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#### Research article



## Field aging declines the regulatory effects of biochar on cadmium uptake by pepper in the soil

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#### ABSTRACT

Biochar application is not only being widely promoted as an ideal strategy to mitigate global climate warming, but it also has the advantage of reducing heavy metal bioavailability and migration in the soil. However, studies on the effects of field aging on biochar to reduce heavy metals from the soil are still limited. The present study aimed to explore the effects and mechanisms of aged biochar added to the soil planted with pepper plants on cadmium (Cd) uptake. To achieve this, un-amended soil (control), soil amended with fresh biochar, and aged biochar recovered from a long-term field trial after 9 years) were used to investigate the effects of field aging on biochar adsorption efficiency. The results revealed that the amount of Cd in the plant planted in control soil, amended with fresh and aged biochar, accounted for  $40 \pm 6.10$ ,  $17.18 \pm 1.19$ , and  $18.68 \pm 0.79$ , respectively. There was a significant difference (P < 0.05) in the amount of Cd that was uptaken by plants among all treatments. However, soil amended with fresh biochar significantly (P < 0.05) decreased the amount of Cd in plants compared with soil amended with aged biochar. This indicates that field aging declines the potential of biochar to lower heavy metal bioavailability and retention in the soil. This study demonstrates that long-term burial lessens the ability of biochar to interact with Cd and suggests that biochar amendment can lower Cd in the soil, depending on the freshness and aging of biochar.

#### 1. Introduction

As a result of human activities like mining, smelting, municipal sludge, and the use of pesticides or fertilizers in farming, various heavy metals are getting more concentrated in the soil (Gallego et al., 2012; Kumar et al., 2017). This is one of the biggest environmental problems attracting more attention in the global community. Among toxic severe heavy metals, Cd is one of them because of its threats to human health through the food chain and irreversible effects on ecosystems (Murtaza et al., 2015). Several studies have reported that Cd toxicity inhibits seed germination, root elongation, and induces leaf rolling, necrosis, and damage to chloroplast structures (Hussain et al., 2015; Naeem et al.,

2016), which decreases crop yield and plant biomass. Cd can be accumulated in the human body through the food chain or smoking (Xiong et al., 2019), inducing liver, kidney, and lung diseases, diabetes, damaging coronary arteries, and oxidative stress (Ghoochani et al., 2019), and can also increase the risk of heart failure. Recently, techniques to lower soil Cd mobility and bioavailability have been developed to avoid or minimize Cd toxicity in agricultural production and human health (Bolan et al., 2014; Rizwan et al., 2016). Among developed techniques, soil amendments are frequently used in the soil polluted by Cd (Bashir et al., 2020; Jing et al., 2020).

Due to biochar's large surface area, high pH value, strong cation exchange capacity (CEC), and sizeable microporous structure and active

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functional groups (Abbas et al., 2017; Tu et al., 2020), a form of pyrogenic carbon produced by slow pyrolysis of organic waste materials is regarded as an excellent modifier to reduce the bioavailability of cadmium in soil, its absorption, and transportation in the plants (Alaboudi et al., 2019; Kamran et al., 2019). Some studies have reported that biochar (rice and wheat) can significantly reduce Cd activity in a variety of plant-soil systems, thus reducing cadmium that should be absorbed by the rice (Jing et al., 2020) and wheat (Bashir et al., 2020). Accordingly, biochar amendment can be used as an effective method for regulating the transport of Cd in contaminated soil. However, the mechanism by which the aging process affects the performance of the soil is still unclear.

