Effects of Modification and Co-Aging with Soils on Cd(II) Adsorption Behaviors and Quantitative Mechanisms by Biochar

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Abstract

In this study, original rice straw biochar and two KMnO_4 -modified 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 MnO_x through modification. Original and premodified biochars were then conducted four types of aging process, namely, aging without soil, co-aging with acid ($\text{pH}=5.00$), neutral ($\text{pH}=7.00$) and alkaline ($\text{pH}=8.30$) soils, using an improved three-layer mesh method. 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 KMnO_4 -modified biochar was always better than original biochar after co-aging with soils. The dominant adsorption mechanism of original and premodified 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.

1. 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, 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, etc. (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; Deng et al., 2019). However, it is difficult to produce biochar pyrolyzed at relatively high temperatures (i.e. $500\sim700^\circ\text{C}$) 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. $300\sim400^\circ\text{C}$) 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, KMnO_4 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 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 can not 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 is 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, it is still unclear the effects of modification and co-aging with soils on Cd(II) adsorption mechanisms by biochar.

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; 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.

2. Materials And Methods

2.1 Preparation of original and modified biochars

Original biochar (BC) was prepared as a control, in brief, rice straw biomass (< 0.3 mm) 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

hours before cooling to room temperature.

Premodified and postmodified biochars were prepared using $0.1 \text{ mol}\cdot\text{L}^{-1} \text{ KMnO}_4$ solution (Wang et al., 2015a). For premodified biochar (MBC), briefly, 50 g of rice straw biomass was immersed in 250 mL of $0.1 \text{ mol}\cdot\text{L}^{-1} \text{ KMnO}_4$ solution and sonicated for two hours to make them react adequately, and the mixture was then dried in an oven, ground and sieved to $<0.3 \text{ mm}$, and the subsequent pyrolyzing process was the same as BC. Postmodified biochar (OBC) was prepared by reacting BC with $0.1 \text{ mol}\cdot\text{L}^{-1} \text{ KMnO}_4$ solution using the same method described above and then dried in an oven, ground and sieved to $<0.3 \text{ mm}$.

2.2 Biochar characterization

Carbonate contents of biochars were measured according to the hydrochloric acid titration method, and the elemental analyzer (RARIO 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 2020M, 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 MnO_x 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 respectively shown in Fig. 3, Fig. 4, Fig. 5 and Fig. S1.

Table 1
The basic physicochemical properties of ten types of biochar.

Property	pH (CaCl ₂)	C (%)	H (%)	N (%)	BET-SA (m ² ·g ⁻¹)	Yield (%)	Carbonate content (%)
BC	9.70±0.02	49.8	3.1	0.8	3.6	37	1.6
MBC	9.60±0.1	38.3	3.2	0.8	19.4	52.4	5.7
OBC	8.80±0.05	42.8	3.2	0.9	3.9	37	1.3
PBC	8.05±0.03	51.7	3.5	0.8	6.43		
PMBC	7.92±0.01	46.7	3.9	0.8	4.42		
ABC	5.05±0.02	48.6	3.6	0.9	10.91		
AMBC	6.00±0.03	41.7	3.7	0.9	7.44		
BBC	5.90±0.02	52.3	3.6	0.9	9.96		
BMBC	6.10±0.05	45.4	3.9	0.9	9.01		
CBC	7.38±0.03	52.8	3.8	0.9	7.21		
CMBC	7.56±0.01	43.1	4	0.8	9.77		
Notes:							
BC is original biochar;							
MBC is KMnO ₄ -premodified biochar;							
OBC is KMnO ₄ -postmodified biochar;							
PBC is aged original biochar without soil;							
PMBC is aged KMnO ₄ -premodified biochar without soil;							
ABC is original biochar co-aged with acid soil;							
AMBC is KMnO ₄ -premodified biochar co-aged with acid soil;							
BBC is original biochar co-aged with neutral soil;							
BMBC is KMnO ₄ -premodified biochar co-aged with neutral soil;							
CBC is original biochar co-aged with alkaline soil;							
CMBC is KMnO ₄ -premodified biochar co-aged with alkaline soil.							

2.3 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 hours at 25°C, the sample was then withdrawn, and subsequently filtered through 0.45µm 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 hours 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 hours, and the pH value was measured, of which this operation was repeated for 8 times.

2.4 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) divided 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.

In addition to BC and MBC, 8 aged biochar 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 section 2.3.

