubation, the C_{DGT} (Cu) was below the detection limit (1 ug/l) and C_{DGT} (Pb) was almost 40% lower than in the blank.

The biochar had positive effects on the porewater concentration (C_p), and reductions were more closely related to the incubation times than to the biochar doses. In the Cu stabilization test, the C_p always decreased as the stabilization time increased. However, in the Pb stabilization test, the C_p decreased when incubated for 30 days but increased when incubated for 60 days. This may reflect the high affinity of the biochar for Pb as almost all dissolved Pb was adsorbed by SBIO without enough sustainable resupply from the sediment phase, which cannot be detected by centrifugation (C_p) but DGT extraction due to labile metals measured by DGT not only existed as a dissolved fraction but also as a solid fraction (Yin et al., 2014). In addition, the pH and ORP both decreased during the incubation period (Figure S4). Because the ability of the biochar to adsorb Pb was sensitive to changes in the pH (Figure S2), the dissolved Pb detected at 60 d may reflect the decreases in the pH, and this phenomenon can be alleviated largely by adding biochar.

Figure 1.

2.2 Metal fractions in the treated and untreated sediments

The distribution of the Cu and Pb fractions in the treated and untreated sediments incubated for different periods are shown in Figure 2. When treated with the biochar, the contaminated sediment was more stable than the blank treatment. The potentially available fractions of Cu (F1+F2+F3) gradually decreased as the biochar amount and incubation time increased, and the residual fraction (F4) was 61.4%, 54.7%, and 87.7% higher in the CR, SR, and AC contaminated sediments, respectively, than in the blank samples for a biochar dose of 10% and an incubation of 60 days. The acid-soluble fraction (F1) of Pb decreased, and the F1 fraction in the SR sediments treated with biochar were 64.4% largely lower than that in the blank at the end of the experiment for a 10% dose. As well as Cu, the residual fraction (F4) of Pb increased as the biochar dose and the length of the incubation period increased. In fact, the chemical reagents used in the sequential extraction to classify the metal fractions, especially the reagents for F3 (H_2O_2-NH_4Ac) and F4 (HNO_3-HF-$HClO_4$), were very harsh. In the real environment, such harsh conditions would not occur; both F3 and F4 would be stable in the environment and they were more sensitive to the biochar in our experiments.

Figure 2.

2.3 Effect of SBIO on the leachability of Cu and Pb

As shown in Figure 3, the results from the leachability tests were similar to those from the DGT and BCR tests. As the proportion of biochar in the sediment sludge increased, the stability of the metal pollutant also increased and the metal concentrations in the leachate decreased. Over a period of 60 days, the stabilization of both Cu (58.6% and 27.5%) and Pb (37.1% and 17.7%) were highest and lowest in CR and AC.

Figure 3.

3 Discussion

3.1 Relationship between DGT and other extraction methods

The DGT method has been used for several years to predict the supply of heavy metals and the bioavailability of other pollutants in soil and sediment (Zhang et al., 2001). Various studies have shown that there is a good correlation between the amount of metal taken up by plants and the metal concentration measured by DGT (Zhang et al., 2014; Zhang et al., 2001). To obtain better insights into the relationships between the extraction assessment methods used in this study, the relationships between DGT, C_p, BCR, and TCLP (from Pearson correlation analysis) were compared (Tables S3–S8). The DGT results were strongly correlated with those of BCR and TCLP, but weakly correlated with the C_p results. There were significant correlations between DGT and TCLP for all treatments and different sediments at least at the $P<0.05$ level. The highest R^2 values for Cu and Pb were 0.71 ($P<0.01$) and 0.79 ($P<0.01$), respectively, in the SR sediments.

The Cu and Pb that are weakly bound with carbonates through specific adsorption and covalent forces, such as Fe/Mn oxides or hydroxides or weaker stable organic matter, are labile and can be captured by DGT (Roulier et al., 2010). In the sequential extraction, the F1 and F2 fractions that were classified as easily-exchangeable and weakly-bound to organic or inorganic sites were well correlated with C_{DGT} and

F1+F2+F3 (Figure 4). This further indicates that the DGT measurement is not specifically confined to a single metal fraction (Ernstberger et al., 2002; Roulier et al., 2010). The results of metal isotope tracer experiments have also shown that labile Zn was strongly correlated with the extractable fractions (Roulier et al., 2010; Young et al., 2010), and that there was a good correlation between C_{DGT} and the labile isotopic exchange (Ernstberger et al., 2002). Therefore, a DGT device can be used to replace predictions of the bioavailability of metals from the BCR and TCLP methods.

Figure 4

3.2 Possible mechanisms of stabilization induced by biochar

Regardless of whether biochar, in this case SBIO, is added to sediments or not, the stability of the Cu and Pb fractions in sediments always increases. Nevertheless, when SBIO is added, the process of natural stabilization may be reinforced or the metal fractions may be redistributed, and metals may also be incorporated into the lattice of the treatment agent as the incubation time increases (Yin and Zhu, 2016). The mechanisms used by biochar to stabilize metals are complicated, and, to date, are not fully understood. In prior studies, metal adsorption by biochar has been regarded as the major driver for metal stabilization (Fang et al., 2016; Roulier et al., 2010; Zhu et al., 2017). The main mechanisms of metal adsorption by biochar include (i) electrostatic complexation resulting from ion exchange, (ii) surface complexation with active functional groups on biochar surfaces (such as carboxyl and hydroxyl), (iii) metal transport from the outer sphere to the inner sphere, and (iv) the formation of inner-sphere complexes with metals (Fang et al., 2016; Yin and Zhu, 2016; Zhu et al., 2017).

The results from this study also support these mechanisms for metal adsorption by biochar. The results from the FTIR and XPS analysis (Figures S5 and S6) show that the surface oxygen functional groups of SBIO changed after adsorption of Cu and Pb. Also, the SEM measurements demonstrate that the surface morphology of SBIO changed considerably after reacting with heavy metals, which indicates that surface precipitation contributes to the adsorption process. Further, a recent study reported that the crystal morphology of biochar-Cu could be transformed as the contact time increased. The XRD analysis (Figures S7) showed that the crystal signal of *Gerhardtite* and *Malachite* gradually weakened with time. Until the 30-day point, *Gerhardtite, Malachite*, *Paramelaconite*, and *Posnjakite* were detected, and were perhaps related to metal stabilization in sediment-metal-biochar systems. This phenomenon however has not been observed in Pb adsorption tests in this study. However, in another study, over a period of 30 days, a new compound formed on the surface of Pb-loaded biochar, but was not observed in the early stages (Fang et al., 2016). This therefore shows that time has a positive influence on the metal stability.

Because of the biochar, the pH was higher in all the SBIO tests than in the blank systems, and the ORP was also lower. During incubation, all treatment systems became weakly alkaline and showed stronger reducibility (Figure S4). At the end of the incubation, the pH had increased by almost one unit and the ORP was between 150 and 200 mV lower in the tests with 10% biochar than in the blank. The carbonates and functional groups such as $–COO^-$ ($–COOH$) and $–O^-$ ($–OH$) contained in the biochar are mainly responsible for enhancing the pH value (Shen et al., 2016; Yuan et al., 2011). Under a higher pH, there is less competition between the H^+ and heavy metal ions for ligands ($CO_3^{2−}$, $SO_4^{2−}$, $S^{2−}$, $Cl^−$, $OH^−$, phosphate, *etc*.), the sorption and/or precipitation is enhanced, and metal ions combine more easily with ligands into a relatively more stable form (Peng et al., 2009; Shaheen et al., 2013).

In this current study, the F3 and F3+F4 fractions were considerably higher in the control tests than in the blank, which shows that the biochar transformed metals into stable fractions. As a sorbent treatment, biochar has a high solid organic matter (SOM) content and so the content of SOM in sediment increases when mixed with biochar (Shaheen and Rinklebe, 2015). Metals, therefore, may bind to organic matter, like humic substances, and form metal-organic complexes, which can reduce the metals' mobility (Srivastava et al., 2008). Several related studies have also shown that, under enhanced organic matter, more stable metal fractions could form (Ahmad et al., 2014; Bian et al., 2013; Ok et al., 2011).

However, while the results indicate that biochar may be able to stabilize metals in contaminated sediments under certain conditions as clear decreases in C_p and C_{DGT} and clear increases in F3 and F4 in this study, it is clear that biochar is not as effective as phosphate or iron-bearing materials, the removals and transformations reported in other related studies are much higher than those reported in this and other biochar-related studies (Zhang et al., 2017; Igalavithana et al., 2017; Lu et al., 2017). For example, when phosphate compounds were added to contaminated soils, the concentrations of extractable heavy metals decreased by more than 90% (Ahn et al., 2015; Sima et al., 2015), while the oxidizable and residual phases of Pb and Cu increased by between 70% and 90% when nano-zero-valent iron, an activated carbon composite, and ferrihydrite were added (Chen et al., 2016; Qian et al., 2009). The lower efficiencies in this study may be related to the inherent physico-chemical properties of both the sediments and the biochar. First, metals in sediments exist as different fractions bound to, or enveloped by, Fe or Mn oxides, hydroxides, or organic matter that account for a large amount of the total metal, and it is difficult for biochar to increase the stability of these fractions by directly participating in physico-chemical reactions; on the other hand, soluble and carbonate metals only account for a smaller fraction of sediment and can be easily captured and bound by biochar. So, while the C_p and C_{DGT} results showed that the stabilization was effective, these tests could not show obviously changes in the distributions of the metal fraction. Second, when biochar is mixed with sediment slurry, the SOM and finer particulates will either be adsorbed onto the surface of the biochar or may block the pore structure, which further reduces the possibility of contact between the metal and the treatment agent (Wang et al., 2017). Meanwhile, the outer surface of biochar may undergo oxidation or aging first, followed by the interior pores, which may cause the CEC to shift and reduce element retention (Ahmad et al., 2014). Finally, the stabilization period also has an important influence on the metals' stability. In fact, regardless of whether a treatment is applied or not, metals can gradually stabilize because of natural attenuation. This natural process may be accelerated by adding biochar, but short-term incubations do not support the formation of stable compounds (Fang et al., 2016; Rajapaksha et al., 2015).

