Passivation and Remediation of Pb and Cr in Contaminated Soil by Sewage Sludge Biochar Tubule

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Abstract

Currently, numerous studies have carried out to research the effect of biochars remediation soil heavy metals (HMs) contaminated, but there have been fewer explorations of the effect of biochars tubule on soil HMs remediation. This work aimed was to study the effect of passivation and remediation of lead (Pb) and chromium (Cr) contaminated soil after insert sewage sludge biochar (SSB) tubule. The results showed that the high risky fractions of Pb and Cr could be transformed into more stable fractions, also, Pb and Cr total contents are significantly decreased by SSB tubule. The mechanisms including adsorption, ion exchange, complexation and precipitation which are concluded from the characteristic analysis. Detailly, the passivation of Pb and Cr are better when the moisture at 25% and 35%, respectively, [Pb: exchangeable (F1), carbonate bound (F2) decreased by 25.1%, 16.8%, Fe-Mn oxides bound (F3) increased by 18.5%; Cr: F1 decreased by 73.0%, F2, F3, Organic matter bound (F4) increased by 13.2%, 23.9%, 30.8%), respectively]. The remediation of Pb and Cr is better when the moisture at 25% and 35%, respectively, (Pb: decreased by 23.3%; Cr: decreased by 38.4%, respectively). The findings showed that the SSB tubule is effective when used for soil HMs contaminated.

Introduction

The soil environment has been a global concern due to its complexity and significance. However, with the rapid urbanization and industrialization various contaminants [such as HMs, radioactive elements and organics, etc.] are being introduced into the soil system through directly discharged to contain more than the allowable standard contaminant concentrations (Wang et al. 2020; Rybak et al. 2018; Feng et al. 2018). HMs have ranked the first among all soil contaminant types due to their high toxicity, bioaccumulation, persistence and mobility in soils (He et al. 2020; Yang et al. 2020). These HMs (Pb, Cr, Cd, Hg, As, etc.) can lead to potential health risks to predators and humans through the accumulation of food chains. For instance, Pb is a commonly recognized carcinogen and led to neurotoxicity, stomach and lung lesions; Cr(VI) is a strong oxidant and also act as carcinogenic and teratogenic characteristics, and both of them have been listed as priority monitoring and control pollutants (Hu et al. 2020). Excess of Pb and Cr in soil is mainly derived from intensifying anthropogenic activities including mining, sewage irrigation, and pesticide abuse (He et al. 2020), which could lead to a deterioration in various functions and stability of soil systems (Duan et al. 2018).

In the last several decades, various remediation technologies, including phytoremediation, excavation, landfilling, electrokinetic remediation, soil washing and their blending, have been used to Pb and Cr contaminated soils for removing or reducing high toxic element amounts (Liu et al. 2018; Sarwar et al. 2017; Trellu et al. 2016). However, most of these technologies due to their long remediation cycle, high energy consumption, low efficiency and generating significant secondary environmental impacts (Gerhardt et al. 2009), which are unsuitable for the most area to decelerate their development. Accordingly, there is an urgent need for inexpensive, efficient and stable amendment materials.

To date, various materials [resin (Chen et al. 2020); activated carbon (Dong et al. 2016); peat (Lee et al. 2015)] are used to adsorb HMs. Unfortunately, the resin has a potential risk with secondary pollution, activated carbon is expensive and peat has a characteristically low surface. Biochar is a material with carbon-rich, porous and high aromaticity which is obtained from the pyrolysis of biomass at relatively low temperature ($< 700^{\circ}\text{C}$) under the presence of limited oxygen (Yu et al. 2020; Chen et al. 2020). Biochar as an environmental sorbent has become one of the most attractive research hotspots due to having abundant raw materials, easy preparation and stable performance, etc. (Hung et al. 2020; Zhang et al. 2020; Xiao et al. 2019). In addition, biochar can increase crop yield through improve soil fertility and remediate soil by immobilizing HMs (Azeem et al. 2020; Xi et al. 2020). Numerous researches have showed that biochar plays important role in decreasing the HMs (such as Cr, Cd, Pb, Cu and Zn, etc.) total and unstable concentration (Puga et al. 2015; Gao et al. 2020; Liu et al. 2018). Thus, Biochar has great advantages as a green environmental sorbent in remediating HMs contaminated soil.

Biochar can be prepared from a wide variety of raw materials such as municipal sludge, livestock manure, crop straw (Al-Wabel et al. 2018). In recent years, municipal sewage sludge has increased sharply with the increasing improvement of sewage treatment facilities (Zhou et al. 2020a), it is a by-product of the sewage treatment municipal and contains a variety of harmful substances (pathogens, refractory organics and toxic HMs, etc.), which is easy to cause secondary pollution (Zhou et al. 2020b). Pyrolysis of sewage sludge is promising since it enables to decrease the harmful substances and volume. Meanwhile, the solid carbonaceous residues after pyrolysis (SSB) may be used as the amendment of HMs in soil (Zhang et al. 2018). At present, Some researches have showed that the excellent effect of sludge biochar on the remediation of HMs contaminated soil, For example, Penido et al. (2019) observed a significant reduction of Cd, Pb, and Zn bioavailability in HMs contaminated soil from a Zn-mining area by applying SSB. Fang et al. (2016) used the SSB to remediate soils that had been contaminated with cationic Pb(II), etc. and anionic Cr(VI), etc. respectively. However, there are still concerns regarding potential soil secondary contamination with toxic HMs due to SSB were thoroughly mixed with soil and require further investigations to the assessment of long-term risks (Fang et al. 2016; Figueiredo et al. 2019). Thereby, it is requisite to obtain a piece of equipment which is able to separate biochar from the soil when remediation ended.

