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Sorption mechanisms of lead on silicon-rich biochar in aqueous solution: Spectroscopic investigation

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Abstract

Unraveling sorption mechanisms of lead (Pb) to silicon (Si)-rich biochar at molecular scale in aqueous solution are essential for the effective application of the biochars to the remediation of Pb and other metal(loid)s pollution in the environment. Thus, this study investigated the contributions of phytoliths and other compounds to the Pb sorption on Si-rich coconut fiber biochar (CFB500) and the corresponding sorption mechanisms using spectroscopic techniques, including the micro-X-ray fluorescence (μ -XRF), X-ray absorption fine structure (XAFS), scanning electron microscopy combined with energy dispersive X-ray spectroscopy, and X-ray diffraction. The μ -XRF and XAFS results showed that K, Ca, Cu, Mn, and Fe were released and significantly related to Pb in Pb-loaded CFB500; four major Pb species were formed with similar structures to lead carboxylate (e.g., $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$), $\text{Pb}_3(\text{PO}_4)_2$, PbSiO_3 , and PbCO_3 . On phytoliths in CFB500, Pb^{2+} ions were mainly sorbed on the sites of silicate with a structure similar to PbSiO_3 . The contribution of binding sites for Pb^{2+} sorption was ascribed to the outer-wall of carbon skeleton of CFB500, which was stronger than that provided by the mineral oxide aggregate and phytoliths on CFB500. Organic carbon functional groups, inorganic carbonates, silicates and phosphates on CFB500 mostly dominated the sorption sites for Pb^{2+} . Our results suggest that CFB500 was a promising material for the remediation of Pb-contaminated aqueous environments (e.g., wastewater).

Keywords: Phytoliths skeleton; Toxic metal(loid)s; Sorption sites; SEM-EDS; XAFS; μ -XRF.

Abbreviations:

CFB, coconut fiber biochar; CFB500, Si-rich coconut fiber biochar pyrolyzed at 500 °C; PTEs, potentially toxic elements; μ -XRF, micro-X-ray fluorescence; XAFS, X-ray absorption fine structure; EXAFS, extended X-ray absorption fine structure; LCF, linear combination fitting; FTIR, Fourier transformation infrared spectroscopy;

SEM-EDS, scanning electron microscopy combined with energy dispersive X-ray spectroscopy; XRD, X-ray diffraction; SR-FTIR, Synchrotron radiation FTIR; SSRF, Shanghai Synchrotron Radiation Facility; EDTA, ethylenediaminetetraacetic acid; ICP-MS, inductively coupled plasma mass spectrometer.

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1. Introduction

Contamination of soil, sediment, and water with potentially toxic elements (PTEs) is a global environmental, agricultural and human health issue due to their toxic nature (World Health Organization, 2017; Niazi et al., 2017; Li et al., 2018a). Lead (Pb) is one of the widespread PTEs given its worldwide use and emission from various processes, such as mining and smelting, battery recycling, soil pollution in shooting range, use of Pb additives in gasoline, irrigation with Pb-containing wastewater (Laidlaw et al., 2017). Lead exposure can pose a serious threat to human health, and young children are particularly vulnerable to Pb toxicity that can affect their nervous system and brain adversely (World Health Organization, 2017). To reduce Pb exposure, significant efforts have been dedicated to decontaminate Pb^{2+} in water systems (Shaheen et al., 2015; Ahmad et al., 2014), there is a dearth of understanding needed to identify various suitable product materials (such as biochar, inorganic compounds and mineral oxides) for developing low-cost and eco-friendly solutions for restoration and remediation of Pb-contaminated soil and water bodies (Xu et al., 2013; Li et al., 2018b; Li et al., 2019a).

Biochar production through pyrolysis of agricultural and woody residues not only provides renewable energy, but also contributes to potential economic and environmental benefits through upcycling the residues (Wu et al., 2012; Shaheen et al., 2019). In recent years, increasing scientific attention on biochars is ascribed to their potential benefits in soil amendment (Liu et al., 2018; He et al., 2018; Li et al., 2019b), immobilization of PTEs in soils (Lu et al., 2017; Nie et al., 2018; Qin et al., 2018), and removal of contaminants from water (Vikrant et al., 2018; Vithanage et al., 2017; Shaheen et al., 2019). Previous studies have reported that biochars derived from feedstock materials such as bamboo, rice straw, oak bark and pine wood can remove PTEs effectively from aqueous solutions (Ahmad et al., 2014; Liao et al., 2018; Shaheen et al., 2019). Among those biochars, Si-rich coconut fiber biochar (CFB) is considered as a promising material that can be applied to removing or immobilizing PTEs in contaminated soil and water, because of its abundant availability, high

sorption capacity, cost-effectiveness and renewability (Bhatnagar et al., 2010; Nakadi et al., 2018; Lu et al., 2018). Understanding the sorption mechanism of CFB for PTEs is essential for providing sufficient theoretical basis on the application of Si-rich biochars for PTEs remediation in the environment (Lu et al., 2017; Wu et al., 2017).

Phytoliths are found abundant in Si-rich feedstock materials such as Ericaceae (Buján, 2013), rice straw (Anala and Nambisan, 2015), rice husk, and wheat husk (Qadri et al., 2017). Buján (2013) even discovered that phytoliths act as alleviates of metal stress in heathers (Ericaceae). Phytoliths are mainly amorphous silicate particles embedded in plant materials and have various sizes and shapes in different plants (Qadri et al., 2017). As such, silicon is generally abundant in plant fibers (Nakadi et al., 2018). For example, silicon contents in the biomass and ash of coconut fiber ranges from 0.08~0.15% (m/m) and 0.30~0.52% (m/m), respectively (Nakadi et al., 2018), which are considered to be relatively high compared with other agricultural waste materials such as rice straw, palm tree fiber, and peach pit (Wu et al., 2012; Nakadi et al., 2018). When Si-rich feedstock materials are pyrolyzed at high temperatures to produce biochars, phytoliths remain in the skeleton of the resultant biochars (e.g., miscanthus straws derived-biochar) (Houben et al., 2014). As Si-rich biochars, including CFBs, can effectively sorb PTEs in water, phytoliths in the biochars may have a significant contribution to the overall sorption capacity of the biochars for PTEs, which, however, has been overlooked in the literature (Vithanage et al., 2017).

Several studies have investigated the removal of heavy metal ions including Pb^{2+} by various pristine and engineered biochars in aqueous solutions (Lee et al., 2016; Wu et al., 2017; Shaheen et al., 2019). To further understand the sorption mechanism, the composition and structure of sorbed metals on biochars have been assessed using various spectroscopic and microscopic techniques including scanning electron microscopy combined with energy dispersive X-ray spectroscopy (SEM-EDS), X-ray diffraction (XRD) and Fourier

transformation infrared (FTIR) spectroscopy (Lu et al., 2012). However, few studies have provided the sorption mechanism of Pb^{2+} by biochars using traditional methods coupled with advanced characterization techniques such as X-ray absorption fine structure (XAFS) and micro X-ray fluorescence (μ -XRF) (Wu et al., 2017; Lu et al., 2012).

Synchrotron-based XAFS and μ -XRF are powerful tools for providing information on bonding characteristics at molecular scale, and spatial localization of PTEs and their relationship with other elements of interest with a minimal perturbation of the sample (Liu et al., 2016; Sun et al., 2017). The XAFS spectroscopy is a non-destructive and sensitive technique which has been used to determine the local structures of PTEs bound to environmental particles and biochars (Wu et al., 2017; Nevidomskaya et al., 2016). The μ -XRF could describe the spatial distributions of elements in samples at micro scale, which are more intuitive to show the association between PTEs and other elements in the micro-region (Liu et al., 2016). In addition, SEM-EDS is an effective method to examine surface morphology and elemental distribution in micro-region of environmental samples and biochars (Lu et al., 2012). The combined use of these techniques is a novel approach that may provide insights into the sorption mechanism of PTEs by biochar. To the best of our knowledge, little information is available to delineate the Pb sorption mechanisms of CFB at molecular scale using integrated spectroscopic and microscopic techniques (Wu et al., 2017).

