Effects of Mg-modified Biochar on the Bioavailability of Cadmium in Soil

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The remediation effects of peanut shell biochar (HBC) and Mg-modified peanut shell biochar (MHBC) prepared under pyrolysis temperatures of 300 °C and 600 °C on Cd^{2+} polluted brown soil were investigated in a pot experiment. The results showed that the biochar treatment increased soil pH and decreased the bioavailable Cd^{2+} content in the soil. Compared with the control treatment (CK), the pH value increased by 0.32 to 2.5 upon treatment with 1% and 2% of HBC and MHBC. Bioavailable Cd^{2+} in the soil decreased by 5.64% to 21.33% with HBC. The MHBC presented better amendment effects than HBC; bioavailable Cd^{2+} in the soil decreased by 26.2% to 50.1% with the addition of MHBC. The addition of HBC and MHBC increased the shoot height and decreased the root length of the spinach. Moreover, they significantly decreased the accumulation of Cd^{2+} in the shoots and roots of the spinach. Compared to CK, the Cd^{2+} content in the shoots decreased by 7.0% to 46.8% upon treatment with 1% and 2% of HBC and MHBC, while the Cd^{2+} content in the roots decreased by 7.3% to 52.7%. The Cd^{2+} content in the shoots and roots was more greatly decreased with MHBC than with HBC.

Keywords: Magnesium-modified biochar; Cadmium; Remediation; Spinach; Bioavailability

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INTRODUCTION

Cadmium (Cd) is widely used in electroplating and metallurgy. The toxicity of Cd causes major environmental problems in soils worldwide. Soils are the largest source and sink of Cd. In China, according to the National Soil Pollution Survey, the standard pollution rate of Cd in 4,095 typical sampling sites was 7% greater than those of other heavy metals (Wang *et al*. 2015). Research shows that Cd can cause stress to plant growth, resulting in reduced plant biomass even at trace concentrations (Dai *et al*. 2020). Cadmium(II) induces plant cells to produce excessive reactive oxygen species, generating oxidation products such as hydrogen peroxide and peroxide ions. These species affect the redox balance in the plants and damage the integrity of plant cell membranes to varying degrees (Laspina *et al*. 2005; Guo *et al*. 2019; Sidhu *et al*. 2020). The bioavailability of heavy metals is closely related to the extent of damage to plants and animals. Heavy metals with high bioavailability are more likely to be absorbed by plants. Vegetables, fruits, and crops planted in heavy-metal-contaminated soils or irrigated with sewage containing a high content of heavy metals pose potential threats to human health (Farrag *et al*. 2012). Therefore, technologies to control the bioavailability of soil Cd should be studied. Present amendment technologies for Cd removal include physical remediation, chemical remediation, and bioremediation. Soil amendments can decrease the bioavailability of heavy metals through adsorption, complexation, and other mechanisms to fix heavy metals and decrease uptake by animals and plants. Soil amendment is an economical, efficient, and environmentally friendly remediation method (Ashrafi *et al*. 2015; Bashir *et al*. 2020), but the results of different soil amendments vary greatly (Zhang *et al*. 2020). At present, the addition of biochar to soil is one of the most promising soil remediation methods.

Biochars are porous carbonaceous materials with high specific surface area, and they are produced by the pyrolysis of organic matter under high temperature (> 300 °C) in anoxic or anaerobic environments (Sun *et al*. 2017; Cairns *et al*. 2020; Shan *et al*. 2020). The addition of biochar can improve soil quality, thereby promoting plant growth. Moreover, biochar has a well-developed pore structure, high specific surface area, and abundant surface functional groups (Sun *et al*. 2017; Chen *et al*. 2020). Therefore, biochar is an efficient and low-cost adsorbent that can effectively adsorb inorganic and organic pollutants, thereby decreasing their concentrations and bioavailabilities (Jin *et al*. 2016; Awad *et al*. 2020). Ali *et al*. (2020) used apricot shell and apple tree biochars to transform Cd and Zn from acid-soluble and reducible forms to organic-bound and residue fractions, which are less bioavailable. Consequently, their accumulation in the roots and shoots of mustard were decreased. In recent years, biochar has been widely used for the remediation of soil pollution. However, the remediation efficiency of a single type of pristine biochar for the removal of organic and inorganic pollutants in soil is limited (Fan *et al.* 2018). Therefore, researchers have combined biochar with other substances such as iron oxides (Micháleková-Richveisová *et al*. 2017), copper oxide (Li *et al*. 2020b), calcium carbonate (Wu *et al*. 2020), and graphene oxide (Shang *et al*. 2016) to remediate soils contaminated by heavy metals. Moreover, heavy metal fixation by biochar in soils is influenced by the pyrolysis temperature, concentration, and physicochemical properties of the biochar. Wang *et al*. (2020) observed that the content of Cd accumulated in maize decreased upon the addition of biochar prepared at 300 °C compared to that prepared at 700 °C. In another study, as the concentration of bamboo and rice stalk biochars increased from 0% to 5%, the concentration of $CaCl_2$-extractable Cd in the soil gradually decreased (Yang *et al*. 2016). Awad *et al*. (2020) suggested that the contents of heavy metal in the soil and plant issues decreased after adding garden waste biochar and the reduction was higher in 6% of the biochar treatment than 4%. According to the aforementioned studies, the concentration and pyrolysis temperature of the biochar can affect the fraction of heavy metals in the soil, but the mechanisms of the reactions are not clear. Therefore, a new modified biochar should be developed to improve the remediation efficiency of biochar, and its pyrolysis temperature, concentration, mechanisms, and influencing factors should be investigated.