2.5 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_{ci}), precipitation with minerals (Q_{cp}), complexation with acid functional groups (Q_{cf}) and other mechanisms (Q_{co}). In this study, due to the modification with $KMnO_4$, there was a considerable amount of Mn(II) and MnO_x on modified biochars; therefore, the previous mechanism division method was improved and the calculation methods are as follows:

Q_c is the total amount of Cd(II) adsorbed by biochar when $C_e=100 \text{ mg}\cdot\text{L}^{-1}$, and Q_a is the amount of Cd(II) adsorbed by acidified biochar, which was reacted with 1M hydrochloric acid solution and rinsed with ultrapure water until the pH of filtrate was stable, and the mineral components of biochar basically disappeared after such a treatment. Both Q_c and Q_a can be directly determined. Q_{cm} is the adsorption amount of Cd(II) due to the interaction with minerals, which is obtained by the difference between Q_c and Q_a .

$$Q_{cm} = Q_c - Q_a \quad (1)$$

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^+ , Ca^{2+} and Mg^{2+} , and Q_{cp} is obtained by subtracting Q_{cic} and Q_{Mn} from Q_{cm} .

$$Q_{cic} = Q_K + Q_{Na} + Q_{Ca} + Q_{Mg} \quad (2)$$

$$Q_{cp} = Q_{cm} - Q_{cic} - Q_{Mn} \quad (3)$$

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_{co} , 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_{co} was calculated as the difference between Q_a and Q_{cf} .

$$Q_{co} = Q_a - Q_{cf} \quad (4)$$

2.6 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 $0.002\text{mg}\cdot\text{L}^{-1}$.

3. Results And Discussion

3.1 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 $60.52\text{ mg}\cdot\text{g}^{-1}$, 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 $3.9\text{ m}^2\cdot\text{g}^{-1}$, 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 ($117.33\text{ mg}\cdot\text{g}^{-1}$) 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).

3.2 Effects of pH and ionic strength

Figure 2a showed 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 $\text{mg}\cdot\text{g}^{-1}$, 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 was 5.0, the adsorption capacities of BC, MBC and OBC increased to 46.00, 115.21 and 60.26 $\text{mg}\cdot\text{g}^{-1}$, respectively. As solution pH increased, the surface groups of biochars gradually deprotonated; therefore, the chance of Cd(II) binding to biochar structure increased, which resulted in a higher adsorption capacity (Bogusz et al., 2015). 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 $\text{mg}\cdot\text{g}^{-1}$, 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 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 HNO_3 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 MnO_x 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).

3.3 Effects of modification and co-aging on biochar characterizations

To analyze the existing forms of MnO_x on MBC and OBC, XPS analysis of modified biochars was carried out. As shown in Fig. 3c and 3d, the existing forms of MnO_x were determined to be MnO on MBC while MnO_2 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 MnO_x on the biochar premodified by KMnO_4 was mainly MnO (Fan et al., 2018; Yin et al., 2019), whereas that on postmodified biochar was mainly MnO_2 (Liang et al., 2017; Xiao et al., 2019), and the effect of premodification was basically better than that of postmodification in terms of improving heavy metal adsorption of biochars.

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 could also be seen in Table 2 that after co-aging with BC and MBC, the pH of acid, neutral and alkaline soils increased from 5.00, 7.00 and 8.30 to 6.02/6.61, 7.06/7.21 and 8.26/8.33, 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 could be found in Table 1 that the specific surface area of BC increased while that of MBC decreased after all aging treatments.

Table 2
The basic physicochemical properties of three soils.

Property	Acidic soil	Neutral soil	Alkaline soil
Initial pH (CaCl ₂)	5.00±0.10	7.00±0.05	8.30±0.12
Texture	Loamy clay	Silty loam	Sandy clay loam
Sand (%)	45	40	64
Silt (%)	20	56	16
Clay (%)	35	4	20
Organic matter (g·kg ⁻¹)	4.42	10.81	5.32
CEC (cmolc·kg ⁻¹)	9.53	14.92	4.52
pH (after co-aging with BC)	6.02±0.04	7.06±0.01	8.26±0.12
pH (after co-aging with MBC)	6.61±0.05	7.21±0.08	8.33±0.06

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-H₂, C-O, and C-H, respectively (Inyang et al., 2010; Yao et al., 2011). 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 CaCO_3 , CdCO_3 and CaC_2O_4 ; however, after aging without soil or co-aging with soils, due to the consumption of alkaline mineral precipitation during the aging process, CaCO_3 and CdCO_3 disappeared while SiO_2 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.