The effect of biochar in the soil to remove Cd is based on immediate observation after its application. However, there is a lack of studies on Cd's migration and speciation changes in farmland after applying biochar that was buried in the soil for several years. Once biochar is applied to agricultural soil, its chemical and physical properties change over time due to environmental factors such as microbial activity, humidity, and temperature variation. The evidence obtained in anthropogenic soils demonstrated that biochar that had been aged for more than 100 years developed many functional groups at its surfaces (Mao et al., 2012) and changed the surface charge (Mia et al., 2017). Those alterations are linked to changes in biochar functionality, such as the adsorption of nutrients and heavy metals (Nagodavithane et al., 2014; Dong et al., 2017; Mia et al., 2017). Therefore, considering the long-term period of biochar in the soil and its irreversible application clarifies the biochar changes in the soil and their impact on remediation, which is essential for the systematic evaluation of the biochar amendment in agricultural soil and future farmland optimal quality management. Several studies on aged biochar are based on artificial aging in controlled laboratory circumstances or focus on changes in the properties of biochar (Dong et al., 2017; Mia et al., 2017; Yi et al., 2020). Therefore, adding fresh and aged biochar in the soil can be hypothesized to determine their role in Cd interaction with the soil and pepper plants. Generally, a large specific surface area of biochar may also promote the ability of the soil to intercept heavy metals, which also enhances the quality of the soil and the growth of the plants. A few short-term natural aging studies showed noticeable differences or even diametrically opposite results, either because the time was too short (a few months or 1-2 years) or because of the differences in soil properties and/or biochar, etc. (Bandara et al., 2021; Nie et al., 2021). However, recent studies focusing on the effect of aging on biochar in the soil on the reduction of heavy metal uptake by plants are limited.

Taken together, this study was aimed at evaluating the effects of biochar, which was aged under natural conditions on Cd adsorption in the soil and uptake by pepper plants. In this study, aged and fresh biochar were used to perform lab and pilot experiments to investigate the effects of weathering on biochar adsorption capacity on Cd. In addition, the impact of fresh and aged biochar on the ability of plants to uptake Cd was also assessed.

#### 2. Experimental study

#### 2.1. Biochar and artificial Cd-contaminated soil preparation

Fresh biochar was purchased from BioRegional Charcoal Company Ltd. (Bioregional HomeGrown®; Wallington, Surrey, UK), which started to produce biochar from pyrolyzed (450 °C for 48 h) chipped trunks and large branches of Fraxinus excelsior L., Quercus robur L., and Fagus sylvatica L. since around 2009. Afterward, it was sealed and then stored for subsequent use in the experimental field at Abergwyngregyn, Wales (53°14′N, 4°01′W). Aged biochar was taken from the experimental field at Abergwyngregyn, Wales (53°14′N, 4°01′W) in September 2018. The collected materials were a mixture of soil and biochar, but biochar was clearly distinguished by the naked eye and was obviously picked out directly by hand. After that, the collected sample was taken to the

laboratory, followed by washing it on gauze with a particle size of less than 0.5 mm to remove soil from biochar. However, biochar was separated from gravel and mud by density. Biochar, organic matter, roots, and plant debris were separated by manual distinction. In addition, biochar was cleaned again with a brush to re-density separation. The above processes were repeated 3 times. However, biochar which was still mixed with the crumbs was manually extracted, and the remainder was discarded. All the procedures were carried out to get pristine aged biochar. Aged and fresh biochar were grounded and sieved through a 60-mesh sieve and then stored at 4 °C for physicochemical analyses and subsequent use. The physicochemical properties of biochar were determined based on the method of Jones et al. (2011, 2012).

Uncontaminated soil was gathered from a field in the Guizhou Academy of Agricultural Sciences, Jinzhu Town, Huaxi District, Guiyang City, Guizhou Province (26°34′N, 106°30′E) in April 2017. However, it is called "yellow soil" based on Chinese soil classification and belongs to the Dystric Cambisols based on FAO soil classification. It was excavated and corrected at a surface depth of 0-20 cm, followed by drying it with air exposure before being sieved through a 2 mm sieve to remove any stones or debris that may have been retained. Soil properties are presented in Table 1. Therefore, the soil was mixed with cadmium nitrate (Cd(NO<sub>3</sub>)<sub>2</sub>) in the high-density polyethylene containers to achieve 3.00 mg kg<sup>-1</sup>. Afterward, the containers were placed in the greenhouse for the drying mixture until they reached 60% of their water holding capacity (WHC). Every two weeks, some quantity of deionized water is fed to the soil to keep the moisture content consistent in all treatments. Soil amended with biochar was prepared in March 2019. Soil contaminated with and without Cd was naturally dried into 20% of WHC. Fresh and aged biochar were blended with soil at 2% (weight basis).

