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Original article

Chemical speciation distribution, desorption characteristics, and quantitative adsorption mechanisms of cadmium/lead ions adsorbed on biochars

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ABSTRACT

The adsorption characteristics of Cd^{2+} and Pb^{2+} with biochars have been widely reported. However, the desorption characteristics, chemical speciation, and stability of Cd^{2+} and Pb^{2+} adsorbed on biochars remain unclear. In this work, rice straw biochars were obtained at different pyrolysis temperatures (RSBC300, RSBC500, RSBC700). The chemical speciation and desorption characteristics of Cd- and Pb-loaded on biochars were investigated through Tessier sequential extraction and different desorption agents, and possible quantitative mechanisms of metal-laden biochars were revealed. Pyrolysis temperature influenced the properties of biochars obviously, including surface morphology, element and mineral composition, and carbon structure defects. RSBC700 and RSBC500 exhibited the highest adsorption capacity toward Cd^{2+} and Pb^{2+} , respectively. The majority of adsorbed metal ions on rice straw biochars are distributed in the carbonate fraction and the exchangeable fraction. Cd and Pb in all metal-loaded biochars showed a high risk with risk assessment code values larger than 50 %. HCl and EDTA-2Na could desorb most of the Cd²⁺ from the Cd-laden biochars, and desorb most of Pb^{2+} from high-temperature Pb-laden biochars. Precipitation with minerals (Q_{pre} , 52.77 %–82.37 %) and interaction with π -electrons (Q_{π} , 16.57 %–30.26 %) were the main Cd²⁺ adsorption mechanisms for all biochars, whereas precipitation with minerals (Q_{pre} , 18.82 %–58.71 %) and ion exchange (Q_{exc} , 19.18 %–48.81 %) were the main removal mechanisms for Pb^{2+} . Therefore, Cd^{2+} and Pb^{2+} adsorbed on biochars were not stable and easily released to the environment, which showed a high potential environmental risk.

1. Introduction

Cadmium (Cd) and lead (Pb) belong to the typical toxic heavy metals in wastewater, which can pose a potential threat to human health through the food chain (Lian et al., 2020). Among the different methods for metal elimination in wastewater, adsorption technology is widely applied because of its simple, cheap, and effective (Liu et al., 2022b). It is crucial to select a suitable cleanup, eco-friendly, and inexpensive adsorbent for heavy metal ions purification from wastewater efficiently.

Nowdays, biochar has caused great attention as a promising adsorbent because of its well-developed porous structure, abundant functional groups, good aromatic structure, and endogenous minerals (Qin et al., 2020; Pang et al., 2023; Vuppaladadiyam et al., 2023). The adsorption performance of biochar is highly relied on its physicochemical properties (Luo et al., 2022; Cheng et al., 2023; Li et al., 2023; Pinky et al., 2023). The pyrolysis temperature strongly determined the basic properties of biochars, which influenced their adsorption performance toward metal ions (Li et al., 2022; Zhang et al., 2023).

To date, adsorption characteristics of Cd^{2+} and Pb^{2+} on various biochars have been widely investigated (Qiu et al., 2021). In most cases, typical kinetic equations, and the isotherm equations were the most frequently used models to describe the adsorption characteristics of Cd^{2+} and Pb^{2+} on biochars (Liu and Zhang, 2022; Pathy et al., 2023). In addition, adsorption mechanisms of Cd^{2+} and Pb^{2+} by biochars were also fully explored, including mineral ion participation, surface functional groups action, and aromatic structure (Li et al., 2017). The dominant adsorption mechanisms depended considerably on the feedstocks and pyrolysis conditions (Lakshmi et al., 2021). Furthermore, the quantification of multiple adsorption mechanisms of Cd^{2+} and Pb^{2+} on biochars was also studied. For instance, some studies had quantified the

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different Cd²⁺ adsorption mechanisms, referring to cation exchange and precipitation: 59.55 %–76.05 %: 59.55–76.05 % (Huang et al., 2020); Cd²⁺– π interaction: 61.83–82.17 % (Wang et al., 2018); complexation and coordination: 22.4–62.0 % (Huang et al., 2018). Meanwhile, previous studies also quantified the contribution of different Pb²⁺ adsorption mechanisms, including precipitation and cation exchange: 85.6–92.6 % (Wang et al., 2015b); complexation and coordination: 7.6–24.9 %, 30.3–35.5 %, and 4.9–15.6 % (Lu et al., 2012); Pb²⁺– π interaction: 19.5–39.1 % (Gong and Chi, 2022), respectively. These abovementioned studies focused on exploration of the adsorption mechanisms and quantification of Cd²⁺ and Pb²⁺ on biochars. However, the speciation distribution of heavy metals adsorbed on biochars lacks attention, and their desorption characteristics have a shortage of studies.