Spinach is one of the most popular vegetables in China. High concentration of Cd can accumulate in edible parts of leafy vegetables, such as spinach and lettuce. The human consumption of such a vegetable which contains a great amount of heavy metal presents a potential risk for human health (Huang *et al*. 2017). Magnesium ion is an essential element for its growth which can lead to exchange of heavy metal ions in the soil, thereby improving the adsorption efficiency of the biochar. Tao's team found that the sorption capacity of the *Thalia dealbata* biochar for Cd in sediment was improved by 24.2 to 25.6% after loading $MgCl_2$ (Tao *et al.* 2019). Li *et al*. (2020) suggested that the maximum theoretical saturation adsorption amount of Mg-modified biochar for Cd in wastewater was up to 370 mg/g. These research studies about Mg-modified biochar mainly focused on its sorption behavior in two different environmental matrixes. However, the influence of Mg-modified biochar on the bioavailability of Cd in soil and the effect on plant growth status have not been well understood. Further efforts are necessary to evaluate the effect of the Mg-modified biochar on Cd in soil from the aspect of bioavailability. Therefore, this study attempts to prepare Mg-modified biochar and explore its optimum concentration and pyrolysis temperature to reduce the bioavailability of Cd. Peanut shell biochar (HBC) and Mg-modified peanut shell biochar (MHBC) were prepared *via* 300 °C and 600 °C pyrolysis and added to soil samples at 1% and 2% concentrations. The growth and Cd content of spinach were used to evaluate the passivation effect of Cd by HBC and MHBC at different concentrations and pyrolysis temperatures.

EXPERIMENTAL

Preparation and Treatment of Soil Samples

Brown surface soil (0 cm to 20 cm) samples were collected from Rizhao, Shandong Province, China. The soil samples were dried, ground, and sieved through 2-mm, 1-mm, and 0.15-mm sieves to prepare for the pot experiment, pH detection, and analysis of total organic matter and heavy metal content, respectively. The basic physicochemical properties of the soil samples are shown in Table 1.

Table 1. Basic Physicochemical Properties of Soil Samples

Type of Soil	pH	Organic Matter Content (g/kg)	Total N (%)	Total P (%)
Brown soil	6.17	2.4	0.057	0.063

Preparation and Characterization of Biochar

The pristine biochar was prepared from peanut shells. Peanut shells were first washed three times with deionized water, and they were then dried to a constant weight at 50 °C before being ground into powder. The biochar was produced from the obtained powder by placing it in a porcelain crucible with a cap and pyrolyzing it in a muffle furnace for 2 h at 300 °C (300HBC) and 600 °C (600HBC) under an oxygen-limited N_2 atmosphere. The N_2 gas was inserted at 10 L/min, and the heating rate was approximately 15 °C/min. The samples were then ground and sieved through a 0.6-mm sieve after the temperature decreased to room temperature.

To prepare the Mg-modified peanut biochar, peanut shells were first soaked in an $MgCl_2$ solution (at a solid–liquid ratio of 1:10 w/v) in an ultrasonic oscillator for 6 h (Tao *et al*. 2019). They were then cleaned with deionized water, placed in a crucible, and dried at 105 °C before being ground into powder. The pyrolysis process was the same as mentioned above, and the samples were labeled as “300MHBC” and “600MHBC.” The characterization of the biochar is described in Chen *et al*. (2020).

Experimental Methods

The bioavailability of Cd in the biochar-amended soil was investigated through experiments. The soil treatments were the control treatment (CK), 1%300HBC, 2%300HBC, 1%600HBC, 2%600HBC, 1%300MHBC, 2%300MHBC, 1%600MHBC, and 2%600MHBC. The percentages refer to the mass ratio in the soil (*i.e.*, biochar concentration), 300 and 600 indicate the corresponding pyrolysis temperature (°C), HBC refers to pristine biochar, and MHBC refers to Mg-modified biochar.

A stock solution of 1000 mg/L $Cd(NO_3)_2{\cdot}4H_2O$ was added to the soil and mixed evenly. A soil sample with a Cd content of 10 mg/kg was prepared and air dried, followed by homogenization. The polluted soil was added to the plastic pots, and the moisture content of the soil was maintained at 60% of the water holding capacity. After 2 weeks, 1 g of urea was added as base fertilizer and mixed evenly. The pristine biochar and Mg-modified biochar (300HBC, 600HBC, 300MHBC, 600MHBC) were then mixed with the soil at 0%, 1%, and 2% mass fractions. The moisture contents of the soil samples were maintained at 65% of water holding capacity by adding distilled water, and the soil was cultured alternately under moist and dry conditions in a greenhouse for 1 week. All experiments were conducted in triplicate, and the average values were used for the analysis. A total of 27 treatments were established and performed.

Spinach was selected as the indicator of Cd bioavailability in the soil. The spinach seeds were disinfected by soaking in 6% NaClO solution for 20 min. Then, the seeds were removed and rinsed with tap water three times, followed by washing with distilled water. Three seeds were planted in each plastic pot filled with 500 g of soil. The plastic pots were placed in an artificial greenhouse, and their positions were randomly changed every two weeks. The spinach samples were harvested after five weeks of cultivation.

Soil Sampling and Analysis

Soil samples were collected and then air-dried on the 30th day after the spinach was planted in the plastic pots. The soil pH was measured by a pH meter. For that, 5.0 g of soil sample was weighed and sieved (1 mm). The soil sample was placed in a 50-mL centrifuge tube, and 25 mL of deionized water was added to it for a soil:water ratio of 1:5 (w/v). The centrifuge tubes were oscillated at 180 rpm for 30 min, then centrifuged at 4000 rpm for 10 min. Finally, the pH of the supernatant was measured with the pH meter.

Next, soil samples of 5.0 g were screened by a 0.15-mm sieve, then weighed in a 50-mL centrifuge tube. Subsequently, a 0.1 mol/L $CaCl_2$ solution (1:25 soil:water ratio) was added to the tube and oscillated for 2 h at 180 rpm and 25 °C ± 1 °C. The samples were then centrifuged at 4000 rpm for 10 min and filtered through a 0.22-μm membrane. The supernatant was collected to determine the concentration of bioavailable Cd^{2+}.

A soil sample of 0.2 g was moistened with distilled water and placed in a crucible, and 10 mL of HCl was added to it. The sample was heated at 80 °C for evaporation until the solution in the crucible was approximately 3 mL. A mixture solution of HNO_3, HF, and $HClO_4$ (5:5:3 v/v/v) was added and heated at 180 °C for 1 h with a lid. Afterwards, the lid was opened to remove silicon and then closed to decompose the black organic carbide when the thick white perchloric acid smoke emerged. Before the lid was opened to remove the white smoke, the black organic matter on the crucible wall was already absent. The crucible was cooled to room temperature, and 1 mL of HNO_3 solution was added. The mixture was transferred into a 25-mL colorimetric tube, mixed evenly, and left to stand overnight. The results of atomic absorption testing (see later) determined the total Cd in the soil.

