Effects of modification and co-aging with soils on Cd(II) adsorption behaviors and quantitative mechanisms by biochar

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Received: 18 November 2021 / Accepted: 8 January 2022 / Published online: 18 January 2022
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Abstract
In this study, original and two KMnO4-modified rice straw biochars (pre- and postmodification) were prepared, which were all pyrolysed at 400 °C. Premodified biochar had the largest Cd adsorption capacity, strongest acid and solute buffering capacity, which benefited from the increase of carbonate content, specific surface area, and the emergence of Mn(II) and MnOx through modification. Original and premodeled biochars were then conducted four types of aging process by an improved three-layer mesh method, namely, aging without soil and co-aging with acid (pH = 5.00), neutral (pH = 7.00), and alkaline (pH = 8.30) soils. The adsorption capacities of modified biochar were always larger than those of original biochar after aging processes. After four aging processes, Cd(II) adsorption capacities were basically in the order of aged biochar without soil > biochar co-aged with alkaline soil > biochar co-aged with neutral soil > biochar co-aged with acid soil, and KMnO4-modified biochar was always better than original biochar after co-aging with soils. The dominant adsorption mechanism of original and premodeled biochars (fresh and aged) for Cd(II) was all the precipitation and adsorption with minerals (accounted for 58.55 ~ 85.55%). In this study, we highlighted that biochar remediation for Cd should be evaluated by co-aging with soil instead of aging without soil participation.

Keywords Biochar · Modification · Cadmium · Adsorption · Mechanisms · Co-aging

Introduction
In recent years, farmland soils have been seriously polluted by heavy metals from exhaust gas emissions, mining, and smelting, of which cadmium (Cd) is recognized as one of the most dangerous heavy metals due to its high toxicity and fluidity; more seriously, it can be enriched in fruits, vegetables, and aquatic organisms and eventually enter the human body through food chain, causing kidney failure and other diseases (Chen et al., 2008; Li et al., 2010; Liu et al., 2010; Rizwan et al., 2016). Currently, in situ technology is considered as one of the most cost-effective remediation methods to deal with heavy metal pollution (Inyang et al., 2012; Sun et al., 2013). As an in situ remediation agent, the high efficiency of biochar on Cd remediation in the soil has been verified due to its unique physicochemical properties, including high pH value, large cation amounts, and huge specific surface area (Ahmad et al., 2018; Cai et al., 2021; Fan et al., 2020; Trakal et al., 2014; Meng et al., 2013; Qian et al., 2016).

Many studies indicated that Cd(II) adsorption capacities of biochars prepared in laboratory muffle furnace basically increased with increasing pyrolysis temperatures from 300 to 700 °C (Deng et al., 2018, 2019). However, it is difficult to produce biochar pyrolyzed at relatively high temperatures (i.e., 500 ~ 700 °C) under large-scale factory conditions, but Cd(II) adsorption capacities of original biochars pyrolyzed at relatively low temperatures were limited (Han et al., 2013b; Liu & Fan, 2018). Therefore, to realize the large-scale application of biochar in the field, researches of modified biochars pyrolyzed at relatively low temperature (i.e., 300 ~ 400 °C) should be increasingly carried out (Wang et al., 2017). Currently, modification methods are mainly divided into physical modification (Lyu et al., 2018; Rajapaksha et al., 2015) and chemical modification (Hadjittofi
et al., 2014; Song et al., 2014). As a relatively inexpensive reagent, KMnO₄ has been increasingly applied to modify biochars in recent years, and the maximum Cd(II) adsorption capacities of KMnO₄-modified biochars were 2.16~5.9 times than original ones (Li et al., 2017; Liang et al., 2017; Wang et al., 2015a; Yin et al., 2019).

Although stable properties have been frequently reported for biochars, once applied in soil, biochar will interact with soil and inevitably experience a series of aging processes in the field. Aging in soils can cause property changes of biochar, and further affect Cd(II) adsorption behaviors of biochar (Wang et al., 2020). The modification effects of KMnO₄ cannot be judged only by Cd(II) adsorption capacity of fresh biochar, but also the property changes and Cd(II) adsorption behaviors of modified biochar after co-aging with soil. Moreover, Cd(II) adsorption behaviors of biochars after co-aging with soil might vary in soils with different pH. Therefore, it is necessary to investigate the effects of co-aging with different soils on Cd(II) adsorption behaviors by biochars. Due to the long time cost of natural aging, artificial accelerated aging methods have been increasingly employed to simulate long-term aging process in the field (Chang et al. 2019; Fan et al., 2018; Quan et al. 2020).