In the current study, advanced characterization methods (e.g., μ -XRF, XAFS, XRD and SEM-EDS) were used to investigate the sorption of Pb in aqueous solution by a Si-rich CFB produced at 500 °C (CFB500) at a molecular scale, in hope to clarify the Pb sorption mechanism of phytoliths and other components in the CFB. It is hypothesized that CFB can provide various sorption sites for Pb, which are attributed to phytoliths along with organic functional groups and inorganic oxides such as phosphate, carbonate, and other compounds in CFB. Thus, the specific objectives of this study were to: (i) quantify Pb^{2+} sorption by CFB500 in aqueous solutions; (ii)

determine the spatial distribution of Pb and correlated elements on Pb-loaded CFB500; (iii) explore the speciation and local coordination environment of Pb bound to inorganic components and organic functional groups of Pb-loaded CFB500; and (iv) reveal the sorption sites of Pb^{2+} offered by different compounds in CFB500 and establish the sorption model of CFB500 for Pb^{2+} in aqueous solution.

2. Materials and methods

2.1 Production of biochar

Coconut (*Cocos nucifera* L.) fiber was obtained from a coconut grove in the eastern suburbs of Wenchang (110.9°E, 19.6°N), Hainan Province, China and used for biochar production (Text S1 of the Supporting Information for details) based on the procedure in Wu et al (2016). In our previous studies (Wu et al., 2016; Wu et al., 2017), CFB produced at 500 °C (referred to as CFB500) was suggested to be used for further study of PTEs sorption mechanism, considering the cost of biochar preparation and the efficiency of biochar to remove Pb from aqueous solutions. Accordingly, coconut fiber was pyrolyzed under oxygen-limited conditions in an SX210-12 Muffle furnace with a heating rate of about 20 °C per min (Wu et al., 2016), and maintained at 500 °C for 4 h before cooling to room temperature. The biochar sample was passed through a 2 mm sieve and stored for further use.

Lead-loaded CFB500 was prepared by adding 0.5 g of biochar into 250 mL Pb^{2+} solution of 300 mg L^{-1} at pH 6.0 in a 500 mL Erlenmeyer flask. The pH of the solution was adjusted every hour using HNO_3 0.1 mol L^{-1} . The suspension was agitated on a thermostatic reciprocating shaker at 220 rpm and 25 °C for 24 h, and filtered using 0.45- μm cellulose-acetate membrane filter to collect the solids. The solids on the filter were then washed with ultrapure water, and air-dried at ambient temperature prior to desorption experiments and spectroscopic

analysis. The result of a preliminary study indicated that the highest Pb adsorption of CFB500 was achieved at Pb concentration of 300 mg L^{-1} and a CFB500: solution ratio of 1:500 (w/v).

2.2 Characterization of biochar

The pH of CFB500 was measured in a 1:20 (w/v) biochar to water suspension after stirring this mixture for 1 h (Wu et al., 2016). The ash content of CFB500 was determined according to the American Society for Testing and Materials (ASTM) method D1762-84 (2007). The cation exchange capacity of CFB500 was determined using the 1 M ammonium acetate (pH 7.0) method (Wu et al., 2017). The amounts of alkaline and acidic functional groups of CFB500 were determined by the Boehm titration method (Boehm, 1994). Specific surface area and Fourier transform infrared (FTIR) spectroscopy of the biochar were determined according to Wu et al. (2017). The total carbon (C), nitrogen (N), and hydrogen (H) contents were measured using an elemental analyzer (Vario EL III - Elementary Company, Germany).

Major elements (P, Mg, Ca, K, Na, S) were determined after melting digestion according to a standard method (Schmidt et al., 2016). One hundred mg of the biochar was weighed into a platinum crucible and thoroughly mixed with 1 g of lithium metaborate. The platinum crucible was placed in a SX210–12 Muffle furnace (Longkou Xian Ke Electricity Furnace Inc., Shandong, China), remaining at 1050°C in the oven for 15 minutes. The digestate was dissolved in 10% (w/w) hydrochloric acid and filled to a 250-mL volumetric flask and stored in polyethylene bottles for further analysis. Trace metals (Cu, Zn, Fe and Mn) were determined after microwave-assisted digestion according to Schmidt et al. (2016). One hundred mg biochar was placed in the reaction vessel of the microwave. Then, 6 ml of nitric acid, 2 ml of hydrogen peroxide and 0.4 ml of hydrofluoric acid were added to the vessel. The reaction vessel was sealed and placed in the microwave digester system (Sineo, MDS-6, Shanghai, China) and digested at 190°C for 15 min, and then holding at 190°C for 20

minutes. After complete cooling, the digestion solution was transferred to a 50-mL plastic volumetric flask and filled with deionized water. The concentrations of elements in filtrates and digested solutions were measured using an inductively coupled plasma mass spectrometer (ICP-MS, Thermo Fisher-X series).

2.3 Lead sorption and desorption experiments

In sorption kinetics, 500 mL of 300 mg L⁻¹ Pb²⁺ solution in 0.01 M NaNO₃ was placed in different reaction vessels and pre-adjusted to pH 3.0, 4.0, 5.0 and 6.0 following by addition of 1.0 g of CFB500, modified from Lu et al. (2012). The pH of solution was adjusted to the desired values every hour with HNO₃ 0.1 mol L⁻¹. Then, flasks were placed on a rotating shaker and agitated (220 rpm) at 25 °C for 24 h. A 5 mL aliquot was withdrawn from the suspension at given time intervals (10 min, 30 min, 60 min, 180 min, 360 min, 540 min, 900 min, and 1440 min) and filtered using 0.45-μm cellulose-acetate membrane filter. Lead concentrations in the filtrate were determined using an ICP-MS.

In sorption isotherms, 25 mL aqueous solution with different initial Pb concentrations (i.e., 50, 100, 200, 300, 400 and 500 mg L⁻¹) in 0.01 M NaNO₃ at different pH (3.0, 4.0, 5.0 and 6.0) was placed in each 50-mL plastic centrifuge tube following by addition of 0.05 g of CFB500, respectively, modified from Lu et al. (2012). The tubes were agitated on a rotating shaker at 220 rpm and 25 °C for 24 h. Finally, the solutions were filtered using 0.45-μm cellulose-acetate membrane filter. Concentrations of Pb in the filtrate were measured using an ICP-MS.

Sorption kinetics models the pseudo-first-order and the pseudo-second-order are showed in Eqs. 1 and 2, respectively (Lu et al., 2012).

$$q_t = q_e(1 - e^{-k_1 t}) \quad 1$$

$$t/q_t = 1/(k_2 q_e^2) + t/q_e \quad 2$$

where k_1 and k_2 are sorption rate constant of the pseudo-first order and the pseudo-second order in min⁻¹ and

$\text{min}^{-1} \cdot (\text{g mg}^{-1})$, respectively. While q_e and q_t are the values of the mass adsorbed per unit mass at equilibrium and at time “t” in mg g^{-1} , respectively.

Sorption isotherm models the Langmuir (1918) and the Freundlich (1939) are presented in Eqs. 3 and 4, respectively.

$$\text{Langmuir model : } q_e = kq_m C_e / (1 + kC_e) \quad 3$$

$$\text{Freundlich model : } q_e = K_F C_e^{1/n} \quad 4$$

where, q_e is the amount of Pb sorbed at equilibrium for a given initial concentration in mg g^{-1} , C_e is the concentration in solution at equilibrium in mg L^{-1} . And k is the Langmuir constant in L mg^{-1} , q_m is the maximum amount of Pb adsorbed at equilibrium in mg g^{-1} ; K_F and n are equilibrium constants relating to sorption capacity and sorption intensity of the Freundlich, respectively.

In order to estimate available Pb on Pb-loaded CFB500 to plants, 0.050 g of Pb-loaded CFB500 was reacted with 25 mL of different extraction solutions, 0.01 M NaNO_3 , 1.0 M citric acid, 0.05 M ethylenediaminetetraacetic acid (EDTA) and 1.0 M HCl in 50 mL plastic tubes on a reciprocating shaker at 220 rpm and 25°C for 24 h (Lu et al., 2012). The suspensions were centrifuged and the supernatant solutions were filtered using a cellulose-acetate membrane filter (0.45 μm) to collect the filtrates for the analysis of Pb concentration using ICP-MS.