Adsorption stability is involved in the release behavior, environmental risk, bioavailability, and final disposal of heavy-metal-laden biochars. Desorption studies and sequential extraction procedures were widely used to evaluate the stability of heavy metals in solid waste. In general, a desorption experiment is conducted to regenerate the adsorbent and assess its recycling potential. Among the desorption reagents, HCl and EDTA-2Na are the most widely used agents, which can desorb most metal ions from biochars. Many studies found that HCl and EDTA could desorb most of the Cd/Pb from the Cd/Pb-laden biochars, and were used as eluents for the regeneration of biochars (Wang et al., 2015a; Huang et al., 2019; Zhang et al., 2019). However, the comparison of different reagents and the desorption kinetics of Cd^{2+} and Pb^{2+} on biochars were rarely investigated. Meanwhile, speciation distribution can reflect the leaching assessment and ecological risk of heavy metals in biochars (Shen et al., 2020). The sequential extraction procedure was more adopted to evaluate the remediation effect of biochars on heavymetal-contaminated soil. The majority of adsorbed Cd2+ and Pb2+ onto the biochars was located in the acid-soluble fraction (Shen et al., 2017; Wang et al., 2021; Yang et al., 2022). Cd²⁺ was mainly distributed in the carbonate fraction (61.35-92.96 %) and the exchangeable fraction (5.59–29.78 %) in biochars after adsorption, and Pb²⁺ was mainly located in carbonate fraction (79.30-98.06 %) (Tian et al., 2021). But little information has been reported on the speciation of Cd²⁺ and Pb²⁺ adsorbed on biochars using the Tessier sequential extraction procedure. Furthermore, the potential ecological risk of Cd/Pb adsorbed on biochars has rarely been assessed.

In this work, rice straw biochars were obtained at 300, 500, and 700 °C. Then, the properties of biochars were elucidated using SEM–EDS, BET, XRD, Raman, FTIR, XPS, and element analysis, and used to adsorb Cd^{2+}/Pb^{2+} . A desorption study and Tessier sequential extraction procedure was conducted to assess the stability of Cd^{2+} and Pb^{2+} in Cd/Pb-loaded biochars. The detailed purposes of this work were as follows: (1) to investigate the influence of pyrolysis temperature on the physicochemical properties of biochars, (2) to study the desorption behavior of Cd^{2+}/Pb^{2+} from Cd/Pb-loaded biochars, (3) to assess the speciation distribution of Cd/Pb in Cd/Pb-loaded biochars, and (4) to quantify the main adsorption mechanisms of Cd^{2+}/Pb^{2+} on biochars. Therefore, this study could provide insight into the quantitative contribution of Cd^{2+}/Pb^{2+} adsorption mechanisms by rice straw biochars, and the stability of Cd^{2+} Pb²⁺ on biochars after adsorption.

2. Materials and methods

2.1. Biochar preparation

The procedure of pristine and demineralized biochars preparation could be seen in our previous study (Liu and Fan, 2018), which was shown in the Supplementary Information (SI).

2.2. Biochar characterization

The biochars was fully analyzed and the specific information was shown in **SI**, including scanning electron microscope and energy dispersive spectroscopy (SEM–EDS), N_2 adsorption–desorption isotherms (BET), X-ray diffraction (XRD), Raman, Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), and element analysis.

2.3. Adsorption experiments

The adsorption experiments were also showed in the SI.

2.4. Tessier sequential extraction and risk assessment code

To assess the adsorption stability of Cd^{2+}/Pb^{2+} on biochar and the potential release risk of Cd^{2+}/Pb^{2+} from biochar, Tessier sequential extraction procedure (Tessier et al., 1979) and the risk assessment code (RAC) method (Liu et al., 2016) was performed. The detailed experimental processes and calculation procedure was shown in the **SI**.

2.5. Desorption study

The detailed desorption study was shown in the SI.

2.6. Exploration of adsorption mechanisms

Many characterizations and measurements were performed to elucidate the adsorption mechanisms. In particular, Cd/Pb-loaded biochars were characterized using SEM–EDS, XRD, XPS, FTIR, and Raman analysis. In addition, the pH values of supernatants after Cd^{2+}/Pb^{2+} adsorption onto biochars and acid-washed biochars were also measured. The concentration of PO_4^{3-} in the supernatant after Cd^{2+}/Pb^{2+} adsorption was determined using ion chromatography (ICS-3000, Dionex Inc., USA). The concentrations of CO_3^{2-} and HCO_3^{-} in the supernatant were obtained through the titration method, whereas the concentrations of Ca^{2+} , Mg^{2+} , Na^+ , and K^+ in the supernatant were measured using ICP–OES.