#### 2.2. Soil and biochar characterization

All analyses of the collected samples were performed in quadruplicate. Two solutions were prepared by mixing soil samples and deionized water (1:2.5, w: v); biochar and deionized water (1:5, w: v) under suspension with standard electrodes. The electrical conductivity (EC) and pH were measured using electrical conductivity (DDS-307, Leici, Shanghai) and pH meters (PHS-3C, Leici, Shanghai), respectively. NO<sub>3</sub> and NH<sub>4</sub> were determined using 0.5 M K<sub>2</sub>SO<sub>4</sub> soil and biochar extracts based on a colorimetric method as revealed by Mulvaney (1996) and Miranda et al. (2001). Soil organic carbon was measured using the K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> oxidation method. The available K was estimated based on the flame photometry method in the extract (1 mol  ${\rm L}^{-1}$  ammonium acetate soil). The total K was measured using flame photometry after digesting in a nickel crucible with sodium hydroxide at 750 °C (Jing et al., 2020). The ash content of biochar was assessed based on the weight loss that occurred when biochar was combusted at 575 °C for 16 h. Elemental C, N, H, and S abundances were obtained using a Vario MACRO cube analyzer. After the ash content was subtracted, the O content was obtained under the assumption that biochar is only composed of C, N, H, and O. The cation exchange capacity (CEC) of the biochar was determined based on the modified ammonium acetate method (Gaskin et al., 2008). The WHC of the biochar was determined based on EBC and

**Table 1** The characterization of contaminated soil. All values are represented as means  $\pm$  SEM (n = 4). The symbols EC, AK, TK, and SOC, indicate electrical conductivity, available K, total K, and soil organic carbon.

Parameters	Contaminated soil	
pН	$6.69 \pm 0.06$	
EC (us cm <sup>-1</sup> )	$218.75 \pm 0.063$	
SOC (%)	$2.87\pm0.23$	
AK (mg/kg)	$593.25 \pm 1.94$	
TK (g/kg)	$11.82\pm0.13$	
Cd <sup>2+</sup> (mg/kg)	$0.032 \pm 0.002$	

Foundation, 2012. Biochar's specific surface area (SSA) was determined using an Autosorb iQ/monosorb surface area analyzer (Quantachrome Instruments, Boynton Beach, FL, USA). Functional groups were assessed using a Fourier transform infrared spectrometer (FTIR). The zeta potential was determined using a Malvern Zeta meter (Nano ZSE + MPT2, Malvern Panalytical Instruments Ltd., UK). The surface morphology of biochar was observed using scanning electron microscopy (SEM) (JSM-6460 LV Scanning Microscope (JEOL, Tokyo, Japan).

#### 2.3. Adsorption experiment

The adsorption experiment was carried out on the soil without artificial stimulation of Cd contamination to minimize the influence of Cd release in the soil. Herein, 2.00 g of uncontaminated soil, soil amended with fresh biochar, and gaged biochar were accurately weighed into a 50 mL centrifuge tube. Then, 20 mL of 0.01 M CaCl<sub>2</sub> solution containing Cd was added to each tube. To obtain the sorption isotherm, experiments were carried out with Cd concentrations of 0, 0.05, 0.20, 0.40, 0.80, and 1.60 mg L $^{-1}$ . Then, the tubes were agitated for 24 h on a reciprocating shaker (25  $\pm$  1  $^{\circ}$ C) at a rate of 120 rpm. The tubes were subsequently centrifuged to separate the solid and liquid phases. After that, the supernatant was carefully aspirated using a disposable pipette. The aspirated supernatant was acidified with 0.2% (v/v) of HNO<sub>3</sub>.

