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Remediation of cadmium and lead polluted soil using thiol-modified biochar

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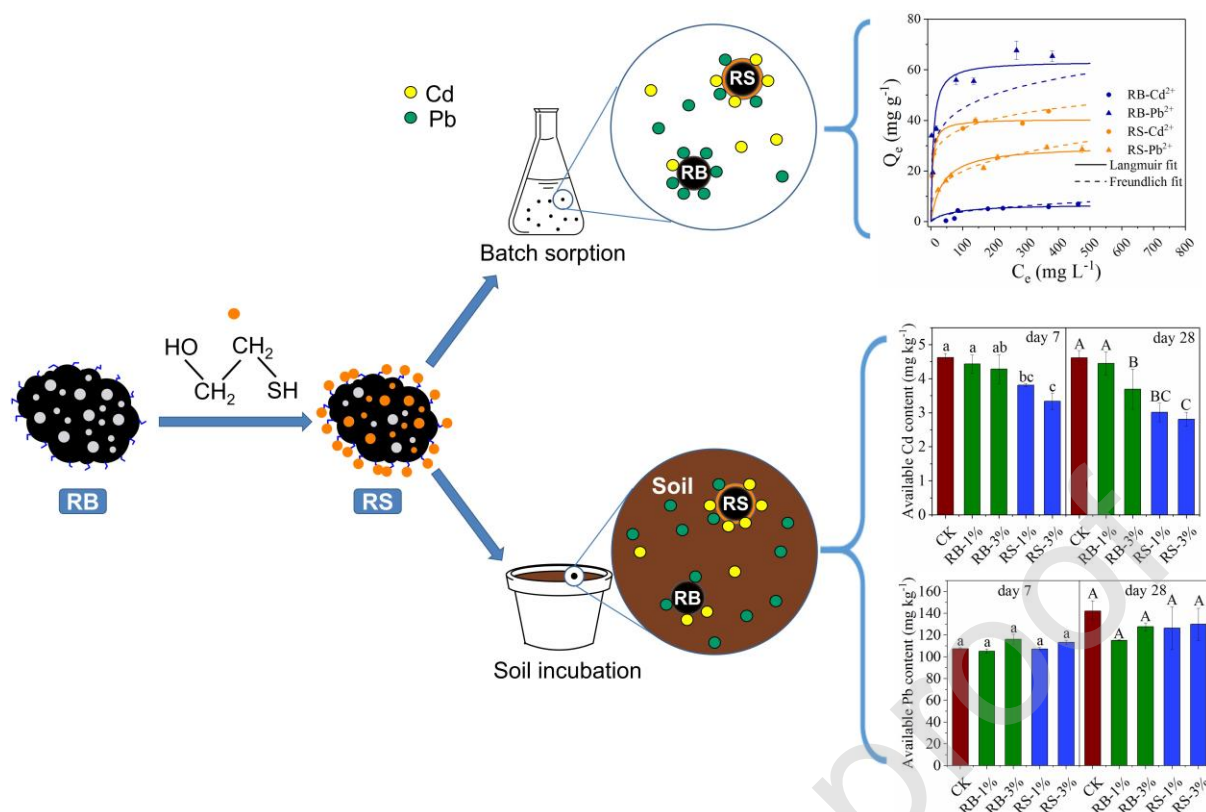
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Graphical abstract



Highlights

- A novel thiol-modified biochar was prepared via esterification with β -mercaptoethanol.
- In binary-metal system, RS selectively adsorbed Cd^{2+} over Pb^{2+} .
- RS reduced Cd availability by up to 40%, and afforded limited immobilized of Pb.
- RS could be effective amendment for remediation of soil pollution.

Abstract

Thiol-modified rice straw biochar (RS) was prepared by an esterification reaction with β -mercaptoethanol and used for the remediation of Cd and Pb polluted soils. Modified biochar was characterized through elemental analysis, BET analysis, FE-SEM, FT-IR and XPS. These analytical results revealed that thiol groups were successfully grafted onto the surface of the biochar and were involved in metal ion complexation. Batch sorption experiments indicated

that Cd^{2+} and Pb^{2+} sorption onto RS described well by a pseudo second order kinetic model and a Langmuir isotherm. The maximum adsorption capacities for Cd^{2+} and Pb^{2+} , in the single-metal systems, were 45.1 and 61.4 mg g^{-1} , respectively. In the binary-metal systems, RS selectively adsorbed Cd^{2+} over Pb^{2+} . Cd^{2+} and Pb^{2+} were removed mainly through surface complexation. In the soil incubation experiments (28 days), RS reduced the available Cd by 34.8-39.2%; while, RS reduced the available Pb by 8.6%-11.1%. This research demonstrates RS as a potentially effective amendment for the remediation of heavy metal polluted soils.

Keywords: Thiol-modification, Rice straw biochar, Heavy metal pollution, Surface complexation, Soil remediation.

1 Introduction

Cd and Pb contamination of soil throughout the world has become a priority environmental concern^[1, 2]. As typical heavy metals, Cd and Pb are identified as priority pollutants by the US Environmental Protection Agency. Anthropogenic activities such as mining, smelting, chemical production and factory emissions dispose large amounts of Cd and Pb into soil, and cause widespread soil contamination^[3, 4]. A soil survey in China reported approximately 19.4% of survey sites of farmland soils to be polluted; cadmium and lead are two of the major metal pollutants in these soils^[5]. Shi et al.(2019) suggest Cd concentrations of soils in China gradually increase from 1981 to 2016, and that mining, sewage irrigation, and fertilizer application significantly contribute to Cd accumulation in agricultural soils^[6]. Significantly, these metals can be transferred, through the soil-crop-food linkages, to cause threats to human health. Considerable research effort has been devoted to developing methods for the remediation of heavy metal contaminated soils. Current used soil remediation technologies include chemical immobilisation^[7, 8], chemical washing^[9], physical technologies^[10], phytoremediation^[11, 12] and microbial remediation^[13, 14]. These technologies have been reported to have variable remediation efficiency and drawback, and their associated cost are different. Based on its simplicity, low cost and high efficiency, chemical immobilisation has been reported to be a superior choice^[15]. Chemical immobilisation can decrease mobility and bioavailability of heavy metals through a series of reactions (including: ion exchange, adsorption, complexation and precipitation) by addition of organic or inorganic amendments into soil^[16-18]. To date, a

wide range of novel materials have been proposed as immobilisation agents, including biochar materials, phosphates-containing materials, Si-rich minerals, and so on^[19-21].

Biochar is an organic carbon-rich material produced by pyrolysis of organic matter, such as agricultural bio-waste, under an oxygen-limited environment^[22]. Biochars have been reported to immobilize heavy metals in soil^[22, 23]. However, practical applications have not consistently shown high levels of success^[24, 25]. Thus, there is a need to optimise biochar to obtain better remediation outcomes. To enhance the remediation efficiency of biochar, a number of modification methods have been developed, including acid/base treatment^[26, 27], loading with minerals^[28, 29] and/or nano-particles^[30, 31], and addition of organic functional groups^[32-34].

Surface modification, by grafting thiol functional groups, has been proposed as a potentially effective strategy to increase the heavy metal adsorption capacity; these thiol groups showing high affinity for heavy metal ions (such as Hg^{2+} , Cu^{2+} , Cd^{2+} , Zn^{2+} and Pb^{2+}) present in solution^[35-37]. According to previous reports, thiol-modified adsorbent can be considered as efficient heavy metal immobilisation agent. Liang et al. ^[38, 39] applied thiol-functionalized sepiolite and palygorskite to enhance the immobilisation of Cd and successfully reduced the bioavailability of Cd through plant physiological and soil chemistry mechanisms. Huang et al.^[40] used thiol-functionalized graphene oxide/Fe-Mn composite for *in situ* immobilisation of mercury-contaminated soil; reporting extractable Hg to be reduced, through chemical precipitation and surface complexation, by more than 90%.

