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Animal or plant waste-derived biochar for Cd(II) immobilization: effects of freeze-thaw-wet-dry cyclic aging on adsorption behavior in tea garden soils

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ABSTRACT

Biochar aging has attracted increasing attention for heavy metals removal from soils. Equilibrium experiment and soil column leaching experiment were conducted to investigate the effect of wheat-straw-derived biochar (BWS) and chicken-manure-derived biochar (BCM) at 650°C on the Cd(II) adsorption in tea garden soils, and the feasibility of using biochar to remediate the Cd(II) contaminated tea garden soils was assessed. The results showed that the Cd(II) adsorption capacity in tea garden soils increased with the application of biochar. Compared with no application, the Cd(II) adsorption capacity increased by 10%–70% and 17.5%–95% in tea garden soils amended with BWS and BCM by 0.1, 0.5, and 1 WT%, respectively. Compared with the application of fresh biochar, the Cd(II) adsorption capacity of tea garden soils amended with the aged BWS and BCM decreased by 22% and 14%, respectively. The biochar application increased the pH value of soils leachate and decreased the Cd(II) leaching loss in contaminated tea garden soils. Compared with the control, the Cd(II) cumulative leaching amounts in tea garden soils amended with the BWS and BCM decreased by 36.75% and 86.81%, respectively. These results suggest that the application of both types of biochar significantly improves the soil buffering capability and the Cd(II) retention capacity in tea garden soils, in which the effect of BCM is more obvious than biochar.

Keywords: Biochar; Aging; Immobilization; Adsorption; Tea garden soil; Cd(II)

1. Introduction

The situation of soil heavy metal pollution in China is not optimistic. The soil cadmium exceeding the standard rate was as high as 7.0% [1]. Lu et al. [2] reported that the Cd(II) average value in tea garden soils in Rizhao City was higher than that in eastern Shandong Province in China and the accumulation trend was increasingly serious. Cao et al. [3] revealed a potential ecological risk of Cd(II) in tea garden soils at An'xi County in southeast China [3]. Therefore, repairing or relieving heavy metal pollution in tea garden soil is of great significance for ensuring the safety of agricultural products.

Biochar has the advantages of strong adsorption capacity, wide material sources and low cost, and has become a hot spot in soil pollution remediation research [4–6]. Numerous studies demonstrated that biochar application could increase the pH of soil, causing heavy metal ions in the soil to form carbonate or phosphate precipitation [7,8]. At the same time, the surface of biochar could provide a large number of active adsorption sites through ion exchange and cation-π action to adsorb heavy metal ions,

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thereby reducing the plant availability of heavy metals in the soil [7,9]. However, most of these studies were concentrated in solution systems or soil systems, rarely in contaminated soils under simulated rainfall conditions. In addition, freeze-thaw and dry-wet alternation are common climatic phenomena in northern China, and repeated changes in hydrothermal conditions affect the physicochemical properties of environmental media such as soil [10,11]. A large number of studies reported that with the prolongation of biochar residence time in the soil, changes in ambient temperature and humidity would cause a slow change in the properties of biochar, affecting its ability to adsorb pollutants [12,13]. In addition, most of the current studies are limited to the short-term adsorption of pollutants in the soil by aged biochar, while the long-term adsorption of pollutants in the soil is less studied [14]. And the research object only focused on biochar from single animal or plant sources, but seldom reported the comparative study of Cd(II) adsorption characteristics in the soil by choosing biochar from two different animal and plant sources.

Rizhao City is located in the southeast of Shandong Province in northern China. "Rizhao Green Tea" enjoys a good reputation at home and abroad and has become the pillar industry of Rizhao City. However, with the rapid development of the tea industry, heavy metal pollution of tea garden soil is becoming increasingly serious [15,16]. Wheat straw and chicken manure, the raw material for biochar preparation, are common agricultural solid wastes in northern China. The objectives of this study is to investigate the effect of biochars amendment (including types, application ratios, and aging treatment) on Cd(II) adsorption in tea garden soil by batch equilibrium experiments, and to explore the feasibility of both types of biochars in remediation of Cd(II)-contaminated tea garden soil by simulating the effects of rainfall on the Cd(II) leaching in tea garden soil.

2. Materials and methods

2.1. Chemicals

All characterization studies were made in triplicate. All chemical reagents were of analytical reagent grade. The stock solution of Cd(II) was prepared with $Cd(NO_3)_2 \cdot 4H_2O$ and distilled deionized water.

2.2. Materials

The soil was collected from the surface layer (0~20 cm) of a green tea garden which is located at Jufeng Town (N 35°19′46″, E 119°16′45″), Lanshan District, Rizhao City, Shandong Province, China. The soil samples were air-dried, amended and ground to pass a 2 mm sieve. The soil properties including pH value and organic matter (OM) content were determined. The amount of soil OM was determined by the potassium dichromate dilution heat colorimetric method [17]. The pH value of the soil samples was measured in a 1:10 solid:liquid ratio suspension using a combination pH value electrode (PHS-3C, Shanghai, China). The basic properties of the soils are listed in Table 1.