4 Conclusion

The bioavailability and mobilization of metals, rather than the total metal content, were used to predict the risks of heavy metals to the environment. The degree to which biochar was able to stabilize metals in contaminated sediments in laboratory incubations was evaluated using DGT, the porewater concentration, the BCR sequential extraction, and the TCLP. The DGT and TCLP tests showed that the bioavailability and labile fractions of the metals decreased because of the biochar. The results of the C_p tests improved more when the incubation time increased than when the amount of biochar was increased. The stable F3 and F4 fractions increased as the dose of biochar increased. Adsorption, transformations in the crystal morphology, and changes in the environmental conditions (e.g. pH and SOM) induced by the biochar were the main mechanisms of metal stabilization. There were good correlations between the DGT, BCR, and TCLP, but these methods were more weakly correlated with the porewater concentrations. These methods are interchangeable in field applications, but the DGT method should be considered the main approach for assessing the bioavailability because of its convenience, analysis capacity, and speed. These results represent an initial application of biochar in sediment management. The approach needs to be refined and field studies should be carried out before any real-life practical applications are attempted. We would hope that this approach using biochar will be useful for curbing the release of metals during sediment dredging and re-suspension; alternatively, biochar-treated sediments could be used in land reclamation initiatives.

Acknowledgements

This work was supported by the Science and Technology Project of Beijing (No. D161100000216001) and the National Science Foundation of China (No. 41672227).

References:

Ahmad M, Lee SS, Lim JE, Lee SE, Cho JS, Moon DH, Hashimoto Y, Ok YS (2014) Speciation and phytoavailability of lead and antimony in a small arms range soil amended with mussel shell, cow bone and biochar: EXAFS spectroscopy and chemical extractions. Chemosphere. 95:421-433.

Ahmad M, Upamali A, Lim JE, Zhang M, Bolan N, Yong SO (2014) Biochar as a sorbent for contaminant management in soil and water: A review. Chemosphere. 99:19-33.

Ahn J, Kang S, Hwang K, Kim H, Kim J, Song H, Hwang I (2015) Evaluation of phosphate fertilizers and red mud in reducing plant availability of Cd, Pb, and Zn in mine tailings. Environ. Earth. Sci 74:2659-2668.

Akcil A, Erust C, Ozdemiroglu S, Fonti V, Beolchini F (2015) A review of approaches and techniques used in aquatic contaminated sediments: metal removal and stabilization by chemical and biotechnological processes. J. Clean. Prod. 86:24-36.

Atkinson CJ, Fitzgerald JD, Hipps NA (2010) Potential mechanisms for achieving agricultural benefits from biochar application to temperate soils: a review. Plant Soil 337:1-18.

Bian R, Chen D, Liu X, Cui L, Li L, Pan G, Xie D, Zheng J, Zhang X, Zheng J (2013) Biochar soil amendment as a solution to prevent Cd-tainted rice from China: Results from a cross-site field experiment. Ecol. Eng. 58:378-383.

Bolan N, Kunhikrishnan A, Thangarajan R, Kumpiene J, Park J, Makino T, Kirkham M, Scheckel K (2014) Remediation of heavy metal(loid)s contaminated soils--to mobilize or to immobilize? J. Hazard. Mater. 266:141-166.

Chen W, Zhang J, Zhang X, Wang W, Li Y (2016a) Investigation of heavy metal (Cu, Pb, Cd, and Cr) stabilization in river sediment by nano-zero-valent iron/activated carbon composite. Environ. Sci. Pollut. R. 23:1460-1470.

Chen W, Zhang J, Zhang X, Wang W, Li Y (2016b) Investigation of heavy metal (Cu, Pb, Cd, and Cr) stabilization in river sediment by nano-zero-valent iron/activated carbon composite. Environ .Sci. Pollut. R. 23:1460-1470.

Chen Z, Wang Y, Xia D, Jiang X, Fu D, Shen L, Wang H, Li QB (2016) Enhanced bioreduction of iron and arsenic in sediment by biochar amendment influencing microbial community composition and dissolved organic matter content and composition. J. Hazard. Mater. 311:20-29.

Du LG, Rinklebe J, Vandecasteele B, Meers E, Tack FM (2009) Trace metal behaviour in estuarine and riverine floodplain soils and sediments: a review. Sci. Total Environ. 407:3972-3985.

Ernstberger H, Davison W, Zhang H, Tye A, Young S (2002) Measurement and dynamic modeling of trace metal mobilization in soils using DGT and DIFS. Environ. Sci. Technol. 36:349-354.

Fang S, Tsang DC, Zhou F, Zhang W, Qiu R (2016) Stabilization of cationic and anionic metal species in contaminated soils using sludge-derived biochar. Chemosphere. 149:263-271.

Ghosh U, Luthy RG, Cornelissen G, Werner D, Menzie CA (2011) In-situ Sorbent Amendments: A New Direction in ContaminatedSediment Management. Environ. Sci. Technol. 45:1163-1168.

Gu L, Hua L (2006) The heavy metal pollution assessmen for Chinese lake sediment. Soil (Chinese) 38:366-373.

Gunes A, Inal A, Taskin MB, Sahin O, Kaya EC, Atakol A (2014) Effect of phosphorus-enriched biochar and poultry manure on growth and mineral composition of lettuce (Lactuca sativa L. cv.) grown in alkaline soil. Soil Use & Management 30:182-188.

Hasan M, Kausar D, Akhter G, Shah MH (2018) Evaluation of the mobility and pollution index of selected essential/toxic metals in paddy soil by sequential extraction method. Ecotox. Environ. Safe. 147:283-291.

Igalavithana AD, Lee SE, Lee YH, Tsang DCW, Rinklebe J, Kwon EE, Yong SO (2017) Heavy metal immobilization and microbial community abundance by vegetable waste and pine cone biochar of agricultural soils. Chemosphere. 174:593-603.

Jeffery S, Bezemer TM, Cornelissen G, Kuyper TW, Lehmann J, Mommer L, Sohi SP, Voorde TF, Wardle DA, Groenigen JW (2015) The way forward in biochar research: targeting trade - offs between the potential wins. Gcb. Bioenergy. 7:1-13.

Kazi TG, Jamali MK, Kazi GH, Arain MB, Afridi HI, Siddiqui A (2005) Evaluating the mobility of toxic metals in untreated industrial wastewater sludge using a BCR sequential extraction procedure and a leaching test. Anal. Bioanal. Chem. 383:297-304.

Keiluweit M, Nico PS, Johnson MG, Kleber M (2010) Dynamic molecular structure of plant biomass-derived black carbon (biochar). Environ. Sci. Technol. 44:1247-1253.

Lin YC, Changchien GP, Chiang PC, Chen WH, Lin YC (2013) Multivariate analysis of heavy metal contaminations in seawater and sediments from a heavily industrialized harbor in Southern Taiwan. Mar. Pollut. Bull. 76:266-275.

Liu P, Ptacek CJ, Blowes DW, Finfrock YZ, Gordon RA (2016) Stabilization of mercury in sediment by using biochars under reducing conditions. J. Hazard. Mater. 325:120-128.

Lu K, Yang X, Gielen G, Bolan N, Ok YS, Niazi NK, Xu S, Yuan G, Chen X, Zhang X (2017) Effect of bamboo and rice straw biochars on the mobility and redistribution of heavy metals (Cd, Cu, Pb and Zn) in contaminated soil. J. Environ. Manage. 186:285-292.

Major J, Rondon M, Molina D, Riha SJ, Lehmann J (2010) Maize yield and nutrition during 4 years after biochar application to a Colombian savanna oxisol. Plant Soil. 333:117-128.

Ojeda G, Patrício J, Mattana S, Sobral AJFN (2016) Effects of biochar addition to estuarine sediments. Journal of Soils & Sediments 16:2482-2491.

Ok YS, Usman AR, Lee SS, Abd El-Azeem SA, Choi B, Hashimoto Y, Yang JE (2011) Effects of rapeseed residue on lead and cadmium availability and uptake by rice plants in heavy metal contaminated paddy soil. Chemosphere 85:677-682.

Peng JF, Song YH, Peng Y, Cui XY, Qiu GL (2009) The remediation of heavy metals contaminated sediment. J. Hazard. Mater. 161:633-640.

Qian G, Chen W, Lim TT, Chui P (2009) In-situ stabilization of Pb, Zn, Cu, Cd and Ni in the multi-contaminated sediments with ferrihydrite and apatite composite additives. J. Hazard. Mater. 170:1093.

Rajapaksha AU, Ahmad M, Vithanage M, Kim KR, Chang JY, Lee SS, Ok YS (2015) The role of biochar, natural iron oxides, and nanomaterials as soil amendments for immobilizing metals in shooting range soil. Environ. Geochem. Health. 37:931-942.

Roulier JL, Belaud S, Coquery M (2010) Comparison of dynamic mobilization of Co, Cd and Pb in sediments using DGT and metal mobility assessed by sequential extraction. Chemosphere. 79:839-843.

Shaheen SM, Rinklebe J (2015) Impact of emerging and low cost alternative amendments on the (im)mobilization and phytoavailability of Cd and Pb in a contaminated floodplain soil. Ecol. Eng. 74:319-326.

Shaheen SM, Tsadilas CD, Rinklebe J (2013) A review of the distribution coefficients of trace elements in soils: Influence of sorption system, element characteristics, and soil colloidal properties. Advances in Colloid & Interface Science s 201-202:43-56.

Shen X, Huang DY, Ren XF, Zhu HH, Wang S, Xu C, He YB, Luo ZC, Zhu QH (2016) Phytoavailability of Cd and Pb in crop straw biochar-amended soil is related to the heavy metal content of both biochar and soil. J. Environ. Manage. 168:245.

Sima J, Cao X, Zhao L, Luo Q (2015) Toxicity characteristic leaching procedure over- or under-estimates leachability of lead in phosphate-amended contaminated soils. Chemosphere. 138:744-750.

Song B, Zeng G, Gong J, Liang J, Xu P, Liu Z, Zhang Y, Zhang C, Cheng M, Liu Y, Ye S, Yi H, Ren X (2017) Evaluation methods for assessing effectiveness of in situ remediation of soil and sediment contaminated with organic pollutants and heavy metals. Environ. Int. 105:43-55.

Srivastava VC, Mall ID, Mishra IM (2008) Adsorption of toxic metal ions onto activated carbon : Study of sorption behaviour through characterization and kinetics. Chemical Engineering & Processing Process Intensification 47:1269-1280.

Tong X, Li J, Yuan J, Xu R (2011) Adsorption of Cu (II) by biochars generated from three crop straws. Chem. Eng. J 172:828-834.

USEPA (1984) Method 1311 Toxicity characteristic leaching procedure (TCLP).: Washington DC.