In view of biochar modification, there are several studies concerning biochar modified with thiol groups. Xia et al.(2019) conducted thiol modified material using 3-mercaptopropyltrimethoxysilane(3-MPTS), and found thiol modification increased the adsorption capacity of mercury onto biochar^[41, 42]. However, this adsorption capacity was lower than that of thiol modified active carbon or thiol modified graphene oxide. Huang et al.(2019) reported thiol-functionalized biochar to effectively removed Hg^{2+} and CH_3Hg^+ from solution, and natural organic matter (NOM), glucose and humic acid (up to 24 mg/L) had little effect on the adsorption^[41, 42]. However, the research on thiol-functionalized biochar is still limited, particularly for typical soil metal pollutants such as Cd^{2+} and Pb^{2+} . In addition, previous researches mainly focus on the performance of thiol-functionalized biochar on metal adsorption in solution; the application of thiol-functionalized biochar for soil remediation remains unconfirmed. Here we adopt a simple and novel path, using β -mercaptoethanol, to prepare thiol-modified biochar and use the prepared material to remediate Cd and Pb contaminated soils. This research aimed to: characterize the properties of thiol modified biochar; to investigate the adsorption on Cd and Pb in water (both individually and as binary mixtures), and; to use thiol-modified biochar to remediate Cd and Pb contaminated soil.

2 Materials and methods

2.1 Rice straw biochar and thiol-modified biochar production and characterisation

Before charring, rice straw was collected, air-dried and cut to lengths less than 2cm. Rice straw biochar (RB) was produced by slowly pyrolysis under N_2 in a muffle furnace (KSL, Kejing

Inc., China). The furnace was heated to 500°C at a heating rate of 20°C min⁻¹ and held at this temperature for 5 h. Then biochar samples were collected, crushed and ground to pass through a 60 mesh sieve.

In brief, thiol-modification was achieved as follows: 1 g of RB was placed in a brown glass bottle with 4 mL of β -mercaptoethanol (>99%, AR), followed by adding acetic anhydride (>98.5, AR, 2.8 mL) and concentrated sulphuric acid (>95.0%, AR, 0.2 mL). The bottle was then sealed and shaken for 18 h at 80 °C. After filtration, the product was washed thoroughly with ultrapure water and then dried in a vacuum oven for 12 h at 35 °C. Thereafter, the product (RS) was crushed and ground to pass through a 60 mesh sieve.

pH was measured by a pH meter (STARTER 3100/F, Ohaus Inc., China) at the ratio of 1 g biochar : 20 mL ultrapure water. The content of thiol group on biochar was analysed using Ellman reagent^[43]. Briefly, biochar (2 mg) was suspended in ethanol (0.2 mL) using ultrasound. Thereafter, 0.2 mol L⁻¹ phosphate buffered solution (PBS, pH 7.8, 1 mL) and 5,5'-dithiobis-(2-nitrobenzoic acid) solution (2g L⁻¹ in PBS, 0.2 mL) were added to the biochar suspension. After 5 min of incubation, the solution was filtered and the absorbance at 412 nm was measured. Carbon, nitrogen, and sulphur content were determined using a CNS elemental analyzer (Vario Max, Elementar Analysensysteme GmbH Inc., German). The pH_{pzc} was measured according to the protocol reported by Mohan et al^[44]. The morphologies and surface features were characterized by a field emission scanning electron microscope (FE-SEM) (S-4800, Hitachi

Inc., Japan). The specific surface area and pore size distribution were determined by Brunauer-Emmett-Teller (BET) and Barret-Joyner-Halenda (BJH) methods with N₂ adsorption isotherms, respectively. Fourier transform infrared (FT-IR) (Thermo Scientific Nicolet iS10, Thermo Fisher Scientific Inc., USA) analysis was carried out over a range of 400 - 4000 cm⁻¹ using the KBr pellet technique. X-ray photoelectron spectroscopy (XPS) analysis was determined using a spectrophotometer (*K-Alpha*⁺, Thermo Fisher Scientific Inc., USA) with an Al K α source (1486.6 eV of photons).

2.2 Batch sorption experiment

Batch adsorption experiments were conducted to investigate the adsorption characterisation of RB and RS. Both single-(either Cd²⁺ or Pb²⁺) and binary-(both Cd²⁺ and Pb²⁺) metal adsorption experiments were conducted to determine the sorption capacities of RB and RS at a buffer system (pH 5, 0.05 mol L⁻¹ acetic acid). Briefly, 25 mg of RB or RS was added to centrifuge tubes containing 10 mL of single metal ion (Cd²⁺ or Pb²⁺) solutions or binary metal ion solutions (the mass ratio of Cd²⁺ to Pb²⁺ was 1:1) of various initial concentrations (50 - 600 mg L⁻¹). The centrifuge tubes were shaken (180 rpm for 24 h) and the suspension was filtered through a 0.22 μ m membrane filter. After filtration, the concentrations of heavy metals in the filtrate were determined by an inductively coupled plasma optical emission spectrometer (ICP-OES) (Optima, Perkin Elmer Inc., America). Sorption kinetic experiments of Cd²⁺ and Pb²⁺ on RB and RS were carried using 250 mL conical flasks, containing 100 mL of 200 mg L⁻¹ single metal ions (Cd²⁺ or Pb²⁺) solutions buffered to pH 5 (0.05 mol L⁻¹ acetic acid), and flasks were

sampled periodically (0 - 24h). The effect of pH on sorption of metal ion (Cd^{2+} or Pb^{2+}) was determined using solutions of 50 mg L^{-1} concentrations of metal ion adjusted to the desired pH (2 - 7). All the adsorption experiments were conducted in triplicate.

2.3 Soil incubation experiments

A soil sample from the surface layer (0 - 20 cm) was collected from a contaminated vegetable field in Longyan (Fujian Province, China). The soil sample was air dried and passed through a 2-mm sieve. Soil physicochemical properties are reported in Table 1. The concentration of soil Cd and Pb were 9.18 and 1182 mg kg^{-1} , respectively; both metals present in soil were above the risk intervention values, enacted by the government of China^[45], for agricultural land (3.0 mg kg^{-1} for Cd and 700 mg kg^{-1} for Pb).

The soil incubation experiments were performed with soil (30 g) enclosed in the 50 mL centrifuge tube. Dosages of 0, 1%, and 3% RB or RS were homogenously mixed into the soil. Thus, the incubation experiment included five treatments: Soil (CK), Soil + 1% RB (RB-1%), Soil + 3% RB (RB-3%), Soil + 1% RS (RS-1%) and Soil + 3% RS (RS-3%). All the mixtures were incubated at 80% water holding capacity at 25°C . Two batches of samples were prepared for destructive sampling after incubation time of 7 and 28 days. At the designated time, soil samples were air dried, and ground to pass through a 2-mm sieve. Three replicates of each treatment were performed. Soil pH, cation exchange capacity (CEC) and organic matter (O.M) were measured. The available Cd and Pb concentrations of soil samples were estimated by

diethylenetriaminepentaacetic acid (DTPA) solution extraction^[46, 47]. Chemical fractionations of Cd and Pb were determined using a sequential extraction procedure^[48]. These fractions were: exchangeable fraction (EX), carbonate-bound fraction (CB), Fe/Mn oxides-bound fraction (OX), organic matter-bound fraction (OM) and residual fraction (RES). The metal concentrations in the extracts were detected using ICP-MS (Agilent 7500cx, Agilent, America).