In this study, biochar derived from sewage sludge and was placed in polymethyl methacrylate (PMMA) tubule and as an amendment inserted HMs contaminated soils. Herein, Pb and Cr were selected as representative of toxic HMs. The objectives of this study are to 1) investigate the effect of SSB on the fractions of Pb and Cr in soil, to 2) determine the changes of the total content of Pb and Cr in soil with the remediation distance from the SSB tubule and time. The research results will provide some theoretical references for HMs-contaminated soil remediation and passivation by biochar in future research and application.

Material And Method

Biochar preparation

In this study, sewage sludge (SS) was collected from the dewatering workshop of the Xintian Wastewater Treatment Plant (XWTP) in Wanzhou District, Chongqing City, China, where an Orbal oxidation ditch wastewater treatment system is operated. The basic properties of sewage sludge were given in Table 1. The raw sewage sludge was dewatered through a vacuum pump (SHZ-DIII, Yuezhong, China) and then was placed in an oven (DHG-9420A, Honghua, China) at a temperature of 103 ± 2 °C to constant weight. The dried samples were ground and passed through 20-mesh nylon sieves, The samples were thoroughly mixed and stored in plastic bags for further study.

Table 1

Properties of sewage sludge

MLSS mg·L ⁻¹	MLVSS / mg·L ⁻¹	SVI / mL·g ⁻¹	Moisture / %
2425.5	1659.4	128.5	99.1

The oxygen-limited pyrolysis method was used to prepare the biochar. In brief, approximate 50.0g of sewage sludge samples loaded in the crucible and covered with fitting lids and alumina foils, which were loaded into the muffle furnace (SX-10-12, Yiheng, China), the pyrolysis process was performed by raising the target temperature to 500°C with a heating rate of 10°C min⁻¹ and residence time of 2 h. The obtained sewage sludge biochar (SSB) was grounded to pass through 100-mesh nylon sieves, and dip in hydrochloric acid for 24 h to eliminate effects of surface and internal impurities, and improve the porous structure of SSB (Liu et al. 2018), then the SSB was cleaned with deionized water until reaching a neutral pH. Finally, SSB was dried and store in plastic bags.

Characterization of biochar

The yield was calculated from the ratio between the mass of SSB and the raw materials. Ash was measured as the residual remaining after heating to 800°C and maintaining for 4 h. The pH values were measured with a pH meter (FE28, Mettler Toledo, China) and the method from wang et al. (2020). Levels of Pb and Cr were determined by inductively coupled plasma optical emission spectrometry (ICP-OES; Optima7000DV, Perkin Elmer, USA) after acid digestion according to Figueiredo et al. (2020). The surface structure of SSB was analyzed using a scanning electron microscopy (SEM; Supra55, Zeiss Germany). The surface functional groups of SSB were determined through Fourier transform infrared (FTIR) spectroscopy (Nicolet iS 10, Thermo Fisher Scientific, USA), the infrared spectra were obtained over the 4000 ~ 500 cm⁻¹. The crystal structure of the SSB was characterized by X-ray diffraction (XRD; D8 ADVANCE, Bruker, Germany).

Test soil collection and preparation

Surface soil (0–20 cm) was collected from Three Gorges Reservoir area located in Wanzhou District, Chongqing City, China (30°42' 53" N, 108°25' 55" E). The soil sample was thoroughly mixed, air-dried at room temperature, excess roots and gravels were removed, ground to pass through 20-mesh nylon sieves

before initiating the experiments. The physiochemical properties of the soil were determined according to Chinese standard methods (Liu et al. 1996) and were given in Table 2.

To obtain a more significant remediation effect of SSB on Pb and Cr and reduce influences of other HMs in the soil, we replenish external Pb ($\text{Pb}(\text{NO}_3)_2$) or Cr ($\text{K}_2\text{Cr}_2\text{O}_7$) to the air-dried soil and to reach the First or Second type of Risk Intervention Values for Soil Contamination of Development Land (RIVSCDL) of China, respectively. Meanwhile, the soil moisture content was controlled at 25% or 35% in each test group. Finally, all test soils were allowed to incubate for 7 days before the experiments. The type of soils required and marking was given in Table 3.

Table 2
The properties of the raw soil.

Volume-weight / ($\text{g}\cdot\text{cm}^{-3}$)	Moisture / %	pH	Total Pb / ($\text{mg}\cdot\text{kg}^{-1}$)	Total Cr / ($\text{mg}\cdot\text{kg}^{-1}$)
1.3 ± 0.1	29.4 ± 2.1	7.3 ± 0.4	26.4 ± 1.3	35.6 ± 1.5

Table 3
The types of soils required

Adscititious HMs	Value / ($\text{mg}\cdot\text{kg}^{-1}$) expectantly / actually	Moisture / %	Amendments	Marking
Pb	800 / 707.3	25 and 35	Raw soil	CN
Pb	800 / 707.3	25 and 35	SSB	SSB-F
Pb	2500 / 1998.2	25 and 35	SSB	SSB-S
Cr	30 / 31.8	25 and 35	Raw soil	CN
Cr	30 / 31.8	25 and 35	SSB	SSB-F
Cr	80 / 76.5	25 and 35	SSB	SSB-S
Notes: CN: Control. HMs contaminated soil (concentration were controlled at the First type of RIVSCDL) which were remediated by raw soil.				
SSB-F and SSB-S: Treatment groups. HMs contaminated soil (concentration was controlled at the First and Second type of RIVSCDL) which were remediated by SSB.				