The distribution coefficient  $(K_d)$  was calculated using Eq. (1).

$$\mathbf{K}_d = (C_0 - C_e) \times \frac{\mathbf{V}}{\mathbf{W}} / C_0 \tag{1}$$

where W is the weight of the soil sample, V is the volume of solution that contains  $CaCl_2$  and Cd,  $C_0$  is the concentration of Cd in solution at the starting point,  $C_e$  is the concentration of Cd in solution after adsorption, and  $K_d$  is the amount of Cd adsorbed by soil.

#### 2.4. Incubation experiment

An incubation experiment was conducted in the greenhouse located at the Guizhou Academy of Agricultural Sciences, Jinzhu Town, Huaxi District, Guiyang City, Guizhou Province. In March 2019, a compound fertilizer (N, P, and K) was blended into the soil according to the base dose of 112.5 kg/ha for N, P, and K. Then, 50 g of soil was loaded into a switch-equipped polyethylene syringe, where the moisture content was adjusted to 60% of WHC with deionized water. After an equilibrium period of two weeks, one pepper seedling was transplanted into each tube. While plants were growing, they were consistently watered with deionized water. They were harvested after 40 days. The plants with above-ground biomass and roots were washed and scrubbed gently to remove the soil thoroughly, followed by drying them in an oven at 80 °C to maintain a constant weight. The dry weight was recorded as the biomass yield. The dry plant samples were grounded and sieved through a 100-mesh sieve for physicochemical analysis. Inductively coupled plasma mass spectrometry (US PE Company) was used to determine the Cd content in the plant, in which it was first oxidized by H2O2 and then wholly dissolved with HF-HClO<sub>4</sub>-HNO<sub>3</sub>. After that, the soil was taken back out of the tube and mixed well before being left to dry naturally. It was abraded and sieved through a 100 mesh for physicochemical analysis.

Four steps of the optimized BCR sequential extraction procedure were performed based on the method indicated by Ure et al. (1993) to identify the changes in bonding forms and redistribution of Cd in the soil. After centrifugation of 4000 g for 10 min in the I-III step, 10 mL of supernatant liquid was collected and quantified. Residual solids were entirely digested with HF–HClO<sub>4</sub>–HNO<sub>3</sub> and then diluted to 50 mL with 2% (v/v) HNO<sub>3</sub> solution. The concentration of Cd in all samples was measured using an inductively coupled plasma mass spectrometry (US PE Company) for the soil and plants. The standard reference of soil

GBW07405 with a value of 0.45  $\pm$  0.06 (ug/g) and the reference of the rice biological component GBW10010 with a value of 87  $\pm$  5 (ug/g) (the National Institute of Standard Materials, China) was used in the quality analysis. The result of soil standard reference samples was 0.46  $\pm$  0.04 (ug/g), and its recovered rate was 102.5  $\pm$  8.1%. The development of the rice biological component was 83.83  $\pm$  5.95 (ug/g), and its recovered rate was 96.36  $\pm$  6.8%.

#### 2.5. Statistical analysis

Data calculation, statistical analysis, and chart production were done using SPSS version 20.0 (SPSS Inc., Chicago, IL, U.S.A) and Origin Pro 2019 (Origin Lab Corporation). The variances among treatments were tested using standard distribution and homogeneity of variance and analyzed using one-way ANOVA with Fisher's least significant difference (LSD) test. All data were calculated based on a significance level of P-value < 0.05. The Freundlich models were used to fit the adsorbed results, as shown in Eq. (2).

$$\ln q_{\rm e} = \ln K_{\rm F} + \frac{1}{\rm n} \ln C_{\rm e} \tag{2}$$

where qe is the equilibrium adsorption capacity (mg g-1), Ce is the equilibrium concentration of the adsorbate in an aqueous phase (mg L-1), KF is the Freundlich adsorption capacity, and n is the adsorption intensity.