Plant Sampling and Analysis

After 5 weeks of culturing, three spinach samples were randomly selected from each treatment group to measure the plant height and root length with a ruler. The average value was used as the indicator of spinach growth.

The harvested spinach samples were washed with distilled water three times. The shoots and roots of the spinach were separated and dried at 105 °C for 30 min, dried to constant weight at 60 °C, and then ground into powder. A sample of 0.25 g was placed in a crucible, to which 10 mL of HNO_3-$HClO_4$ (4:1, v/v) mixture solution was added. The mixture was heated to digest, and the Cd content in the plant tissue was analyzed.

Detection and Statistical Analysis

An atomic absorption spectrophotometer (GFA-7000A, Shimadzu Corporation, Shimadzu, Japan) was used to determine the Cd content in the soil and digested plant tissue solutions. Origin 8.0 software (OriginLab, Northampton, MA, USA) was used for statistical processing of all test data.

RESULTS AND DISCUSSION

Effects of Different Biochar Treatments on Soil pH

Soil pH is the main factor controlling the adsorption, desorption, and precipitation balance of heavy metals. Moreover, it determines the migration and transformation behavior of heavy metals in the soil. Therefore, the soil pH can notably influence the bioavailability of heavy metals in the soil and the extent of the stress caused by them on plant growth. The effects of the different biochar treatments on the soil pH are shown in Fig. 1. The pH of the soil treated with HBC and MHBC increased by 0.32 to 2.50 units compared with CK. This result was consistent with the results of other studies. For example, Wu *et al*. (2020) reported that the addition of calcium-based magnetic biochar significantly increased the pH of rice rhizosphere and non-rhizosphere soil. The ash produced by the pyrolysis of biomass generates many inorganic salt ions, such as Mg^{2+}, Ca^{2+}, Na^+, and K^+, which mostly exist as metal oxides and carbonates. Adding them to the soil increases the soil pH. The salt ions of the biochar can also lead to H^+ and Al^{3+} exchange on the surface of soil colloids, thereby increasing the soil pH (Yuan *et al*. 2010). In addition, when the biochar is alkaline, it can increase the soil pH, to some extent decreasing the content of exchangeable Cd^{2+} and thereby decreasing the consequent damage to the growth processes of crops (Van Zwieten *et al*. 2010). The soil pH values for 300HBC, 600HBC, 300MHBC, and 600MHBC at 1% increased by 0.32, 1.43, 0.92, and 2.21 units, respectively, compared with CK. When the biochar concentration was increased to 2%, the soil pH values increased by 1.36, 2.11, 1.89, and 2.50 units, respectively, in comparison with CK. This result suggests that the soil pH increased with increasing concentration of biochar. These results are consistent with the findings of Yang *et al*. (2016), who reported that the addition of corn stalk biochar significantly increased soil pH, and the improvement caused by 5% corn stalk biochar treatment was greater than with the 1% treatments. This result may be because biochar is an alkaline material, and more alkaline ions carried by the biochar enter the soil with increasing addition of biochar, thereby leading to a greater soil pH. Moreover, the capacities of the HBC and MHBC to increase soil pH increased with increasing pyrolysis temperature. At the same concentration, the biochar produced at higher pyrolysis temperature increased the soil pH to a greater extent. Compared with the HBC, the soil pH increased by 0.39 to 0.78 units with the addition of MHBC, and the soil pH was greatest with the 2%600MHBC treatment. This result demonstrates that the additions of magnesium and biochar had a synergistic effect on soil pH. The Mg^{2+} loaded on the biochar surface can adsorb negatively charged OH^- and CO_3^{2-}. Consequently, the inorganic magnesium led to a relatively high biochar pH, thereby increasing the soil pH to a greater extent (Lee *et al*. 2017).

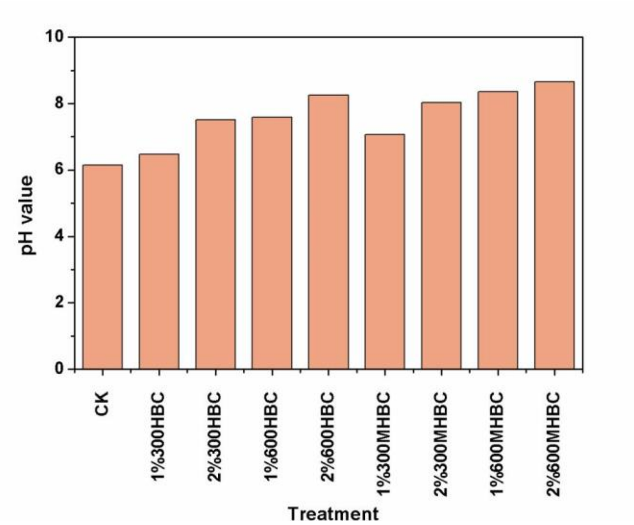

Fig. 1. Effects of different biochar treatments on soil pH

Effects of Different Biochar Treatments on the Bioavailable Cd Content in the Soil