3 Results and discussion

3.1 Physicochemical properties

Physicochemical properties of RB and RS are presented in Table 2. The elemental analysis revealed that the composition of RS was markedly changed after thiol-modification. The nitrogen content and carbon content of RS were lower than RB. The sulphur content of RS was 24.04% (while it was only ~1% in RB). The accessible thiol contents, which is available for heavy metal adsorption, were 0.83 and 0.01 mmol g⁻¹ for RS and RB, respectively. The increased sulphur content and accessible thiol contents of RS confirmed that thiol groups had been successfully introduced. After thiol-modification, the pH and pH_{pzc} of RS decreased dramatically with respect to RB. As the pH of biochar is mainly affected by surface functional groups^[49], the decrease of pH of RS indicated that thiol-modification increased acidic functional groups on the surface of RS. The low pH_{pzc} of RS suggested that the incorporation of thiol groups led to an enhancement of surface negative charges (these will have likely influenced adsorption of metal cations favourably^[50]).

The surface area of RS decreased from 7.82 m² g⁻¹ to 0.34 m² g⁻¹ and pore diameter of RS

decreased from 20.8 nm to 16.7 nm due to infilling of the pores with thiol groups^[43]. Fig. S1 shows typical FE-SEM images of RB and RS. RB had regular pore structure with rough surface and some particles attached. After thiol-modification, the surface of RS was covered with a layer of smooth membranous material and the pores were visually observed to be blocked. These observations are consistent with previous reports that pore blockage caused by grafting of the thiol groups^[43, 51].

To identify the chemical changes of the functional groups on the adsorbent surface, FT-IR spectra were obtained (Fig. 1). In the RB spectrum, the peaks at 1573, 1419, 1066, 617 and 459 cm^{-1} were attributed to the vibration of $\text{C}=\text{O}/\text{C}=\text{C}$, $\text{C}-\text{OH}$ (phenolic), $\text{C}-\text{O}$ (carboxylic), $\text{C}-\text{O}$ (alkyl), and $\text{C}-\text{C}$, respectively^[52-57]. Comparing the spectra before and after thiol-modification, the spectrum of RS changed obviously. In the RS spectrum, the broad adsorption peak at 3446 cm^{-1} was ascribed to the $\text{O}-\text{H}$ stretching vibrations. New peaks observed at 1233 cm^{-1} and 1028 cm^{-1} were attributed to the lactones and the stretching vibration of $\text{C}-\text{O}$ ^[58, 59], respectively. The peaks observed at 2929 and 2560 cm^{-1} , corresponded to the $-\text{CH}_2-$ vibrations of β -mercaptoethanol and thiol group, respectively^[35, 60]. These results confirm that the β -mercaptoethanol was successfully introduced on the biochar support. The adsorption band at 1739 cm^{-1} was assigned to ester carbonyl stretching^[61], while the peak at 1066 cm^{-1} belonging to carboxylic acids, markedly reduced^[55]. Furthermore, these results confirm the β -mercaptoethanol grafting had been achieved via ester linkages. The peak at 671 cm^{-1} was

assigned to C–S^[62], it also confirmed the presence of β -mercaptoethanol. Additionally, the FT-IR spectra suggests that sulfonic groups were not formed during thiol-modification of RS although there was concentrated H₂SO₄ addition during the preparation. The vibration band at 1040 cm⁻¹ (attributed to S=O symmetric stretching), that would indicate the presence of sulfonic groups, was not visible in the FT-IR spectrum. The absence of this band in the FT-IR spectra confirms the absence of -SO₃H groups on thiol-modified RS^[63]. In summary, the β -mercaptoethanol was successfully introduced onto RS by esterification (see reaction route presented in Fig. 2)^[35, 64].

3.2 Sorption of Cd and Pb from aqueous solution

3.2.1 Sorption kinetics

The adsorption of Cd²⁺ on RB was observed to be slow, and the equilibrium was achieved after approximately 24 h (Fig. 3a). The adsorption of Cd²⁺ on RS initially increased rapidly, this rate subsequently decreased, and sorption reached equilibrium within 2 h. The equilibrium adsorption capacity of RS was three times higher than that of RB.

In order to probe the sorption mechanisms, the sorption kinetics data were fitted using a pseudo-first-order kinetic model and a pseudo-second-order kinetic model (Table 3). Cd²⁺ sorption kinetics on RB was better described by the pseudo-first-order kinetic model, this suggested that mononuclear sorption of Cd²⁺ was underpinning Cd²⁺ sorption by RB^[65]. In contrast, the pseudo-second-order kinetic model better fitted the kinetic data of Cd²⁺ on RS, indicating that the rate-limiting step was chemical sorption. As shown in Fig. 3b, the adsorption

of Pb^{2+} on RB was initially more rapid than its adsorption on RS, and thereafter decreased considerably with the extension of time until equilibrium was achieved. Pb^{2+} adsorption by RB and RS was better described by the pseudo-second-order kinetic models, suggesting that the rate-limiting step was chemical sorption.

These results demonstrated that, in comparison to RB, RS had a large affinity for Cd^{2+} and relatively low affinity to Pb^{2+} , while RB had a high affinity for Pb^{2+} and a far lower affinity for Cd^{2+} .

3.2.2 Sorption isotherms of Cd and Pb in single- and binary-metal systems

The adsorption isotherms of Cd^{2+} and Pb^{2+} on RB and RS in the single-metal systems are illustrated in Fig. 4, and the model parameters fitted by the Langmuir and Freundlich models are listed in Table 4. The adsorption capacities of RB for Cd^{2+} were greatly enhanced, while the adsorption capacities of RB for Pb^{2+} were slightly decreased after thiol-modification.

For Cd^{2+} , the maximum adsorption capacity on RS was 45.1 mg g^{-1} , about 3-fold higher than that of RB. For Pb^{2+} , the maximum adsorption capacities on RB and RS were 67.4 and 61.4 mg g^{-1} , respectively. Correlation coefficients indicated that the Langmuir model fitted adsorption isotherms of Cd^{2+} and Pb^{2+} on RB and RS better than the Freundlich model. This observation implies that metal ion adsorption occurred at a homogeneous surface by monolayer sorption without interaction between the adsorbed ions^[66].

The increase in adsorption capacity of RS for Cd^{2+} was ascribed to the incorporation of thiol

groups on RS. The characteristic band of thiol groups at 2560 cm^{-1} in the FT-IR spectra of RS- Cd^{2+} disappeared after adsorption (Fig. S2); this indicates the interactions between thiol groups and Cd^{2+} or Pb^{2+} [67]. The lone pair of electrons on the sulphur atoms of the thiol groups have been reported to coordinate with heavy metals, thus promoting their adsorption[35].

However, the adsorption capacity of RS for Pb^{2+} was slightly decreased. This result might be attributed to the significant reduction in carboxylic groups remaining on RS following thiol groups; these carboxylic groups act as reaction sites for the esterification (Fig. 2). It can be inferred that in the adsorption of heavy metals, the main adsorption sites on RB were oxygen-containing functional groups such as carboxyl groups, etc, while the thiol groups on RS played a great role. Comparing the FT-IR spectra of RB before and after Cd^{2+} or Pb^{2+} adsorption (Fig. S2), the shift of carboxylic group related band at 1066 cm^{-1} suggest the binding of metal ion with carboxylic groups on RB[55]. Meantime, the disappearance of O1s peaks at 534.2 eV (Fig. S3) and the shift of C1s peak at 288.0 eV (Fig. S4) also indicate that the carboxyl groups on RB were involved in adsorption[68, 69]. However, the carboxyl groups were markedly reduced after thiol-modification, as confirmed by FT-IR spectra (Fig. 1) and XPS O1s spectra (Fig. S3)[70]. According to Lewis' HSAB (hard and soft acids and bases) theory, soft acids (acceptors) tend to form strong bonds with soft bases (donors), but bind reluctantly or weakly to harder bases, while hard acids (acceptors) tend to form strong bonds with hard bases (donors), but bind reluctantly or weakly to softer bases[71]. Carboxyl groups (a hard base) are more favourable to adsorb Pb^{2+} (Pb^{2+} is a borderline acid while Cd^{2+} is a soft acid) [72]. In contrast,

the interaction between thiol groups (soft base) and Cd^{2+} is more favourable comparing to Pb^{2+} [69]. Therefore, although the content of thiol groups on RS was increased, the loss of carboxylic groups during the thiol-modification lead to the slight decrease of adsorption capacity of Pb^{2+} .