2.7. Quantification of different adsorption mechanisms

Based on the previous literatures (Wang et al., 2015b; Cui et al., 2016), the main adsorption mechanisms of Cd^{2+}/Pb^{2+} onto biochars are ion exchange, precipitation with minerals, complexation with organic functional groups (OFGs), and Cd/Pb- π interaction. Quantification of different adsorption mechanisms was performed and shown in Supplementary Information (SI).

2.8. Practical application of biochars

The detailed practical application of biochars was presented in the SI.

3. Results and discussion

3.1. Characterization of biochars

The SEM-EDS of biochars are displayed in Fig. S1. As the increase in pyrolysis temperature, the surface of the biochar became more irregular, coarse, and porous. More particles could be observed on the surface of the biochars. Moreover, more minerals could be condensed in high-temperature biochars.

As shown in Fig. S2a, the biochars exhibit typical I/IV-type isothermal curves, indicating the presence of micropores structure (Ye et al., 2019). Moreover, the small hysteresis loop of the desorption branch extending from P/P_0 at 0.5 to 0.9 demonstrates the existence of abundant mesopores structure (Cheng et al., 2020). Thus, the pore structure of biochars showed multilayer and hierarchical. According to Fig. S2b, adsorption pores of biochars are mainly distributed in micropores and mesopores with the pore size ranging from 2 to 50 nm. The

Table 1

Basic properties of rice straw biochars.

Biochars	RSBC300	RSBC500	RSBC700
$S_{Total}/(m^2 \cdot g^{-1})$	70	98	155
$S_{Micro}/(m^2 \cdot g^{-1})$	61.0056	83.5069	134.0205
$S_{External}/(m^2 \cdot g^{-1})$	9.3974	14.9701	20.9314
$V_{Total}/(cm^3 \cdot g^{-1})$	0.045659	0.071233	0.100370
$V_{Micro}/(cm^3 \cdot g^{-1})$	0.031606	0.043078	0.071451
average pore diameter (nm)	16.4860	22.0595	11.3716
C (%)	52.31	54.50	60.27
Н (%)	3.435	1.857	0.82
O (%)	18.761	13.389	6.377
N (%)	1.09	0.93	0.61
S (%)	0.184	0.244	0.293
Ash (%)	24.22	29.08	31.63
H/C	0.0657	0.0341	0.0136
O/C	0.3587	0.2457	0.1058
(N + O)/C	0.3795	0.2627	0.1159
pH	8.54	9.67	9.73

pore size distribution of biochar at three temperatures was different, and RSBC700 presented a high mesoporous volume, followed by RSBC500 and RSBC300.

The textural parameters of biochars are listed in Table 1. With the



pyrolysis temperature increasing from 300 to 700 °C, the surface area of biochars increased from 70 to 155 $m^2\,g^{-1},$ and the pore volume of biochars increased from 0.045659 to 0.100370 cm³·g⁻¹. The micropore surface area and micropore volume also increased with the increase in pyrolysis temperature, suggesting that they were predominant in the biochars. The average pore diameter of RSBC700 was less than that of RSBC300 and RSBC500, which was beneficial for the diffusion of metal ions (Yuan et al., 2024).

The contents of elements, ash, and elemental ratio are presented in Table 1. The contents of C, S, and ash in the biochars increased, whereas the contents of H, O, and N decreased with increasing pyrolysis temperature. These changes were attributed to several reactions such as decarboxylation, dehydrogenation, decarbonylation, and deoxygenation that occurred during the pyrolysis process (Chen et al., 2020; Gupta et al., 2022). The H/C, O/C, and (N + O)/C ratios are generally used to evaluate the aromaticity, polarity, and hydrophilicity of biochars (Wang et al., 2016). As the pyrolysis temperature increased, the atomic ratios of H/C, O/C, and (N + O)/C decreased, suggesting that higher aromaticity, lower polarity, and hydrophilicity were observed in RSBC700. The pH value of the biochars increased with increasing pyrolysis temperature, which was ascribed to the condensation of mineral components in biochars (Yuan et al., 2011).



Binding energy (eV)

100

Fig. 1. XRD (a), Raman (b), FTIR (c), and XPS survey (d) of biochars.