Wang M, Zhu Y, Cheng L, Andserson B, Zhao X, Wang D, Ding A (2017) Review on utilization of biochar for metal-contaminated soil and sediment remediation. J. Environ. Sci. 63:156-173.

Yin H, Cai Y, Duan H, Gao J, Fan C (2014) Use of DGT and conventional methods to predict sediment metal bioavailability to a field inhabitant freshwater snail (Bellamya aeruginosa) from Chinese eutrophic lakes. J. Hazard. Mater. 264:184.

Yin H, Zhu J (2016) In situ remediation of metal contaminated lake sediment using naturally occurring, calcium-rich clay mineral-based low-cost amendment. Chem. Eng. J. 285:112-120.

Young SD, Zhang H, Tye AM, Maxted A, Thums C, Thornton I (2010) Characterizing the availability of metals in contaminated soils. I. The solid phase: sequential extraction and isotopic dilution. Soil Use & Management 21:450-458.

Yuan JH, Xu RK, Zhang H (2011) The forms of alkalis in the biochar produced from crop residues at different temperatures. Bioresource. Technol. 102:3488-3497.

Zhang C, Ding S, Xu D, Tang Y, Wong MH (2014) Bioavailability assessment of phosphorus and metals in soils and sediments: a review of diffusive gradients in thin films (DGT). Environ. Monit. Assess. 186:7367-7378.

Zhang H, Zhao F, Sun B, Davison W, Mcgrath SP (2001) A new method to measure effective soil solution concentration predicts copper availability to plants. Environ. Sci. Technol. 35:2602-2607.

Zhang RH, Li ZG, Liu XD, Wang BC, Zhou GL, Huang XX, Lin CF, Wang AH, Brooks M (2017) Immobilization and bioavailability of heavy metals in greenhouse soils amended with rice straw-derived biochar. Ecol. Eng. 98:183-188.

Zhang X, Wang H, He L, Lu K, Sarmah A, Li J, Bolan NS, Pei J, Huang H (2013) Using biochar for remediation of soils contaminated with heavy metals and organic pollutants. Environ. Sci. Pollut. R. 20:8472-8483.

Zhu Q, Wang Z (2012) Heavy metals distributing characteristic and source analyzing in Chinese major river sediments. Earth And Environment (Chinese) 40:305-312.

Zhu X, Chen B, Zhu L, Xing B (2017) Effects and mechanisms of biochar-microbe interactions in soil improvement and pollution remediation: A review. Environ. Pollut. 227:98-115.

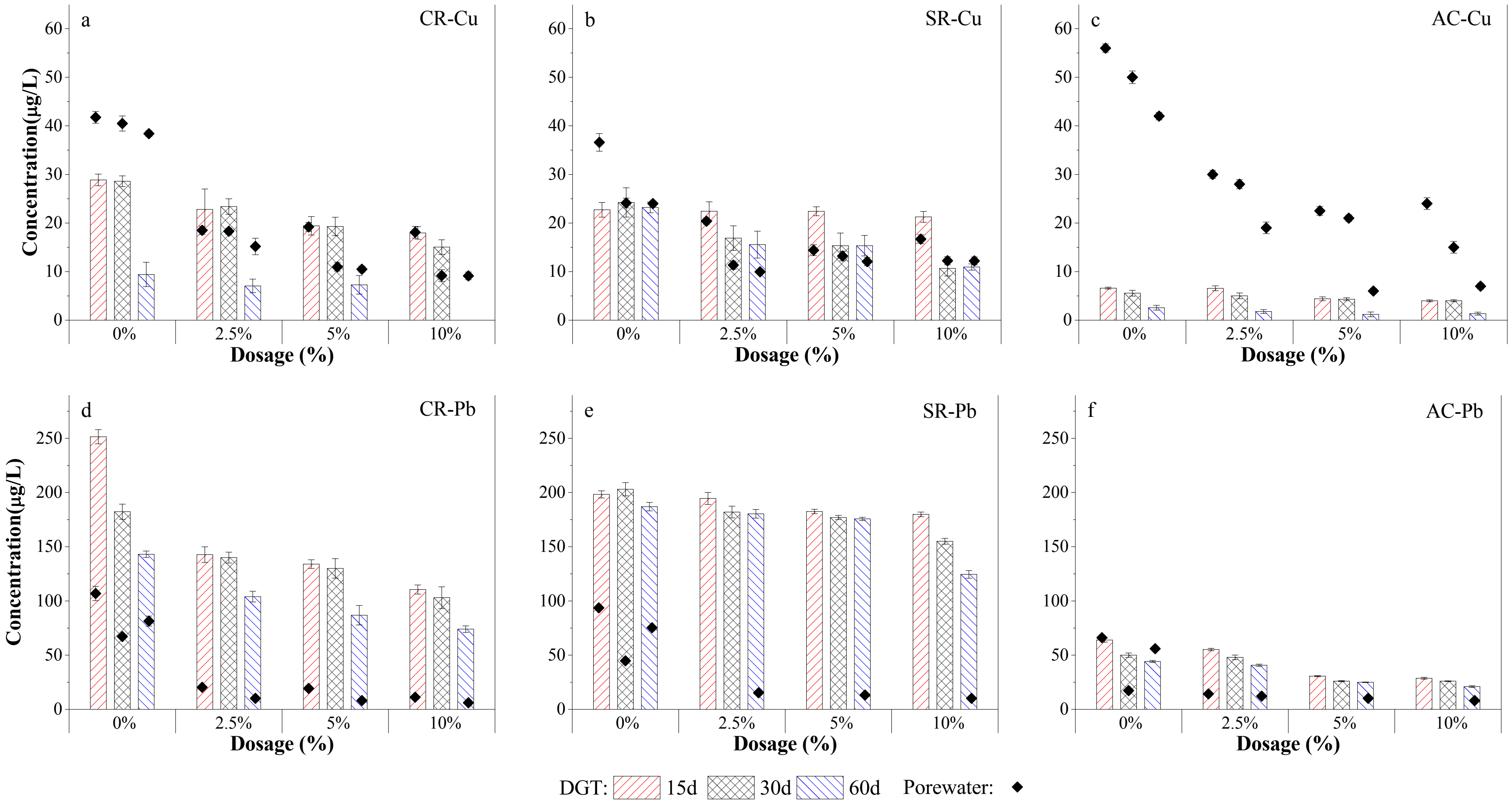


Fig.1 DGT-labile and porewater metal concentration in different treatment sediments. The figure of a, b and c were CR, SR and AC contaminated by Cu, respectively; and d, e and f were CR, SR and AC contaminated by Pb, respectively. No marked porewater sign is indicated below the detection limit of ICP-MC.

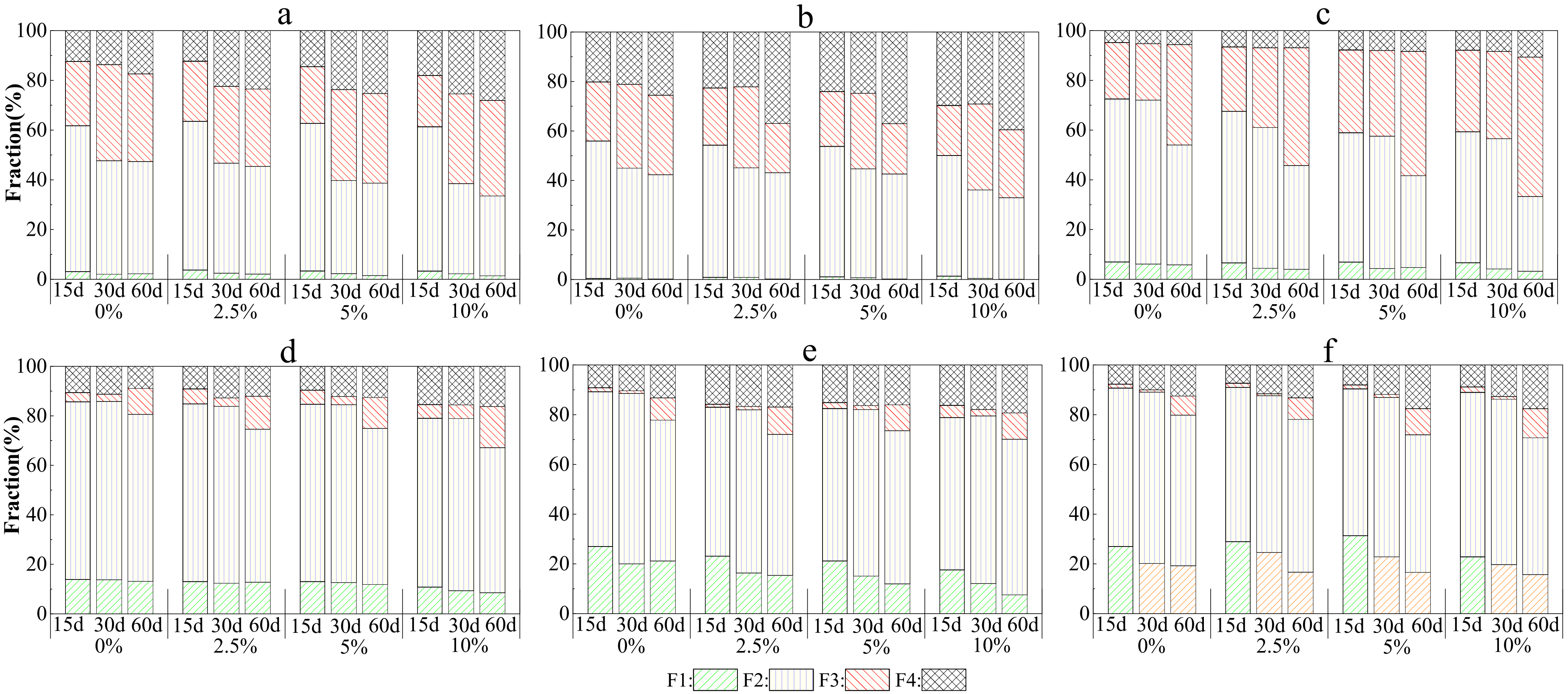


Fig.2 Metal fraction in (un)treated sediment with the addition of various amounts (%) of SBIO and incubation time (day). The figure of a, b and c were CR, SR and AC contaminated by Cu, respectively; and d, e and f were CR, SR and AC contaminated by Pb, respectively.