However, most previous studies investigated aging effects on biochar adsorption behaviors only based on aged biochars without soil participation, which was far from natural aging of biochar in field soils (Deng et al., 2020), because it is a big challenge to separate biochar from soil. Therefore, it is necessary to investigate biochar remediation effects for Cd by co-aging with soil.

Cd(II) adsorption mechanisms are important to reveal the modification effects of biochar. Currently, the adsorption mechanisms between biochar and heavy metal ions mainly include cation exchange, complexation, precipitation, and other potential mechanisms (Cui et al., 2016; Wang et al., 2015b). Deng et al. (2019) indicated that cation exchange and precipitation with minerals were respectively the main Cd(II) adsorption mechanisms of rice straw biochars pyrolyzed at 400 and 700 °C. However, the effects of modification and co-aging with soils on Cd(II) adsorption mechanisms by biochar are still unclear.

In this study, an improved three-layer mesh method was conducted to ensure the close contact between soil and biochar during aging, meanwhile realizing the easy separation of biochars after aging. Thereby, biochars after co-aging with acid, neutral, and alkaline soils were obtained, then the acid and solute buffering capacity, Cd(II) adsorption behaviors, and mechanisms of co-aged biochars were investigated. Here we test the hypothesis that both modification and co-aging with soils affect Cd(II) adsorption behaviors and mechanisms of biochar. The main objects of this study were (1) to compare the adsorption capacities, acid and solute buffering capacity of original and modified biochars; and (2) to investigate effects of aging without soil participation and co-aging with soil on Cd(II) adsorption behaviors and mechanisms by original and modified biochars.

Materials and methods

Preparation of original and modified biochars

Original biochar (BC) was prepared as a control, in brief, rice straw sample gathered from a farmland in Jingmen City, Hubei Province, was rinsed several times with pure water, air dried in an oven, ground, and sieved to <0.3 mm to obtain rice straw biomass. Rice straw biomass was filled into a crucible sealed with tin foil, which was then placed in a muffle furnace, heated to 400 °C and held for 4 h before cooling to room temperature.

Premodified and postmodified biochars were prepared using 0.1 mol·L⁻¹ KMnO₄ solution (Wang et al., 2015a). For premodified biochar (MBC), briefly, 50 g of rice straw biomass was immersed in 250 mL of 0.1 mol·L⁻¹ KMnO₄ solution and sonicated for 2 h to make them react adequately, and the mixture was then dried in an oven, ground, and sieved to <0.3 mm, and the subsequent pyrolyzing process was the same as BC. Postmodified biochar (OBC) was prepared by reacting BC with 0.1 mol·L⁻¹ KMnO₄ solution using the same method described above and then dried in an oven, ground, and sieved to <0.3 mm.

Biochar characterization

Carbonate contents of biochars were measured according to the hydrochloric acid titration method, and the elemental analyzer (ARARIO EL III, Elementar, Germany) was employed to analyze the contents of carbon, hydrogen, and nitrogen in biochars. The surface areas of biochars were detected using the BET method and porosity analyzer (ASAP 2020 M, Mike, USA). Field Emission Scanning Electron Microscope (FESEM, Zeiss SIGMA, Carl Zeiss, England) was applied to detect the changes in the element contents and surface morphology of biochars. The surface functional groups were determined by using Fourier Transform Infrared Spectrometer (FTIR5700, Thermo, USA) by measuring the absorbance from 400 to 4000 cm⁻¹. X-Ray Diffractometer (XRD, XPert Pro, Panaco, Holland) was used to study the crystalline minerals on biochars, especially the crystalline Mn minerals. X-ray Photoelectron Spectroscopy (XPS, Thermo, USA) was carried out to determine the existing forms of MnOₓ on two modified biochars. The basic properties of three biochars are listed in Table 1, and the images of XPS, FTIR, XRD, and FESEM-EDS are shown in Fig. 3, Fig. 4, Fig. 5, and Fig. S1, respectively.
Adsorption isotherms and adaptability of original and modified biochars

To determine Cd(II) adsorption isotherms of biochars, 0.02 g of biochar sample was added to a centrifuge tube containing 20 mL of Cd(II) solution (pH = 5.5) with a background electrolyte of 0.01 mol·L⁻¹ NaNO₃ solution, and the Cd(II) concentrations ranged from 5 to 200 mg·L⁻¹. After centrifuge tubes were shaken in a water bath shaker at 200 rpm for 24 h at 25 °C, the sample was then withdrawn, and subsequently filtered through 0.45 µm nylon membrane filters. The Cd(II) concentration in the filtrate was detected by flame atomic absorption spectrometry (AAS, Agilent 240 Duo AA, USA).