As shown in Fig. 5, the maximum adsorption capacity of Cd^{2+} and Pb^{2+} on RB and RS decreased considerably in the binary-metal system compared to in the single-metal system. Competition between Cd^{2+} and Pb^{2+} in the binary-metal systems affected the adsorption of Cd^{2+} and Pb^{2+} on RB and RS and all the experimental data was well fitted by the Langmuir model (Table 5). The decreasing amplitude of Cd^{2+} adsorption on RB caused by competition was larger than the decreasing amplitude of Pb^{2+} adsorption; the decrease in adsorption capacities of RB for Cd^{2+} and Pb^{2+} were 52% and 6%, respectively. The decreasing amplitude of Pb^{2+} adsorption on RS caused by competition was larger than the decreasing amplitude of Cd^{2+} adsorption on RS; the decrease in adsorption capacities of RS for Cd^{2+} and Pb^{2+} were 10% and 51%, respectively. Furthermore, the analysis of distribution coefficient (K_d) shown the difference between adsorption preference for Cd^{2+} and Pb^{2+} on RB and RS (Table 6). RB showed more prominent selectivity for Pb^{2+} over Cd^{2+} . On the contrary, RS had adsorption selectivity for Cd^{2+} over Pb^{2+} . The adsorption preference for Pb^{2+} by biochar has been reported in other studies. Park^[72] found that sesame straw biochar adsorbed more Pb^{2+} from a multimetal system (of Pb^{2+} , Cu^{2+} , Cr^{2+} , Zn^{2+} and Cd^{2+}). This might be attributed to the lower hydrated radius of Pb^{2+} and greater affinity of Pb^{2+} for most functional groups, including phenolic and

carboxylic groups (hard Lewis bases), on the sesame straw biochar. A reasonable explanation for more favourably adsorbed of Cd^{2+} on RS than Pb^{2+} is that thiol groups (soft Lewis bases) had higher affinity for cadmium ions (soft Lewis acids)^[73].

3.2.3 Effects of pH on sorption

pH is a crucial parameter in adsorption process as it can affect the surface charge of adsorbents and metal speciation^[74]. Changes in the initial pH of the adsorbent/solution systems affected Cd^{2+} and Pb^{2+} adsorption by RB and RS (Fig. S5). In general, the removal efficiency of the metals by RB and RS increased with increasing pH until reaching maximum. The removal of Cd^{2+} by RS was much higher than RB with the increase of pH from 2 to 4. The removal of Cd^{2+} by RS remained constant beyond pH 5. The removal of Cd^{2+} by RB continued to increase beyond pH 5. With the increase in pH, the removal of Pb^{2+} by RB and RS increased. These phenomena were likely due to the presence of a large number of H^+ and H_3O^+ ions in aqueous solution at low pH (these ions competing with the metal ions for adsorption sites). With increasing of pH, the competition between metal ions and protons for binding sites decreased and more binding sites were released^[75]. Furthermore, the surface charge of the adsorbent would be positive below the pH_{PZC} , or be negative above the pH_{PZC} . While solution pH exceeds pH_{PZC} , the negative surface charge on adsorbent increase with the increase of solution pH and therefore shows better heavy metal removal efficiency at higher pH^[76]. These observations suggest that ion exchange mechanisms underpin the adsorption of Cd^{2+} and Pb^{2+} on RB and RS^[55].

3.2.4 Sorption mechanism

To further elucidate the mechanism of Cd^{2+} and Pb^{2+} adsorption onto RS and RB, XPS data were collected (Fig. 6). Fig. 6a showed S2p spectrum of sulphur of RS before and after adsorption of Cd^{2+} and Pb^{2+} . The S2p binding energy of RS at 162.9 eV and 164.0 eV were ascribed to the grafted thiol monolayers and thiol group^[77]. For Cd^{2+} - and Pb^{2+} -laden RS, the decrease in thiol groups from 42.1% to 28.9% and 26.8%, were ascribed to the interaction between thiol groups and Cd^{2+} or Pb^{2+} , respectively. Similarly, Huang et al. found that thiol groups on thiol-functionalized graphene oxide/Fe-Mn composite decreased by 30.3% and 10.4%, respectively, after Hg^{2+} and CH_3Hg^+ adsorption, indicating surface complexation^[78]. From Fig. 6b, the $\text{Cd}3\text{d}_{3/2}$ (412.3 eV) and $\text{Cd}3\text{d}_{5/2}$ (405.5 eV) indicated the formation of precipitation, such as cadmium hydroxide and carbon oxides, associated with the adsorption of Cd^{2+} ^[79]. From Fig. 6c, two peaks at 411.4 and 404.6 eV of RS, assigned to $\text{Cd}3\text{d}_{3/2}$ and $\text{Cd}3\text{d}_{5/2}$ of Cd^{2+} in CdS ^[80], indicating that cadmium species were adsorbed via binding reactions between cadmium ions and thiol groups. For the spectrum of Pb4f of Pb loaded RB (Fig. 6d), the binding energies of 144.7 eV for $\text{Pb}4\text{f}_{5/2}$, and 139.8 eV for $\text{Pb}4\text{f}_{7/2}$ denoted the complexation of PbO ^[81]. From Fig. 6e it can be seen that the Pb4f spectrum of Pb loaded RS had $\text{Pb}4\text{f}_{7/2}$ binding energy at 137.4 eV and $\text{Pb}4\text{f}_{5/2}$ binding energy at 142.3 eV; these are in good agreement with data obtained for PbS ^[82]. The interaction between thiol groups and metal ions played important role in the adsorption of Pb^{2+} onto RS. Collectively these results indicate, that after

thiol-modification surface complexation reactions involving grafted thiol groups and metal ions facilitated their adsorption/precipitation^[42, 83].

3.3 Remediation of Cd and Pb in soil

3.3.1 Effects on soil pH, O.M and CEC

The influence of RB and RS on soil pH, O.M and CEC was assessed (Fig. S6). These attributes are important influences upon the chemical behaviour of heavy metals in soil.

Compared with the control soil (pH 7.42), RB addition to soil resulted in a significant ($p < 0.05$) increase in pH (Fig. S6a). In contrast, RS addition significantly decreased soil pH ($p < 0.05$).

Across all the incubation times, RB increased the pH of soil by 0-0.49 units and the addition of RS decreased the pH of soil by 0.07-0.36 units across all the incubation times. No time-related trends in pH were observed over the 28 days. However, the significant ($p < 0.05$) relationships between pH and increasing RB/RS application doses were observed. The high pH RB (pH = 10.2) likely underpinned increases in soil pH^[84]. The decrease of soil pH after addition of RS was likely caused by the acidity of RS (pH = 2.4).

With increasing application, RB and RS significantly increased soil O.M compared to the CK (Fig. S6b) ($p < 0.05$). The soil O.M increased respectively by 28-115% and 33-130% following RB and RS addition (28 days). There was no significant difference observed between RB and RS on soil O.M ($p > 0.05$). The addition of biochar to soil has previously been reported to significantly increase the content of soil O.M due to its high carbon content^[85].