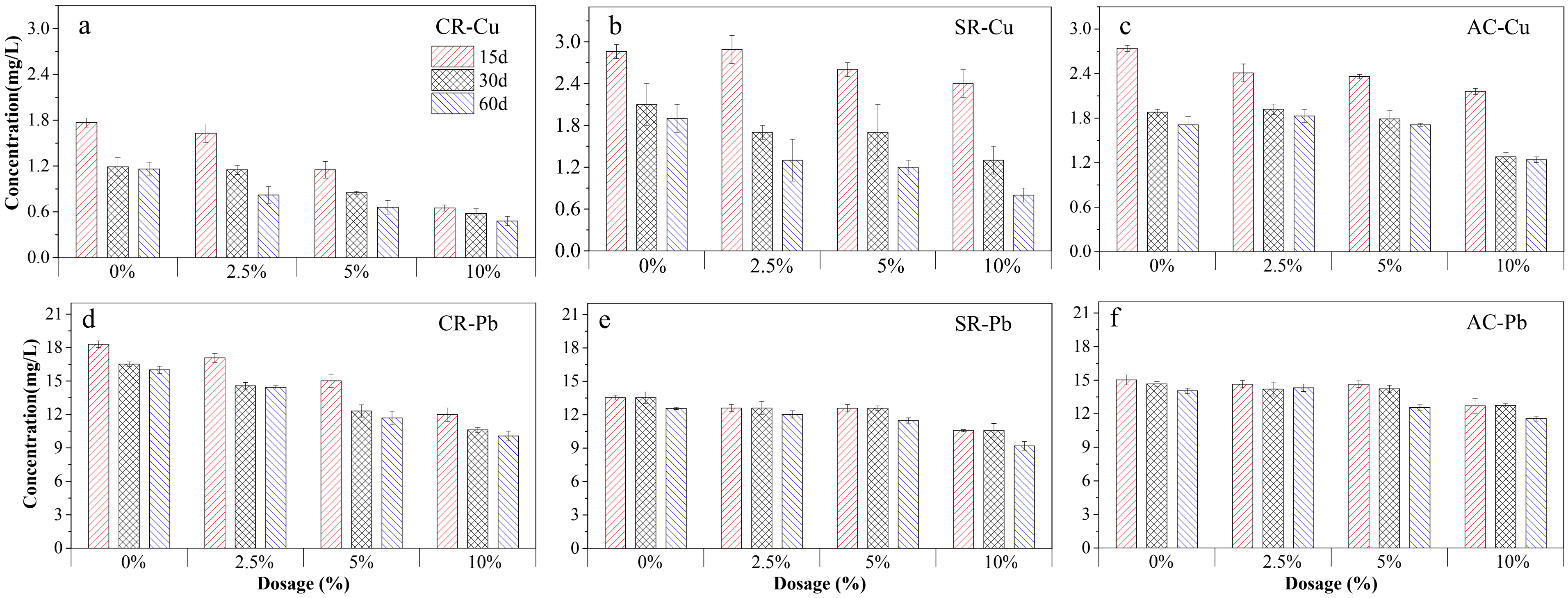


Fig.3 Leaching Cu and Pb from (un)treated sediment by TCLP. The figure of a, b and c were CR, SR and AC contaminated by Cu, respectively; and d, e and f were CR, SR and AC contaminated by Pb, respectively.

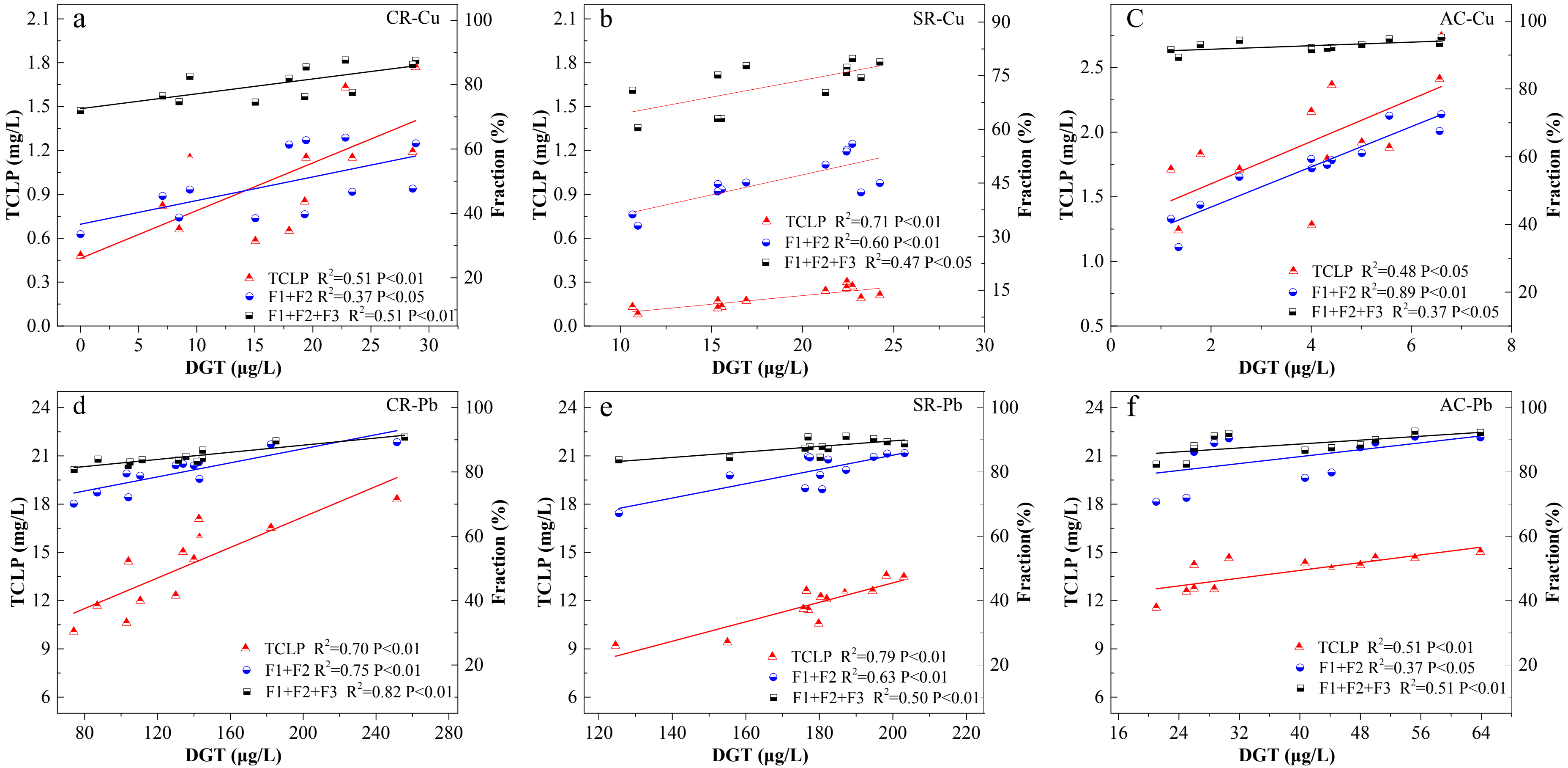


Fig.4 Correlation between DGT concentration and TCLP/ BCR. The figure of a, b and c were CR, SR and AC contaminated by Cu, respectively; and d, e and f were CR, SR and AC contaminated by Pb, respectively.

Table 1. Characterization of sediments and SBIO samples

Materials	SR	CR	AC	SBIO
pH	7.2	7.28	7.14	11.7
TOC (g/kg)	39.1	43.08	18.34	275.75
Water content (%)	52.2	42.5	45.1	-
BET (m^2/g)	-	-	-	90.4
[1]K (mg/kg)	20445	19943	21134	41700
[1]Ca (mg/kg)	58279	104274	22974	132576
[1]Mg (mg/kg)	13793	19322	11684	11906
[1]Na (mg/kg)	13175	6650	17772	3563
*Cu (mg/kg)	35.3	43.9	30.6	55.3
*Pb (mg/kg)	30.8	40.9	25.3	40.2
Zn (mg/kg)	77.5	105.3	56.2	170.3
Cu spiked (mg/kg)	635.3	643.9	630.6	-
Pb spiked (mg/kg)	730.8	740.9	725.3	-
[2]SiO_2 (%)	51.22	54.85	63.27	53.35
[2]CaO (%)	12.69	14.05	5.01	21.48
[2]Al_2O_3 (%)	18.194	15.16	16.06	4.12
[2]K_2O (%)	2.63	2.35	2.68	6.19
[2]Fe_2O_3 (%)	7.89	5.31	5.07	2.34
[2]MgO (%)	4.11	4.92	3.28	2.64
[2]MnO (%)	0.1	0.1	0.1	0.93

[1]: the result from ICP-MS

[2]: the result from XRF

*: the original concentration without Cu(II) or Pb(II) spiking

Table 2. Extraction conditions used for the fractionation process of BCR

Step	Fraction	Reagents/conditions
1	F1, acid-soluble fractions	20 mL of 0.11M HAc, shaken for 16 h
2	F2, reducible fractions	20 mL of 0.5M (pH 2) NH_2OH•HCl, shaken for 16 h
3	F3,oxidizable fractions	5 mL of 8.8M H_2O_2, placed in a water bath at 85℃ for 1 h; an additional 5 mL of 8.8M H_2O_2, placed in a water bath at 85℃ until the solution was evaporated to a few millilitres; 25 mL of 1M (pH 2) NH_4Ac, shaken for 16 h
4	F4, reducible fractions	And dry residuals were digested as solid sample for metal content analysis

*all shaking was conducted at a temperature of 25℃ and centrifuged at 160 rpm.

JOURNAL OF ENVIRONMENTAL SCIENCES

Editorial Department
P. O. Box 2871
Beijing 100085
China
Tel: 86-10-62920553
E-mail: jesc@rcees.ac.cn

Journal Publishing Agreement

Author(s): Mingming Wang, Liangsuo Ren, Dayang Wang
Cai Zuansi, Xuefeng Xia. Qizhong Ding

Title: Assessing biochar stabilization trace metal in contaminated sediment using chemical and extraction methods

The undersigned authors, with the consent of all authors, hereby assign to *Journal of Environmental Sciences*, the copyright in the above identified article to be transferred, including supplemental tables, illustrations or other information submitted in all forms and media throughout the world, in all languages and format, effective when and if the article is accepted for publication.

Authors also agree to the following terms:

A. The article submitted is not subject to any prior claim or agreement and is not under consideration for publication elsewhere.

B. The article contains no libelous or other unlawful statements and does not contain any materials that violate proprietary right of any other person, company, organization, and nation.