To evaluate the adaptability of modified biochars, the adsorption capacities of biochars under different pH and ionic strength conditions were also tested. Biochars were added to Cd(II) solutions (200 mg·L⁻¹) with different pH values (3.0–7.0) and ionic strength (0–0.1 mol·L⁻¹ Na(I)). After the 24 h of shaking at 200 rpm in a water bath shaker at room temperature, the same procedures were conducted as described above to determine Cd(II) concentrations. To further study the adaptability of modified biochars under acidic contaminated conditions, an acid buffer experiment was carried out. In brief, 1 g of biochar was added to 20 mL of 0.01 mol·L⁻¹ CaCl₂ solution, and 0.5 mL of 2% HNO₃ solution was added each time, then the sample was shaken at 200 rpm for 12 h, and the pH value was measured, of which this operation was repeated for 8 times.

Preparation of co-aged biochars

According to the results of Cd(II) adsorption capacities and adaptability of biochars in aqueous solutions, MBC was obviously better than OBC; therefore, only MBC was selected to co-age with soils in the following experiments, and BC was used as comparison. Three kinds of non-cadmium contaminated soil, acid (pH = 5.00), neutral (pH = 7.00), and alkaline (pH = 8.30), were employed in this experiment, which were respectively gathered from Nanchang City (116.045°E, 28.635°N), Jingmen City (112.044°E, 31.097°N), and Bayannur City (107.398°E, 41.027°N), China. An improved three-layer mesh method was employed, which not only ensured close contact between soil and biochar during aging, but also realized the separation of biochars after aging (Meng et al., 2020). Briefly, four 600-mesh nylon nets (15 cm × 20 cm) were divided into three inside layer spaces, which were filled with 50 g soil, 3 g fresh biochar (BC or MBC), and 50 g soil in order, and the outermost four sides of nylon nets were tightly sealed with glue, and finally the bottom and top of sample were fixed with stainless steel plates by clips.
Wang et al. (2020) indicated that quantitative artificial aging methods should be applied to make predictions of biochar’s long-term performance. Therefore, in this experiment, freeze–thaw cycling and dry–wet cycling were combined to closely simulate the natural aging in the field, and the 54-day aging process simulated 6-year natural aging according to the multi-year average meteorological data of Wuhan city, China (Xu et al., 2018). Additionally, aged biochars without soil participation were also prepared for comparison. According to the meteorological data in Wuhan city, the average time that the precipitation amount is over 50 mm was approximately 6 days per year, and the average time that the minimum air temperature is lower than −5 °C was approximately 3 days per year. We assumed that one combined aging process consisted of dry–wet cycling and freeze–thaw cycling in a ratio of 2:1, and every 2 days of dry–wet cycling followed by 1-day freeze–thaw cycling. For each dry–wet cycling (1 day), three-layer mesh samples were saturated to 100% water-holding capacity with pure water, kept at 25 °C for 12 h, and then dried at 60 °C for 12 h in an oven (Hale et al., 2011). For each freeze–thaw cycling (1 day), samples were saturated to 100% water-holding capacity with pure water, kept at −20 °C for 12 h, and then thawed at 25 °C for 12 h (Naisse et al., 2015).

In addition to BC and MBC, 8 aged biochars were obtained after aging, namely, aged biochars without soil (original: PBC; modified: PMBC), biochars co-aged with acid soil (original: ABC; modified: AMBC), biochars co-aged with neutral soil (original: BBC; modified: BMBC), and biochars co-aged with alkaline soil (original: CBC; modified: CMBC). The basic properties of these aged biochars are also listed in Table 1; moreover, their adsorption experiments were also conducted as the same method described in the “Adsorption isotherms and adaptability of original and modified biochars” section.

Quantitative adsorption mechanisms of biochars

The contributions of various mechanisms to Cd(II) adsorption capacities of biochars were determined based on the researches of Wang et al. (2015b), Cui et al. (2016), and Deng et al. (2019), which calculated the contributions of cation exchange with K(I), Ca(II), Na(I), and Mg(II) (Q_{c}) precipitation with minerals (Q_{cp}); complexation with acid functional groups (Q_{sf}); and other mechanisms (Q_{co}). In this study, due to the modification with KMnO4, there was a considerable amount of Mn(II) and MnO2 on modified biochars; therefore, the previous mechanism division method was improved and the calculation methods are as follows:

\[ Q_c = Q_{c} - Q_{a} \] (1)

\[ Q_{cm} \] includes three parts, namely, Q_{cic}, Q_{Mn}, and Q_{cp}, where Q_{cic} represents the amount of Cd(II) adsorption by cation exchange with K+, Na+, Ca2+, and Mg2+, and Q_{cp} is obtained by subtracting Q_{cic} and Q_{Mn} from Q_{cm}.