The addition of RB and RS, across all incubation periods, resulted in a slight but insignificant

enhancement of soil compared with the control; there was no significant difference in soil cation exchange capacity between RB and RS treated soil (Fig. S6c) ($p > 0.05$). As the effect of biochar on soil cation exchange capacity has been reported to related to the incubation time^[86], the insignificant effect of RB/RS on soil cation exchange capacity may be linked to the short period of incubation used in this study.

3.3.2 Effects on availability of Cd and Pb

The effect of RB/RS on the concentration of available Cd and Pb in the soil was determined by DTPA extraction (Fig. 7). These results revealed that available Cd in RB treated soils and RS treated soils were lower than in CK. The influence of RB treatment on available Cd content were not significant ($p > 0.05$), except RB-3% at 28th day. In comparison, RS had a better immobilisation effect than RB; available Cd content in all RS treated soils decreased significantly ($p < 0.05$) by 17.5-27.7% (7 days) and 34.8-39.2% (28 days), respectively. The available Pb content in soil fluctuated with the addition of RB and RS at 7th day. After 28 days, the available Pb decreased by 10.2-19.0% (RB treated soils) and 8.6-11.1% (RS treated soils), but there was no significant difference compared with CK ($p > 0.05$).

Biochar has been reported to mainly influences the mobility of heavy metals by changing cation exchange capacity and pH of soil^[87]. In this study, RB had no significant effect on soil CEC. On the other hand, RB significantly increased soil pH but less than 0.5 unit, while the control soil was alkaline. Increasing soil pH with biochar dose not always reduce the availability of

heavy metals, especially in alkaline soils. It has been reported that the pH changes of biochar added to alkaline soil has no significant correlation with the availability of heavy metals^[25]. These two reasons might led to poor immobilisation effect of RB on Cd and Pb. Unlike other pH-regulating immobilization agents such as biochar and lime, RS addition decreased the soil pH. The loading of thiol groups on RS enhanced the retention of Cd in soil through the formation of metal complexes and thus the availability of heavy metals was decreased^[18]. Similarly, He et al.(2018) suggested thiol groups grafted palygorskite (MP) decreased soil available Cd by 89.51%, and reduced Cd concentration of pak choi^[88]. The schematic of the general remediation mechanism was presented: There did not occur pH regulation effect. Thiol groups on MP directly adsorb metal ions from soil. Meanwhile MP changed soil properties including surface zeta potential, which increased the chemical reaction between soil and Cd pollutant. Lian et al.(2019) reported that thiol functionalized reactive nanosilica reduced soil bioavailable-Cd from 12.46 mg/kg to 0.22 mg/kg, and most Cd was transformed into more stable species due to the chemical reaction between Cd and thiol groups^[89]. In this study, the addition of RS shifted the phytoavailable Cd fractions (EX and CB fractions) to the less available fractions (OX and OM fractions) over time as described in section 3.3.3. For Pb, there was limited immobilisation effect for RS or RB. This was probably due to the high concentration of Pb in the soil, so the magnitude of the decrease was not so significant.

3.3.3 Influence of RB and RS on Cd and Pb speciation in soils

The speciation of Cd and Pb in soils are shown in Fig. 8. Cd was mainly bound to exchangeable,

carbonate-bound and Fe/Mn oxides-bound fractions, the sum of the three fractions accounted to more than 90% of total Cd in CK. Pb mainly existed in Fe/Mn oxides-bound and residual fractions, and the sum of the two fractions accounts for more than 80% of total Pb in CK. In the CK, 57.1-61.6% of Cd and 6.9-13.7% of Pb were found in the exchangeable and carbonate-bound fractions; these fractions have been called as the phytoavailable fractions of heavy metal in soil^[90, 91].

Over the 28-day periods, the application of RB did not have an obvious influence on Cd speciation in soil. RB decreased phytoavailable Cd of total Cd by 2 and 5%. In contrast, additions of RS shifted Cd species from carbonate fraction to Fe/Mn oxides fraction. The percentages of carbonate-bound fraction of total Cd decreased 5 and 13% following RS application, while the percentages of Fe/Mn oxides-bound fractions of total Cd increased 9 and 16%. Thus, RS treatment decreased phytoavailable Cd between 10 and 14%. The RB and RS treatment did not have a significant influence on Pb speciation during the incubation. The percentages of phytoavailable Pb of total Pb decreased 1 and 4%, 1 and 6% after RB and RS application, respectively.

Biochar can not only directly reduce the available content of heavy metals in soil by means of adsorption or precipitation, but also indirectly reduce the available content of heavy metals in soil by improving pH, electrical conductivity and other soil properties^[92, 93]. However, in this study, RB had limited immobilisation effect on both Cd and Pb in the soil. Addition of thiol-

modified sepiolite to Cd contaminated farmland soil can transform the exchangeable fraction and carbonate-bound fraction of Cd into the Fe/Mn oxides-bound fraction, organic matter-bound fraction and residual fraction^[38]. The increase of Fe/Mn oxides-bound fraction of Cd has been reported to be due to the adsorption of Cd on Fe/Mn oxides-bound indirectly promoted by thiol-modified sepiolite; while the increase of organic matter-bound fraction of Cd has been reported to be due to the adsorption of Cd by thiol functional groups directly. In this study, RS had a better immobilisation effect on Cd in the soil and the addition of RS transformed carbonate-bound fraction of Cd into Fe/Mn oxides-bound fraction. A reasonable explanation is that the carbonate-bound fraction of Cd, which may solubilise under acidic condition^[94], was released into the soil solution as the pH decreased following RS addition, and re-adsorbed onto RS^[40]. However, RS had negligible impacts on the chemical fraction of Pb in the soil, which could be partially attributed to the adsorption selectivity of RS for Cd over Pb when Cd and Pb coexisted in soil solution. However, again, extreme high level of Pb contamination (1182 mg kg⁻¹) in soils might be the main reason for the limited immobilisation effect of RS on Pb distribution in soils.

4 Conclusions

Thiol-modified biochar was successfully prepared by esterification with β -mercaptoethanol. The kinetics of adsorption of Cd²⁺ and Pb²⁺ on RS were found to be rapid, and the experimental data was well described by pseudo-second order kinetics; indicating that the adsorption was controlled by chemisorption. The thiol-modification tripled the sorption capacity for Cd²⁺ and

slightly decrease the sorption capacity for Pb^{2+} . Cd^{2+} and Pb^{2+} were removed mainly via surface complexation. The RS exhibited an adsorption preference for Cd^{2+} over Pb^{2+} in the binary-metal system. The laboratory-scale incubation test showed that RS had better performance in immobilizing Cd and shifting Cd to less phytoavailable phases in the soil than RB. Both RB and RS significantly increased the organic matter content of soil and slightly increase cation exchange capacity in the soil. These results suggest RS could be a useful remediation option for heavy metal contamination in water and soil. Further studies should be conducted to provide more understanding of the interaction between thiol groups on RS and metal ions, and the effects of RS on soil metal migration in field application which involved the influences of plantation and microbial activities needed to verified.

Author contribution

Zhang Youchi: Conceptualization, Methodology, Investigation, Writing- Reviewing and Editing. **Jiajun Fan:** Investigation, Writing- Original draft preparation. **Chao Cai :** Conceptualization, Investigation **Haifeng Chi:** Investigation. **Brian J. Reid:** Writing- Reviewing and Editing, Data curation. **Frédéric Coulon:** Writing- Reviewing and Editing. **Yanwei Hou:** Investigation, Data curation, Writing- Reviewing and Editing.

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Figure caption

Fig. 1 FT-IR spectra of RB and RS.

Fig. 2 The scheme of the preparation of RS.

Fig. 3 Sorption kinetic of (a) Cd^{2+} and (b) Pb^{2+} onto RB and RS (initial concentration of metal ions: 200 mg L^{-1} , adsorbent dosage: 2.5 g L^{-1} , pH 5, buffered by 0.05 mol L^{-1} acetic acid).