C. If the article was prepared jointly with other authors, the author(s) agree with the authorship sequence.

Please sign and date the document.

First Author: Qizhong Ding
Corresponding author: Mingming Wang

Date: 2018.6.7
Date: 2018. 6. 7

Supplementary materials

1. Metal adsorption kinetics and isotherm by biochar

1.1 Adsorption and fitting method

Adsorption kinetics and isotherm characteristics of Cu and Pb by SBIO were studied through a batch of experiments. In the study of adsorption kinetics, SBIO passed through a 100 mesh sieve was mixed with a 1000-mg/L stock solution in 50-mL polyethylene centrifuge tubes. The tubes were placed on a reciprocating shaker and the sorption results were analyzed at time intervals ranging from 0.5 to 60 hours. In the study of adsorption isotherm, powdered SBIO (100 mesh) was added to metal solutions of various concentrations (100~1000 mg/L) with shaking at 15, 25, and 35℃. At the end of each sorption, the solution was centrifuged at 5,000 rpm for 15 min and the supernatant was filtered through a 0.45-μm membrane, 2mol/L nitric acid, and stored at 4℃ until analysis. All sorption experiments were conducted at a solid/liquid ratio of 4:1 for Cu and 1:2 for Pb under free pH conditions, with shaking at 160 rpm and were performed in triplicate.

In this study, the adsorption kinetics data at were fit using the Pseudo-first-order (Eq. 1) and the Pseudo-second-order (Eq. 2) models, and the adsorption isotherm date were analyzed using the Langmuir (Eq. 3) and Freundlich (E. 4) models.

$$\log\left(q_e - q_t\right) = \log q_e - \frac{k_1}{2.303} \cdot t \qquad \text{Eq. 1}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad \text{Eq. 2}$$

$$Q_e = \frac{K_L Q_{max} C_e}{1 + K_L C_e} \qquad \text{Eq. 3}$$

$$Q_e = K_f C_e^m \qquad \text{Eq. 4}$$

where q_t and q_e (mg/g) are sorbate removed at time t and at equilibrium, respectively, k_1 and k_2 (h^{-1}) are the sorption rate constants of the first-order and second-order, respectively, K_L (L/mg) and K_F ($mg^{(1-n)}L^n g^{-1}$) are the Langmuir equilibrium adsorption constant related to the affinity of binding sites and the roughly Freundich affinity coefficient, respectively, Q_{max} (mg/g) is the maximum capacity of sorbent, C_e (mg/L) is the equilibrium concentration of the sorbate, m is the Freundlich linearity constant, and Q_e is the adsorbed capacity (mg/g).

Moreover, the shifted Langmuir (Eq.5) and Freundlich (Eq.6) mode were employed to describe multi-layer adsorption:

$$Q_e^n = Q_{max}^{n-1} + \frac{K_L^n Q_{max}^n (C_e - C_s)}{1 + K_L^n (C_e - C_s)} \qquad \text{Eq.5}$$

$$Q_e^n = Q_{max}^{n-1} + K_f^n C_e^m \qquad \text{Eq.6}$$

where n is the layer of sorbate, and the other parameters are defined as previously described. So the maximum capacity in multi-layer adsorption is the sum of Q_{max} from layer 1 to layer n.

1.1 Adsorption kinetic analysis

The adsorption behaviour of Cu(II) and Pb(II) onto SBIO were examined at 1000 mg/L of Pb and Cu solution to investigate the equilibrium process, respectively. As presented in Fig.1S, the sorption process of Pb and Cu were similar, most Cu or Pb sorption by SBIO taking place at the initial process (<12h) and then slowly reached equilibrium within 20 h. The maximum sorption capacity of Pb and Cu were approximately 665 and 55 mg/g, and the sorption ability for Pb was greatly higher than Cu by over 10 times.

Table S1 Best-fit model parameters of lead adsorption on SBIO

	Model	First-order	Second-order	Langmuir	Freundlich
Pb	Parameter 1	k_1=1.23	k_2=0.0032	$K_L = 273.4$	$K_f = 421.1$
	Parameter 2	q_e=663.8	q_e=683.7	$Q_{max} = 635.7$	m=0.07
	R^2	0.88	0.94	0.94	0.91
Cu	Parameter 1	k_1=0.14	k_2=0.0024	$K_L^1 = 1.94$ $K_L^2 = 0.011$	$K_f^1 = 10.59$ $K_f^2 = 1.29$
	Parameter 2	q_e=57.57	q_e=67.61	$Q_{max}^1 = 19.1$ $Q_{max}^2 = 33.7$	m^1=0.504 m^2=0.104
	R^2	0.98	0.97	0.99^*/0.98**	0.92^*/0.92**

*: first layer, **: second layer

Through fitting with the *Pseudo-first-order* and *Pseudo-second-order* model, the effect of reaction time on adsorption metals onto SBIO and related parameters were analyzed and are presented in Fig.1S and Table S1. These sorption results demonstrated that SBIO provides adsorption sites with both Pb and Cu. Surface complexation with active functional groups of the biochar contributed more to metal bonding, as shown in Fig.S4-S8. Due to increasing pH introduced by SBIO, the biochar surface potentials could become more negative and the surface functional groups (e.g. –COOH ,-OH and phenolic hydroxyl) further dissociated which promoted the metal sorption process as well as adsorption capability (Tong et al., 2011a; Uchimiya et al., 2011). Besides, co-precipitation, surface/innersphere complexation and physical adsorption also play a critical role in the metal sorption process (Zhang et al., 2013). Otherwise, the model fitting result indicates that the correlation coefficient (R^2) between Pseudo-first-order and Pseudo-second-order were hardly different, but the calculated value of q_e by the Pseudo-first-order was closer to the real value, which indicated that diffusion/ion exchange was the limiting step to adsorption rather than chemisorption (Yin and Zhu, 2016).

1.2 Adsorption isotherm analysis

The maximum adsorption capacity of Cu and Pb onto SBIO was estimated using *Langmuir* and *Freundlich* isotherm models, which present the surface properties and affinity of SBIO and describe the relationship between adsorption capacity and equilibrium concentration at given temperatures as shown in Fig.1S. According to the shape of the adsorption isotherms within given concentrations, the adsorption can be classified as single-layer adsorption for Pb and multi-layer adsorption for Cu, respectively. The multi-layer adsorption seemed to be caused by adsorption hysteresis at larger pores and disappearance of this phenomenon was attributed to an increased chemical potential of the pore walls (Wang and Hwang, 2000). Besides, cooperative adsorption also contributed to this process, for which it was assumed that a shift in concentration was necessary for special adsorption to readily occur (Grant et al., 1998). So both the *shifted Langmuir* and *shifted Freundlich* isotherm were employed to characterize the adsorption process of Cu onto SBIO at both the first and second layers. Table S1 lists the parameters of the *Langmuir* and *Freundlich* model and their correlation coefficients. The results demonstrate that the *Langmuir* model is suitable to explain the sorption behaviour of Cu and Pb onto SBIO, and the adsorption capacity (Q_{max}, Langmuir model) for Pb (635.7 mg/g) is much higher than for Cu (52.8 mg/g) at a given temperature.

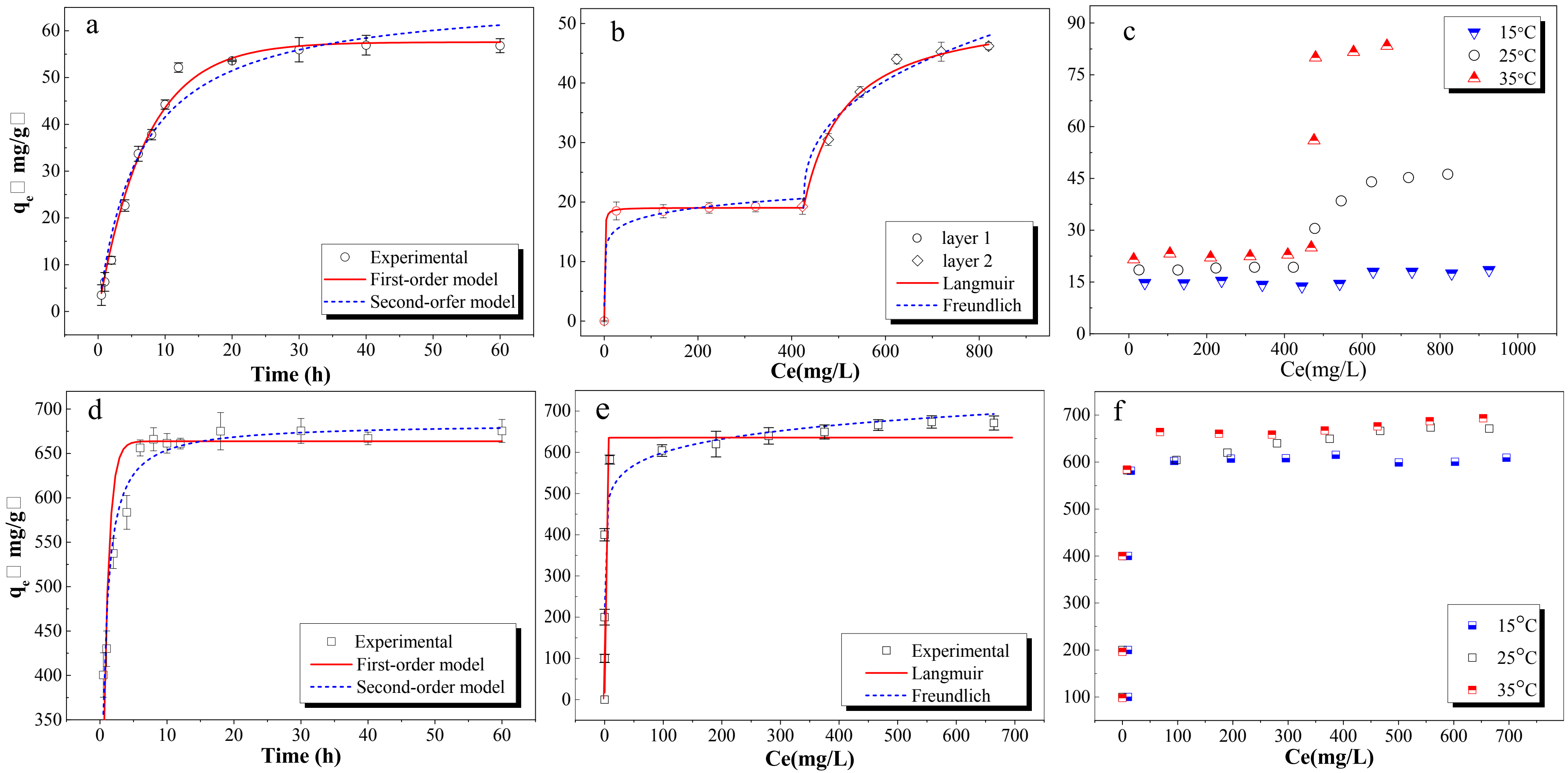


Fig.S1 Kinetic model for Cu (a) and Pb (d) adsorption; adsorption isotherms at room temperature for Cu (b) and Pb (e); adsorption isotherms at different temperatures for Cu (c) and Pb (f)