Experimental design

The tested soils and SSB were placed in PMMA column [H (height) = 10, D (diameter) = 30 cm] and PMMA tubule (H = 10, d = 1.5 cm, many pores is full of the tubule wall), respectively, and the tubule was located center of the column (Fig. 1). To minimize the migration of Pb and Cr through the column sidewalls, PMMA columns were coated with a thin layer of paraffin wax and spread a layer of 1.5 cm gravel. Then, the soil was filled with layer upon layer and packed. The filling height up to 8.0 cm both soil and biochar

and at a ratio of 1:600 (dry mass, biochar/soils). Finally, they were incubated in a lightproof, sealed, and room temperature sustain 35 days, soil samples were collected every 5 days and 8 times in total. Approximate 0.5 g of soil samples were collected at equal depth and distance to measure the total contents of Pb or Cr, and the needless soil was backfilled and compacted. After the last collection, SSB tubules were recycled, soil in the PMMA column was thoroughly mixed and measure the Pb and Cr concentration of fractions. All of the soil samples were dried, grounded to pass through 100-mesh nylon sieves and stores. Each experiment was implemented in duplicate. The schematic diagram of the experimental design was showed in Fig. 1.

Analyses of Pb and Cr

Total contents of Pb and Cr

In this study, total Pb and Cr were determined using a microwave digester (Speedwave Xpert, Berghof, Germany). Particularly, samples (0.2 g) were digested with a dup-acid mixture of HF (1 mL) and HNO₃ (8 mL) according to Khadhar et al. (2020) and the residual solution through membrane filters (0.22 µm) and diluted to 50 mL.

Chemical fractions of Pb and Cr

Pb and Cr potentially toxic were measured according to Tessier sequential extraction method (Tessier et al. 1979), this method divides HMs into five fractions due to their are successively less bioavailability and mobility effect (Chen et al. 2020). In brief, extraction steps were as follows: (F1) exchangeable (1 mol/L MgCl₂); (F2) carbonate bound (1 mol/L NaAc); (F3) Fe-Mn oxides bound (0.04 mol/L NH₂OH·HCl in 25% HAc); (F4) organic matter bound [(0.02 mol/L HNO₃), (30% H₂O₂), (3.2 mol/L NH₄Ac in 20% HNO₃)]; (F5) residual (digested with HF-HNO₃ acids). After each step, the sample was separated at 4000 rpm for 20min, supernatants were used for detecting the concentration of F1- F5 through membrane filters (0.22 µm). The Pb and Cr concentrations were measured by ICP-OES.

Results And Discussion

Passivation effect of SSB on Pb and Cr

HMs exist in the soil with diverse chemical fractions and the bioavailability and potentially toxic mainly depend on their specific fraction. F1 presents the most unstable and high risky and F2 slightly, F5 was identified as a stable fraction. bioavailability and toxic of those five fractions from high to low was F1 > F2 > F3 > F4 > F5 (Chen et al. 2020).

Fraction distribution of Pb and Cr obtained from Tessier sequential extraction method and were showed in Fig. 2 which reveal the fraction distribution difference of initially and finally. In brief, the results showed that CN had a varied slightly of fraction distribution and SSB had was significant. Compare SSB-F with SSB-S groups. The F1 and F2 decreased by 25.1% and 16.8%, F3 increased by 18.5%; the F1 and F2

decreased by 28.8% and 2.9%, F3 increased by 9.8% (Fig. 4a). The F2 and F3 decreased by 8.8% and 4.8%, F4 increased by 75.1%; the F1 decreased by 42.1%, F3 and F4 increased by 4.5% and 12.9% (Fig. 4b). The F1 decreased by 33.6%, F3 and F4 increased by 10.1% and 22.1%; the F1 decreased by 25.3%, F3 and F4 increased by 13.8% and 14.8% (Fig. 4c). The F1 decreased by 73.0%, F2, F3 and F4 increased by 13.2%, 23.9% and 30.8%; the F1 decreased by 37.2%, F3 and F4 increased by 25.4% and 33.5% (Fig. 4d). Munir et al. (2020) found that Cr and Pb be immobilized and removed by -OH and -COOH groups in biochar.

Results showed that SSB could decrease Pb and Cr bioavailability and mobility through transforming the F1 and F2 to more stable forms and that is better when the moisture at 25% and 35%, respectively, (Pb: F1, F2 decreased by 25.1%, 16.8%. Cr: F1 decreased by 73.0%, respectively). These results were compared with others. Liu et al. (2018) added 5% (w/w) modified coconut shell biochar to multi-metals contaminated soil in Mianzhu, Sichuan, China, which decreased the acid-soluble Cd, Ni and Zn concentration by 30.1%, 57.2% and 12.7%, respectively. Munir et al. (2020) added 2% (w/w) bamboo-biochar to Pb and Cr contaminated soil in Huainan, Anhui, China, which decreased their F1 concentration by 8.5% and 29%, respectively. Therefore, SSB tubules have a practical effect on soil passivation.