To evaluate the environmental safety of Pb sorbed on CFB500, Pb fractionation of the Pb-loaded CFB500 was conducted using the sequential extraction method, modified from Tessier et al. (1979). The Pb-loaded CFB500 was extracted sequentially at room temperature to discriminate Pb into (i) exchangeable, (ii) Fe/Mn oxides bound, (iii) organic matter bound, and (iv) residual fractions.

2.4 Characterization techniques

2.4.1 Synchrotron-based micro-X-ray fluorescence (μ -XRF) spectroscopy

The Pb-loaded CFB500 without embedding was frozen at $-20\text{ }^{\circ}\text{C}$ and directly sectioned with a cryomicrotome (Leica CM1950) for μ -XRF analysis at beamline 15U1 of Shanghai Synchrotron Radiation Facility (SSRF). Thin sections ($30\text{ }\mu\text{m}$ thick) were subsequently freeze-dried for 48 h. Chemical images of Pb and several other elements in the thin sections were collected by scanning the samples under a monochromatic beam at 14 keV with a step size of $3 \times 3\text{ }\mu\text{m}^2$ and a dwell time of 5 sec (Sun et al., 2017).

2.4.2 X-ray diffraction (XRD) analysis

The crystalline components of CFB500 were examined using powder X-ray diffractometer (D8, Bruker AXS, Germany), equipped with a graphite monochromator in the diffracted beam (at 40 kV and 30 mA). The XRD pattern of the sample, which was packed into an aluminum holder, was collected in a 2θ range from 10° to 60° with a step size of 0.04° . The software of Jade 6 (Material Data, Inc.) was used to process the XRD pattern and identify the components in the sample.

2.4.3 X-ray absorption fine structure (XAFS) spectroscopy

Based on the total elemental analysis of Pb-loaded CFB500, reference compounds that might represent the binding sites for the sorption of Pb^{2+} were prepared. The XAFS spectra of Pb-loaded CFB500 and reference compounds were taken at room temperature on the 1W1B beamline at the Beijing Synchrotron Radiation Facility (BSRF), China. The XAFS measurements (Wu et al., 2017; Xiong et al., 2013) and data processing were conducted according to published methods (Hill, 1985; Ravel and Newville, 2005; Rehr et al., 1991). The detailed experimental procedures are shown in Text S3.

2.4.4 Scanning electron microscopy (SEM) combined with EDS

Surface morphology of CFB500 and Pb-loaded CFB500 were examined with scanning electron microscopy (SEM) (model S-3000N; Hitachi Company, Japan). The SEM combined with energy dispersive X-ray

spectroscopy (EDS) was employed to estimate the elemental compositions of the biochars.

2.5 Statistical analyses

Results are shown as the mean of three replicates per treatment and are expressed on a dry biochar basis. The Pearson correlation coefficients between Pb and other elements on Pb-loaded CFB500 were analyzed using SPSS 19 (IBM Corporation, USA). Statistical analysis was performed using SAS 9.1 (SAS Institute Inc., USA). The fitting of Langmuir and Freundlich models and the graphing of FTIR spectra were done using the software Origin 9.0 (Origin Lab, USA).

3. Results and discussion

3.1. Sorption-desorption experiments

Basic properties of the CFB500 are presented in Table S1 and Text S4 in Supporting Information. Fig. S1 in the Supporting Information presents the kinetics and isotherms of Pb²⁺ sorption on CFB500 at the initial pH of 3-6. The sorption kinetics of Pb²⁺ on CFB500 can be expressed well by the pseudo-second-order model (Table S2). Because Pb sorption on CFB500 required several hours to reach the equilibrium, electrostatic interaction, which reaches equilibrium in few minutes, may play an insignificant role in the Pb sorption reaction (Lu et al., 2012). The sorption isotherms of Pb²⁺ on CFB500 were found to be well fitted by the Langmuir model (Table S3 and Text S5), indicating the occurrence of a sorption maximum (Wu et al., 2017). The Langmuir- q_m value of CFB500 was 89.7 mg g⁻¹ for Pb, which was higher than the value (i.e., 81.9 mg g⁻¹) of raw sugarcane bagasse biochar (another fiber biochar; Inyang et al., 2011) and most of those of non-modified biochars, ranging from 2.25 to 175.4 mg g⁻¹ (Table S4). Sorption of metal ions is more effective when the adsorbent has low zeta potential (Jiang et al., 2012); Meanwhile, the zeta potential of biochars would decrease

with increasing pH value in solution (Fahmi et al., 2018). The lower zeta potential is attributed to an increase in negative charges and a decrease in positive charges on the surface of a sorbent. With an increase in solution pH, the increase in net negative charges on the surface of CFB500 facilitates the sorption of Pb^{2+} ions, and consequently the Langmuir- q_m value of CFB500 for Pb increased.

Several agents were used to extract Pb on the Pb-loaded CFB500 (details in Text S5). As shown in Table 1, Pb released from the Pb-loaded CFB500 by 1.0 M HCl, 0.05 M EDTA and 1.0M citric acids solutions were 34.0, 35.1 and 21.1 mg g^{-1} , respectively. The desorbing agent 0.05 mol L^{-1} EDTA presented to be a strong extractant for Pb. The EDTA-extractable concentrations of Pb from solid samples are potential available, while the residual fraction of those elements is regarded as non-available for plant uptake in natural environments (Feng et al., 2005).

3.2. Sequential extraction of Pb from the Pb-loaded CFB500

The amount of Pb sorbed on CFB500 was determined to be 66.5 mg g^{-1} (Table 1). As revealed by the results of sequential extraction, the two major Pb fractions in the Pb-loaded CFB500 were exchangeable Pb (27.1 mg g^{-1}) and organic-bound Pb (35.4 mg g^{-1}), accounting for 40.7% and 53.2% of the total sorbed Pb (Fig. S2). Small amounts of Fe/Mn oxides bound (0.21 mg g^{-1}) and residual (3.82 mg g^{-1}) Pb fractions were detected (accounting for 0.32% and 5.78%, respectively). The bioavailability and mobility of PTEs are related to their fractions in the natural environment (Maiz et al., 2000). The PTEs in exchangeable and Fe/Mn-oxide bound pool fractions are relatively mobile and, therefore, have a higher risk for plant uptake and animal/human consumption (Ratuzny et al., 2009). The organic-bound and residual fractions of heavy metals are considered to have a lower environmental risk compared with other fractions. The relatively stable fractions (organic bound and residual) of

Pb on Pb-loaded CFB500 make up approximately 60%, indicating that CFB500 can effectively immobilize Pb^{2+} in solutions.

Desorption results showed that Na^+ , K^+ , Ca^{2+} and Mg^{2+} of CFB500 were released during the Pb sorption on the CFB500 (Table 1). The amounts of the released Na^+ , K^+ , Ca^{2+} and Mg^{2+} were equivalent to 3.83, 6.42, 3.11 and 6.63 mg g^{-1} of the sorbed Pb on the basis of ionic charges, which accounted for 5.76%, 9.65%, 4.68%, 9.97% of the total sorbed Pb on Pb-loaded CFB500, respectively (Fig. S2). These cations were released from the exchange sites of mineral oxides and various functional groups of inorganic and organic compounds on biochars (Xu et al., 2013; Lu et al., 2012). Thus, ion-exchange, chelating and surface complexation reactions may occur during the sorption of Pb by CFB500, leading to the releases of Na^+ , K^+ , Ca^{2+} and Mg^{2+} . The occurrences of these reactions will be further verified in Section 3.3 and 3.4.

3.3. Spatial distributions of Pb and mineral elements on Pb-loaded CFB500

In general, Pb and mineral elements (K, Ca, Cu, Mn and Fe) were distributed heterogeneously on the surface of the Pb-loaded CFB500 (Fig. 1). As revealed by the image of μ -XRF spectroscopy, higher concentrations of Pb were observed mainly in the regions of a, b and c on Pb-loaded CFB500 (Fig. 1A). However, mineral elements K, Ca, Cu, Fe and Mn had a contrary distribution pattern with Pb, i.e., lower concentrations in the regions a, b and c on Pb-loaded CFB500 (Fig. 1B-F). According to the Pearson correlation coefficient, Pb was significantly related with K (0.916**), Ca (0.422**), Cu (0.926**), Fe (0.238**), Mn (0.682**). Although K, Ca, Cu, Fe and Mn were also heterogeneously distributed on Pb free CFB500 (Fig. S3), there is no significant correlation between the spatial distributions of these elements on CFB500.