The addition of HBC and MHBC significantly affected the bioavailable Cd^{2+} content in the soil. As shown in Fig. 2a, in comparison with CK, the content of bioavailable Cd^{2+} decreased by 5.6%, 6.4%, 26.2%, and 45.0% with 1% concentration of 300HBC, 600HBC, 300MHBC, and 600MHBC, respectively, and the content of bioavailable Cd^{2+} ranged from 4.35 mg/kg to 5.32 mg/kg. The content of bioavailable Cd^{2+} in the soil decreased by 21.3%, 19.5%, 40.8%, and 50.1% with 2% 300HBC, 600HBC, 300MHBC, and 600MHBC, respectively, and the bioavailable Cd^{2+} ranged from 2.16 mg/kg to 3.37 mg/kg. Therefore, the addition of biochar can effectively decrease the content of bioavailable Cd^{2+} in the soil, which decreased as the concentration of biochar increased from 1% to 2%. This result is consistent with the results of Yang *et al*. (2016), who reported that the content of $CaCl_2$-extractable Cd^{2+} in soil decreased as the concentration of biochar increased from 0% to 5%. This result probably occurred because more active adsorption sites were provided for the soil with greater biochar concentrations, which increased the soil pH to a greater extent, thereby improving the fixation capacity of the soil for Cd^{2+}. Moreover, as the biochar concentration increased, the desorption rate of the Cd^{2+}, which was adsorbed by the soil surface, decreased (Abbas *et al*. 2017). However, Qayyum *et al*. (2019) demonstrated that the content of bioavailable Cd^{2+} significantly decreased and was effectively fixed in a soil contaminated by a relatively low Cd^{2+} level (25 mg/kg) as the concentration of cotton stalk biochar increased from 2% to 5%. However, the results were contrary for soils with relatively greater Cd^{2+} contamination (50 mg/kg and 100 mg/kg). These results illustrate that the effect of biochar on the fixation of Cd^{2+} can also be affected by the contamination level of Cd in the soil. Furthermore, for the same concentration, the content of bioavailable Cd^{2+} in the soil decreased as the pyrolysis temperature increased, and the values were ranked as follows: 300HBC > 600HBC > 300MHBC > 600MHBC. Karimi *et al*. (2020) reported that a sludge biochar prepared at 600 °C effectively decreased the exchangeable form of Pb^{2+} and Cd^{2+} in the soil, and its effect was more significant than that of the biochar prepared at 300 °C. This result further illustrates that the greater pyrolysis temperatures correspond to greater fixation capacity of the biochar for Pb^{2+} and Cd^{2+} in the soil. Studies have shown that biochar prepared *via* low-temperature pyrolysis

(< 300 °C) mainly produces aliphatic alkylated oxygen, whereas biochars formed by high-temperature pyrolysis (> 300 °C) contain abundant aromatic structures (Li *et al*. 2013). Therefore, a greater pyrolysis temperature contributes to the formation of aromatic functional groups on the surface of the biochar, such as O-H, C=C, and C=O. These structures can enhance the adsorption capacity of the biochar by strengthening hydrogen and dipole bonds (Chen *et al*. 2019). The abundant surface functional groups and aromatic structures of the biochar can also act as electron donors or receptors to adsorb Cd^{2+} by π-π electron donor–receptor interactions (EDA), thereby decreasing the content of bioavailable Cd^{2+} in the soil. Compared with the HBC, the MHBC had a stronger inhibitory effect on the bioavailable Cd^{2+} content in the soil in a short period of time (30 d). The content of bioavailable Cd^{2+} after the MHBC treatment decreased by 26.2% to 50.1% compared with the CK treatment, which was a greater reduction than that of the HBC treatment (5.6% to 21.3%). This result demonstrates that the Cd^{2+} fixation capacity of the biochar in the soil was improved by the Mg loading, and the passivation effect of the 2% MHBC prepared at 600 °C was the greatest. This result might be due to the magnesium loaded on the biochar surface after the pyrolysis process in preparing the MHBC. Magnesium hydroxide was precipitated due to the increased soil pH, which promoted the co-precipitation of Mg^{2+} and Cd^{2+} in the soil solution (Ngambia *et al*. 2019; Li *et al*. 2020), thereby decreasing the content of bioavailable Cd^{2+} in the soil.

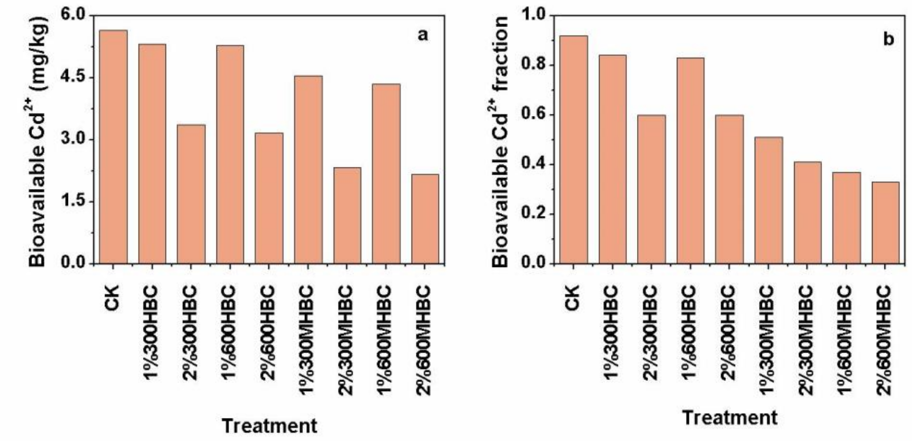

Fig. 2. Effects of different treatments on (a) bioavailable Cd^{2+} and (b) fraction of bioavailable Cd^{2+} to total Cd^{2+}

The fraction of bioavailable Cd^{2+} to total Cd^{2+} under different biochar treatments are shown in Fig. 2b. The addition of HBC or MHBC decreased the fraction of bioavailable Cd^{2+} to total Cd^{2+} in the soil, and as the biochar concentration increased, the fraction of bioavailable Cd^{2+} tended to decrease. Compared with the CK treatment, the fractions of bioavailable Cd^{2+} treated with 1%300HBC, 2%300HBC, 1%600HBC, and 2%600HBC decreased by 8.7%, 34.8%, 9.8%, and 34.8%, respectively. By contrast, the fractions of bioavailable Cd^{2+} in the soil treated with 1%300MHBC, 2%300MHBC, 1%600MHBC, and 2%600MHBC decreased by 44.6%, 55.4%, 59.8%, and 64.1%, respectively. The fractions of bioavailable Cd^{2+} to total Cd^{2+} were ranked as 300HBC > 600HBC > 300MHBC > 600MHBC for the same concentration of HBC and MHBC, thus indicating that the fraction of bioavailable Cd^{2+} in the soil decreased as the pyrolysis temperature increased.