The remediation effect of SSB on Pb and Cr

The variation of Pb and Cr total contents in the soil with the incubation period and distance were showed in Fig. 3 (A line represents the variation of the Pb or Cr total content in this sampling point with time). Insert SSB tubules in contaminated soils resulted showed that Pb and Cr total contents were significantly decreased. Presented diverse trends under different experiment conditions which phenomenons indicate these conditions (moisture and pollution intensity) have a definite influence on the remediation results.

At end of the remediation, results revealed that CN had a varied slightly of Pb and Cr concentration compares with initially (concentration decreased by -2.1%~8.0% and -10.3%~4.0%). On the contrary, the effect were significantly of SSB-F and SSB-S [Pb concentration decreased by 8.5%~21.8% and 14.6%~23.3% (Fig. 3a), 13.0%~17.3% and 8.2%~16.2% (Fig. 3b); Cr concentration decreased by 9.5%~22.2% and 5.0%~15.5% (Fig. 3c), 25.1%~38.4% and 24.8%~36.1% (Fig. 3d), respectively]. Maximum of Pb is located at the farthest and the closest point when moisture was 25% and 35%, respectively, and maximum of Cr located were showed in Fig. 3c-d. Results indicated that a better remediation effect of Pb and Cr when the soil moisture content was 25% and 35% (concentration of Pb and Cr decreased by 23.3% and 38.4%, maximally). This remediation effect was compared with others. Wang et al. (2020) added 10% (w/w) kitchen waste-based biochar to Ba contaminated soil in landfill areas, Tibet, China, which decreased the concentration by 10.1%. Li et al. (2016) added biochar to Cd contaminated soil, found decreased the total content by 46.4%. These studies indicate that added biochars could remove HMs in soil.

In addition, for Pb contaminated soil, these points ($\leq 7.5\text{cm}$) presented initial decrease, subsequent increased and final decreased with the remediation time, and others presented initial increased, finally decreased. These phenomena could be attributed to SSB had a rich porous structure (Fig. 4b). Lin et al.

(2020) indicated biochars adsorb HMs are divided into the surface monolayer sorption initially and the intraparticle diffusion sorption later. Initially, SSB adsorbs Pb ion at closer points, with the adsorption persistent, Pb ion could gradually migrate to SSB tubule from a broader area, which leads to Pb ion short-dated increase and final continuous decrease, Mitzia et al. (2020) consider that cause this phenomenon may attribute multiple interactions (such as soil matrix and water content), which can provoke an Eh-pH fluctuation. For Cr contaminated soil, presented a similar trend for all lines which are rapid initial decrease, subsequent increase (starting on the 5th day), and final decrease (starting on the 20th day) and presented an indistinctive effect at remediation distance.

Characteristics of SSB and its removal mechanisms of Pb and Cr

Characteristics of SSB

The basic properties of SSB were given in Table 4. Results showed that yield and ash of SSB were higher compare with other biochar (biochars derived from rice straw, sawdust and phragmites etc.) which was mainly due to the SSB have high contents of inorganic constituents (Pellera et al. 2020) Furthermore, SSB was alkaline which was due to the surface of SSB including multitudinous alkaline aromatization groups and them could immobilize HMs through increase the pH of the soil (Mitzia et al. 2020). Pellera et al. (2020) found that biochar leads to higher soil pH and ECE and causes metal precipitation, finally.

Table 4 Basic properties of SSB				
Yield / %	Ash / %	pH	Total Pb / mg·kg ⁻¹	Total Cr / mg·kg ⁻¹
47.8 ± 0.2	30.6 ± 0.3	8.2 ± 0.1	18.8 ± 2.4	53.5 ± 4.0

SEM analysis

The SEM was carried out to characterize the microstructure of SSB and different magnifications are showed in Fig. 4. Results showed that the SSB had uneven size distribution and visible loose fold (Fig. 4a), and had a rich porous structure (Fig. 4b), which could be due to the breakdown of the volatile compounds at higher temperatures that leadto the energy (gas) to escape from sewage sludge (Shakya et al. 2019). These forming mesopores and micropores to obtain greater surface area and porous volume, these porous structures could provide enough adsorption area for metal binding (Wang et al. 2018). Furthermore, visible inorganic ash particles were random distributed around of porous structure, Yuan et al. (2020) found that these particles would via ion exchange, complexation and precipitation reactions to reduce metal ions.

FTIR spectra analysis

Figure 5a shows the infrared spectrum of SSB. Five main absorption peaks centered at 3734, 2360, 1540, 1015 and 775 cm⁻¹ were recorded. The peaks observed near 3734 cm⁻¹ was attributed to the stretching

and bending vibration of -OH (Lin et al. 2017), the peaks at 2360 cm^{-1} were corresponded to the stretching vibration of CO_2 (Lin et al. 2017) and the peaks at 1540 cm^{-1} was ascribed to the stretching vibration of $\text{C}=\text{O}$, $\text{C}=\text{C}$ aromatic rings (Shin et al. 2020), the peaks at 1015 cm^{-1} and 775 cm^{-1} were attributed to the stretching vibration of -OH and C-H of aromatic rings (Liu et al. 2020), respectively. Indicating that SSB contained several kinds of functional groups, These groups play a heavy role to reduce Pb and Cr in soil have been widely reported, for example, Zhao et al. (2021) found that O-containing groups positive participation Cr(VI) removal, Wang et al. (2018) reported that -OH was involved in the interaction with Pb(II) ion by the ion exchange reaction.