#### 3. Results and discussion

#### 3.1. The influence of aging on biochar characterization

After 9 years of aging, the pH value decreased from 9.61 in the fresh biochar to 7.65 in the aged biochar. SSA declined from  $46.04 \text{ m}^2 \text{ g}^{-1}$  in the fresh biochar to  $38.16 \text{ m}^2\text{ g}^{-1}$  in the aged biochar. The Zeta potential decreased from-38.58 mv in the fresh biochar to-40.69 mv in the aged biochar. CEC decreased from 43.47 cmol kg<sup>-1</sup> in the fresh biochar to 24.33 cmol kg<sup>-1</sup> in the aged biochar. Typically, when biochar is applied to the soil, it undergoes physical, chemical, and biological changes (Rechberger et al., 2017; Ren et al., 2018). Most studies that mimicked aging artificially showed that aging reduced the volatile organic compounds from biochar, which enhanced SSA (Shi et al., 2015; Vithanage et al., 2015). In contrast, other research has shown that aging decreases biochar SSA due to structural degradation (Wang et al., 2018). The SSA level was lowered after nine years of natural aging. SEM images evinced that fresh biochar surface was smooth, and its pores were empty (Fig. 1a). However, the aged biochar surface was rough. Its pores were filled with some particles (Fig. 1b). Long-term aging in the natural environment (nine years) seems to reduce the surface area of biochar by filling it with fine particles, letting microbes take over, and even making the structure fall apart (Ameloot et al., 2013; Ren et al., 2018). Table 2 shows the physicochemical properties of fresh and aged biochar.

The C, H, N, and O content of biochar are shown in Fig. 2. After aging, the C content in the biochar increased from 56.68% (fresh biochar) to 74.46% (aged biochar). The O content in aged biochar (14.53%) was substantially lower than that of fresh biochar (22.08%). Generally, biochar is regarded as a very stable form due to its aromatic structures (Lehmann et al., 2006). However, several reports have demonstrated that biochar is slowly oxidized in soil, resulting in changes in biochar elemental composition with aging (Mukherjee et al., 2014; Ren et al., 2018). In this study, the C content (74.46%) in aged biochar was higher (17.78%) than that of fresh biochar, while the O content (14.53%) was small compared with that of fresh biochar (22.08%). Similarly, these findings are consistent with the previous studies conducted by Dong et al. (2017) and Mukherjee et al. (2014) due to the labile matter in biochar, which was decomposed into carbohydrates, decreasing O content. Several studies have found that biochar was oxidized during

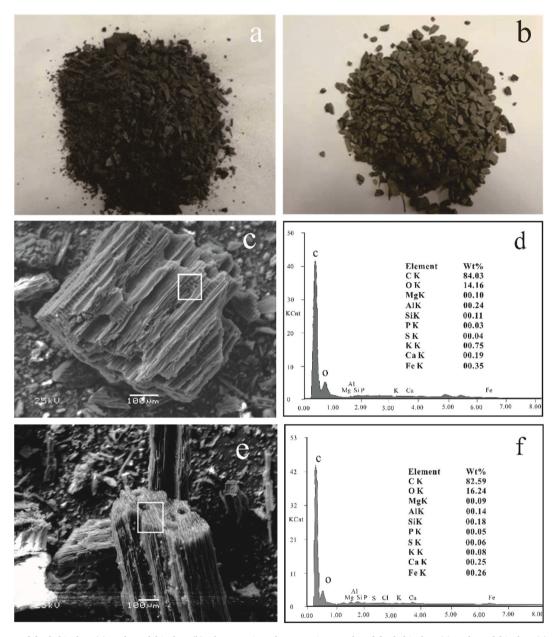


Fig. 1. The picture of fresh biochar (a) and aged biochar (b); the scanning electron micrographs of fresh biochar (c) and aged biochar (e); and the element composition of the biochar site in fresh biochar (d) and age biochar (f).