To explore the mechanism of the effect of biochar addition on the content of bioavailable Cd^{2+} in the soil, the correlation between soil pH and fraction of bioavailable Cd^{2+} to total Cd^{2+} was analyzed. As shown in Fig. 3, this correlation was significant ($p < 0.01$), which further demonstrates that the biochar immobilized Cd^{2+} in the soil mainly by increasing soil pH and weakening its bioavailability. Huang *et al*. (2020) reported that the proportion of bioavailable Cd^{2+} to total Cd^{2+} was 48.5% in an acidic soil and 5.0% in an alkaline soil. This result is consistent with the results of Ali *et al*. (2020), which suggested that the addition of biochar derived from apricot shells can decrease the bioavailability of Cd^{2+} in soil by increasing soil pH and ultimately decreasing crop uptake. Such results can be attributed to two reasons.

First, the addition of HBC and MHBC increased the soil pH, and the consequent greater concentration of OH^- in the soil led to the hydrolyzation of Cd^{2+}, which precipitated to $Cd(OH)_2$. The adsorption of Cd^{2+} was enhanced because the adsorption affinity of the soil for metal hydroxides was greater than that for free metal cations. Consequently, the bioavailability of Cd^{2+} was decreased (Yuan *et al*. 2010). Second, in addition to increasing the negative surface charge of clay minerals in the soil, greater soil pH also weakens the competitive adsorption of H^+ and Cd^{2+}. Therefore, the adsorption capacity of negatively charged soil colloids for Cd^{2+} was promoted. Meanwhile, precipitation of compounds such as $Cd(OH)_2$, $CdCO_3$, and $Cd_3(PO_4)_2$ also occurred, which decreased the bioavailability of Cd^{2+}. However, the fraction of bioavailable Cd^{2+} to total Cd^{2+} was not fully consistent with the variation trend of soil pH. For instance, the pH of the soil treated with 1%600HBC was 0.28 units larger than that of the soil treated with 2%300HBC, and the fraction of bioavailable Cd^{2+} in the former sample was 23% greater, which did not follow the negative correlation (Figs. 1 and 2b). This result indicates that the content of bioavailable Cd^{2+} in the soil was not completely determined by soil pH, and it may be closely related to the adsorption and desorption processes of HBC and MHBC for Cd^{2+} in the soil.

The structure of the biochar determines if it can effectively adsorb Cd^{2+} in the soil through surface adsorption and pore filling, thereby fixating the Cd^{2+} and decreasing its bioavailability. As shown in scanning electron microscopy (SEM) analysis of HBC and MHBC (Chen *et al*. 2020), the pristine biochar and Mg-modified biochar had well-developed pore structures and high specific surface area, which exhibited a significant increase after loading $MgCl_2$ on the surface of peanut shell biochar. The pristine biochar presented a relative smooth surface with lesser pores than Mg-modified biochar, which can also explain the adsorption capacity of MHBC for Cd was better than HBC and thus posing a more significant effect on decreasing the bioavailability of Cd in soil. Moreover, according to the SEM analysis, the surface of MHBC was covered with irregular particles, which has been corroborated MgO and $Mg(OH)_2$ crystal particle by Energy Dispersive Spectrometer (EDS) analysis in our previous study (Chen *et al*. 2020). This indicated that Mg was successfully deposited on the surface of biochar and may improve the adsorption capacity of biochar-soil system for Cd by ion exchange process to some extent. Fourier-transform infrared spectroscopy of HBC and MHBC suggests that their surfaces are rich in functional groups such as -OH corresponded to the peak of 3462 cm^{-1}, $-CH_3$ (2944 cm^{-1}), carbonate (833 cm^{-1}), -C=O (1633 cm^{-1}), and C=C (1450 cm^{-1}), among which acidic oxygen-containing functional groups such as carboxyl can complex with Cd^{2+} in the soil, thereby decreasing its bioavailability (Chen *et al*. 2020). In addition, biochars are rich in organic matter, which can also promote the formation of stable complexes between heavy metals (such as Cd^{2+}) and organic matter, thereby decreasing the Cd^{2+} bioavailability (Zia ur Rehman *et al*. 2017). In this study, the inherent properties of biochar were changed by

$MgCl_2$ modification, and the content of cation ions also increased. These transformation can account for the more significant reduction effect of MHBC on the bioavailability of Cd in soil.

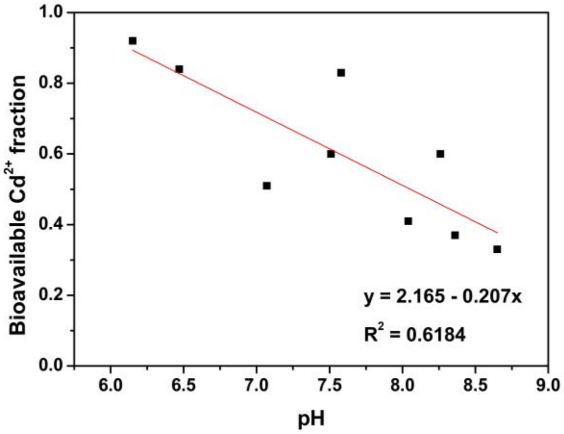

Fig. 3. Correlation between soil pH and fraction of bioavailable Cd^{2+} to total Cd^{2+} upon different treatments

Effects of Different Treatments on the Biomass of Spinach

The effects of the HBC and MHBC treatments on the growth of spinach shoots and roots are shown in Fig. 4. The addition of HBC and MHBC increased the shoot height by 37.2% to 80.1% compared with CK. This result can be attributed to the biochar’s alkalinity, which was conducive to the deprotonation of hydroxyl, carboxyl, and other acidic functional groups in the soil. As the negative surface charge of the soil colloids and biochar increased, free heavy metal ions with positive charge were adsorbed to neutralize the surface charge, thus improving the adsorption capacity of the soil and, consequently, its Cd^{2+} amendment potential. Therefore, the addition of biochar could decrease the bioavailability of Cd^{2+} in the soil, thereby decreasing the toxic stress on spinach and increasing its yield. The shoot height of the spinach increased with increasing concentrations of HBC and MHBC. Compared with CK, the shoot heights of 1%300HBC, 2%300HBC, 1%600HBC, and 2%600HBC increased by 37.2%, 50.1%, 48.9%, and 49.8%, respectively. Moreover, the shoot heights of 1%300MHBC, 2%300MHBC, 1%600MHBC, and 2%600MHBC increased by 66.5%, 70.8%, 73.8%, and 80.8%, respectively. This result is contrary to the findings of Wu *et al*. (2020), whose results show that the effect of 1% magnetic calcium-based rice straw biochar on the growth of rice was stronger than that of 2% addition to an As polluted soil. This probably occurred because the negative charges on the surfaces of the soil colloids increased with increasing biochar concentration, which resulted in the repulsion of As anions in the soil. Therefore, the bioavailability of As was enhanced, and the bioavailable As was absorbed more easily by the plant, thereby inhibiting its growth. In contrast, Tao *et al*. (2019) reported results consistent with the present study. In their study, the Cd^{2+} stress in the soil was alleviated as the biochar concentration increased from 0% to 5%, which significantly promoted the germination and growth of pakchoi. The differences between these results may be due to the different valence (Cd^{2+}, As anions) which determined the repulsion and adsorption behavior of heavy metal ions then influencing their bioavailability when the negative charges on the surfaces of the soil colloids increased after adding biochar.