Fig. 2. Adsorption capacity of Cd^{2+} (a) and Pb^{2+} (b) by biochars and acid washed biochars, and the chemical speciation distribution of Cd^{2+} (c) and Pb^{2+} (d) on biochars.

Fig. 1a shows the main minerals in biochars, namely, SiO₂, CaCO₃, and KCl. Two broad and weak peaks at $2\theta = 24^{\circ}$ ((002)) and 42° (100) were observed in the XRD pattern of the biochars (Hu et al., 2020; Tang et al., 2020). The appearance of the (002) peak implies the formation of amorphous carbon in the biochars. The intensity of peak (100) became more obvious in RSBC700, suggesting that more graphitic carbon structure was formed in biochar prepared at higher temperatures.

Two prominent peaks, the D band ($\approx 1360 \text{ cm}^{-1}$) and G band ($\approx 1580 \text{ cm}^{-1}$) in biochars, were found in the Raman spectra (Fig. 1b). The D-band intensity originated from sp³ hybridization, and the G band was induced by crystalline graphitic/sp² carbon atoms (Ma et al., 2020). The area ratio of the D band to the G band (A_D/A_G) of RSBC300 was larger than that of RSBC500 and RSBC700, suggesting the existence of structural defects and disorder in RSBC300. As the pyrolysis temperature increased from 500 to 700 °C, the A_D/A_G ratio increased from 3.71 to 5.17, indicating the increase in the proportion of condensed aromatic ring structures with defects (Mei et al., 2021; Xu et al., 2022; Huang et al., 2023).

The surface functional groups of the biochars are presented in Fig. 1c; the pyrolysis temperature also influenced the surface functional groups in biochars. In the FTIR spectra, the position of the C=C (1630 cm⁻¹), $-CH_2$ (1401 cm⁻¹), Si-O—Si (1111 and 557 cm⁻¹) significantly changed with the increasing pyrolysis temperature (Fan et al., 2018). The change of surface functional groups may influence the binding ability toward Cd²⁺ and Pb²⁺ ions.

The valence states of the surface elements and composition of the biochars were measured using XPS (Fig. 1d). The peaks of C 1s, O 1s, N 1s, Si 2p, Ca 2p, and Mg 2p were observed on the surface of the biochars.

The relative content of various elements also changed with the increase in pyrolysis temperature. Obviously, minerals also could be found on the surface of the biochars.

According to the XPS peak fitting results (Fig. S2), the highresolution spectra of the C 1s peak of RSBC300 show that the C 1s peaks located at 284.73, 285.66, and 288.35 eV are ascribed to C–C/ C=C/C–H, C–O, and C=O, respectively (Yang et al., 2016). The O 1s spectrum of RSBC300 could be decomposed into two peaks at 533.08 and 531.42 eV, which are ascribed to the C=O and C–O, respectively (Yao et al., 2022), respectively. In addition, pyrolysis temperature affected the types and relative percentage of functional groups (C=O and C–O).

3.2. Adsorption capacity of Cd^{2+} and Pb^{2+} by biochars and acid washed biochars

The adsorption capacity of Cd^{2+} and Pb^{2+} by biochars and acidwashed biochars are presented in Fig. 2a and 2b. Specifically, RSBC700 exhibited the highest adsorption capacity for Cd^{2+} and were 62.45 mg•g⁻¹, whereas RSBC500 showed the greatest adsorption capacity for Pb^{2+} and reached 167.49 mg•g⁻¹. However, the adsorption capacity of Cd^{2+} and Pb^{2+} by biochars extremely decreased after acid demineralization treatment, implying that soluble minerals played a crucial role in the adsorption process of Cd^{2+} and Pb^{2+} , which contributed 50 %–80 % for Cd^{2+} adsorption, 61 %–75 % for Pb^{2+} adsorption. In addition, RSBC300-A showed the highest adsorption capacity toward Cd^{2+} and Pb^{2+} among the acid-washed biochars, which could be ascribed to the presence of functional groups in low-

Table 2

Risk assessment code (RAC) of toxic elements in the metal-laden biochars.

Biochars	Cd (%)	Pb (%)
RSBC300	90.22	57.70
RSBC500	95.56	83.49
RSBC700	97.24	87.40

temperature biochars.

Other studies have also confirmed that minerals could play an crucial role and take part in the adsorption process through ion exchange and precipitation mechanisms, especially for Cd^{2+} , Pb^{2+} , Cu^{2+} , etc (Xu et al., 2017; Gholizadeh and Hu, 2021; Wu et al., 2021). Meanwhile, surface functional groups and the aromatic graphite structure of biochars could bind with heavy-metal ions via complexation and cation– π interaction. (Berslin et al., 2022).