**Table 2** The physicochemical properties of fresh and aged biochar. All values are represented as means  $\pm$  SEM (n = 4). A significant difference (P < 0.05) between the treatments is represented by superscript letters behind the data. The symbols EC, CEC, WHC, and SSA, indicate electrical conductivity, cation exchange capacity, water holding capacity, and specific surface area.

Parameters	Fresh biochar	Aged biochar
pH	$9.61\pm0.47^a$	$7.65\pm0.49^{b}$
EC (uScm <sup>-1</sup> )	$1381.33 \pm 21.07^{\mathrm{a}}$	$122.87 \pm 10.19^{\rm b}$
CEC (cmol kg <sup>-1</sup> )	$43.47 \pm 6.38^{a}$	$24.33 \pm 1.64^{b}$
WHC (%)	$166.04 \pm 5.04^{a}$	$187.03 \pm 5.05^{\mathrm{b}}$
SSA $(m^2g^{-1})$	$46.04 \pm 0.32^{a}$	$38.16 \pm 0.49^{b}$
Zeta potential (mv)	$-38.58 \pm 1.00^{a}$	$-40.69 \pm 0.83^{\rm b}$

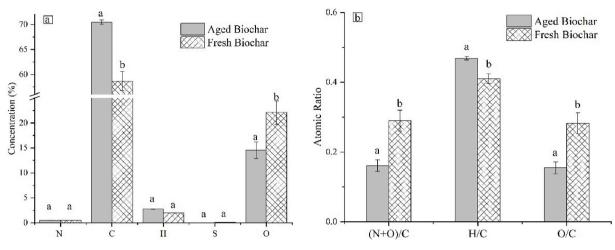
aging to increase the quantity of O-containing functional groups (Cheng et al., 2008; Mia et al., 2017), accompanied by an increase in CEC and surface negative change (Cheng et al., 2008). However, CEC and O

content in this study decreased, whereas FTIR indicated that the O content in the functional groups weakened or disappeared during the aging process (Fig. 3).

Overall, aging processes have greatly influenced the physicochemical properties of biochar, such as a decrease in pH value, CEC, and SSA, and also an increase in Zeta potential. Inevitably, these alterations in the physicochemical properties of biochar impact the regulation of heavy metals.

#### 3.2. The influence of biochar aging on Cd adsorption

As shown in Fig. 4, the adsorption of Cd increased as equilibrium concentrations increased. According to the parameters of the isotherm calculated from the mode of Freundlich (Table 3),  $R^2$  values of the Freundlich model were more than 0.97, indicating that the Freundlich model is suitable for explaining the Cd adsorption. The  $K_f$  values in the fresh biochar (36.53) were significantly higher (P < 0.05) than those in the aged biochar (13.42) and in control (11.65). The parameters  $K_f$ 



**Fig. 2.** Carbon (C), hydrogen (H), oxygen (O), nitrogen (N), and sulfur (S) content in the biochar (a) and the atomic ratios in biochar (b). A significant difference (*P* < 0.05) between the treatments is represented by superscript letters behind the data.

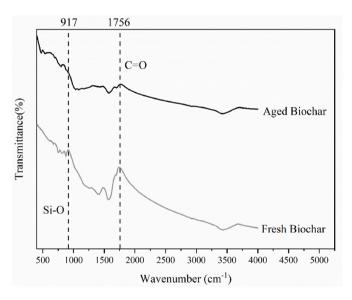


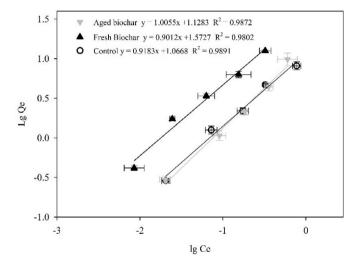
Fig. 3. FTIR spectra of fresh and aged biochar. The blank and gray lines represent aged biochar and fresh biochar, respectively.