The main reason for the negative correlation between the distributions of Pb and other cations may be that

mineral elements like K, Ca, Cu, Fe and Mn were exchanged by sorbed Pb and consequently released into solution during the Pb sorption of CFB500 (Lu et al., 2012). It was found that Na^+ , K^+ , Ca^{2+} , Mg^{2+} were released during the Pb sorption on CFB500 (Table 1). Thus, sorbed Pb ions replaced these cations on the surface binding sites of CFB500, leading to the decreases of their contents in the regions where Pb ions were accumulated in the μ -XRF image.

A previous study reported that the surface of magnetic biochar derived from eucalyptus leaf residue contained reversible sorption sites, which could contribute to exchangeable Pb fraction on Pb-loaded biochar. Upon the release of K, Ca, and Fe from the surface of the biochar, more reusable sorption sites were exposed to Pb ions in solution (Wang et al., 2015). Deashing experiment of Sun et al. (2013) on biochar structural properties revealed that the removal of mineral elements in biochars resulted in more sorption sites on the biochars. Similarly to our finding, a portion of the sorption sites associated with mineral elements K, Na, Ca, and Mg were transferred to Pb during the sorption of Pb by sludge-derived biochar (Lu et al., 2012). In order to clarify the Pb sorption mechanism of CFB500, it is necessary to determine the exact Pb species on Pb-loaded CFB500 and identify the compounds that provide sorption sites for Pb.

3.4. Pb speciation on Pb-loaded CFB500

Elemental analysis showed that CFB500 was rich in C, Si and P, which were 760 g kg^{-1} , 6.47 g kg^{-1} and 2.55 g kg^{-1} , respectively (Table S1). The presence of these elements lead to the hypothesis that Pb sorption by biochar may be attributed to the formations of Pb-carbonate or Pb-organic carbon groups, Pb-silicate and Pb-phosphate precipitates, which were confirmed using X-ray diffraction (XRD) and X-ray absorption fine structure (XAFS) analysis (Fig. 2 and 3).

The XRD pattern of CFB500 exhibits only a broad peak, indicating the presence of amorphous materials. Comparatively, several diffraction peaks appeared in the XRD pattern that of Pb-loaded CFB500 (Fig. 2). The diffraction peaks in Pb-loaded CFB500 were contributed by inorganic crystalline components, including lead silicate (PbSiO_3 ; 4.25 Å), lead phosphate ($\text{Pb}_3(\text{PO}_4)_2$; 4.46 Å and 3.61 Å) and hydrocerussite ($\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$; 3.34 Å, 2.62 Å, and 2.23 Å), based on the Powder Diffraction and Standards (PDF). Lead phosphate ($\beta\text{-Pb}_9(\text{PO}_4)_6$) and hydrocerussite ($\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$) were previously reported to exist in Pb-loaded dairy-manure derived biochar (BC) as revealed by XRD analysis (Cao et al., 2009).

The peak position and peak shape of the EXAFS spectra of Pb-loaded CFB500 were similar to those of the Pb reference materials, including $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$, PbSiO_3 , $\text{Pb}_3(\text{PO}_4)_2$, PbCO_3 and Pb-loaded goethite (Fig. 3a), but they were different from those of PbSO_4 , PbS, Pb-loaded Al_2O_3 and PbO (Fig. S4). The best fit of Pb-loaded CFB500 (red line) is presented in Fig. 3a. The relative contents of Pb species with a similar structure to $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$, $\text{Pb}_3(\text{PO}_4)_2$, PbSiO_3 , PbCO_3 , and Pb-loaded goethite were determined to be 43.8%, 33.2%, 12.0%, 7.3%, and 3.6%, respectively (Table 2). These Pb species may be contributed by the sorption of Pb on the organic functional groups (e.g., $-\text{OH}$, $-\text{COOH}$, $\text{C}=\text{O}$), phosphate, silicate, $-\text{CO}_3$ like inorganic compounds and iron oxide in CFB500. In particular, the predominance of $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ and $\text{Pb}_3(\text{PO}_4)_2$ in Pb-loaded CFB500 may be attributed to the high contents of carboxyl functional group and phosphorus in CFB500.

Our EXAFS data was slightly different from those of Wu et al. (2017), showing that the five most predominant Pb species in Pb-loaded chemically modified CFB were $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$, $\text{Pb}_3(\text{PO}_4)_2$, Pb-loaded montmorillonite, PbSO_4 and Pb- Al_2O_3 . Indeed, Pb-loaded montmorillonite is a type of lead silicate similar to PbSiO_3 . However, few studies presented XAFS results of Pb species on Pb-loaded biochars independently (Wu et al., 2017). Nevertheless, some researchers have found that phosphate, clay minerals and oxides (such as Al/Fe/Mn-OH), $-\text{CO}_3$ and oxygen-containing functional groups exist in dairy manure-derived and

sludge-derived biochars, and their contents in the biochars determine the sorption capacity of the biochars for Zn, Cd and Pb (Xu et al., 2013; Lu et al., 2012). Similar with our results, inorganic components such as KCl, CaCO_3 , silicate, phosphate and abundant organic groups in rice straw-derived biochar could also contribute to the sorption of PTEs (Wu et al., 2012).

The LCF results of EXAFS spectra of Pb-loaded CFBs (CFB300, CFB500 and CFB700) are presented in Table 2. The relative contents of Pb species on Pb-loaded CFBs, indicating Pb-carbonate (PbCO_3), Pb-silicate (PbSiO_3) and Pb-mineral iron oxides (Pb-loaded FeOOH), increased with the increasing pyrolysis temperature of CFBs; Contrarily, Pb-phosphate ($\text{Pb}_3(\text{PO}_4)_2$) and Pb-organic carbon functional groups (with similar structure to $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$) decreased with the increasing temperature. These changes in the contents of Pb species may be attributed to the loss of sorption sites of phosphate and organic carbon functional groups and the increase of silicate, carbonate and mineral oxides sorption sites on CFBs for Pb with the increasing charring temperature. Previous studies showed that the organic functional groups of O–H, C=O, C=C and available P on biochar were reduced, while content of CaCO_3 , ash (mineral oxides contained) and groups of O–Si–O were raised with increasing pyrolysis temperature (Wu et al., 2012; Wu et al., 2016). The adsorption capacity of biochar (for Pb) commonly increased with increasing pyrolysis temperature (Wu et al., 2017; Shen et al., 2019). Similarly, the Pb species on Pb-loaded rice-straw biochar was significantly different under different pyrolysis temperatures: lead oxalate (PbC_2O_4) was precipitated on biochar produced at 300 °C, and hydrocerussite ($(\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2)$) was precipitated on biochar produced at 500 and 700 °C, attributing to the decomposition of calcium oxalate (CaC_2O_4) and the formation of calcite (CaCO_3) on rice-straw biochar with the increase of pyrolysis temperature (Shen et al., 2019).

It was noticed that $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$ was the exact Pb species on CFB500, rather than the distinct PbCO_3 and $\text{Pb}(\text{OH})_2$ phases. XAFS technique provides only the percentage of Pb forms a similar structure to reference

compounds of lead on Pb-loaded biochar (Wu et al., 2017), but XRD technique can be used to obtain the crystal structure information of the corresponding Pb species (Lu et al., 2012). Lead was present mainly as Pb^{2+} , $\text{Pb}(\text{OH})^+$, and $\text{Pb}(\text{OH})_2^\circ$ at pH near 5.5 in natural aquatic system (Ucun et al., 2003); thus, Pb^{2+} , $\text{Pb}(\text{OH})^+$, and $\text{Pb}(\text{OH})_2^\circ$ can all sorbed by CO_3^{2-} on CFB500 in aqueous solution since Pb-loaded CFB500 was prepared at pH 6, which may promote the formation of $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$. Similarly, $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$ (hydrocerussite) was also a dominant Pb species on Pb-loaded dairy-manure derived biochar pyrolyzed at 350 °C and rice-straw biochar produced at 500 °C (Cao et al., 2009; Shen et al., 2019).