3.3. Speciation distribution and RAC of Cd^{2+} and Pb^{2+} on biochars

Fig. 2c and 2d shows the chemical distribution of Cd and Pb adsorbed on the Tessier fractions of biochars. The majority of adsorbed Cd^{2+} on rice straw biochars was in the F1 and F2 fractions. Cd^{2+} was bound to the carbonate fraction (45.52 %–61.77 %) and the exchangeable fraction (33.79 %–44.70 %). For Pb²⁺, the majority of adsorbed Pb²⁺ on RSBC300 was in the F1 (39.9 %) and F3 (29.96 %) fractions, followed by the F2 fraction (18.30 %). However, most of the adsorbed Pb²⁺ on RSBC500 and RSBC700 was distributed in the F2 fraction (82.00 %–85.56 %). The speciation of heavy metals adsorbed on biochars also could reflect the adsorption mechanisms. In this work, the majority of adsorbed Cd²⁺ and Pb²⁺ on rice straw biochars were in the F1 and F2 fractions, suggesting that occurrence of precipitation and ion exchange (Frišták et al., 2014; Ke et al., 2023).

Among these five fractions, the exchangeable fraction is the most threatening fraction, and the sum of the exchangeable and carbonate fractions can be regarded as the bioavailable fraction (Sun et al., 2022). In this work, Cd^{2+} and Pb^{2+} adsorbed on rice straw biochars were not stable and easily released to the environment, which poses a potential environmental threat. Compared with Pb^{2+} , Cd^{2+} displayed a high environmental risk due to its high F1 fraction.

Furthermore, the values of RAC for the Cd and Pb in metal-loaded biochars are displayed in Table 2. Cd and Pb in all metal-loaded biochars showed a high risk with RAC values greater than 50 %. In particular, Cd^{2+} and Pb^{2+} loaded on RSBC700 presented a higher risk. Furthermore, the environmental risk of Cd was greater than that of Pb.

Therefore, the biochars after Cd^{2+} and Pb^{2+} adsorption should be disposed of suitably to avoid secondary pollution or environmental risk.

3.4. Desorption characteristics of Cd^{2+} and Pb^{2+} from biochars after adsorption

The desorption amount of Cd^{2+} from Cd-laden biochars with different desorption agents is shown in Fig. 3a-3d. With the increase in desorption time, more Cd^{2+} ions were released into the solution. The desorption capacity was larger at the initial stage, and gradually tended to be stable at the later stage. The desorption deficiency of different desorption agents showed the order of HCl > EDTA-2Na > H₂O > NaOH. When H₂O acted as the desorption reagent, RSBC500 presents a high desorption capacity. In contrast, when HCl, NaOH, and EDTA-2Na were used as the desorption reagents, RSBC700 showed a high desorption capacity due to its high adsorption capacity toward Cd^{2+} .

For Pb²⁺, the desorption capacity from Pb-laden biochars with different desorption agents is shown in Fig. 3e-3 h. As desorption time increased, the desorption amount was larger at the initial stage, and gradually decreased at a later stage. The order of different desorption agents toward Pb desorption from biochar was EDTA-2Na > HCl > $NaOH > H_2O$. When H_2O was acting as the desorption reagent, RSBC700 showed a high desorption capacity, followed by RSBC500 and RSBC300. RSBC500, RSBC700, and RSBC300 exhibited a high desorption amount when HCl was used as the desorption agent. The desorption capacity from RSBC500 and RSBC700 was greater than that from RSBC300. When NaOH acted as the desorption agent, the desorption amount first increased but then decreased with increasing desorption time. The desorption capacity of Pb from biochars became low when the desorption time was 12 h because most Pb had been desorbed from the metalladen biochars or the desorbed Pb²⁺ occurred secondary adsorption on the surface of biochars. When EDTA-2Na was applied as the desorption agent, the desorption amount of Pb from RSBC300 and RSBC700 first

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Desorption rate of Cd^{2+} and Pb^{2+} from biochars.

	Biochars	H ₂ O (%)	HCl (%)	NaOH (%)	EDTA-2Na (%)
Cd^{2+}	RSBC300	8.72	100.00	1.63	93.64
	RSBC500	6.96	100.00	0.62	95.61
	RSBC700	3.05	96.95	0.83	85.40
Pb^{2+}	RSBC300	1.59	34.94	6.38	50.45
	RSBC500	2.89	68.66	3.59	67.11
	RSBC700	1.87	73.53	1.26	84.15



Fig. 3. Desorption kinetics of Cd^{2+} from Cd-laden biochars (a-d), and Pb^{2+} from Pb-laden biochars (e-h).