\[ Q_{cic} = Q_K + Q_{Na} + Q_{Ca} + Q_{Mg} \] (2)

\[ Q_{cp} = Q_{cm} - Q_{cic} - Q_{Mn} \] (3)

where Q_{K}, Q_{Na}, Q_{Ca}, Q_{Mg}, and Q_{Mn} are respectively the net contents of K(I), Na(I), Ca(II), Mg(II), and Mn(II) released from biochar to solution after the adsorption of Cd(II).

\[ Q_a \] includes two parts, namely, Q_{cf} and Q_{cco}, and Q_{cf} was calculated from the amount of H+ released after the adsorption of Cd(II) on acidified biochar, i.e., the drop of pH value, and Q_{cco} was calculated as the difference between Q_{a} and Q_{cf}.

\[ Q_{co} = Q_{a} - Q_{cf} \] (4)

Quality assurance and quality control

The adsorption data of Cd(II) were fitted by Langmuir (LM) and Freundlich (FM) isotherm models, and the specific equations are shown in the supplementary material. Parameters of Cd(II) adsorption on biochars obtained from Langmuir and Freundlich isotherm models are shown in Table S1. Statistical analysis was conducted on all experimental data using EXCEL 2013 software, and Origin 8.0 was used to fit the isotherm models and plotting data. All data shown in figures are the average values of three replicate experiments, and the error bars represent the standard deviation of three replicates. The relative standard deviation (RSD) of Cd determined by AAS was 2%, and the detection limit was 0.002 mg·L^{-1}.

Results and discussion

Adsorption behaviors of fresh biochars (BC, MBC, and OBC)

Cd(II) adsorption isotherms on BC, MBC, and OBC at pH = 5.5 are given in Fig. 1, the adsorption isotherms were all typical “L”-shaped isotherms and reached steady state.
at higher concentrations. For all fresh biochars, the fitting results of Langmuir isotherm model all had larger $R^2$ values (0.996, 0.969, and 0.965 for BC, MBC, and OBC, respectively), indicating that the chemisorption of Cd(II) mainly occurred on the homogeneous surface of BC, MBC, and OBC (Cui et al., 2016; Li et al., 2017). The maximum Cd(II) adsorption capacities ($Q_m$) of BC, MBC, and OBC based on the Langmuir isotherm model were 54.26, 117.33, and 60.52 mg·g$^{-1}$, respectively, which indicated that modification enhanced Cd(II) adsorption ability of rice straw biochar in aqueous solutions, especially the premodification.

The presence of Cd in EDS images proved that all three biochars adsorbed Cd(II), and the content of Cd in MBC was the largest, which was consistent with the adsorption results (Fig. S1). The SEM images showed that the surface of BC was complete and smooth, while that of MBC was relatively rough with several fine particles and crystals evenly distributed on the surface (Fig. S1), which was similar to several previous studies (Liang et al., 2017; Yin et al., 2019), and OBC was more broken compared to BC. The specific surface areas of BC, MBC, and OBC were 3.6, 19.4, and 3.9 m$^2$·g$^{-1}$, respectively, and the specific surface area of MBC was 5.4 times that of BC, which might result in the significant increase in the adsorption capacity of MBC compared with BC. The maximum adsorption capacity of MBC (117.33 mg·g$^{-1}$) in this study was much larger than other reported Mn-loaded biochars, indicating that rice straw is more suitable than other substrates as the raw material for KMnO$_4$ modification (Liang et al., 2017; Fan et al., 2018; Li et al., 2017; Yin et al., 2019).

**Effects of pH and ionic strength**

Figure 2a shows that initial solution pH significantly affected Cd(II) adsorption by biochars. When the pH of Cd(II) solution was 3.0, the adsorption capacities of BC, MBC, and OBC were 24.47, 108.67, and 55.53 mg·g$^{-1}$, respectively, indicating that premodified biochar still had the largest Cd(II) adsorption capacity even under extremely acidic condition. When the pH of Cd(II) solution further increased to 7.0, the adsorption capacities of BC, MBC, and OBC increased to 78.00, 144.93, and 86.53 mg·g$^{-1}$, respectively. We concluded that the adsorption capacities of MBC in Cd(II) solutions with pH from 3.0 to 7.0 were always significantly higher than those of BC and OBC, especially under the strong acidic condition.