3.5. Coordination environment of Pb on Pb-loaded CFB500

The shape and position of Pb–O shell (black dashed line) (Xia et al., 1997) in Fourier transform EXAFS spectra of Pb-loaded CFB500 were similar to those of $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ and $\text{Pb}_3(\text{PO}_4)_2$ (Fig. 3b), indicating that the oxidation state of Pb did not change upon binding to CFB500 (Xiong et al., 2013); and the bonding configurations of the predominant Pb species in Pb-loaded CFB500 were similar to those of $\text{Pb}_3(\text{PO}_4)_2$ and $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ (Rajaram and Rao, 1982). The results indicated that Pb is mainly bound to the functional groups of CFB500 through inner-sphere complexation with a structure of P–O–Pb and C–O–Pb or C–O–Pb–O–C (Lu et al., 2012; Xiong et al., 2013). Consistent with our findings, phenolic and carboxylic groups of biochar were the dominant binding sites for heavy metals (Lu et al., 2012); and Pb complexation to phenolic or carboxylic groups in humic substances could lead to the formation of inner-sphere complexes with C and O atoms (Xiong et al., 2013). Qin et al. (2014) found that the P atom is tetrahedrally coordinated by O atoms and Pb atoms occupy two types of metal sites, which can be characterized as $\text{PO}_4\text{--Pb}(2)\text{O}_{10}\text{--Pb}(1)\text{O}_{12}\text{--Pb}(2)\text{O}_{10}\text{--PO}_4$ in the direction of c-axis within $\text{Pb}_3(\text{PO}_4)_2$ crystal, and $[\text{PO}_4]^{3-}$ groups were basically incompressible units.

As revealed by the shell fitting of the EXAFS spectra, the Pb atom is coordinated with two O atoms at a distance of 2.36 Å, and two other O atoms at a distance of 2.58 Å (Table S5). Previous studies showed that the Pb-O bond distance with a bidentate configuration is 2.59–2.74 Å in the crystal structure of $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ (Bryant et al., 1985). In the crystal structure of PbSiO_3 , Pb atoms are coordinated to oxygen atoms, with one or two distances in the range of 2.45–2.60 Å and the other two in the range of 2.23–2.31 Å (Boucher and Peacor, 1968). The Pb atoms in $\text{Pb}_3(\text{PO}_4)_2$ possess lone-pair electrons, which could affect the bond polarizabilities such as the $\text{P}-\text{O}_\text{p}-\text{Pb}$ linkages (Mihailova et al., 2001). With similar bonding distances, it is plausible to suggest that the Pb-O-C, Pb-O-Si and Pb-O-P chains occurred in the coordination environment of Pb in Pb-loaded CFB500.

The FTIR spectra of CFB500 and Pb-loaded CFB500 were obtained to gain information about the binding mechanism of Pb with the organic functional groups on CFB500 (Fig. 4). The vertical dashed lines represent peak positions of specific functional groups on CFB500 (Fig. 4). The spectral bands at 1730–1690 cm^{-1} indicated C=O stretching of carboxyl (Lin et al., 1999). In the range of 1620 and 1580 cm^{-1} , the peak at 1587 cm^{-1} assigned to a smaller extent to C=O stretching of β -diketone ligands in aromatic rings (Chen et al., 2008). The peak at 1384 cm^{-1} might correspond to the bending vibration of the carboxylate ion, in the range of 1380 and 1400 cm^{-1} (Vergnoux et al., 2011). Peaks between 1273 and 1246 cm^{-1} were due to the C-O stretching vibration of the ester group or anhydride C-O-C stretching vibration (Lin et al., 1999).

Compared with CFB500, the FTIR spectrum of Pb-loaded CFB500 showed the increasing intensities of carboxylate ion vibration at 1384 cm^{-1} and the C=O stretching of β -diketone ligands ($-\text{COCH}_2\text{CO}-$) at 1587 cm^{-1} (Fig. 4; Vergnoux et al., 2011). These may be contributed by the formation of Pb-carboxylate after the sorption of Pb to CFB500. Similarly, the increased intensity at 1384 cm^{-1} of coconut-fiber derived biochar after Pb sorption was previously attributed to the chelation of Pb with carboxyl groups on the biochar (Wu et al.,

2017).

The FTIR spectra of CFB500 before and after Pb sorption showed that anhydride C–O–C stretching vibration at 1257 cm^{-1} decreased after Pb sorption, but, at the same time, the change in the intensity of carboxyl-C=O stretching at 1695 cm^{-1} was insignificant (Fig. 4). It could be attributed to the release of carboxyl groups through the hydrolysis of anhydride on CFB500. Carboxyl groups could be produced during the hydrolysis of the carboxylic acid anhydride on biochars, which proceeds slowly in aqueous solution (Qian et al., 2014). Thus, when a large number of carboxyl groups on CFB500 were consumed by chelating Pb, carboxylic acid anhydride on CFB500 would be hydrolyzed to produce carboxyl groups, which offered the loss in the sorption sites of carboxyl groups for Pb to form Pb-carboxylate surface complexes. In succession, C–O–Pb–O–C structures (attributing to double carboxyl groups) chelate with Pb as shown in Scheme S1 or S2 formed during the sorption of Pb on CFB500.

The strong intensity of the carboxylate ion vibration at 1384 cm^{-1} in the FTIR spectrum of CFB500 revealed that carboxylate ion was abundant and was bound to cations such as K^+ , Na^+ , Ca^{2+} and Mg^{2+} on CFB500 (Lu et al., 2012). Sorbed Pb ions could replace these cations on CFB500 to form C–O–Pb–O–C structures. Muhanna et al. (2012) reported that carboxyl groups could provide efficient sorption sites for Pb^{2+} , Cd^{2+} , Cu^{2+} , Ni^{2+} , and Zn^{2+} . Similar to our research, the stable five-membered and six-membered rings structures containing C–O–Pb–O–C were detected after Pb reacted with carboxylic acid groups on humic substances (Xiong et al., 2013).

The C–O–Pb–O–C structure is stable (Basolo and Johnson, 1964), so the chelating of sorbed Pb to carboxyl groups could play an important role in the non-bioavailable Pb fractions on Pb-loaded CFB500. Interestingly, Li et al. (2018b) also revealed that Pb was readily chelated by two –COOH groups to form the

structure of $(-O-C=O)_2Pb$ during Pb sorption to MgO hybrid sponge-like carbonaceous material. Another research showed that the MgO@N-biochar has a high performance for sorbing Pb mainly due to the surface coordination of Pb and $O=C-O$ or $C=O$, pyridonic, pyridinic, and pyrrolic N (Ling et al., 2017).

3.6. Sorption capacity of micro-regions on CFB500 for Pb

Rugged surface, honeycomb-like micropores and carbon skeleton like fibrous texture were observed on Pb-loaded CFB500 (Fig. 5). Dramatically, tiny aggregates could also be found on Pb-loaded CFB500, as presented inside the red circular region (Fig. 5). The tiny aggregate was then determined to contain a large amount of Si using EDS (region “a” in Fig. 5). The EDS results of four representative regions corresponding red square regions a, b, c and d on Pb-loaded CFB500 in Fig. 5 are shown at the right half part of Fig. 5.

The major part of the region “a” on Pb-loaded CFB500 was a small aggregate. The weight percentage contents of element C, O, Si and Pb were 68.7, 19.72, 9.07 and 2.50 in the region “a”, respectively. The region “b” on Pb-loaded CFB500 mainly contained a bigger mineral oxide aggregate, which is different from the small aggregates in the region “a” and contained much more elements than other regions (Fig. 5). Elements such as C, O, S, P, Ca and Pb appeared in the large mineral oxide aggregate on the surface of Pb-loaded CFB500, and accounted for 62.88, 32.82, 1.27, 0.71, 1.10 and 1.21% (weight percentage), respectively. The region “c” was a part of the micropore inner-wall of carbon skeleton on Pb-loaded CFB500 (Fig. 5). Only C, Si and S could be found in the region “c”, and accounted for 96.41, 2.75 and 0.84%, respectively. The red region “d” was a part of the outer-wall of carbon skeleton on Pb-loaded CFB500 (Fig. 5). The weight percentage contents of element C, O, P, Si and Pb in the region “d” were 76.35, 15.28, 0.83, 0.89 and 5.34%, respectively.