illustrated that aging decreased biochar adsorption capacity on Cd, which is inconsistent with the study conducted by Nagodavithane et al. (2014). Previous research showed that the adsorption mechanisms of CEC and pH have a close relationship (Kumpiene et al., 2008). The liming potential of biochar (Chan et al., 2008) gradually disappeared during aging. As a result, the pH value was reduced from 9.61 in fresh biochar to 7.65 in aged biochar, and the CEC value was decreased from 43.47 cmol/kg<sup>-1</sup> in fresh biochar to 24.33 cmol/kg<sup>-1</sup> in aged biochar. Evidently, the drop in pH and CEC that occurred throughout the aging process had a significant portion of the reduced Cd adsorption seen in the soil amended with fresh and aged biochar (Shaaban et al., 2018).

Additionally, the decrease in SSA was caused by other soil particles or organisms occupying the potential adsorption site. These factors should share some responsibility for reducing adsorption capacity in aged biochar (Mia et al., 2017). Because of this, the physicochemical properties of biochar may change over time, reducing the amount of cadmium that biochar can absorb.

#### 3.3. The influence of aging on the plant uptake cd

As depicted in Fig. 5b, biochar application in the soil increased the



**Fig. 4.** Freundlich isotherms of Cd adsorption on un-amended soil and soil amended with fresh or aged biochar at 298 K. A significant difference (P < 0.05) between the treatments is represented by superscript letters behind the data.

**Table 3** Fitting Freundlich model parameters to isotherm data for cadmium uptake by biochar. All values are represented as means  $\pm$  SE (n = 4). A significant difference (P < 0.05) between the treatments is represented by superscript letters behind the data.

Treatments		Freundlich		K <sub>d</sub>
	n	K <sub>f</sub>	R <sup>2</sup>	
Control	$1.10\pm0.04^{a}$	$11.649 \pm 0.49^{a}$	$0.97\pm0.01$	$10.52\pm1.33^{\text{a}}$
Fresh biochar	$1.13\pm0.07^a$	$36.526 \pm 2.56^{b}$	$0.98\pm0.01$	$37.71 \pm 3.91^{b}$
Aged biochar	$0.98\pm0.03^a$	$13.415 \pm 1.24^{a}$	$0.99\pm0.02$	$15.76 \pm 2.83^{c}$

biomass, which is consistent with the previous studies (Silva Gonzaga et al., 2019; Nobile et al., 2020). Biochar mitigated Cd toxicity that should inhibit pepper growth, resulting in increased pepper biomass (Fig. 5b). The effect of aged biochar on promoting pepper growth is more noticeable than that of fresh biochar. The reason for this was attributed to the fact that fresh biochar had a higher adsorption capacity (Fig. 4). This means that biochar absorbed more nutrients (Gong et al., 2019), and the increased pepper biomass was less in the fresh biochar treatment than in the aged biochar treatment.

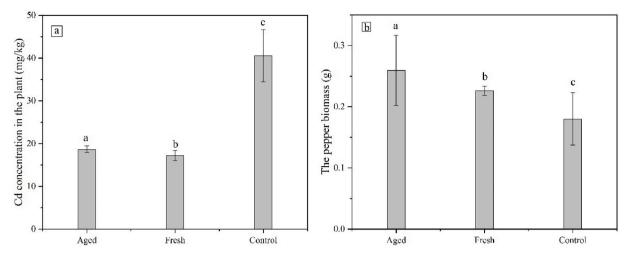
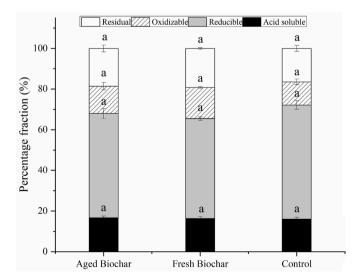


Fig. 5. The Cd concentration in the plant (a) and the plant biomass in the different treatments (b). A significant difference (P < 0.05) between the treatments is represented by superscript letters behind the data.