XRD analysis

Figure 5b shows the mineralogical composition of SSB. Illustrating highly crystalline structures due to revealing numerous sharp peaks (Liu et al. 2020). Results revealed C, SiO_2 , SiS_2 and AlPO_4 as the predominant minerals in SSB. The characteristic peaks of carbon were detected corresponding to the presence of a number of aromatic carbon sheets and this phenomenon was confirmed from the FTIR results. Also, the components of SiO_2 , SiS_2 and AlPO_4 were responsible to immobilize Pb and Cr in soil. Li et al. (2018) found that SiO_2 could induce complexation and coordination with Cr(VI), the SiS_2 could induce reduction what was Cr(VI) reduce to Cr(III) and the AlPO_4 were converted to $\text{Pb}_5(\text{PO}_4)_3\text{OH}$ precipitations (Zhao et al. 2018).

Based on the previous discussions, the potential mechanism of removal and passivation of Pb and Cr are surmised. Generally, SSB could decrease Pb and Cr toxicity and mobility due to form precipitations under alkaline conditions (Khan et al. 2020), on the other hand, abundant pore structures of SSB provide more adsorption sites for metal complexing and precipitating (Wang et al. 2018). Furthermore, the FTIR spectrum revealed that functional groups (such as -OH , $\text{C}=\text{O}$, $\text{C}=\text{C}$, et al.) of SSB could bind Pb and Cr via ion exchange, complexation and coordination (Yuan et al. 2020). XRD analysis indicated that SiO_2 and AlPO_4 could immobilize Pb and Cr via complexation and precipitation (Shakya et al. 2019; Zhao et al. 2018). To sum up, these characters of SSB could reduce the bioavailability and total contents of Pb and Cr in soil.

Cost analysis of SSB

In this study, SSB was prepared in a muffle furnace with an oxygen-limited pyrolysis method. Specific costs of raw materials, reagents and disposal were estimated, which provides a basis for large-scale production in the further. To date, more than 60 million tonnes of municipal sewage sludge were produced in China (Zhang et al. 2020). The raw materials were gathered with costless. Furthermore, the cost of electricity during the production procedures is 0.51 USD/kg (including pyrolysis and dry of biochar). Finally, the cost of chemicals (hydrochloric acid) during removing SSB impurities procedures is 0.71USD/kg. The cost of SSB has a low level compares with anterior reports and the price will lower when large-scale production (Cai et al. 2020). Therefore. the SSB has a great potential in HMs contaminated soil remediation, meanwhile, there are signs to investigate further.

Conclusion

The fraction of unstable and high risky and total content of Pb and Cr could be significantly decreased when inserting a SSB tubule in the contaminated soil, which was achieved via adsorption, ion exchange, complexation and precipitation, etc. This study revealed that have a better passivation effect of Pb and Cr when the soil moisture at 25% and 35%, respectively, [Pb: (F1) decreased by 4.9%, (F2) decreased by 14.8%, (F3) increased by 22.5%; Cr: (F1) decreased by 60.2%, (F3) increased by 21.5%), maximally]. The remediation effect is better of Pb and Cr when the moisture content at 25% and 35% (the total content decreased by 23.3% and 38.4%, maximally) which is located at outermost and innermost, respectively. Furthermore, SSB exhibited higher efficacy in remediating and passivating Cr contamination than Pb.

Declarations

Authors' contributions

LC and CF: Investigation, visualization and writing the original manuscript. QN and YW: Analysis and writing (review and editing). WP and HL: Supervision, resources and writing (review and editing). HB, CH and ML conducting experiments. All authors read and approved the final manuscript.

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Data and materials availability

All data and materials generated or analyzed during this study are included in this article.

Compliance with ethical standards

Conflict of interest

The authors declare that they have no competing interests.

Ethics approval

Not applicable.

Consent to participate

Not applicable.