L. Liu et al.



Fig. 4. XRD (a), FTIR (b), XPS (c), and pH change on biochars after Cd²⁺ adsorption.

increased, then tended to become stable with the increase in desorption time. The desorption amount of Pb from RSBC500 using EDTA-2Na was stable.

The desorption extent of Cd/Pb from the Cd/Pb-laden biochars is listed in Table 3. Herein, HCl and EDTA-2Na exhibited the highest desorption extent, indicating that most of the Cd/Pb can be desorbed from biochars. HCl can destroy the mineral composition and the structure of the biochar, resulting in the release of Cd/Pb into the solution (Zhang et al., 2019). EDTA-2Na has a strong chelating ability and realizes desorption by chelating with Cd/Pb on the surface of the biochar (Pal and Maiti, 2019).

For RSBC300 and RSBC700, the desorption extent of Pb^{2+} by EDTA-2Na was larger than that of HCl. For RSBC500, the desorption extent of Pb^{2+} by HCl was slightly greater than that of EDTA-2Na. The results of the desorption experiment stayed the same with the analysis of the Tessier sequential extraction procedure. Exchangeable and carbonate fractions of Cd/Pb on biochars could be extracted when HCl and EDTA-2Na were used as desorption reagents.

In this study, the desorption kinetic experiment lasted 720 min due to the stable leaching of metal ions. However, future study was required to be performed in a long-term time to validate the results of desorption kinetics. 3.5. Adsorption mechanisms of Cd^{2+} and Pb^{2+}

(1) Precipitation with minerals

Based on the SEM–EDS of biochars after Cd^{2+} and Pb^{2+} adsorption (Fig. S4 and Fig. S5), many particles and crystal minerals were found on the surface of the biochars. The Cd and Pb could be directly found on the surface of the biochars, which confirmed that precipitation with minerals occurred during the adsorption process.

The typical anion concentrations in the supernatant after Cd^{2+} and Pb^{2+} adsorption are showed in Table S1. Compared with the control group, the concentrations of CO_3^{2-} , HCO_3^{-} , and PO_4^{3-} decreased after Cd^{2+} adsorption, indicating that potential precipitation occurred. Furthermore, the decrease in concentration of HCO_3^{-} and PO_4^{3-} after Pb adsorption directly confirmed the presence of precipitation.

As shown in Fig. 4a, CdCO₃ in RSBC300, and CdCO₃ and Cd(OH)₂ in RSBC500 and RSBC700 were formed after Cd adsorption. Therefore, precipitation with minerals was key for the high removal of Cd²⁺ by rice straw biochars (Yang et al., 2021). As shown in Fig. 5a, much Pb-containing precipitation was observed in biochars after Pb²⁺ adsorption. To be specific, PbC₂O₄, Pb₃(PO₄)₂, Pb₂(SO₄)O, and 3PbCO₃·2Pb (OH)₂·H₂O were detected on the surface of RSBC300. For RSBC500 and RSBC700, Pb₅(PO₄)₃Cl, Pb₃(CO₃)₂(OH)₂, Pb₂O₃, Pb₄O(PO₄)₂, Pb₃C₂O₇, Pb₄(SO₄)(CO₃)₂(OH)₂, and Pb₅(PO₄)₃OH were found on the surface of



Fig. 5. XRD (a), FTIR (b), XPS (c), and pH change on biochars after Pb²⁺ adsorption.

the biochars. Thus, precipitation with minerals was responsible for the Pb^{2+} adsorption (Chang et al., 2020).

Overall, the above characterization and analysis confirmed that the occurrence of precipitation during the adsorption process was caused by the anions in the biochars.

(2) Ion exchange

Comparing the results of Fig. S1 with Fig. S4 and Fig. S5, typical minerals cation ions on the surface of biochar disappeared after Cd^{2+} and Pb^{2+} adsorption, suggesting the occurrence of ion exchange.

Comparing the XPS analysis of biochar in Fig. 1d with Fig. 4c and Fig. 5c, the relative content of Ca 2p and Mg 2p of the biochars decreased after Cd and Pb adsorption, which suggested that ion exchange took place during the Cd^{2+} and Pb^{2+} adsorption process.