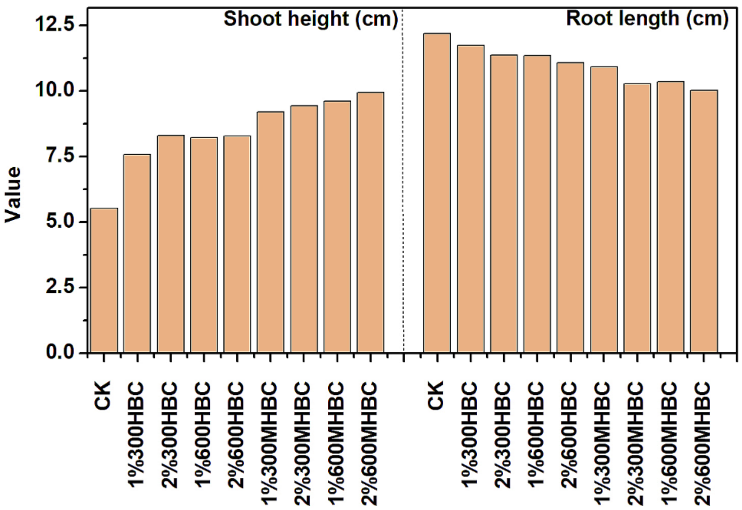

Fig. 4. Effects of different biochar treatments on spinach biomass

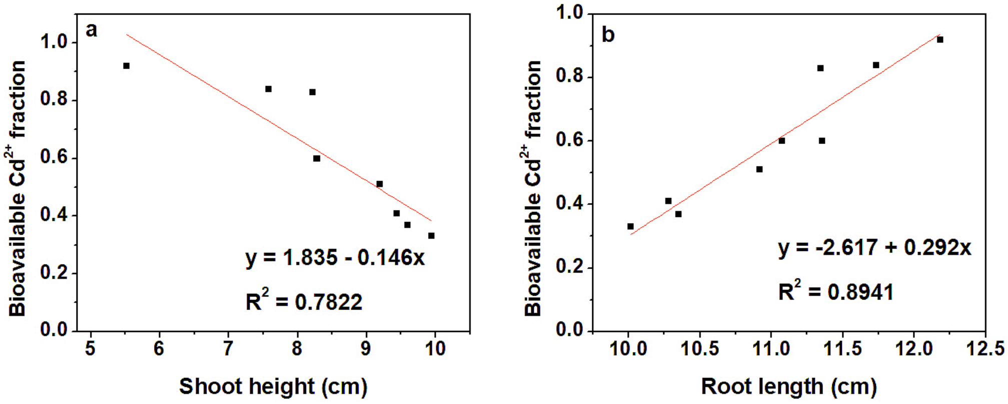

Fig. 5. Correlations between (a) shoot height and (b) root length of spinach and the fraction of bioavailable Cd^{2+} to total Cd^{2+}

Therefore, the effect of biochar on plant growth in a heavy-metal-stressed soil depends on the characteristics of the biochar, plant species, and heavy metal properties, among which valence is the most important factor (Chen *et al*. 2015). The shoot heights of the spinach were ranked as follows: 300HBC < 600HBC < 300MHBC < 600MHBC. This result indicates that the shoot height of the spinach increased with increasing biochar pyrolysis temperature for the same concentration of HBC and MHBC. The shoot height related to the MHBC treatment was 9.20 cm to 9.95 cm, which was significantly greater than those related to the HBC treatment (7.58 cm to 8.29 cm) and CK (5.52 cm). These results indicate that the addition of MHBC was more conducive to the growth of the spinach overground part. This result was consistent with the results of Tao *et al*. (2019), in which the addition of Mg-modified biochar derived from *Thalia dealbata* had a more significantly effect than pristine biochar on the germination and growth of pakchoi. A possible reason for these results is that the biochar was rich in basic cations (Mg^{2+}), whose content increased by the modifying process. Abundant Mg^{2+} can promote the exchange of the Mg^{2+} loaded on the biochar surface with the Cd^{2+} in soil, thereby fixing Cd^{2+} on the biochar surface. In addition, Mg^{2+} can provide nutrients for the spinach, which promote its growth to some extent. Therefore, the shoot height increased with increasing biochar concentration and pyrolysis temperature, and MHBC had more significant effects on the increase of spinach shoot height. Then the shoot height increased the most in the 2%600MHBC treatment compared with CK. This is consistent with the findings of Lu *et al.* (2014), who reported that the shoot biomass of *Sedum plumbizincicola* in 5% bamboo biochar treatment was higher than 1% treatment and CK under Cd stress. On the one hand, this was related to the extractable Cd content which was lower in 5% biochar treatment. The heavy metal Cd has been reported that can decrease spinach biomass (Younis *et al.* 2016). Then the stress effect on plant growth was lesser in 5% biochar treatment. On the other hand, the total shoot nutrient element N content and the shoot N concentration in 5% biochar treatment were significantly higher than that in 1% and CK. Therefore, different concentration of biochar can affect plant biomass by influencing its nutrient absorption capacity. Moreover, in this study, the pH value of biochar-soil system increased with the pyrolysis temperature of biochar increase. This may decrease the bioavailability of Cd and thus improving the plant biomass.