The changes in solution pH after fully reacting with biochars are shown in Fig. 2b. Regardless the initial pH of Cd(II) solution was 3.0, 5.0, or 7.0, after reacting with MBC, the solution pH was obviously higher than that of treated with BC and OBC, indicating that MBC had a stronger
ability in improving the pH of solutions. Moreover, the acid buffer experiment (Fig. 2c) showed that modified biochars (MBC and OBC) had higher acid buffer capacities compared with original biochar. The pH values of Cd(II) solutions treated with BC, MBC, and OBC after the addition of 4 mL of HNO₃ solution were 1.5, 6.3, and 4.4, respectively, which indicated that MBC had an extremely strong acid buffer capacity, and this was one of the most important factors resulting in its largest adsorption capacity under acidic condition. The carbonate contents of BC, MBC, and OBC were 1.6, 5.7, and 1.3%, respectively, of which MBC was 3.5 times that of BC; moreover, the presence of MnOₓ might also enhance the acid buffer capacities of MBC and OBC (Fan et al., 2018).

As shown in Fig. 2d, overall, the adsorption capacities of all biochars decreased as the ionic strength increased, because metal ions and sodium ions competed for the same adsorption sites. Many previous studies also demonstrated that the amounts of target metal ions adsorbed by biochar decreased as other metal ions presented (Deng et al., 2019; Xu et al., 2013).

**Effects of modification and co-aging on biochar characterizations**

To analyze the existing forms of MnOₓ on MBC and OBC, XPS analysis of modified biochars was carried out. As shown in Fig. 3c and d, the existing forms of MnOₓ were determined to be MnO on MBC while MnO₂ on OBC by using the ΔE of Mn 3s (Biesinger et al., 2011). Combining with the results on Mn-modified biochars in recent years, we concluded that the form of MnOₓ on the biochar premodified by KMnO₄ was mainly MnO (Fan et al., 2018; Yin et al., 2019), whereas that on postmodified biochar was mainly MnO₂ (Liang et al., 2017; Xiao et al., 2019), and the effect of premodification was basically better than that of post-modification in terms of improving heavy metal adsorption of biochars.
When the pH of solution was larger than the \( \text{pH}_{\text{pzc}} \) of biochar, the biochar was negatively charged, which was conducive to the adsorption of heavy metals. Therefore, the smaller the \( \text{pH}_{\text{pzc}} \) of biochar, the better the adsorption for heavy metals. The \( \text{pH}_{\text{pzc}} \) of BC and MBC was 2.51 and 1.98, respectively, indicating that premodification of KMnO\(_4\) improved the adsorption of rice straw biochar. The pH values of BC and MBC were 9.70 and 9.60, indicating that premodification had almost no effect on pH improvement of rice straw biochar; however, the pH of biochars varied largely after co-aging with different types of soil. For original biochar, the order of biochar pH was BC (9.70) > PBC (8.05) > CBC (7.38) > BBC (5.90) > ABC (5.05), and that of premodified biochar was MBC (9.60) > PMBC (7.92) > CMBC (7.56) > BMBC (6.10) > AMBC (6.00). For both original and premodified biochars, the pH values after aging without soil were obviously larger than those after co-aging with soils; moreover, for biochars co-aged with soils, the pH values decreased with the increase of soil acidity. It can also be seen in Table 1 that the specific surface area of BC increased while that of MBC decreased after all aging treatments.

EDS analysis showed that O contents of MBC and OBC (27.12% and 21.48%) were higher than that of BC (17.36%) (Fig. S1), which indicated that the degrees of oxidation were significantly improved after modification, and this change increased oxidative functional groups and improved the complexation effects between modified biochars and Cd(II) (Fan et al., 2018). In the FTIR spectra (Fig. 4), the broad band at approximately 3400 cm\(^{-1}\) corresponded to the absorption peak of hydroxyl groups (−OH) (Dutta et al., 2015), and the peaks at 1623, 1382, 1099, and 784 cm\(^{-1}\) corresponded to C = O, C-H\(_2\), C-O, and C-H, respectively. With the increase of soil acidity, the greater the improvement effect of biochar on soil pH, the larger the consumption of its own acid buffer capacity. After co-aging with the same soil, the pH of premodified biochar was always larger than that of original biochar, which showed that MBC was less affected than BC during the aging process in soils, especially in acid soil. It can be found in Table 1 that the specific surface area of BC increased while that of MBC decreased after all aging treatments.
respectively (Inyang et al., 2010; Yao et al., 2011). The XPS spectra of O on BC and MBC are presented in Fig. S2, and the main chemical forms of O were C-O, COOH, and C=O. The percentages of C-O, COOH, and C=O on BC and MBC were different due to the modification of KMnO4. The percentage of C-O had almost no change (from 25.28% on BC to 25.15% on MBC), and the percentage of COOH increased from 36.98% on BC to 58.48% on MBC, but the percentage of C=O decreased from 37.74% on BC to 16.37% on MBC. After Cd(II) adsorption, XRD analysis of biochars was conducted and shown in Fig. 5, and it indicated that the crystal precipitations on fresh biochars (BC and MBC) were mainly existed in the forms of CaCO3, CdCO3, and CaC2O4; however, after aging without soil or co-aging with soils, due to the consumption of alkaline mineral precipitation during the aging process, CaCO3 and CdCO3 disappeared while SiO2 appeared, which might have a greater impact on the contribution of precipitation, and in turn led to a significant decrease in adsorption capacity of biochar.