Table S2 Summary of the literature data on sorption of Pb^{2+} and Cu^{2+} to different biochar

Biochar	Pb^{2+} Qmax (mg/g)	Cu^{2+} Qmax (mg/g)	Ref.
Sludge	31		(Zhang et al., 2013)
Shell	45		(Elaigwu et al., 2014)
Cow manure	230		(Kołodyńska et al., 2012)
Dairy manure	140		(Cao et al., 2009)
Sugar cane	87		(Abdelhafez and Li, 2016)
Orange peel	28		(Abdelhafez and Li, 2016)
Pinewood	4		(Liu and Zhang, 2009)
Begass	135		(Inyang et al., 2011)
Peanut shells	350		(Guocheng, 2014)
Rraditional Chinese medicine waste	400		(Guocheng, 2014)
Peanut straw		50	(Tong et al., 2011b)
Soybean straw		33	(Tong et al., 2011b)
Seed		27	(Mahdi et al., 2018)
Spartina alterniflora		48	(Li et al., 2013)
Cow manure		54	(Xu et al., 2013)
Pinewood		4	(Liu et al., 2010)
Pinewood		3	(Liu et al., 2010)
Raw farmyard manure		39	(Batool et al., 2017)
poultry manure		43	(Batool et al., 2017)
Sawdust	655	55	In this study

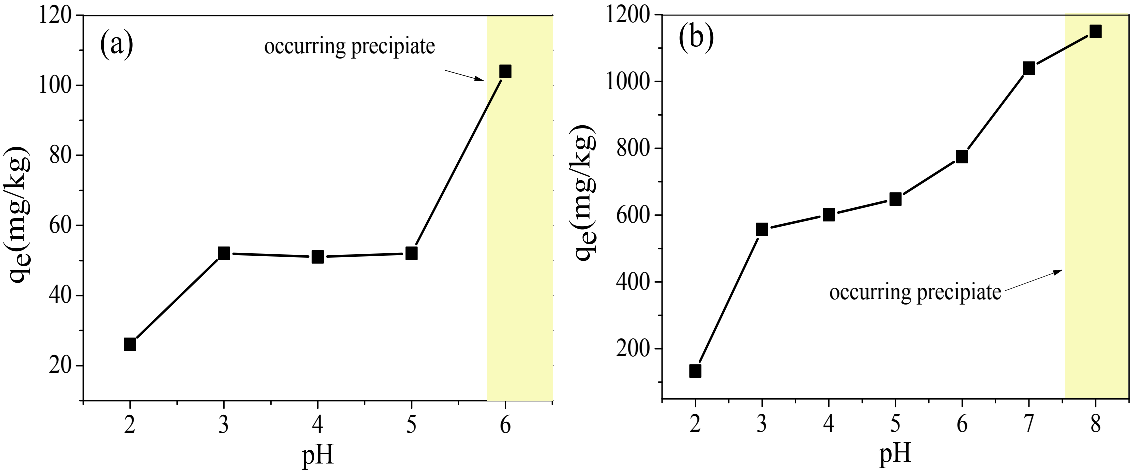


Fig.S2 The effect of pH on SBIO adsorption capability for Cu (a) and Pb (b)

2 The DGT device

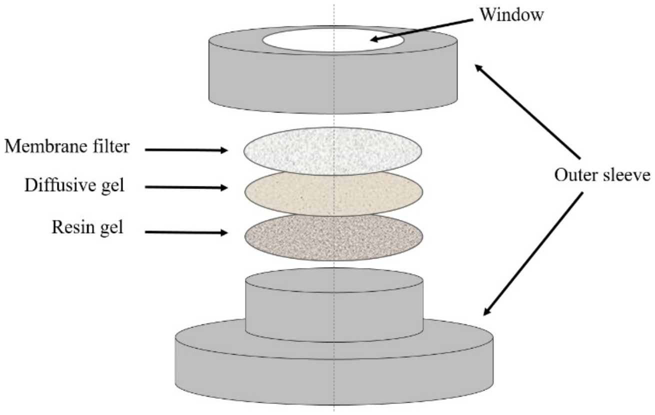


Fig.S3 The structure of the DGT device

The C_{DGT} can be measured from the following equation:

$M=C_e*(V_{acid}+V_{gel})/f_e$ Eq. 7

where M is the mass of metal adsorbed by resin gel, C_e is metal concentration in 1M HNO_3, V_{acid} is the HNO_3 volume used to elute metals bound by resin gel, V_{gel} is the resin gel volume, and f_e is the elute efficiency.

$C_{DGT}=M\Delta g/(DtA)$ Eq. 8

where Δg is the thickness of diffusive gel (cm), D the diffusion coefficient of the metal ion in the diffusive gel (cm^2/s), t is the contact time between the DGT device and sediment (s), and A is the area of window (cm^2).

3 The figure of supporting information

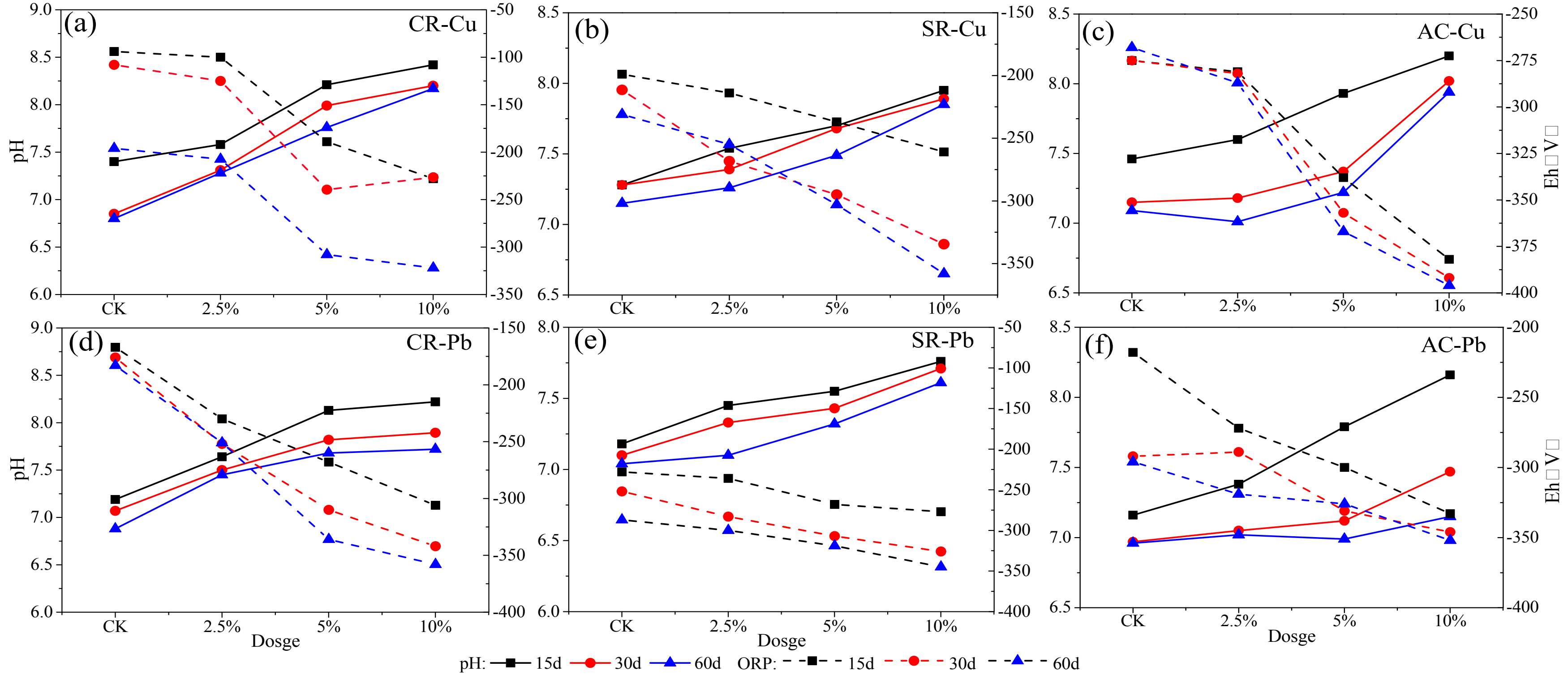


Fig.S4 The change trend of sediment pH and ORP during 60 days of incubation. The figure of a, b and c were SR, CR and AC contaminated by Cu, respectively; and d, e and f were SR, CR and AC contaminated by Pb, respectively.

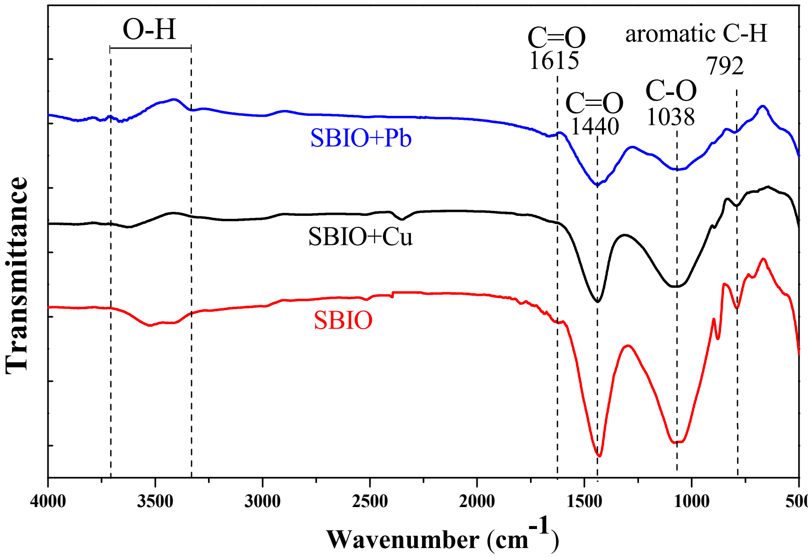


Fig.S5 FTIR spectra of SBIO after adsorption of Cu and Pb

As shown in Fig.S5, obvious signals of –OH, ester C=O, carboxyl C, C-O and aromatic C-H were obtained, and these groups were the major functional groups of SBIO. After reaction with Cu and Pb respectively, the peak for all of these functional groups were obviously either weakened or deviated, especially for C=O, C-O and C-H.