3.4 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 $Q_e=200 \text{ mg}\cdot\text{L}^{-1}$ were used as the maximum adsorption capacities. For original biochars, the order of adsorption capacities was $\text{CBC} (63.50 \text{ mg}\cdot\text{g}^{-1}) > \text{BC} (54.80 \text{ mg}\cdot\text{g}^{-1}) > \text{PBC} (50.08 \text{ mg}\cdot\text{g}^{-1}) > \text{BBC} (36.33 \text{ mg}\cdot\text{g}^{-1}) > \text{ABC} (31.17 \text{ mg}\cdot\text{g}^{-1})$; and for modified biochars, the order of adsorption capacities was $\text{MBC} (126.91 \text{ mg}\cdot\text{g}^{-1}) > \text{PMBC} (105.83 \text{ mg}\cdot\text{g}^{-1}) > \text{CMBC} (86.25 \text{ mg}\cdot\text{g}^{-1}) > \text{AMBC} (83.00 \text{ mg}\cdot\text{g}^{-1}) > \text{BMBC} (82.33 \text{ mg}\cdot\text{g}^{-1})$. 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), 115.9% (CBC); and those of modified biochars were 83.4% (PMBC), 65.4% (AMBC), 64.9% (BMBC), 68.0% (CMBC). Except for the original biochar co-aged with alkaline soil 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 could be seen from Table 1 that the order of modified biochar pH was $\text{MBC} (9.60) > \text{PMBC} (7.92) > \text{CMBC} (7.56) > \text{BMBC} (6.10) > \text{AMBC} (6.00)$, which was basically 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.

3.5 Quantitative adsorption mechanisms of biochars for Cd(II)

3.5.1 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 SiO_2 and Al_2O_3 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 were 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 $\text{mg}\cdot\text{g}^{-1}$, respectively. The Q_{cic} of MBC was close to that of BC, indicating that the premodification of KMnO_4 had almost no effect on this mechanism. Except for aged original biochar without soil, after aging, the contribution 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.

3.5.2 Cation exchange with Mn(II)

The EDS analysis showed that Mn(II) appeared on the surface of MBC by the redox reaction between KMnO_4 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 $\text{mg}\cdot\text{g}^{-1}$, 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.

3.5.3 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 MnO_x on biochar after the modification with KMnO_4 . After premodification with KMnO_4 , 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) analysis showed that crystalline Cd(II) mainly existed in the form of CdCO_3 . The adsorption 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 $\text{mg}\cdot\text{g}^{-1}$, respectively. The XRD analysis (Fig. 5) revealed that almost all the mineral components on biochar

became SiO_2 with the disappear of CaCO_3 and CdCO_3 after aging, and occasionally a small amount of CaC_2O_4 appeared, which resulted in the obvious decrease in the contribution of Q_{cp} .

3.5.4 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 $\text{Cd}(\text{II})$, and the contribution of this mechanism to adsorption capacity was calculated by the pH differences of $\text{Cd}(\text{II})$ solution before and after reaction with demineralized biochar (Cui et al., 2016; Wang et al., 2015b; Xu et al., 2013); moreover, the complexation of $\text{Cd}(\text{II})$ with acidic surface functional groups was accompanied by the release of H^+ , indicating that the lower the pH value of $\text{Cd}(\text{II})$ 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.

3.5.5 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 $\text{Cd}(\text{II})$ 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 $\text{Cd}(\text{II})$. 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 $\text{mg}\cdot\text{g}^{-1}$, 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.

3.5.6 Overall analysis of five mechanisms

It could 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 $\text{Mn}(\text{II})$. Fig. 7b showed 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 $\text{Cd}(\text{II})$ was still the precipitation and adsorption with minerals.

The contributions of all five mechanisms to the adsorption capacities of aged biochars for $\text{Cd}(\text{II})$ basically showed a downward trend. For original biochar, after aging without soil, 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 $\text{mg}\cdot\text{g}^{-1}$, 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 $\text{mg}\cdot\text{g}^{-1}$). 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, 15.65 $\text{mg}\cdot\text{g}^{-1}$ for aging without soil, co-aging with acidic, neutral and alkaline soils, respectively. Deng et al. (2020) conducted a one-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.

4. Conclusion

The premodification of KMnO_4 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 MnO_x . 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.

Declarations

Data availability

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

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Ethics declarations

Consent for publication

The authors agree to participate and publish.

Competing interests

The authors declare no competing interests.

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Figures

Figure 1

Adsorption isotherm data fitted by the Langmuir and Freundlich models for Cd(II) adsorption onto BC, MBC and OBC.

Figure 2

Adsorption capacities of biochars (BC, MBC and OBC) in Cd(II) solution with different pH values (a) and ionic strengths (d). The solution pH values after reaction and the results of the acid buffer experiment are shown in b and c.

Figure 3

XPS scans of MBC and OBC after Cd(II) adsorption: wide scan (a), Cd3d (b), Mn2p (c), Mn3s (d).

Figure 4

FTIR spectra of biochars (BC, MBC, PBC, PMBC, ABC, AMBC, BBC, BMBC, CBC and CMBC), and the specific information has been identified in the figure.

Figure 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.

Figure 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).

Figure 7

The estimated contributions to Cd(II) adsorption on the biochars (BC, MBC, PBC, PMBC, ABC, AMBC, BBC, BMBC, CBC and CMBC) attributed to cation exchange with K(I), Ca(II), Na(I), and Mg(II), cation exchange with Mn(II), precipitation and adsorption with minerals, complexation with acid surface functional groups and other potential mechanism.

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