After a detailed analysis, we found that the atomic percentage content of element O in the region “b” was

14.83 more than that in region “d”; contrarily, the atomic percentage content of element C in the region “b” was 14.43 less than the region “d”. This indicates that the mineral oxide content in the large aggregate was more than that in the outer-wall of carbon skeleton on Pb-loaded CFB500, while the organic groups in outer-wall of carbon skeleton were higher than those in big aggregate on Pb-loaded CFB500.

The atomic percentage content of Pb in the region “d” was four times higher than that in the region “b” (Fig. 5), indicating the ability of binding sites to adsorb Pb provided by outer-wall of the carbon skeleton, which was stronger than that provided by mineral oxide aggregate on Pb-loaded CFB500. It was found that the atomic percentage content of element C in the region “a” was 6.96 less than that in the region “d” but element O in the region “a” was 4.05 more than that in the region “d”; but the atomic percentage content of Si in the region “a” was almost 10-times higher than that in the region “d”. The atomic percentage of Pb in the region “a” was less than half of that in the region “d”. This suggests that the Pb affinity of the binding sites provided by silicon oxide aggregate of phytoliths was weaker than that provided by outer-wall of the carbon skeleton on Pb-loaded CFB500. Lead did not exist in micropore inner-wall of the carbon skeleton on Pb-loaded CFB500, indicating that the Pb sorption of CFB500 mainly occurs on outer-wall of carbon skeleton – seldom on the micropore inner-wall of carbon skeleton. Wu et al. (2017) also found the phytoliths on CFB in their SEM results, and discovered silicate sorption sites (i.e., montmorillonite) on CFB to sorb Pb^{2+} in aqueous solution. However, they did not reveal the association between the PbSiO_3 and the Pb species sorbed by phytoliths on CFB.

3.7. Sorption sites on CFB500 for Pb

Percentage content of Si in the region “a” was notably higher than that in other regions, which suggests that the small aggregate in the region “a” on Pb-loaded CFB500 was a silicon oxide aggregate or phytoliths. Houben et al. (2014) confirmed the presence of Si-rich phytoliths in *Miscanthus* straws derived–biochar based on the

SEM-EDS analysis. Only the large mineral oxide aggregate on the surface of Pb-loaded CFB500 did not contain Si, which indicates that silicon-containing compounds and silicon oxides were embedded in carbon skeleton (Catinon et al., 2009).

Phytoliths particles were abundant on CFB500 (Fig. S5) and Pb-loaded CFB500 (Fig. 5) as shown by the SEM observation. Meanwhile, these phytoliths on CFB500 have a high capacity to sorb Pb (Fig. 5). The Pb-loaded phytoliths may also have a significant contribution to Pb fractions in Pb-loaded CFB500 like PbSiO_3 and albeit, which were not included in the reference compounds for the EXAFS analysis of Pb-loaded CFB500. Instead, we tested another reference compound PbSiO_3 , which was also rich in Si. The Pb species of PbSiO_3 accounted for 12 % Pb on Pb-loaded CFB500 (Table 2); thus, it is plausible that silicate was the main compound of phytoliths on CFB500 to offer sorption sites for Pb.

Similar with our results, previous studies reported that some elements and carbon of phytoliths are released when rice husk and wheat husk are burnt at a certain temperature in air, resulting in the formation of leaving silicates or silicon dioxide (SiO_2) as the major component of the end product (Qadri et al., 2017; Xiong et al., 2009). However, few researchers have reported the sorption of PTEs by phytoliths, except several studies on the sorption of silicate for PTEs. Sodium silicate (magadiite) has a much higher affinity for Cu^{2+} , and the copper ions are probably strongly bound to the terminal Si–O groups (Mokhtar et al., 2018). Lead is sorbed onto tricalcium silicate and calcium silicate hydrate structure via the formation of Pb–O–Si bonds as revealed by $\text{L}_{3\text{-edge}}$ XAFS analysis (Rose et al., 2000).

The EDS spectrum results, corresponding to the red square regions in Fig. 5, further confirmed the presence of C, P and Si, which existed the structures similar to PbCO_3 or $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$, lead carboxylate ($\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$), $\text{Pb}_3(\text{PO}_4)_2$ and PbSiO_3 on Pb-loaded CFB500 (Fig. 3 and Table 2). These Pb species accounted

for 95% of total Pb in Pb-loaded CFB500 (Table 2). Thus, the Pb precipitation of inorganic carbonates, organic carbon groups, phosphates and silicates could be a significant mechanism for the removal of Pb^{2+} from the aqueous solution by CFB500 at initial pH 6.

Adsorption and desorption study of 20 kinds of biochars by Zama et al. (2017) reported that the sorption of Pb, Cd and As was characterized by biochar skeleton sorption with a distribution of sorption sites on the surface of the biochars. Similar to our results, Zama et al. (2017) also found organic functional groups (e.g., $-\text{COOH}$, $\text{C}=\text{O}$, $\text{C}-\text{X}$), inorganic minerals (CaCO_3 , SiO_2 , $\text{Ca}_2\text{Si}_5\text{O}_{10}\cdot 3\text{H}_2\text{O}$) and cations (K^+ , Ca^{2+} , Mg^{2+} , Na^+) controlled Pb, Cd and As sorption significantly. The sorption of Pb to these groups might be attributed to the strong chelating ability of organic functional groups on the outer walls of carbon skeletons of biochar for Pb. Wang et al. (2015) observed that oxygen-containing organic functional groups on KMnO_4 treated hickory wood biochar could chelate heavy metals rapidly. It might also be the reason that outer-wall of the carbon skeleton on CFB500 sorbed high level of Pb (Fig. 5), and lead carboxylate (e.g., $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$) species of accounted for 43.8% of Pb in Pb-loaded CFB500 (Table 2).

It appears that CFB500 has some potential to be used as a safe and efficient material for heavy metal remediation. Further research is required to delineate the molecular structure of phytoliths (special silicate) on CFB500 and its sorption characteristic for Pb to bring insights into the sorption mechanism of PTEs to CFB500 or other biochars that are rich in Si. Synchrotron radiation FTIR (SR-FTIR) and μ -XRD are also powerful analytical tools for characterizing the distribution of organic carbon (OC) forms and clay minerals in environmental matrices (Luo et al., 2014). Thus, a combined of μ -XRF, μ -XAFS, SR-FTIR and μ -XRD spectroscopy is expected to provide further information about the sorption mechanisms of PTEs on biochars, and the performance of biochar in removing or immobilizing PTEs in more complex matrices, such as soils.

4. Conclusions

Heterogeneous distribution of sorbed Pb was significantly related to the K, Ca, Mn, Fe and Cu in Pb-loaded CFB500. The major Pb species on the Pb-loaded CFB500 were determined to be lead carboxylate (e.g., $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$), $\text{Pb}_3(\text{PO}_4)_2$, PbSiO_3 , and PbCO_3 , accounted for 43.8%, 33.2%, 12.0%, and 7.3%, respectively. The precipitation of Pb^{2+} with CO_3^{2-} and OH^- resulted in the formation of $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$ precipitate on the surface of Pb-loaded CFB500. Silicates were the dominant Pb sorption sites on phytoliths in CFB500. The Pb–O–C or C–O–Pb–O–C, Pb–O–Si, Pb–O–P chains occurred in the atomic environment around Pb in Pb-loaded CFB500. The organic carbon groups, inorganic carbonates, silicates, and phosphates on CFB500 were the predominant sorption sites for Pb.

The conceptual model of Pb sorption mechanisms on CFB500 was divided into the following three parts: (1) cation exchange - Pb exchanged with Na^+ , K^+ , Ca^{2+} , Mg^{2+} and other cations in mineral oxides, inorganic compounds and organic carbon skeleton of CFB500; (2) complexation with functional group - surface complexation with free carboxyl and hydroxyl functional groups, resulting in the formation of C–O–Pb–O–C (or C–O–Pb) chain or ring structures; (3) other sorption processes - physical sorption, inner sphere complexation with the free hydroxyl of phytoliths carbon skeleton (mainly owe to silicates), phosphates and mineral oxides, and other surface precipitation.