The release of minerals cation ions by all biochars was measured after Cd^{2+} and Pb^{2+} adsorption and listed in Table S1. More Ca^{2+} , Mg^{2+} , and K^+ were released to the solution after Cd^{2+} and Pb^{2+} adsorption on biochars, implying the occurrence of an ion exchange mechanism.

In short, the above results also confirmed ion exchange happened during the adsorption process.

(3) Complexation interaction

FTIR and XPS of biochars after heavy metal ions adsorption were characterized to elucidate the complexation interaction.

Compared with the FTIR of biochars in Fig. 1c, some peaks shifted after Cd adsorption on biochars (Fig. 4b). For RSBC300, the peaks at 1630, 1111, and 557 cm⁻¹ shifted to 1618, 1104, and 563 cm⁻¹, respectively. For RSBC500, 1420 and 554 cm⁻¹ shifted to 1407 and 580 cm⁻¹, respectively. For RSBC700, 3449, 1625, 1098, and 464 cm⁻¹ shifted to 3442, 1630, 110, and 467 cm⁻¹, respectively. Compared with the FTIR of biochars in Fig. 1c, some peaks also shifted after Pb adsorption on biochar (Fig. 5b). For RSBC300, the peaks at 3443, 1630, and 557 cm⁻¹ shifted to 3439, 1639, and 553 cm⁻¹, respectively. For RSBC500, 3440, 1617, 1420, and 554 cm⁻¹ shifted to 3443, 1629, 1401, and 550 cm⁻¹, respectively. For RSBC700, 3449, 1625, 1098, and 464 cm⁻¹ shifted to 3443, 1633, 1117, and 450 cm⁻¹, respectively. These changes suggested that OFGs in biochar toke prat in the binding of Cd²⁺/ Pb²⁺ through complexation.

Compared with the XPS of biochars in Fig. S3, the binding energy and distribution of carbon- and oxygen-related groups changed after Cd^{2+} adsorption on biochars (Fig. S6). In addition, the OFGs also changed after Cd^{2+} adsorption. Moreover, the Cd $3d_{3/2}$ and Cd $3d_{5/2}$ peaks were observed on the surface of biochars after Cd^{2+} adsorption (Liu et al., 2022a; Tan et al., 2022). Compared with the XPS of biochars in Fig. S3, the binding energy and distribution of carbon- and oxygencontaining groups changed after Pb²⁺ adsorption on biochars



Fig. 6. Adsorption capacity and quantitative contributions of different sorption mechanisms, (a) and (b) for Cd^{2+} , (c) and (d) for Pb^{2+} .

(Fig. S7). Furthermore, the Pb $4f_{5/2}$ and Pb $4f_{7/2}$ peaks were found on the surface of biochars after Pb²⁺ adsorption (Wu et al., 2021).

As shown in Fig. 4d and Fig. 5d, the pH of RSBC-A after Cd^{2+} and Pb^{2+} adsorption was less than the control groups without Cd^{2+} and Pb^{2+} adsorption, illustrating the complexation interaction between Cd^{2+}/Pb^{2+} and OFGs. The complexation reactions can be seen in the following reactions.

$$-$$
 COOH $+$ Cd²⁺/Pb2 $+$ $+$ H₂O \rightarrow $-$ COOCd⁺/Pb $+$ $+$ H₃O⁺

$$-OH + Cd^{2+}/Pb2 + H_2O \rightarrow -OCd^+/Pb + H_3O^+$$

(4) Cd- π interaction

Based on the FTIR and XPS, the aromatic carbon structure (1630 cm⁻¹ in FTIR) and graphene-like structure (C–C/C—H/C==C in XPS) in biochars changed after Cd²⁺ and Pb²⁺ adsorption, suggesting that Cd/Pb– π interaction took place during the adsorption process. In addition, the Cd/Pb– π interaction could be observed directly in the XPS analysis of Cd 3p and Pb 4f.

Raman spectroscopy analysis also could be used to revela the adsorption mechanism (Fan and Zhang, 2021). According to the Raman

spectra (Fig. S8) of biochar after Cd²⁺ and Pb²⁺ adsorption, the decrease in A_D/A_G values indicated the presence of Cd/Pb- π interaction when compared with the results in Fig. 1b.