### Adsorption behaviors of aged biochars

The adsorption isotherms of Cd(II) on aged biochars (PBC, PMBC, ABC, AMBC, BBC, BMBC, CBC, and CMBC) are shown in Fig. 6. For all aged biochars, the fitting results of Freundlich isotherm model basically had larger $R^2$ values (ranging from 0.941 to 0.992), which were quite different from the fitting results of fresh biochars, indicating that aging processes (aging without soil or co-aging with soils) changed the adsorption of biochars into heterogeneous multilayer adsorption (Tran et al., 2017). Deng et al. (2020) also found that the adsorption of fresh biochars for Cd(II) and Ni(II) was better fitted by the Langmuir model, while that of aged biochar was better fitted by the Freundlich model. Tan et al. (2020) showed that the adsorption data of fresh and aged biochars for Pb(II) were more suitable for Langmuir model and Freundlich model, respectively.

Since part of adsorption data could not be well fitted by Langmuir model, in this study, the adsorption capacities of biochars at $Q_e = 200$ mg·L$^{-1}$ were used as the maximum...
adsorption capacities. For original biochars, the order of adsorption capacities was CBC (63.50 mg·g⁻¹) > BC (54.80 mg·g⁻¹) > PBC (50.08 mg·g⁻¹) > BBC (36.33 mg·g⁻¹) > ABC (31.17 mg·g⁻¹); and for modified biochars, the order of adsorption capacities was MBC (126.91 mg·g⁻¹) > PMBC (105.83 mg·g⁻¹) > CMBC (86.25 mg·g⁻¹) > AMBC (83.00 mg·g⁻¹) > BMBC (82.33 mg·g⁻¹). The adsorption capacity percentages of aged biochars divided by fresh biochars were calculated; for original biochars, the percentages were 91.4% (PBC), 56.9% (ABC), 66.3% (BBC), and 115.9% (CBC), and those of modified biochars were 83.4% (PMBC), 65.4% (AMBC), 64.9% (BMBC), and 68.0% (CMBC). Except for the original biochar co-aged with alkaline soil which increased the adsorption capacity, the other aging treatments all decreased the adsorption capacities of biochars. Moreover, for biochars co-aged with soils, the adsorption capacities basically decreased with the increase of soil acidity.

It can be seen from Table 1 that the order of modified biochar pH was MBC (9.60) > PMBC (7.92) > CMBC (7.56) > BMBC (6.10) > AMBC (6.00), which was basically the same as the order of adsorption capacities, indicating that the pH of soil had a crucial influence on the adsorption capacity of co-aged biochar. It was noteworthy that the adsorption result of aged biochar without soil was far from that of co-aged biochars; therefore, the single biochar aging cannot be used to predict the adsorption behaviors of biochar after aging in soils.

Quantitative adsorption mechanisms of biochars for Cd(II)

Cation exchange with K(I), Ca(II), Na(I), and Mg(II)

Cd(II) in solution can be adsorbed on biochars by cation exchange with K(I), Ca(II), Na(I), and Mg(II) (Lu et al., 2012). Monovalent cations (K(I) and Na(I)) and divalent cations (Ca(II) and Mg(II)) present in different forms on biochars; monovalent cations are retained by electrostatic outer-sphere interactions, while divalent cations are retained by precipitation and inner-sphere complexation with oxygen-containing surface functional groups (Cui et al., 2016; Lu et al., 2012). All these four ions can directly exchange with Cd(II), and Zhang et al. (2015) indicated that hydroxylated SiO₂ and Al₂O₃ on the biochar surface provided sites for cation exchange.