To further explore the effect of bioavailable Cd^{2+} on plant growth, the correlation between shoot height and fraction of bioavailable Cd^{2+} to total Cd^{2+} was analyzed. As shown in Fig. 5a, the spinach shoot height was negatively correlated with this fraction ($p < 0.01$). This result may be attributed to the lower content of bioavailable Cd^{2+}, which then caused a lower stress effect on the growth of the spinach. Therefore, the growth inhibition effect of the Cd^{2+} on the spinach was weak, and the shoots were able to grow relatively tall. In addition, Parra *et al.* (2017) observed that Ca^{2+}, Zn^{2+}, and Fe^{2+} were essential elements for plant growth and had similar physical properties to Cd^{2+}, such as charge and ion radius. Other studies have also shown that Cd^{2+} competes with Ca^{2+}, Zn^{2+}, and Fe^{2+} for the same transport channel on the root surface when being absorbed into plant tissue (Tian *et al.* 2016). Therefore, the decreased content of Cd^{2+} decreased the competition between Cd^{2+} and essential elements for plant growth, which was conducive to nutrient uptake by the plant.

As shown in Fig. 4, the addition of HBC and MHBC decreased the length of the spinach root. Compared with CK, the root length decreased by 3.7% to 17.8%, and it decreased the most for the 2%600MHBC treatment. As shown in Fig. 4, the root length decreased with increasing biochar concentration. For the 1%300HBC, 2%300HBC, 1%600HBC, and 2%600HBC treatments, the root lengths decreased by 3.7%, 6.8%, 6.8%, and 9.1% compared to the CK, respectively. For the 1%300MHBC, 2%300MHBC, 1%600MHBC, and 2%600 MHBC treatments, the lengths decreased by 10.3%, 15.6%, 15.0%, and 17.8%, respectively. A possible reason for these results is that the 2% HBC and MHBC have more ions, and the increased soil conductivity led to a salt stress, which further inhibited the growth of spinach roots. The lengths of the spinach roots were ranked as follows: 300HBC > 600HBC > 300MHBC > 600MHBC, for the same concentrations of HBC and MHBC. Therefore, the root length decreased with increasing pyrolysis temperature. In addition, compared with HBC, MHBC had a stronger shortening effect on the root length. This result was consistent with the trend of fraction of bioavailable Cd^{2+} to total Cd^{2+} upon addition of biochar. As shown in Fig. 5b, there was a highly significant positive correlation between root length and fraction of bioavailable Cd^{2+} to total Cd^{2+} ($p < 0.01$). This probably occurred because the spinach roots were directly exposed to Cd^{2+} contaminated soil and were more sensitive to a Cd^{2+} contaminated environment. It was difficult for plant tissues to transport and absorb Cd^{2+} ions due to the decrease of bioavailable Cd^{2+} in the soil. Therefore, the spinach shoot contained less Cd^{2+}, which accumulated more in the spinach root, thereby inhibiting its growth.

Effects of Different Biochar Treatments on the Cd Content of Spinach

The Cd^{2+} contents of the spinach shoots and roots treated with different biochars are shown in Fig. 6. Both treatments decreased the accumulation of Cd^{2+} in the shoots and roots. Compared with CK, the Cd^{2+} content upon HBC and MHBC treatment decreased by 7.0% to 46.8% in the shoots and 7.3% to 52.7% in the roots. This result is likely due to the low molecular organic acid being the most active substance in the root exudates, among which oxalic acid was the main component (Muratova *et al*. 2009). Root exudates decrease soil pH and provide ligands for metal complexation reactions, thereby increasing the concentration of bioavailable Cd^{2+} in the soil. However, the addition of alkaline biochar neutralized organic acids in the plant root exudates, thereby fixing Cd^{2+} and decreasing its absorption by the plant. The biochar addition had a relatively mild effect on the decrease of Cd^{2+} content in the spinach shoots compared with the roots, which suggests that the spinach roots functioned as a barrier to Cd^{2+} absorption and were the main channel for Cd^{2+} to be transported to the aboveground parts of the plant.

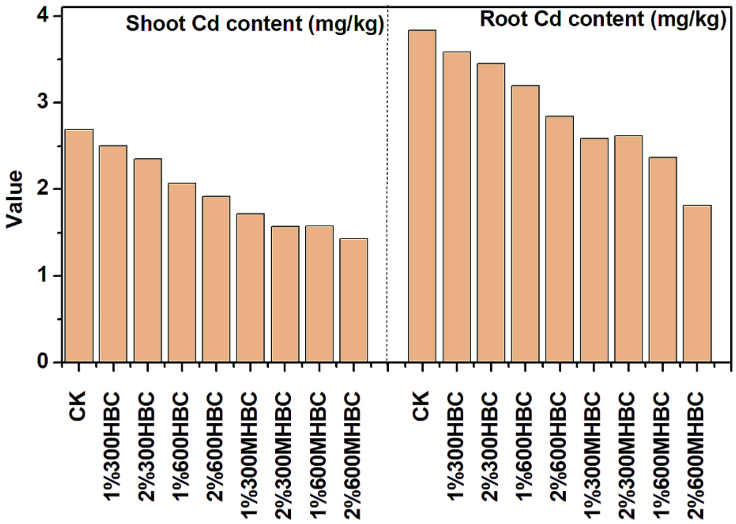

Fig. 6. Effects of different biochar treatments on the Cd^{2+} content in spinach