3.6. Quantitative contributions of different sorption mechanisms

The pyrolysis temperature significantly influenced the heavy metal adsorption mechanisms on biochars. The Q_{exc} , Q_{pre} , Q_{com} , and Q_{π} values of biochars were 0.02–2.36, 21.63–51.44, 0.64–4.60, and 10.35–12.93 mg•g⁻¹, respectively (Fig. 6a.). As the pyrolysis temperature increases, the Q_{exc} values of biochars decreased due to the minerals becoming stable at high temperatures, and Q_{com} values of biochars decreased due to the lower abundance of functional groups. The Q_{pre} values of biochars also greatly increased with the increasing pyrolysis temperature. Precipitation with minerals played a key role in the adsorption of Cd²⁺, especially for the high-temperature biochar. As shown in Fig. 6b, the relative contribution percentage of Q_{exc} , Q_{pre} , Q_{com} , and Q_{π} values of biochars were 0.03 %–5.75 %, 52.77 %–82.37 %, 1.03 %–11.22 %, and 16.57 %–30.26 %, respectively. The contributions of Q_{exc} , Q_{com} , and Q_{π} decreased with increasing temperature, whereas the contribution of Q_{pre} was gradually predominant at high pyrolysis temperatures.

For Pb²⁺ (Fig. 6c), the Q_{exc} , Q_{pre} , Q_{com} , and Q_{π} values of biochars



Fig. 7. Practical application of biochars, (a) and (b) for recycle, (c) and (d) for real waterbodies.

were 30.42–75.93, 25.14–93.17, 0.88–26.22, and 17.00–34.14 mg•g⁻¹, respectively. As the increasing of pyrolysis temperature, the $Q_{\rm pre}$ and Q_{π} values of biochars increased, whereas the $Q_{\rm com}$ values of biochars decreased. The Qexc values of biochars first increased and then decreased with the increasing pyrolysis temperature. Thus, minerals in biochar could participate in the interaction of precipitation and exchange, which became the dominant mechanism during the adsorption process. As shown in Fig. 6d, the relative contribution percentages of Qexc, Qpre, $Q_{\rm com}$, and Q_{π} values of biochars were 19.18 %-48.81 %, 18.82 %-58.71 %, 0.55 %-19.63 %, and 12.73 %-21.52 %, respectively. As the pyrolysis temperature increased, the relative contributions of Q_{pre} and Q_{π} increased, whereas the relative contributions of Q_{exc} and Q_{com} decreased. The increased contributions of Q_{pre} and Q_{π} were attributed to the soluble minerals in biochar and graphitic structure, but the increased contributions of Qexc and Qcom were ascribed to the passivation of minerals in biochar, and the disappearance of OFGs.

Therefore, quantitative contributions of different sorption mechanisms could be used to explain the speciation distribution and environmental risk of Cd^{2+} and Pb^{2+} adsorbed on biochars, and the desorption characteristics of Cd^{2+} and Pb^{2+} from biochars after adsorption.

3.7. Practical application of biochars

The regeneration performance of biochars for metal ions is shown in Fig. 7a and Fig. 7b. The adsorption performance of biochars toward metal ions decreased significantly due to the loss of minerals since the precipitation with minerals and ion exchange were the dominant mechanisms for metal ions adsorption, especially Cd^{2+} . Thus, the

recycle potential of biochars was limited due to the decrease of binding sites.

The real application of biochars toward metal ions removal in various waterbodies is presented in Fig. 7c and Fig. 7d. As seen in the results, biochars exhibited a good adsorption performance toward Cd^{2+} and Pb^{2+} in domestic wastewater and tap water. Furthermore, biochars displayed a high removal rate toward Pb^{2+} in lake water and river water. Further study should be conducted to modify the biochars to improve their adsorption performance.

4. Conclusions

The majority of adsorbed Cd²⁺ on rice straw biochars was in the carbonate fraction and the exchangeable fraction. Cd and Pb in all metal-loaded biochars presented high risk, with RAC values greater than 50 %. HCl and EDTA-2Na could desorb most of the Cd²⁺ and Pb²⁺ from metal-laden biochars. Precipitation with minerals, ion exchange, and interaction with π -electrons were the main Cd²⁺/Pb²⁺ adsorption mechanisms, which was controlled by pyrolysis temperature. Therefore, Cd²⁺ and Pb²⁺ adsorbed on biochar were not stable and easily released to the environment, which shows a potential environmental risk. Biochars after Cd²⁺ adsorption should be treated suitably to avoid causing secondary pollution.

CRediT authorship contribution statement

Li Liu: Methodology, Writing – original draft, Software, Formal analysis, Investigation. Shisuo Fan: Investigation, Conceptualization, Supervision, Project administration. Zixin Wang: Methodology, Formal analysis, Investigation, Data curation. Jingjing Hu: Methodology, Software, Investigation, Data curation.

Declaration of competing interest

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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Appendix A. Supplementary data

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L. Liu et al.

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