Fig. 4 Sorption isotherms of (a) Cd^{2+} and (b) Pb^{2+} on RB and RS in the single-metal systems (adsorbent dosage: 2.5 g L^{-1} , pH 5, buffered by 0.05 mol L^{-1} acetic acid).

Fig. 5 Sorption isotherms of Cd^{2+} and Pb^{2+} on RB and RS in the binary-metal systems (adsorbent dosage: 2.5 g L^{-1} , pH 5, buffered by 0.05 mol L^{-1} acetic acid, contact time: 24 h).

Fig. 6 XPS spectra of (a) S2p for RS before and after cadmium and lead uptake, (b) Cd3d for RB- Cd^{2+} , (c) Cd3d for RS- Cd^{2+} , (d) Pb4f for RB- Pb^{2+} and (e) Pb4f for RS- Pb^{2+} .

Fig. 7 Effect of RB and RS on availability of (a) Cd and (b) Pb. Different lower case and capital letters above the column indicate significant difference between treatments at $p < 0.05$.

Fig. 8 Influence of RB and RS on species distribution of (a) Cd and (b) Pb.

Table 1 Soil properties

pH	CEC (cmol kg ⁻¹)	O.M. (%)	Clay (%)	Silt (%)	Sand (%)	Cd (mg kg ⁻¹)	Pb (mg kg ⁻¹)
7.42	13.53	2.15	0.76	18.74	80.50	9.18	1182

Table 2 Physicochemical properties of RB and RS.

	CNS elements			-SH content (mmol g ⁻¹)	pH	pH _{PZC}	surface	pore diameter
	N (%)	C (%)	S (%)				area (m ² g ⁻¹)	
RB	1.54	48.18	0.98	0.01	10.20	9.92	7.82	20.82
RS	0.59	43.71	24.04	0.83	2.36	2.26	0.34	16.69

Table 3 Sorption kinetic parameters of Cd^{2+} and Pb^{2+} sorption on RB and RS (initial concentration of metal ions: 200 mg L^{-1} , adsorbent dosage: 2.5 g L^{-1} , pH 5, buffered by 0.05 mol L^{-1} acetic acid)

Ions	Sorbent	1 st order kinetics			2 nd order kinetics		
		q_{m1}	k_1	R^2	q_{m2}	k_2	R^2
		(mg g^{-1})	(h^{-1})		(mg g^{-1})	($\text{g mg}^{-1} \text{ h}^{-1}$)	
Cd^{2+}	RB	9.9	0.15	0.9963	11.3	0.01	0.9074
Cd^{2+}	RS	45.2	14.49	0.7221	46.1	0.60	0.9993
Pb^{2+}	RB	55.4	32.60	0.0246	55.6	1.90	0.9998
Pb^{2+}	RS	53.2	22.93	0.9750	54.3	1.13	0.9998

Table 4 Isotherm parameters of Langmuir and Freundlich for the sorption of Cd^{2+} and Pb^{2+} onto RB and RS in the single-metal systems (adsorbent dosage: 2.5 g L^{-1} , pH 5, buffered by 0.05 mol L^{-1} acetic acid, contact time 24 h)

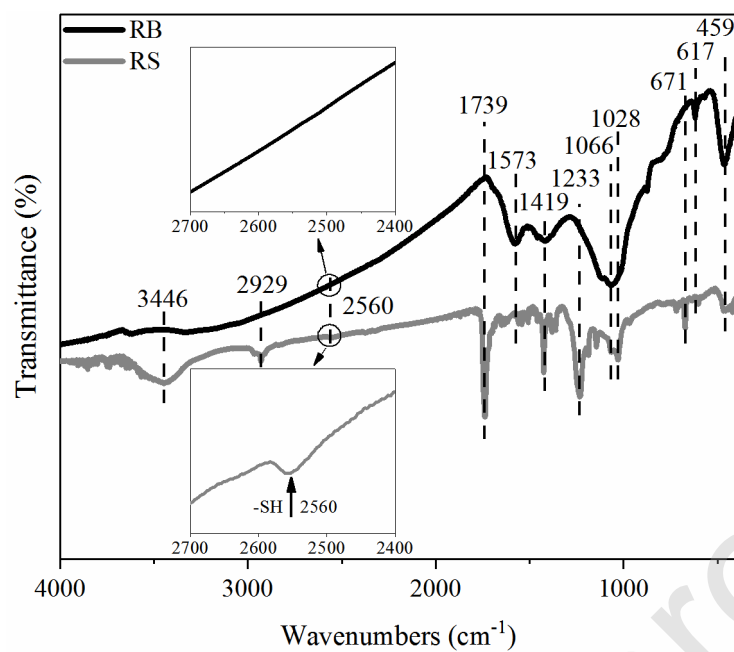
Isotherm	Parameters	Cd^{2+}	Cd^{2+}	Pb^{2+}	Pb^{2+}
		RB	RS	RB	RS
Langmuir	$Q_m (\text{mg g}^{-1})$	14.2	45.1	67.4	61.4
	$K_L (\text{L mg}^{-1})$	0.01	0.22	0.09	0.03
	R^2	0.8143	0.9993	0.9965	0.9982
	$K_F (\text{mg g}^{-1})$	1.8	24.0	20.3	9.5
Freundlich	$1/n$	0.31	0.12	0.25	0.31
	R^2	0.4154	0.9899	0.9168	0.9248

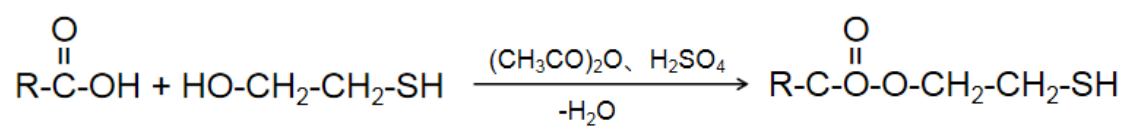
Table 5 Isotherm parameters of Langmuir and Freundlich for the sorption of Cd^{2+} and Pb^{2+} onto RB and RS in the binary-metal systems (adsorbent dosage: 2.5 g L^{-1} , pH 5, buffered by 0.05 mol L^{-1} acetic acid, contact time: 24 h)

Isotherm	Parameters	RB		RS	
		Cd^{2+}	Pb^{2+}	Cd^{2+}	Pb^{2+}
Langmuir	$Q_m (\text{mg g}^{-1})$	6.8	63.3	40.4	30.0
	$K_L (\text{L mg}^{-1})$	0.02	0.14	0.22	0.03
	R^2	0.8410	0.9854	0.9956	0.9824
Freundlich	$K_F (\text{mg g}^{-1})$	0.5	20.5	19.0	5.2
	$1/n$	0.44	0.17	0.14	0.29
	R^2	0.4314	0.4102	0.8272	0.9763

Table 6 Distribution and selectivity coefficient of competitive adsorption

	$K_d \text{ (Cd)}$	$K_d \text{ (Pb)}$	$K_d \text{ (Cd)} / K_d \text{ (Pb)}$	$K_d \text{ (Pb)} / K_d \text{ (Cd)}$
RB	14.39	119.59	0.12	8.31
RS	90.66	52.35	1.73	0.58