Compared with control, Cd content was significantly (P < 0.05) lowered in the plant due to biochar application (Fig. 5a), whereas in the aged biochar treatment, it was significantly (P < 0.05) increased compared with that of the fresh biochar treatment. This indicates that aging weakened the capacity of biochar to inhibit heavy metals in soil, as it is shown in the adsorption results (Fig. 4). Recently, reducing the mobility and transportation of heavy metals in soil using fresh biochar has been seen as a successful technique (Abbas et al., 2017; Kamran et al., 2019), but mechanisms that occur during the reduction of their mobility and transport in the soil and plants using aged biochar are unclear. The Cd concentration in the pepper demonstrated that adding biochar to the soil reduced the Cd bioavailability, resulting in a decreased Cd that should be uptaken by the plants. Aging significantly reduces biochar adsorption capacity, increasing Cd concentration in the plants. There are two possible explanations for this occurrence. Firstly, biochar boosted the adsorption capability of the soil (Kamran et al., 2019; Tu et al., 2020). The difference in fresh and aged biochar demonstrated that biochar adsorption capacity was the main reason for the plant biomass and Cd concentration. Secondly, the variation of Cd bioavailability greatly influences the plant's Cd content uptake (Rizwan et al., 2016). Biochar application improved the physicochemical



**Fig. 6.** Specification percentage of Cd in soil amended with or without biochar. A significant difference (P < 0.05) between the treatments is represented by superscript letters behind the data.

properties of the soil, resulting in a change in Cd speciation in the soil (Yang et al., 2017; Alaboudi et al., 2019). As evinced in Fig. 6, the percentage fraction of Cd speciation showed no significant difference between treatments with biochar and control, which is inconsistent with the previous studies (Yang et al., 2017; Kamran et al., 2019). As evinced in previous studies, the liming effect of biochar enhances the soil pH, which also changes the fractionation of Cd due to the net negative charge and higher density of cation exchange sites in biochar (Houben et al., 2013; Cui et al., 2019). For the following two reasons, there is no difference in Cd fractionation observed between different treatments. On the one hand, the pH of the soil itself is close to neutral, and the liming effect of biochar is not noticeable. On the other hand, due to less recovery of aged biochar, the proportion of biochar added was 2%, and the effect of biochar on the morphological changes of the heavy metal Cd in soil due to the added biochar amount is not apparent.

This study indicates that biochar application can decrease Cd that should be uptaken by plants due to increased adsorption capacity of the soil, while biochar aging reduces adsorption capacity, resulting in more Cd that can be uptaken by plants.

#### 4. Conclusion

The results of this study revealed that aging decreased the surface area, pH value, and cation exchange capacity (CEC), resulting in a decrease in adsorption capacity. It was shown that soil remediation with fresh and aged biochar reduced 57.05 and 53.3% of the amount of Cd that can be uptaken by the plant compared to the treatment without biochar. This shows that aged biochar can solidify Cd and decrease the amount of Cd that can be uptaken by plants. Biochar aging significantly reduced the capacity of biochar to adsorb Cd in the soil. This study shows that the age of the biochar should be considered when using it to clean up soil contaminated by Cd.

#### The author's contribution and conflict of interest statements

Dr Cheng Hongguang and Dr Xing Dan was responsible for the manuscript writing and the experiment design, Dr Zengping Ning and Yizhang Liu analyzed the data, Dr Lin Shan was responsible for the experimental work, Professor Yongfu Li was responsible for the experimental design. Professor Davey, Chadwick and Dr Paul were responsible for the overall planning of the experiment and the revision of the manuscript.

#### 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.

#### Data availability

Data will be made available on request.

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