Consent for publication

References

1. Azeem M, Hassan TU, Tahir MI, Ali A, Jeyasundar PGSA, Hussain Q, Bashir S, Mehmood S, Zhang Z (2021) Tea leaves biochar as a carrier of *Bacillus cereus* improves the soil function and crop productivity. *Appl Soil Ecol* 157: 103732. <https://doi.org/10.1016/j.apsoil.2020.103732>
2. Al-Wabel MI, Hussain Q, Usman ARA, Ahmad M, Abdulazeem A, Abdulazeem SS, Ok YS (2018) Impact of biochar properties on soil conditions and agricultural sustainability: A review. *Land Degrad Dev* 29: 2124-2161. <https://doi.org/10.1002/ldr.2829>
3. Cai T, Liu X, Zhang J, Tie B, Lei M, Wei X, Peng Q, Du H (2021) Silicate-modified oiltea camellia shell-derived biochar: A novel and cost-effective sorbent for cadmium removal. *J Clean Prod* 281: 125390. <https://doi.org/10.1016/j.jclepro.2020.125390>
4. Chen M, Nong S, Zhao Y, Riaz MS, Xiao Y, Molokeev MS, Huang F (2020) Renewable P-type zeolite for superior absorption of heavy metals: Isotherms, kinetics, and mechanism. *Sci Total Environ* 726: 138535. <https://doi.org/10.1016/j.scitotenv.2020.138535>
5. Chen X, Zhao Y, Zhang C, Zhang D, Yao C, Meng Q, Zhao R, Wei Z (2020) Speciation, toxicity mechanism and remediation ways of heavy metals during composting: A novel theoretical microbial remediation method is proposed. *J. Environ. Manage* 272: 111109. <https://doi.org/10.1016/j.jenvman.2020.111109>
6. Chen Y, Wang R, Duan X, Wang S, Ren N, Ho SH (2020) Production, properties, and catalytic applications of sludge derived biochar for environmental remediation. *Water Res* 187: 116390. <https://doi.org/10.1016/j.watres.2020.116390>
7. Dong L, Liu W, Jiang R, Wang Z (2016) Study on the adsorption mechanism of activated carbon removing low concentrations of heavy metals. *Desalin Water Treat* 57: 7812-7822. <https://doi.org/10.1080/19443994.2015.1100140>
8. Duan C, Fang L, Yang C, Chen W, Cui Y, Li S (2018) Reveal the response of enzyme activities to heavy metals through in situ zymography. *Ecotox Environ Safe* 156: 106-115. <https://doi.org/10.1016/j.ecoenv.2018.03.015>
9. Fang S, Tsang DCW, 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. <https://doi.org/10.1016/j.chemosphere.2016.01.060>
10. Figueiredo CC, Chagas JKM, Silva J, Jorge PF (2019) Short-term effects of a sewage sludge biochar amendment on total and available heavy metal content of a tropical soil. *Geoderma* 344: 31-39. <https://doi.org/10.1016/j.geoderma.2019.01.052>
11. Feng LJ, Zhang LQ, Feng L, Li JL (2018) Dissipation of polycyclic aromatic hydrocarbons (PAHs) in soil amended with sewage sludge and sludge compost. *Environ Sci Pollut Res* 25: 34701-34710. <https://doi.org/10.1007/s11356-018-3383-2>

12. Gao R, Hu H, Fu Q, Li Z, Xing Z, Ali U, Zhu J, Liu Y (2020) Remediation of Pb, Cd, and Cu contaminated soil by co-pyrolysis biochar derived from rape straw and orthophosphate: Speciation transformation, risk evaluation and mechanism inquiry. *Sci Total Environ* 730:139119. <https://doi.org/10.1016/j.scitotenv.2020.139119>
13. Gerhardt KE, Huang XD, Glick BR, Greenberg BM (2009) Phytoremediation and rhizoremediation of organic soil contaminants: Potential and challenges. *Plant Sci* 176: 20-30. <https://doi.org/10.1016/j.plantsci.2008.09.014>
14. He M, Yan P, Yu H, Yang S, Xu J, Liu X (2020) Spatiotemporal modeling of soil heavy metals and early warnings from scenarios-based prediction. *Chemosphere* 255: 126908. <https://doi.org/10.1016/j.chemosphere.2020.126908>
15. Hu B, Shao S, Ni H, Fu Z, Hu L, Zhou Y, Min X, She S, Chen S, Huang M, Zhou L, Li Y, Shi Z (2020) Current status, spatial features, health risks, and potential driving factors of soil heavy metal pollution in China at province level. *Environ Pollut* 266: 114961. <https://doi.org/10.1016/j.envpol.2020.114961>
16. Hung CM, Huang CP, Chen CW, Wu CH, Lin YL, Dong CD (2020) Activation of percarbonate by water treatment sludge-derived biochar for the remediation of PAH-contaminated sediments. *Environ Pollut*, 265: 114914. <https://doi.org/10.1016/j.envpol.2020.114914>
17. Khadhar S, Sdiri A, Chekirben A, Azouzi R, Charef A (2020) Integration of sequential extraction, chemical analysis and statistical tools for the availability risk assessment of heavy metals in sludge amended soils. *Environ. Pollut* 263: 114543. <https://doi.org/10.1016/j.envpol.2020.114543>
18. Khan A, Khan S, Lei M, Alam M, Khan MA, Khan A (2020) Biochar characteristics, applications and importance in health risk reduction through metal immobilization. *Environ Technol Innov*, 20: 101121. <https://doi.org/10.1016/j.eti.2020.101121>
19. Lee SJ, Park JH, Ahn YT, Chung JW (2015) Comparison of Heavy Metal Adsorption by Peat Moss and Peat Moss-Derived Biochar Produced Under Different Carbonization Conditions. *Water Air Soil Pollut*, 226(9): 2-11. <https://doi.org/10.1007/s11270-014-2275-4>
20. Li HY, Ye XX, Geng ZG, Zhou HJ, Guo XS, Zhang YX, Zhao HJ, Wang GZ (2016) The influence of biochar type on long-term stabilization for Cd and Cu in contaminated paddy soils. *J Hazard Mater* 304: 40-48. <https://doi.org/10.1016/j.jhazmat.2015.10.048>
21. Li Y, Wei Y, Huang S, Liu X, Jin Z, Zhang M, Qu J, Jin Y (2018) Biosorption of Cr(VI) onto *Auricularia auricula* dreg biochar modified by cationic surfactant: Characteristics and mechanism. *J Mol Liq* 269: 824-832. <https://doi.org/10.1016/j.molliq.2018.08.060>
22. Lin L, Qiu W, Wang D, Huang Q, Song Z, Chau HW (2017) Arsenic removal in aqueous solution by a novel Fe-Mn modified biochar composite: Characterization and mechanism. *Ecotox Environ Safe* 144: 514-521. <https://doi.org/10.1016/j.ecoenv.2017.06.063>
23. Lin S, Huang W, Yang H, Sun S, Yu J (2020) Recycling application of waste long-root *Eichhornia crassipes* in the heavy metal removal using oxidized biochar derived as adsorbents. *Bioresour Technol* 314: 123749. <https://doi.org/10.1016/j.biortech.2020.123749>