**Fig. 1**

**Fig. 2**

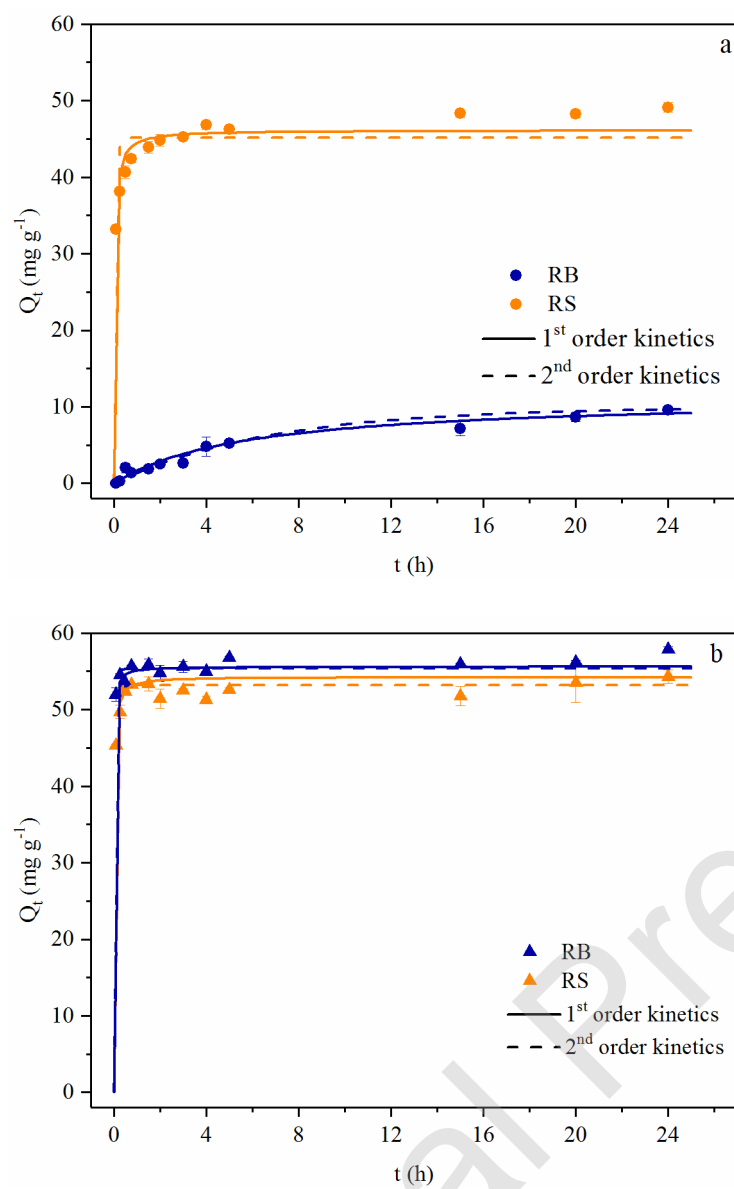
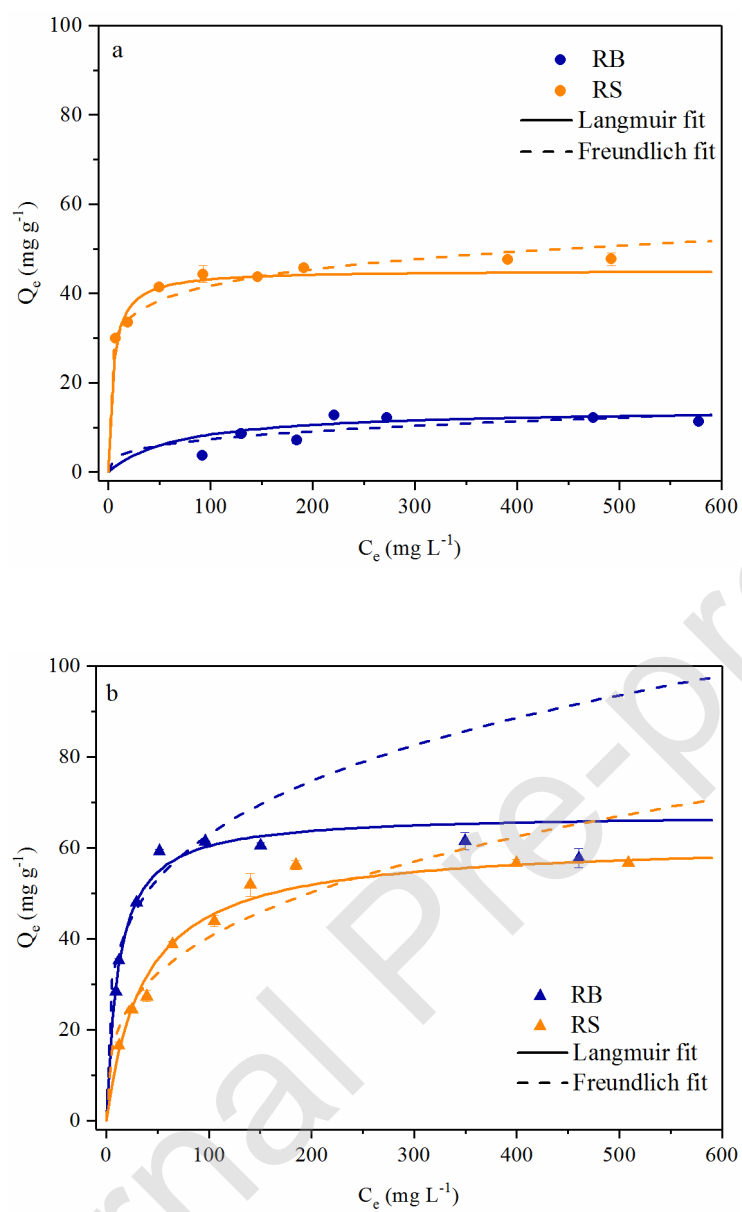
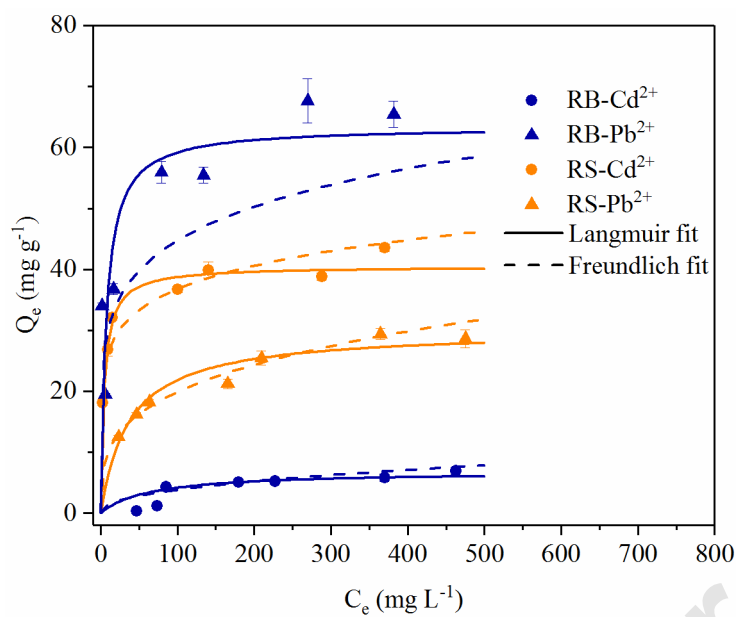