To quantify this mechanism, the net releases of these four ions were calculated, where every two K(I) or Na(I) exchanged one Cd(II), and Ca(II) or Mg(II) exchanged with Cd(II) in equal amount, and the results are shown in Table S1. The adsorption capacities of BC, MBC, PBC, PMBC, ABC, AMBC, BBC, BMBC, CBC, and CMBC due to the cation exchange with K(I), Ca(II), Na(I), and Mg(II) (Q_{cic}) were 6.05, 6.48, 9.22, 4.56, 0.64, 3.63, 2.22, 4.94, 0, and 1.82 mg·g⁻¹, respectively. The Q_{cic} of MBC was close to that of BC, indicating that the premodification of KMnO₄ had almost no effect on this mechanism. Except for aged original biochar without soil, after aging, the contribution

Fig. 5 XRD image of biochars after Cd(II) adsorption (BC, MBC, PBC, PMBC, ABC, AMBC, BBC, BMBC, CBC, and CMBC), and the specific information has been identified in the figure.

![XRD image of biochars after Cd(II) adsorption](image-url)
of cation exchange with K(I), Ca(II), Na(I), and Mg(II) to the adsorption capacities of biochars all decreased, possibly caused by releasing or exchanging with other ions in soil during the aging process.

**Cation exchange with Mn(II)**

The EDS analysis showed that Mn(II) appeared on the surface of MBC by the redox reaction between KMnO₄ and straw powder. The adsorption capacities due to the cation exchange with Mn(II) on MBC, PMBC, AMBC, BMBC, and CMBC were 11.39, 13.02, 2.95, 1.93, and 3.78 mg·g⁻¹, respectively, which indicated that the contributions of cation exchange with Mn(II) were all significantly decreased after co-aging with soils; however, the contribution of this mechanism after aging without soil slightly increased. Moreover, it is noting that the decrease in contribution of this mechanism was obviously larger than that of cation exchange with K(I), Ca(II), Na(I), and Mg(II) after co-aging with soils, indicating that the newly emerged Mn(II) due to the modification was more easily exchanged with other ions or released in soil during the aging process.

**Precipitation and adsorption with minerals**

Minerals on biochars can co-precipitate with Cd(II) to achieve adsorption (Cui et al., 2016); in this study, this mechanism was redefined, which included not only the precipitation, but also the adsorption with minerals due to the existence of MnOₓ on biochar after the modification with KMnO₄. After premodification with KMnO₄, the carbonate content of MBC significantly increased (Table 1), and in turn improved the adsorption capacity caused by precipitation, and both the XRD (Fig. 5) and XPS (Fig. 3a, b) analyses showed that crystalline Cd(II) mainly existed in the form of CdCO₃. The adsorption

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**Fig. 6** Adsorption isotherm data fitted by the Langmuir and Freundlich models for Cd(II) adsorption onto PBC, PMBC (a), ABC, AMBC (b), BBC, BMBC (c), CBC, and CMBC (d)
capacities of BC, MBC, PBC, PMBC, ABC, AMBC, BBC, BMBC, CBC, and CMBC due to the precipitation and adsorption with minerals (Q_{cp}) were 37.85, 64.85, 32.16, 45.19, 21.28, 25.41, 15.98, 31.37, 32.18, and 49.20 mg·g^{-1}, respectively. The XRD analysis (Fig. 5) revealed that almost all the mineral components on biochar became SiO2 with the disappearance of CaCO3 and CdCO3 after aging, and occasionally a small amount of CaC_2O_4 appeared, which resulted in the obvious decrease in the contribution of Q_{cp}.

**Complexation with acidic surface functional groups**

Many previous researchers demonstrated that complexation with acidic surface functional groups was one of the important adsorption mechanisms of biochars for Cd(II), and the contribution of this mechanism to adsorption capacity was calculated by the pH differences of Cd(II) solution before and after reaction with demineralized biochar (Cui et al., 2016; Wang et al., 2015b; Xu et al., 2013); moreover, the complexation of Cd(II) with acidic surface functional groups was accompanied by the release of H^+, indicating that the lower the pH value of Cd(II) solution after reaction, the greater the contribution to adsorption capacity by this mechanism. However, as shown in Fig. 7a, the contributions of complexation with acidic surface functional groups to adsorption capacities of rice straw biochars were the smallest among all five mechanisms.