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Table 1

The equivalent amount of Pb on Pb-loaded biochar (CFB500)

The amount of Pb fractions on Pb-loaded biochar (mg g ⁻¹)				Total Pb ²⁺
Exchangeable	Fe/Mn oxides	Organic matter	Residual	sorbed (mg g ⁻¹)
27.1 ± 0.57	0.21 ± 0.016	35.4 ± 1.3	3.82 ± 0.3	66.5
Equivalent of sorbed Pb ²⁺ by released cations (mg g ⁻¹)				Total Pb ²⁺
K ⁺	Na ⁺	Ca ²⁺	Mg ²⁺	sorbed (mg g ⁻¹)
6.42 ± 0.27	3.83 ± 0.25	3.11 ± 0.29	6.63 ± 0.31	66.5
Equivalent of desorbed Pb ²⁺ with extracting agents (mg g ⁻¹)				Total Pb ²⁺
Water	1.0 M Citric acid	0.05 M EDTA	1.0 M HCl	sorbed (mg g ⁻¹)
0.87 ± 0.03	21.2 ± 0.50	34.0 ± 1.41	35.1 ± 0.88	66.5

Results are means ± SD (n = 3).

Table 2

Percentage of Pb-species in Pb-loaded CFBs determined by linear combination fittings on EXAFS spectra

Sample ID	Pb ₃ (PO ₄) ₂	Pb-loaded goethite	PbCO ₃	Pb(OH) ₂	PbSiO ₃	Pb(C ₂ H ₃ O ₂) ₂	R	χ^2
CFB300	39.8	3.8	3.7	--	6.8	45.9	0.132	0.042
CFB500	33.2	3.6	7.3	--	12.0	43.8	0.11	0.026
CFB700	30.1	13.4	14.9	3.8	9.9	27.9	0.09	0.021

Note: CFB300, CFB500 and CFB700 refer to coconut fiber biochar pyrolyzed at 300, 500 and 700 °C, respectively. R-factor is the comparative goodness of fit, and χ^2 is the measure of the absolute goodness of fit.

Fig. 1. The microscope photos and μ -XRF maps of Pb, K, Ca, Cu, Mn and Fe distribution within Pb-loaded coconut fiber biochar (CFB500) particles. Higher fluorescence intensities are nearer to red and lower intensities (corresponding to lower concentrations) are nearer to blue according to the color bars. (a–c) represent the selected regions of interest.

Fig. 2. (a) Powder X-ray diffraction patterns of CFB500 and Pb-loaded CFB500. (b) The energy dispersive X-ray spectrogram of Pb-loaded CFB500, and the atomic percentage and the weight percentage of different elements in Pb-loaded CFB500.

Fig. 3. (a) The Pb $L_{3\text{-edge}}$ k^3 -weighted (the red line is the best linear combination fitting result of Pb-loaded CFB500) and (b) Fourier transformed (right, no phase shift correction) EXAFS data of Pb-loaded CFB500 and reference compounds.

Fig. 4. The FTIR spectra of CFB500 and Pb-loaded CFB500.

Fig. 5. The SEM photograph (with Pb sorption mechanisms) and SEM–EDS spectra of Pb-loaded CFB500 at initial pH 6. The EDS spectra of (a), (b), (c) and (d) correspond to the red square regions inside “a”, “b”, “c” and “d” in the SEM photograph.

Highlights

- Distribution of Pb in Si-rich coconut biochar was related to K, Ca, Cu, Mn and Fe.
- Lead carboxylate, $\text{Pb}_3(\text{PO}_4)_2$, and PbSiO_3 were major Pb species on Pb-loaded biochar.
- Silicates were the dominant sorption sites on biochar's phytoliths for Pb^{2+} .
- Pb^{2+} was mainly sorbed by organic skeleton of biochar with a C–O–Pb or C–O–Pb–O–C.

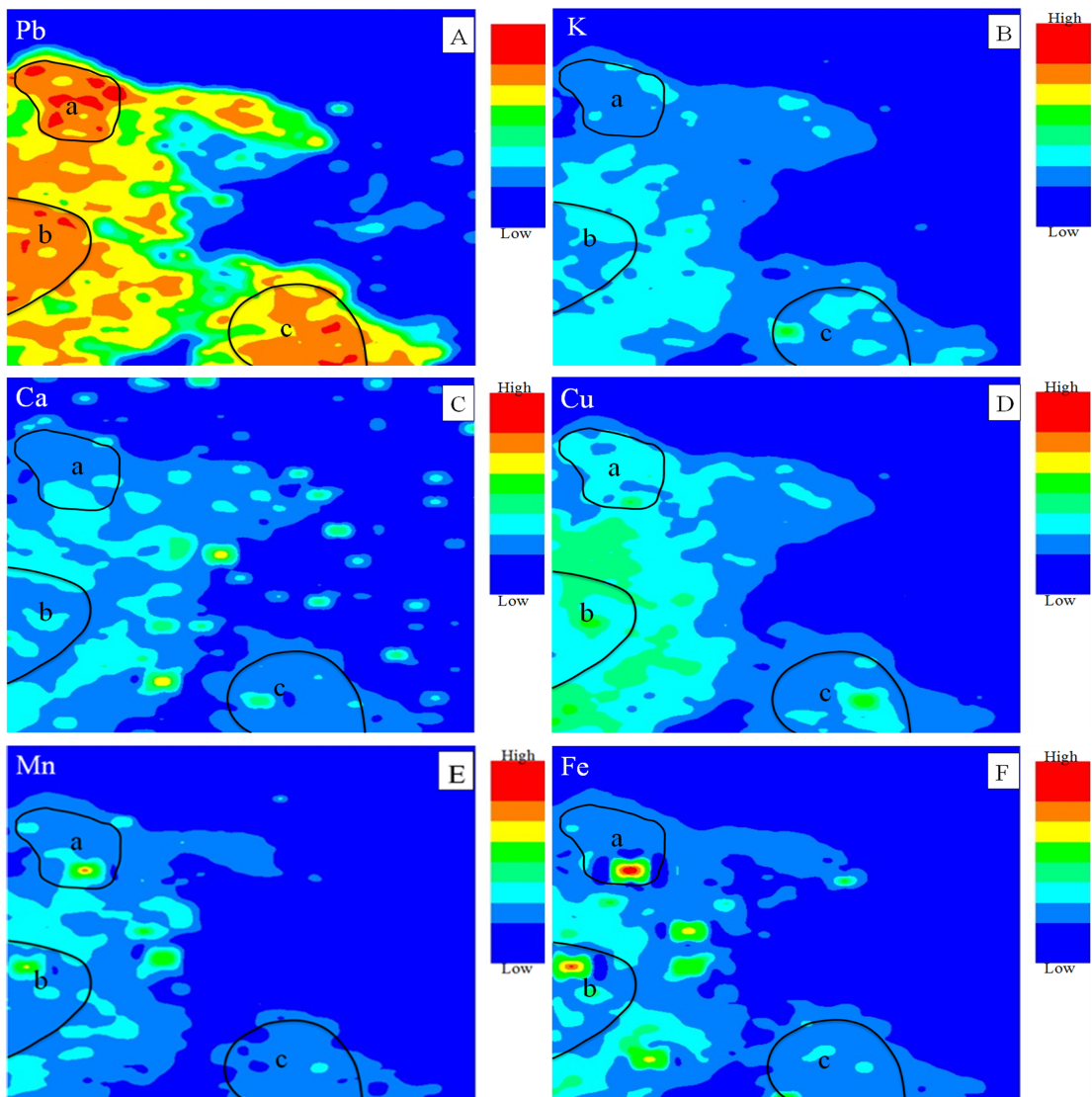
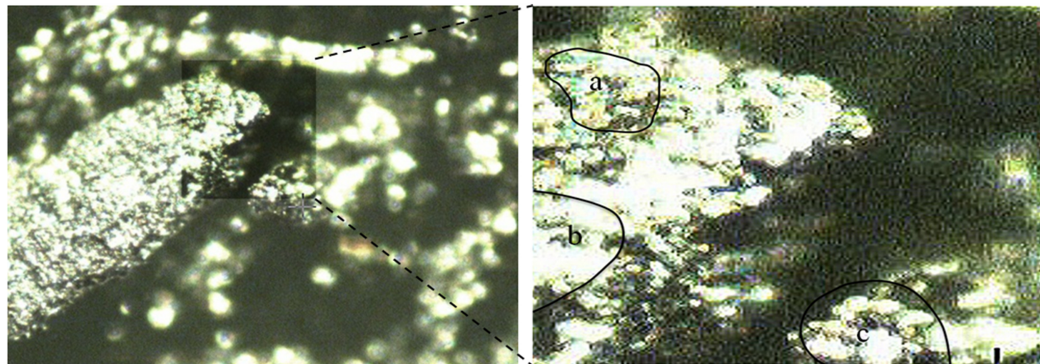