24. Liu GS, Jiang NH, Zhan LD, Liu Z (1996) Soil Physical and Chemical Analysis Description of Soil Profiles Environmental Sampling, China. Standard Methods Press, Beijing
25. Liu H, Xu F, Xie Y, Wang C, Zhang A, Li L, Xu H (2018) Effect of modified coconut shell biochar on availability of heavy metals and biochemical characteristics of soil in multiple heavy metals contaminated soil. *Sci Total Environ* 645: 702-709. <https://doi.org/10.1016/j.scitotenv.2018.07.115>
26. Liu J, Yang X, Liu H, Cheng W, Bao Y (2020) Modification of calcium-rich biochar by loading Si/Mn binary oxide after NaOH activation and its adsorption mechanisms for removal of Cu(II) from aqueous solution. *Colloid Surf A-Physicochem Eng Asp* 601: 124960. <https://doi.org/10.1016/j.colsurfa.2020.124960>
27. Liu L, Li W, Song W, Guo M (2018) Remediation techniques for heavy metal-contaminated soils: Principles and applicability. *Sci Total Environ* 633: 206-219. <https://doi.org/10.1016/j.scitotenv.2018.03.161>
28. Mitzia A, Vítkov M, Komarek M (2020) Assessment of biochar and/or nano zero-valent iron for the stabilisation of Zn, Pb and Cd: A temporal study of solid phase geochemistry under changing soil conditions. *Chemosphere* 24: 125248. <https://doi.org/10.1016/j.chemosphere.2019.125248>
29. Munir MAM, Liu G, Yousaf B, Ali MU, Cheema AI, Rashid MS, Rehman A (2020) Bamboo-biochar and hydrothermally treated-coal mediated geochemical speciation, transformation and uptake of Cd, Cr, and Pb in a polymetal(loid)s-contaminated mine soil. *Environ Pollut* 265: 114816. <https://doi.org/10.1016/j.envpol.2020.114816>
30. Pellera FM, Gidarakos E (2015) Effect of dried olive pomace – derived biochar on the mobility of cadmium and nickel in soil. *J Environ Chem Eng* 3: 1163-1176. <https://doi.org/10.1016/j.jece.2015.04.005>
31. Penido ES, Martins GC, Mendes TBM, Melo LC.A, Guimarães IR, Guilherme LRG (2019) Combining biochar and sewage sludge for immobilization of heavy metals in mining soils. *Ecotox Environ Safe* 172: 326-333. <https://doi.org/10.1016/j.ecoenv.2019.01.110>
32. Puga AP, Abreu CA, Melo LCA, Beesley L (2015) Biochar application to a contaminated soil reduces the availability and plant uptake of zinc, lead and cadmium. *J Environ Manage* 159: 86-93. <https://doi.org/10.1016/j.jenvman.2015.05.036>
33. Rybak AV, Belykh ES, Maystrenko TA, Velegzhaninov IO (2018) Microsatellite polymorphism of *Trifolium pratense* population at the conditions of radioactive and chemical contamination of soil (Komi republic, Russia). *Environ Sci Pollut Res* 26: 34127-34136. <https://doi.org/10.1007/s11356-018-3375-2>
34. Sarwar N, Imran M, Shaheen MR, Ishaque W, Kamran MA, Matloob A, Rehim A, Hussain S (2017) Phytoremediation strategies for soils contaminated with heavy metals: Modifications and future perspectives. *Chemosphere* 171: 710-721. <https://doi.org/10.1016/j.chemosphere.2016.12.116>
35. Shakya A, Agarwal T (2019) Removal of Cr(VI) from water using pineapple peel derived biochars: Adsorption potential and re-usability assessment. *J Mol Liq* 293: 111497. <https://doi.org/10.1016/j.molliq.2019.111497>