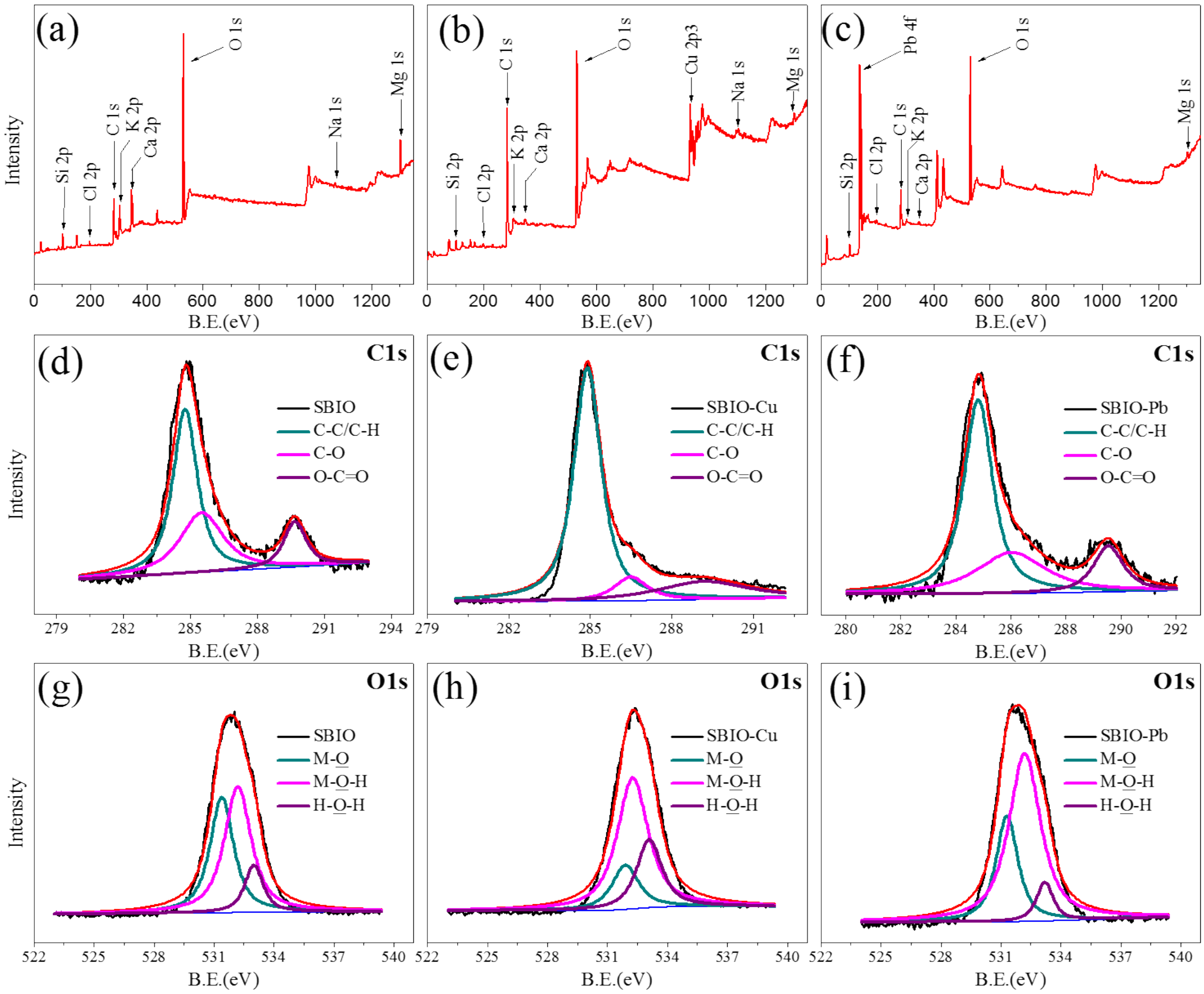


Fig.S6 XPS spectra of wide scan for SBIO (a), SBIO loaded Cu (b) and Pb (c), C 1S and O 1 s before adsorption (d and g) and after adsorption Cu (e and h) and Pb (f and i) onto SBIO

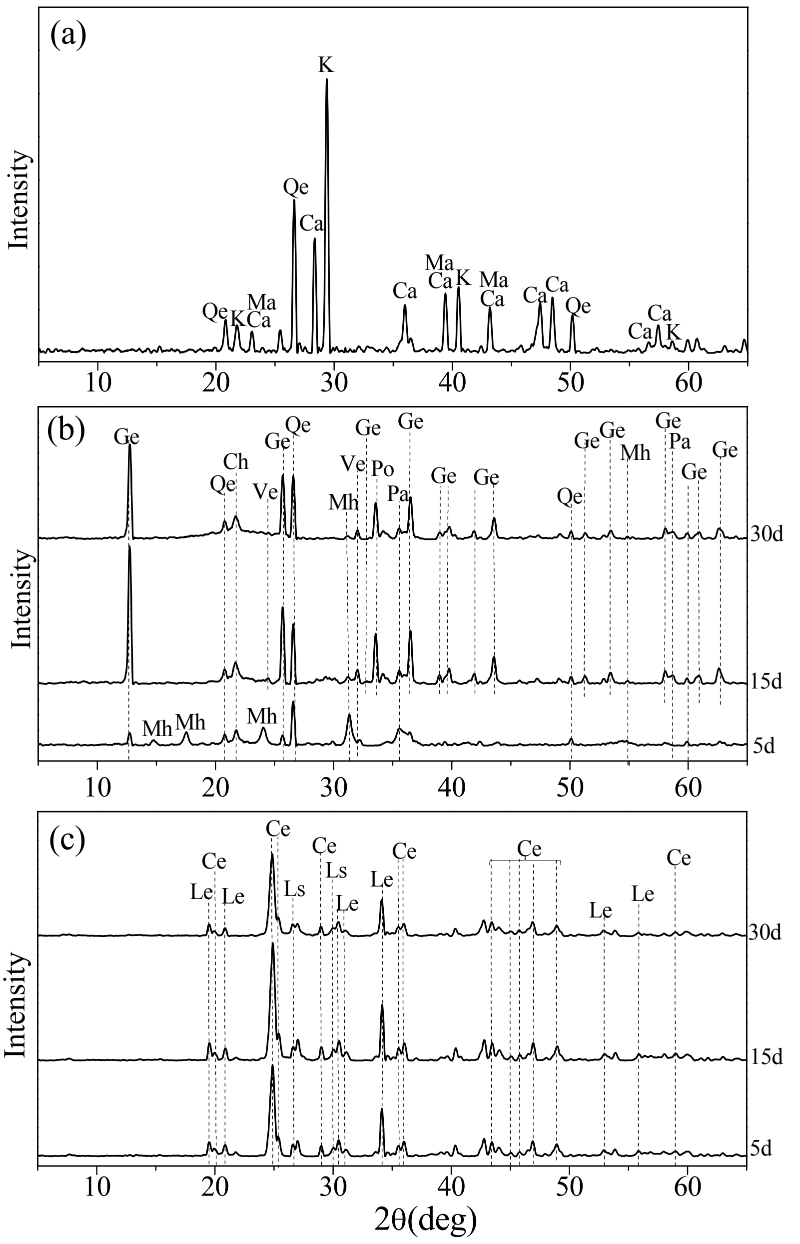


Fig.S7 X-ray diffraction spectrum of SBIO before (a) and after adsorption Cu (b) and Pb (C) during different react times

Ca: $CaCO_3$; Qe: SiO_2; Ma: $MgCa(CO_3)_2$; K: KCl; Fc: $CuFeO_2$, Pc: $Cu_5O_2(PO_4)_2$, Mh: Malachite, Ge: *Gerhardtite*, Pa: *Paramelaconite*, Po: *Posnjakite,* Ve: *Veszelyite*, Ch: *Chalcophanite*, Ce: *Cerussite*, Le: *Leadhillite*, Ls:Pb_2SO_5

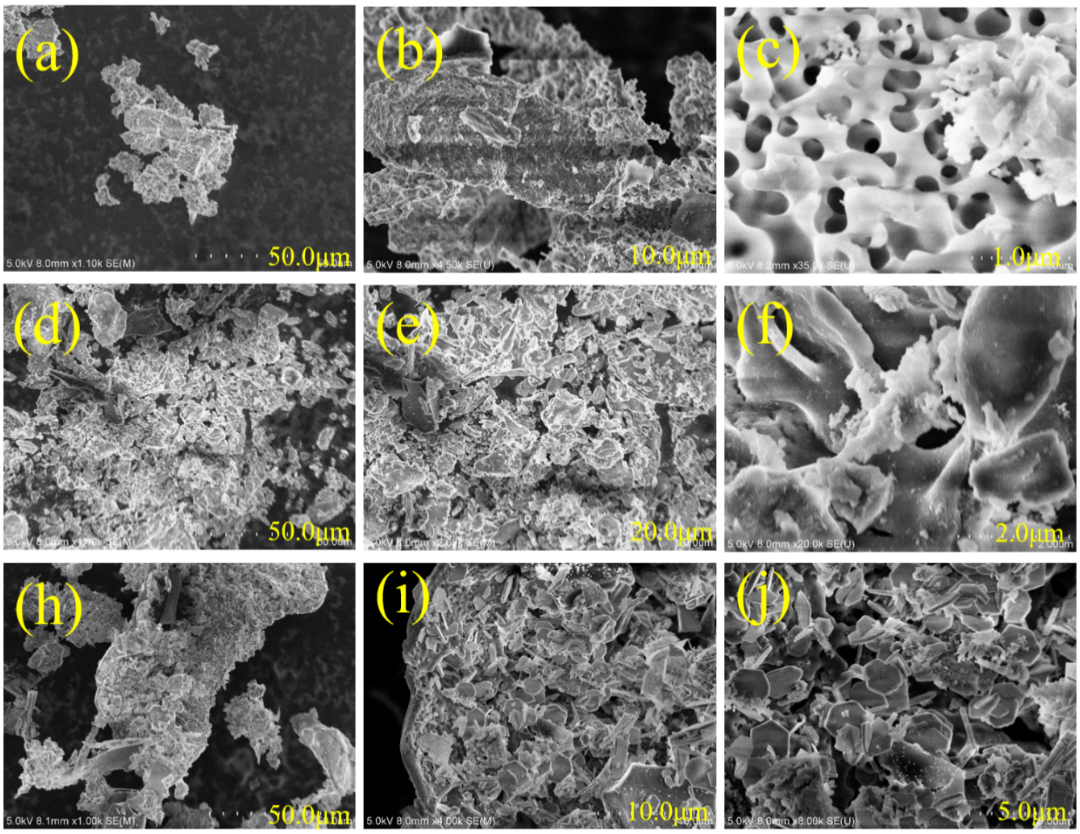


Fig.S8 SEM image of surface SBIO (a-c), SBIO loaded Cu (d-f) and SBIO loaded Pb at different resolutions, respectively