Fig. 3

**Fig. 4**

**Fig. 5**

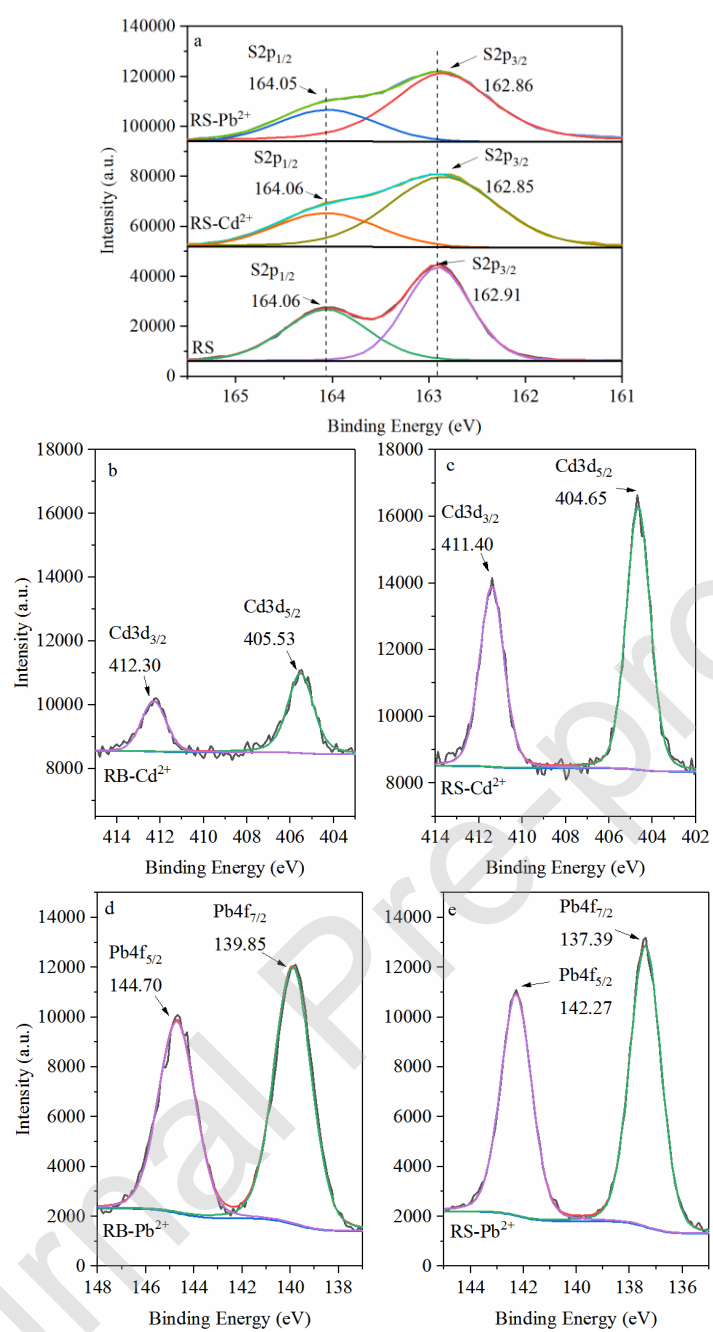


Fig. 6

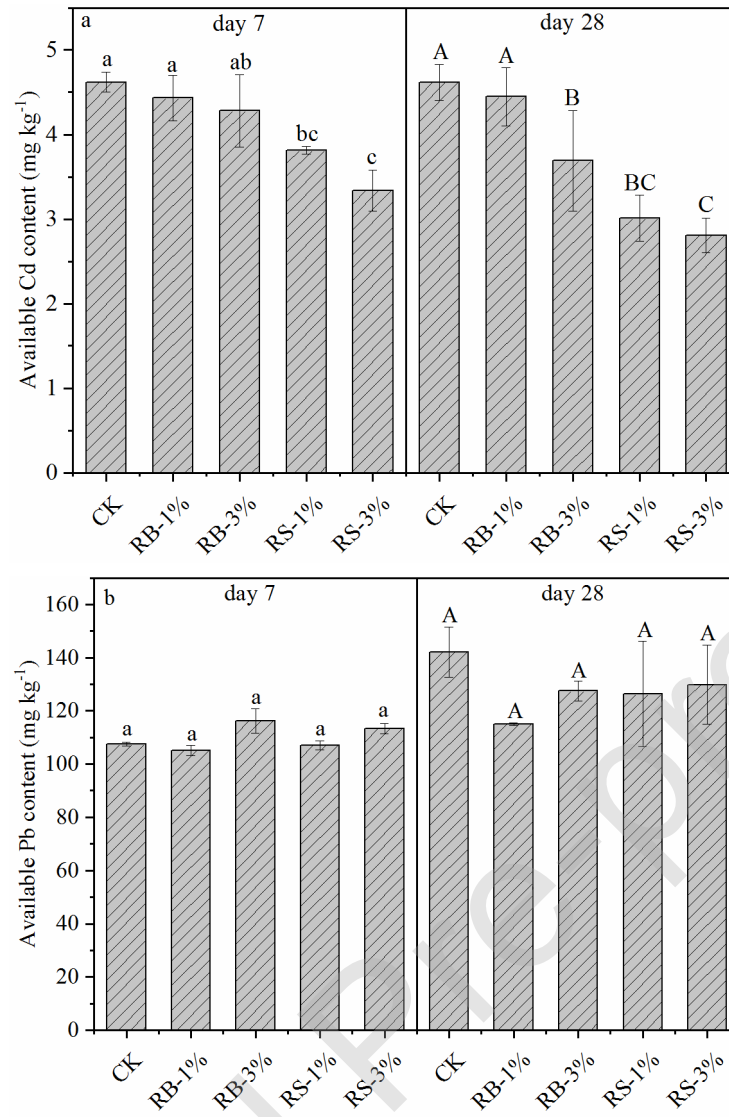


Fig. 7

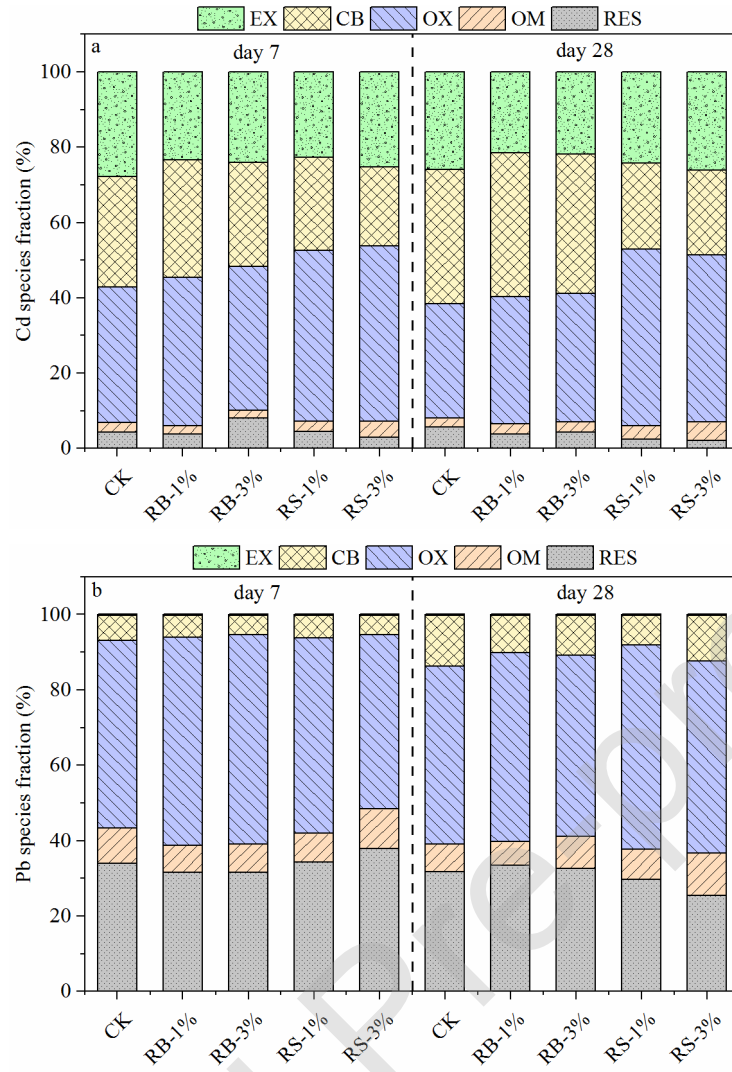


Fig. 8