36. Shin H, Tiwari D, Kim DJ (2020) Phosphate adsorption/desorption kinetics and P bioavailability of Mg-biochar from ground coffee waste. *J Water Process Eng* 637: 101484.
<https://doi.org/10.1016/j.jwpe.2020.101484>
37. Tessier A, Campbell PGC, Bisson M (1979) Sequential extraction procedure for the speciation of particulate trace metals. *Anal Chem* 51: 844–851. <https://doi.org/10.1021/ac50043a017>
38. Trellu C, Mousset E, Pechaud Y, Huguenot D, Hullebusch ED, Esposito G, Oturan MA (2016) Removal of hydrophobic organic pollutants from soil washing/flushing solutions: A critical review. *J Hazard Mater* 306: 149-174. <https://doi.org/10.1016/j.jhazmat.2015.12.008>
39. Wang S, Shi R, Li H, Li Y, Xu Y, Han Z (2020) Effect of terminal temperature on the morphology and potentially toxic metals concentrations of biochars derived from paper and kitchen waste. *Waste Manage* 118: 445-451. <https://doi.org/10.1016/j.wasman.2020.09.012>
40. Wang T, Sun H, Ren X, Li B, Mao H (2018) Adsorption of heavy metals from aqueous solution by UV-mutant *Bacillus subtilis* loaded on biochars derived from different stock materials. *Ecotox. Environ. Safe* 148: 285-292. <https://doi.org/10.1016/j.ecoenv.2017.10.039>
41. Xi J, Li H, Xi J, Tan S, Zheng J, Tan Z (2020) Effect of returning biochar from different pyrolysis temperatures and atmospheres on the growth of leaf-used lettuce. *Environ Sci Pollut Res* 27: 35802-35813. <https://doi.org/10.1007/s11356-020-09840-8>
42. Xiao R, Wang P, Mi S, Ali A, Liu X, Li Y, Guan W, Li R, Zhang Z (2019) Effects of crop straw and its derived biochar on the mobility and bioavailability in Cd and Zn in two smelter-contaminated alkaline soils. *Ecotox Environ Safe* 181: 155-163. <https://doi.org/10.1016/j.ecoenv.2019.06.005>
43. Yang X, Liu L, Tan W, Liu C, Dang Z, Qiu G (2020) Remediation of heavy metal contaminated soils by organic acid extraction and electrochemical adsorption. *Environ Pollut* 264: 114745.
<https://doi.org/10.1016/j.envpol.2020.114745>
44. Yu B, Li D, Wang Y, He H, Li H, Chen G (2020) The compound effects of biochar and iron on watercress in a Cd/Pb–contaminated soil. *Environ Sci Pollut Res* 27: 6312-6325.
<https://doi.org/10.1007/s11356-019-07353-7>
45. Yuan S, Hong M, Li H, Ye Z, Gong H, Zhang J, Huang Q, Tan Z (2020) Contributions and mechanisms of components in modified biochar to adsorb cadmium in aqueous solution. *Sci Total Environ* 733: 139320. <https://doi.org/10.1016/j.scitotenv.2020.139320>
46. Zhang J, Hu H, Wang M, Li Y, Wu S, Cao Y, Lian P, Zhang J, Naidu R, Liu Y, Man YB, Wong MH, Zhang C, Shan S (2021) Land application of sewage sludge biochar: Assessments of soil-plant-human health risks from potentially toxic metals. *Sci Total Environ* 756: 114137.
<https://doi.org/10.1016/j.scitotenv.2020.144137>
47. Zhang J, Jin J, Wang M, Naidu R, Liu Y, Man YB, Liang X, Wong MH, Christie P, Zhang Y, Song C, Shan S (2020) Co-pyrolysis of sewage sludge and rice husk/ bamboo sawdust for biochar with high aromaticity and low metal mobility. *Environ Res* 191: 110034.
<https://doi.org/10.1016/j.envres.2020.110034>

48. Zhang W, Du W, Wang F, Xu H, Zhao T, Zhang H, Ding Y, Zhu W (2020) Comparative study on Pb²⁺ removal from aqueous solutions using biochars derived from cow manure and its vermicompost. *Sci Total Environ* 716: 137108. <https://doi.org/10.1016/j.scitotenv.2020.137108>
49. Zhao N, Zhao C, Tsang DCW, Liu K, Zhu L, Zhang W, Zhang J, Tang Y, Qiu R (2021) Microscopic mechanism about the selective adsorption of Cr(VI) from salt solution on O-rich and N-rich biochars. *J Hazard Mater* 404: 124162. <https://doi.org/10.1016/j.jhazmat.2020.124162>
50. Zhao T, Yao Y, Li D, Wu F, Zhang C, Gao B (2018) Facile low-temperature one-step synthesis of pomelo peel biochar under air atmosphere and its adsorption behaviors for Ag(I) and Pb(II). *Sci Total Environ* 640-641: 73-79. <https://doi.org/10.1016/j.scitotenv.2018.05.251>
51. Zhou G, Gu Y, Yuan H, Gong Y, Wu Y (2020a) Selecting sustainable technologies for disposal of municipal sewage sludge using a multi-criterion decision-making method: A case study from China. *Resour Conserv Recycl* 161: 104881. <https://doi.org/10.1016/j.resconrec.2020.104881>
52. Zhou W, Yang F, Zhu R, Dai G, Wang W, Wang W, Guo X, Jiang J, Wang Z (2020b) Mechanism analysis of pore structure and crystalline phase of thermal insulation bricks with high municipal sewage sludge content. *Constr. Build. Mater* 263:120021. <https://doi.org/10.1016/j.conbuildmat.2020.120021>

Figures

Figure 1

A brief diagram of the experimental design

Figure 2

Fractions distribution of Pb (a-b) and Cr (c-d) in soil. Notes: F1: Exchangeable; F2: Carbonate bound; F3: Fe-Mn oxides bound; F4: Organic matter bound; F5: Residual. (a) and (b): contaminated soil (Pb), at moisture was 25% and 35%; (c) and (d): contaminated soil (Cr), at moisture was 25% and 35%; a and b: Fractions distribution of Pb or Cr from initially and finally; CN, SSB-F and SSB-S were showed in Table 3.

Figure 3

Concentration of total Pb (a-b) and Cr (c-d) during remediating

Figure 4

SEM images of SSB at different magnifications

Figure 5

FTIR spectra (a) and XRD pattern (b) of SSB

Supplementary Files

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- [1.Passivation.xlsx](#)
- [2.Remediation.xlsx](#)