The concentrations of HBC and MHBC had a relatively low effect on the Cd^{2+} content of spinach shoots. The accumulation of Cd^{2+} in the spinach shoot decreased as the biochar concentration increased. The Cd^{2+} content in the shoots decreased by 6% upon treatment with 2%300HBC, compared with that of 1%300HBC, and it decreased by 7.2% with 2%600HBC, compared with that of 1%600HBC. The Cd^{2+} content upon 2%300MHBC treatment was 8.7% less than that of the 1%300MHBC treatment, and it was 9.5% less for 2%600MHBC compared with that of 1%600MHBC. The accumulation of Cd^{2+} in the spinach shoot was the lowest (1.43 mg/kg) for the treatment of 2%600MHBC. The accumulation of Cd^{2+} in the spinach root decreased with increasing biochar concentration. Compared with CK, the greatest reduction occurred for the 2%600MHBC group, at 52.7%. The accumulation of Cd^{2+} in the spinach shoots and roots decreased with increasing biochar concentration, which suggests that the addition of HBC and MHBC inhibited the absorption of Cd^{2+}, and the increase of biochar concentration improved the inhibition of Cd^{2+} absorption. In addition, the shoot height increased with increasing biochar concentration, which had a certain dilution effect on the Cd^{2+} in the spinach shoot. The inhibition effects of biochar on the absorption of Cd^{2+} in both shoots and roots of the spinach were as follows: 300HBC < 600HBC < 300MHBC < 600MHBC. This result indicates that the inhibition of the Cd^{2+} adsorption increased with increasing biochar pyrolysis temperature. This result probably occurred because higher pyrolysis temperatures resulted in higher losses of fatty matter, volatile matter, and water, thereby forming a well-developed pore structure on the biochar surface (Zhang *et al*. 2013), which effectively promotes surface adsorption and pore filling for Cd^{2+} (Chen *et al*. 2019). Consequently, the bioavailability and mobility of Cd^{2+} in the soil decreased, and its absorption was inhibited. Compared with the HBC, the inhibition effect of MHBC on the absorption of Cd^{2+} was greater. The accumulations of Cd^{2+} in the shoots and roots of spinach with MHBC decreased by 23.7% to 33.2% and 24.1% to 52.1%, respectively, compared with the HBC at the same pyrolysis temperature and concentration. This result indicates that the magnesium modification had a synergistic effect on pristine biochar in inhibiting the absorption of Cd^{2+} by the spinach.

As shown in Fig. 6 and Fig. 2b, the variations of the Cd^{2+} content absorbed by the shoots and roots of the spinach for different treatments were mostly consistent with the fraction of bioavailable Cd^{2+} to total Cd^{2+}. To further explore the influence of bioavailable Cd^{2+} in soil on the accumulation of Cd^{2+} in plants, the correlations between the accumulations of Cd^{2+} in the shoots (Fig. 7a) and roots (Fig. 7b) of the spinach and the fractions of bioavailable Cd^{2+} to total Cd^{2+} were analyzed.

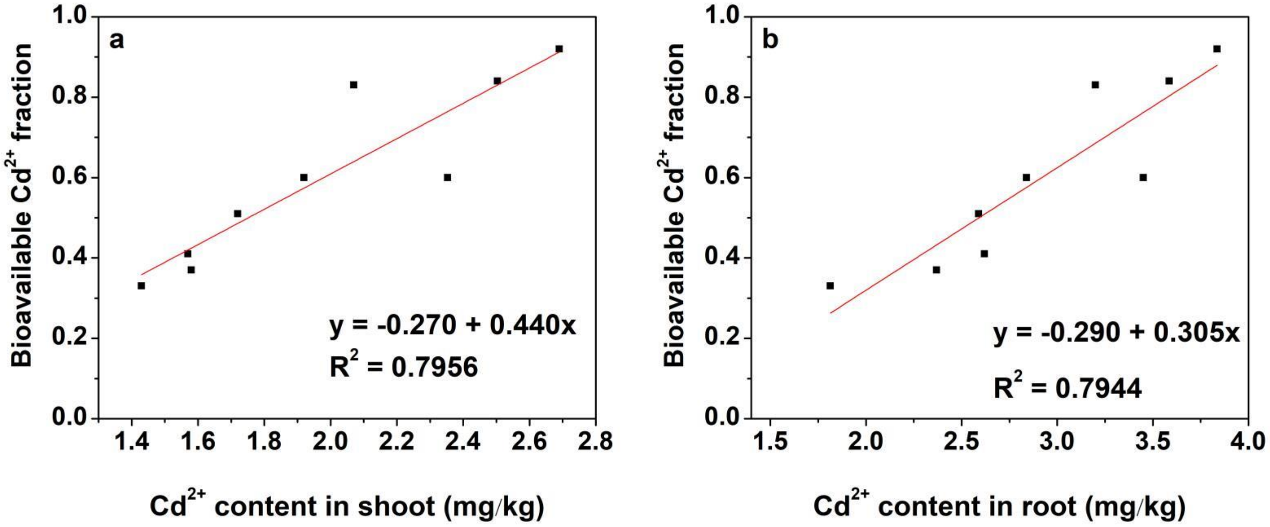

Fig. 7. Correlation between accumulation of Cd^{2+} in spinach (a) shoots and (b) roots and the fraction of bioavailable Cd^{2+} to total Cd^{2+}

As shown in Fig. 7, the contents of Cd^{2+} in both shoots and roots of the spinach were positively correlated with the fraction of bioavailable Cd^{2+} ($p < 0.01$). This result indicates that the Cd^{2+} content in the spinach was mainly affected by the content of bioavailable Cd^{2+} in the soil. This result is consistent with the results of Huang *et al*. (2020), in which the Cd^{2+} absorption by plants was mainly related to bioavailable Cd^{2+}, instead of total Cd^{2+} content in the soil. The addition of HBC and MHBC decreased the content of bioavailable Cd^{2+} in the soil, thus decreasing its uptake by plants. The accumulation of Cd^{2+} in the spinach was greater in the roots than in the shoots, and the average Cd^{2+} content in the roots was 32.2% greater than that in the shoots. Thus, the distribution of Cd^{2+} in the spinach presented an obvious root accumulation effect.

CONCLUSIONS

1. The addition of peanut shell biochar (HBC) and Mg-modified peanut shell biochar (MHBC) effectively increased the soil pH with increasing biochar concentration and pyrolysis temperature. The effect of MHBC on pH increase was greater than that of HBC.
2. Both HBC and MHBC effectively decreased the content of bioavailable Cd^{2+} in the soil, thereby decreasing the amount of Cd^{2+} absorbed by the shoots and roots of the spinach. The bioavailable Cd^{2+} content in the soil and the Cd^{2+} absorbed by the spinach decreased with increasing biochar concentration and pyrolysis temperature. The MHBC had the greater effect on the decrease of bioavailable Cd^{2+}, indicating that the MHBC can better decrease the bioavailability of heavy metals.
3. The addition of the HBC and MHBC significantly increased the shoot height and decreased the root length of the spinach, and the effects were greater as the biochar concentration and pyrolysis temperature increased. The effects of the MHBC on plant height and root length were greater than those of the HBC.

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