Figure 1

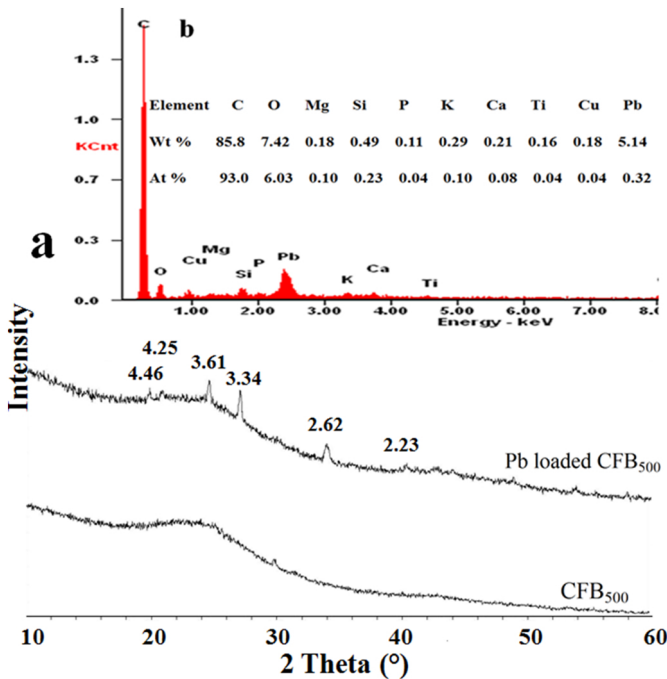


Figure 2

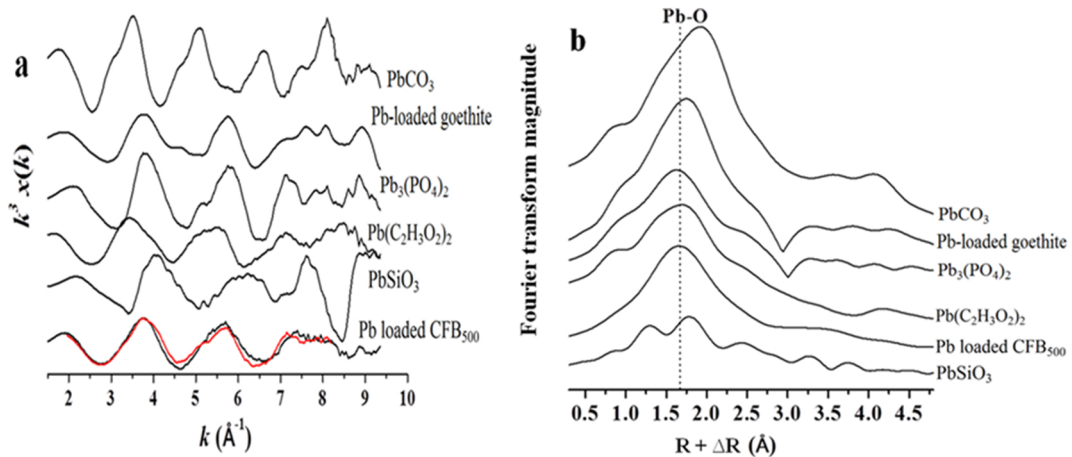


Figure 3

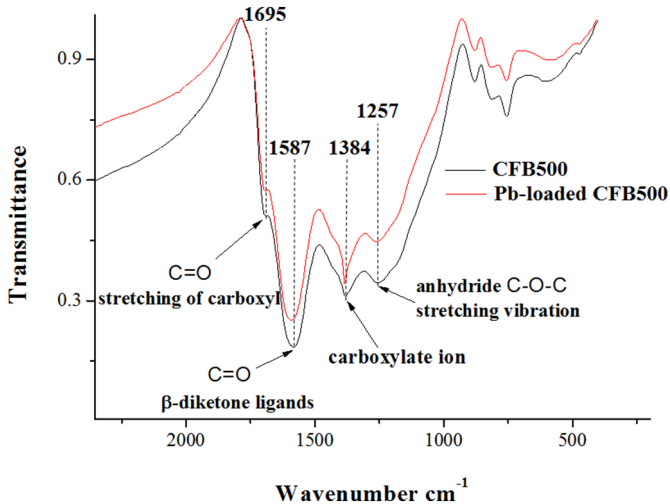


Figure 4

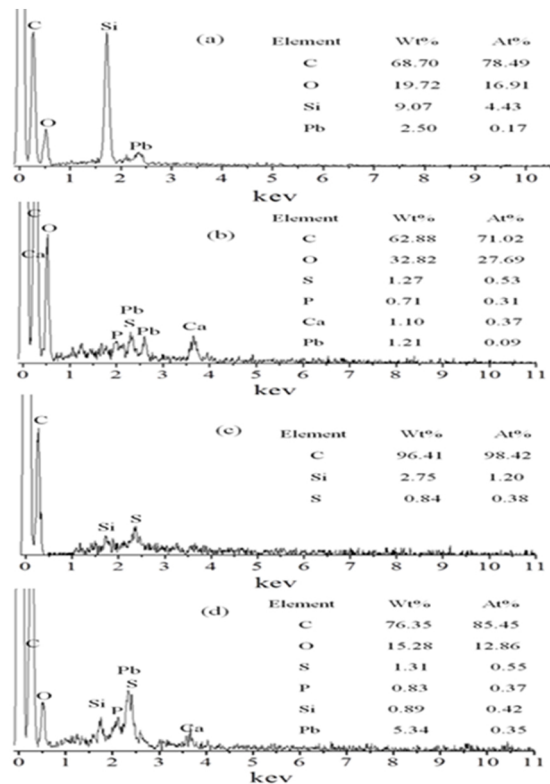
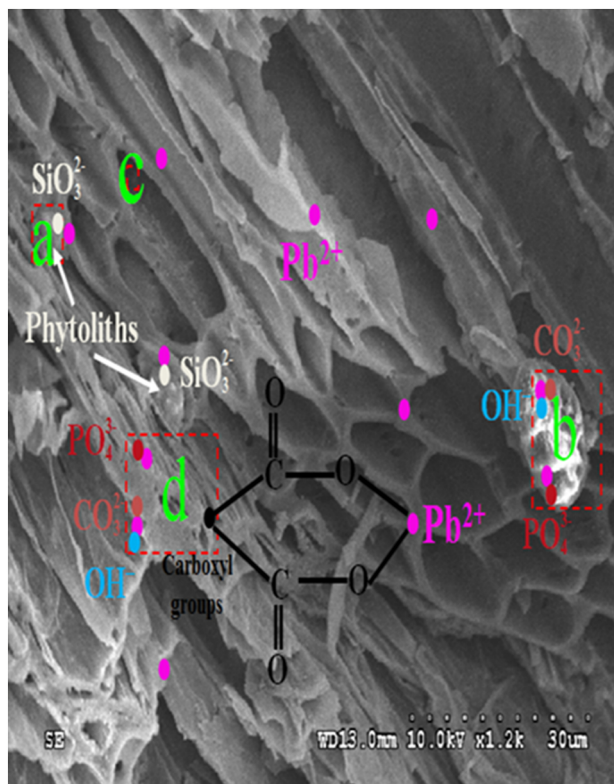


Figure 5