4. The relevance and variability between evaluation methods

Table S3 Correlation coefficient (R^2) between DGT and other extraction methods for Cu at CR

	C_{DGT}	C_P	TCLP	F1	F2	F3	F1+F2	F2+F3	F1+F2+F3
C_{DGT}	1.000								
C_P	0.29	1.000							
TCLP	0.51**	0.48*	1.000						
F1	0.37*	0.05	0.387*	1.000					
F2	0.37*	0.21	0.491*	0.86**	1.000**				
F3	0.14	0.08	0.182	0.82**	0.81**	1.000			
F1+F2	0.37*	0.19	0.488*	0.88**	0.99**	0.82**	1.000		
F2+F3	0.52**	0.62**	0.71**	0.47**	0.69**	0.26	0.69**	1.000	
F1+F2+F3	0.54**	0.55**	0.72**	0.56**	0.77**	0.34*	0.76**	0.99**	1.000

*: P<0.05; **: P<0.01

Table S4 Correlation coefficient (R2) between DGT and other extraction methods for Cu at SR

	CDGT	CP	TCLP	F1	F2	F3	F1+F2	F2+F3	F1+F2+F3
CDGT	1.00								
CP	0.48*	1.00							
TCLP	0.71**	0.38*	1.00						
F1	0.16	0.02	0.41*	1.00					
F2	0.61**	0.31	0.85**	0.32	1.00				
F3	0.02	0.002	0.06	0.03	0.22	1.00			
F1+F2	0.60**	0.29	0.86**	0.36*	1.00**	0.21	1.00		
F2+F3	0.46*	0.38*	0.56**	0.18	0.39*	0.16	0.40*	1.00	
F1+F2+F3	0.47*	0.36*	0.58**	0.23	0.41*	0.14	0.42*	0.99**	1.00

*: P<0.05; **: P<0.01

Table S5 Correlation coefficient (R2) between DGT and other extraction methods for Cu at AC

	C_{DGT}	C_P	TCLP	F1	F2	F3	F1+F2	F2+F3	F1+F2+F3
C_{DGT}	1.00								
C_P	0.47*	1.00							
TCLP	0.48*	0.35*	1.00						
F1	0.42*	0.42*	0.71**	1.00					
F2	0.90**	0.64**	0.42*	0.46*	1.00				
F3	0.92**	0.58**	0.46*	0.52**	0.99**	1.00			
F1+F2	0.89**	0.66**	0.48*	0.54**	0.99**	0.99**	1.00		
F2+F3	0.01	0.22	0.01	0.05	0.08	0.03	0.05	1.00	
F1+F2+F3	0.37*	0.83**	0.39*	0.40*	0.60**	0.52**	0.61**	0.37*	1.00

*: P<0.05; **: P<0.01

Table S6 Correlation coefficient (R2) between DGT and other extraction methods for Pb at CR

	C_{DGT}	C_P	TCLP	F1	F2	F3	F1+F2	F2+F3	F1+F2+F3
C_{DGT}	1.00								
C_P	0.58**	1.00							
TCLP	0.70**	0.45*	1.00						
F1	0.73**	0.38*	0.85**	1.00					
F2	0.02	0.042	0.06	0.05	1.00				
F3	0.36*	0.00	0.17	0.28	0.38*	1.00			
F1+F2	0.75**	0.18	0.47*	0.59**	0.21	0.79**	1.00		
F2+F3	0.30	0.05	0.56**	0.75**	0.14	0.25	0.29	1.00	
F1+F2+F3	0.82**	0.77**	0.64**	0.64**	0.01	0.14	0.58**	0.15	1.00

*: P<0.05; **: P<0.01

Table S7 Correlation coefficient (R2) between DGT and other extraction methods for Pb at SR

	C_{DGT}	C_P	TCLP	F1	F2	F3	F1+F2	F1+F2+F3	F1+F2+F3
C_{DGT}	1.00								
C_P	0.04	1.00							
TCLP	0.79**	0.11	1.00						
F1	0.83**	0.09	0.95**	1.00					
F2	0.43*	0.05	0.27*	0.32	1.00				
F3	0.38*	0.12	0.17	0.21	0.92**	1.00			
F1+F2	0.63**	0.01	0.50*	0.56**	0.94**	0.82**	1.00		
F2+F3	0.03	0.17	0.15	0.14	0.03	0.01	0.07	1.00	
F1+F2+F3	0.50**	0.17	0.75**	0.76**	0.23	0.07	0.41*	0.61**	1.00

*: P<0.05; **: P<0.01

Table S8 Correlation coefficient (R2) between DGT and other extraction methods for Pb at AC

	C_{DGT}	C_P	TCLP	F1	F2	F3	F1+F2	F2+F3	F1+F2+F3
C_{DGT}	1.00								
C_P	0.16	1.00							
TCLP	0.59**	0.03	1.00						
F1	0.19	0.03	0.40*	1.00					
F2	0.13	0.03	0.17	0.05	1.00				
F3	0.15	0.13	0.33	0.53**	0.62**	1.00			
F1+F2	0.26	0.05	0.46*	0.68**	0.54**	0.92**	1.00		
F2+F3	0.00	0.07	0.06	0.58**	0.12	0.10	0.11	1.00	
F1+F2+F3	0.37*	0.01	0.53**	0.73**	0.36*	0.66**	0.89**	0.10	1.00

*: P<0.05; **: P<0.01

References:

Abdelhafez AA, Li J (2016) Removal of Pb(II) from aqueous solution by using biochars derived from sugar cane bagasse and orange peel. J. Taiwan. Inst. Chem. E. 61:367-375.

Batool S, Idrees M, Hussain Q, Kong J (2017) Adsorption of copper (II) by using derived-farmyard and poultry manure biochars: Efficiency and mechanism. CHEM PHYS LETT 689:190-198.

Cao X, Ma L, Gao B, Harris W (2009) Dairy-Manure Derived Biochar Effectively Sorbs Lead and Atrazine. Environ. Sci. Technol. 43:3285-3291.

Elaigwu SE, Rocher V, Kyriakou G, Greenway GM (2014) Removal of Pb and Cd from aqueous solution using chars from pyrolysis and microwave-assisted hydrothermal carbonization of Prosopis africana shell. Journal of Industrial & Engineering Chemistry.20:3467-3473.

Grant PG, Lemke SL, Dwyer MR, Phillips TD (1998) Modified Langmuir equation for S-shaped and multisite isotherm plots. Langmuir. 14:4292-4299.

Guocheng L (2014) Immobilization of Pb(II) in contaminated waters and soils by biochar. Ocean University of China.

Inyang M, Gao B, Ding W, Pullammanappallil P, Zimmerman AR, Cao X (2011) Enhanced Lead Sorption by Biochar Derived from Anaerobically Digested Sugarcane Bagasse. Separation Science & Technology. 46:1950-1956.

Kołodyńska D, Wnętrzak R, Leahy JJ, Hayes MHB, Kwapiński W, Hubicki Z (2012) Kinetic and adsorptive characterization of biochar in metal ions removal. Chem. Eng. J. 197:295-305.

Li M, Liu Q, Guo L, Zhang Y, Lou Z, Wang Y, Qian G (2013) Cu(II) removal from aqueous solution by Spartina alterniflora derived biochar. Bioresource. Technol. 141:83.

Liu Z, Zhang F (2009) Removal of lead from water using biochars prepared from hydrothermal liquefaction of biomass. J. Hazard. Mater. 167:933-939.

Liu Z, Zhang FS, Wu J (2010) Characterization and application of chars produced from pinewood pyrolysis and hydrothermal treatment. Fuel. 89:510-514.

Mahdi Z, Yu QJ, El Hanandeh A (2018) Investigation of the kinetics and mechanisms of nickel and copper ions adsorption from aqueous solutions by date seed derived biochar. J. of Envir. Chem. Eng. 6:1171-1181.

Tong X, Li J, Yuan J, Xu R (2011a) Adsorption of Cu (II) by biochars generated from three crop straws. Chem. Eng. J. 172:828-834.

Tong X, Li J, Yuan J, Xu R (2011b) Adsorption of Cu(II) by biochars generated from three crop straws. Chem. Eng. J. 172:828-834.

Uchimiya M, Chang S, Klasson KT (2011) Screening biochars for heavy metal retention in soil: role of oxygen functional groups. J. Hazard. Mater. 190:432-441.

Wang C, Hwang BJ (2000) A general adsorption isotherm considering multi-layer adsorption and heterogeneity of adsorbent. Chem. Eng. Sci. 55:4311-4321.

Xu X, Cao X, Zhao L, Wang H, Yu H, Gao B (2013) Removal of Cu, Zn, and Cd from aqueous solutions by the dairy manure-derived biochar. Environmental Science & Pollution Research. 20:358-368.

Yin H, Zhu J (2016) In situ remediation of metal contaminated lake sediment using naturally occurring, calcium-rich clay mineral-based low-cost amendment. Chem. Eng. J. 285:112-120.

Zhang W, Mao S, Chen H, Huang L, Qiu R (2013) Pb(II) and Cr(VI) sorption by biochars pyrolyzed from the municipal wastewater sludge under different heating conditions. Bioresource Technol. 147:545-552.

Zhang X, Wang H, He L, Lu K, Sarmah A, Li J, Bolan NS, Pei J, Huang H (2013) Using biochar for remediation of soils contaminated with heavy metals and organic pollutants. Environmental Science & Pollution Research 20:8472-8483.