**Other potential mechanisms**

In addition to the above four adsorption mechanisms, there are some mechanisms that cannot be distinguished, including electrostatic attraction, physical adsorption, and cation-π interactions (Deng et al., 2017; Mahdi et al., 2018). Electrostatic attraction depends on the biochar point of zero charge (pH_{pzc}) and the pH of solution, and when the pH of solution is greater than pH_{pzc}, the surface of the biochar is negatively charged, leading to the Cd(II) adsorption by biochar (Han et al., 2013a). Many previous studies (Jiang et al., 2016; Tran et al., 2017) indicated that physical adsorption was mainly related to the microporous structure and specific surface area of biochar, and aromatic carbon on the biochar surface produced electron-rich π-systems and interacted with Cd(II). The adsorption capacities of BC, MBC, PBC, PMBC, ABC, AMBC, BBC, BMBC, CBC, and CMBC due to this mechanism were 9.88, 15.10, 8.33, 5.39, 2.95, 11.40, 6.81, 3.80, 8.33, and 3.19 mg·g^{-1}, respectively, which showed that aging without soil and co-aging with soils decreased the contributions of other potential mechanisms to the adsorption capacity of biochars.

**Overall analysis of five mechanisms**

It can be seen from Fig. 7a that the increase in the adsorption capacity of MBC compared with BC was mainly caused by precipitation and adsorption with minerals and cation exchange with Mn(II). Figure 7b shows that precipitation and adsorption with minerals accounted for 70.36, 66.29, 64.68, 66.28, 85.55, 58.55, 63.92%, 74.63, 79.40, and
84.83% of the total adsorption capacities of BC, MBC, PBC, PMBC, ABC, AMBC, BBC, BMBC, CBC, and CMBC, respectively, indicating that even if the original and modified rice straw biochars underwent different aging progresses (aging without soil and co-aging with different types of soil), the main adsorption mechanism of biochars for Cd(II) was still the precipitation and adsorption with minerals.

The contributions of all five mechanisms to the adsorption capacities of aged biochars for Cd(II) basically showed a downward trend. For original biochar, after aging without soil and co-aging with acidic and neutral soils, the contributions of the precipitation and adsorption with minerals decreased the most, namely, 5.69, 16.58, and 21.87 mg·g⁻¹, while after co-aging with alkaline soil, the contribution of cation exchange with K(I), Ca(II), Na(I), and Mg(II) decreased the most (6.05 mg·g⁻¹). In terms of modified biochar, all aging processes decreased the contributions of precipitation and adsorption with minerals the most, namely, 19.66, 39.43, 33.48, and 15.65 mg·g⁻¹ for aging without soil and co-aging with acidic, neutral, and alkaline soils, respectively. Deng et al. (2020) conducted a 1-year constant temperature and humidity aging on single biochar, and the adsorption experimental results of Cd(II) and Ni(II) also indicated that aging significantly reduced the contributions of precipitation and cation exchange to the adsorption capacities of biochar. In general, the adsorption capacity of MBC decreased more than that of BC after aging (aging without soil or co-aging with soils); moreover, co-aging with acidic and neutral soils had a greater negative impact on the contributions of all mechanisms than aging without soil and co-aging with alkaline soil.

**Conclusion**

The premodification of KMnO₄ significantly improved Cd(II) adsorption capacity and adaptability of rice straw biochar, which benefited from the increase of carbonate content, specific surface area, and the emergence of Mn(II) and MnOₓ. Even after co-aging with soils, Cd(II) adsorption capacities of modified biochar were always larger than those of original biochar. Moreover, Cd(II) adsorption capacities were basically in the order of aged biochar without soil > biochar co-aged with alkaline soil > biochar co-aged with neutral soil > biochar co-aged with acid soil. The contribution of cation exchange in premodified biochar was always larger than that in original biochar due to the emergence of Mn(II) by modification. Whether aging or not, the dominant adsorption mechanism of original and premodified biochars for Cd(II) was all the precipitation and adsorption with minerals. In this study, we highlighted that biochar remediation for Cd should be evaluated by co-aging with soil instead of aging without soil.

**Supplementary Information** The online version contains supplementary material available at https://doi.org/10.1007/s11356-022-18637-w.

**Author contribution** Zhuowen Meng: data curation, formal analysis, investigation, and writing—original draft. Shuang Huang: conceptualization, writing—review and editing, and resources. Zhongbing Lin: writing—review and editing.

**Funding** This work was supported by the National Natural Science Foundation of China (No. 52179040) and the National Key Research and Development Program of China (No. 2021YFC3201202).

**Data availability** All data gathered or analyzed during this study are included in this paper.

**Declarations**

**Consent for publication** The authors agree to participate and publish.

**Competing interests** The authors declare no competing interests.

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