The biochar derived from wheat straw and chicken manure are referred to as wheat straw biochar (labeled as BWS) and chicken manure biochar (labeled as BCM), respectively. Our previous studies found that the biochar prepared by wheat straw and chicken manure at 650°C had the highest adsorption capacity (39.65~41.53 mg g^{-1}) for Cd(II) in solution at the different pyrolysis temperatures (350°C, 500°C, and 650°C) [18]. Therefore, in this study, BWS and BCM at 650°C were selected as the tested objects.

Pyrolysis yield was calculated according to GB/T17664-1999 (Wood charcoal and test method of wood charcoal). Ash content was calculated according to GB/T12496.3-1999 (Test methods of wooden activated carbon–determination of ash content). The pH value of the biochar was measured according to GB/T12496.7-1999 (Test methods of wooden activated carbon–determination of pH). The elemental C, H, O, and N contents were determined with an elemental analyzer. The properties of biochar are shown in Table 2. No Cd(II) was detected in the leachate of the two types of biochar. The tested biochar was screened by 0.15 mm, thoroughly amended with the soil by 0.1, 0.5, and 1 WT%. The blank soil was set as the control and labeled as CK1. The soils amended with different proportions of both types of biochar were recorded as BWS-X and BCM-X, X represents the amount of biochar applied.

Table 1
Basic properties of the soil

Soil sample	Farmland soil
pH value	6.06 ± 0.03
Organic matter (g kg^{-1})	10.90 ± 2.4
Available Fe (mg kg^{-1})	68.70 ± 15.7
Available Mn (mg kg^{-1})	30.10 ± 9.25
Total C (mg kg^{-1})	18.30 ± 5.32
Total Cd (mg kg^{-1})	1.43 ± 0.04
Total Pb (mg kg^{-1})	27.14 ± 0.12
Total Cu (mg kg^{-1})	32.81 ± 0.08

Table 2
Yield, pH value, ash content and elemental composition of biochar

Samples	Yield/%	pH value	Ash content/%	Elemental composition/%			
				C	N	H	O
BWS	32.14 ± 0.21	9.86 ± 0.12	22.9 ± 0.3	58.5 ± 0.32	0.09 ± 0.01	1.77 ± 0.03	16.51 ± 0.17
BCM	54.63 ± 0.13	10.21 ± 0.09	66.5 ± 0.2	25.61 ± 0.45	0.68 ± 0.02	0.72 ± 0.01	6.44 ± 0.13

BWS and BCM represent the BWS and BCM prepared at 650°C, respectively, the same below.

2.3. Experimental methods

2.3.1. Aging experiment

The aging experiment was carried out with reference to Miao [19] and a slight modification in a plastic box (no cover, L = 30 cm, W = 20 cm, H = 30 cm), which was filled with 20 cm high tea garden soil which had been collected and untreated. The biochar samples were placed horizontally in the middle of the soil layer with 200-mesh nylon bags. Then the plastic boxes with different biochar samples were placed in the ZRQ-400 artificial climate chamber. The freeze-thaw-wet-dry cyclic culture was performed in the chamber, in which –20°C/5 d (40% humidity), 50°C/5 d (40% humidity), 25°C/5 d (100% humidity), 25°C/5 d (20% humidity) for 6 cycles of 120 d. After the aging treatment, the biochar samples were taken out, dried at about 60°C, and labeled as ABWS and ABCM, respectively. The aged biochar was fully amended with the soil by 1 WT% and the soil amended with the aged biochar was classified as ABWS-1 and ABCM-1, respectively.

2.3.2. Isothermal adsorption experiment

Soil samples (1.0 g) of different treatments were placed into a 100 mL centrifuge tube, then a 40 mL Cd(II) solution with a concentration of 5, 10, 15, 20, 30, and 40 mg L^{-1} was added. The pH of the soil solution was adjusted to 6.0. The mixture was shaken at a rate of 200 rpm for 24 h and centrifuged at 3,000 rpm for 10 min. The supernatant was passed through a 0.45 μm acetate filter and diluted to a constant volume. The Cd(II) concentration in the filtrate was measured by an AA-7000 atomic absorption spectrophotometer (Shimadzu Corporation, Japan).

2.3.3. Soil column leaching experiment

Cd(II) was added to the tested soil in the form of $Cd(NO_3)_2{\cdot}4H_2O$ to obtain cadmium contaminated soil, in which the Cd(II) added amount is 1 mg kg^{-1}. The cadmium-contaminated soil was naturally air-dried, passed through 2 mm sieves, and filled with pots of 400 g each. The tested biochar was applied to the contaminated soil by 1 WT% and thoroughly amended with the contaminated soil. The experiment set blank soil as a control, labeled as CK2, and the contaminated soil applied with biochar was labeled as CBWS-1 and CBCM-1, respectively. The indoor soil culture method was used to maintain the water content of the contaminated soil in about 60% of the field water holding capacity. The deionized water was used to replenish the soil moisture every other day, and the mixture was stably balanced for two weeks at room temperature. The soil column leaching experiment was carried out after natural air drying again.

The leaching method was referred to as Tian et al. [20] with minor modifications. The leaching experiment was performed in polyvinyl chloride plastic tubes (d = 5 cm and h = 25 cm). According to bulk density (1.28 g cm^{-3}) of the tested soil, a soil column with a height of about 16 cm was formed by loading 400 g soil into the leaching column. Filter paper and 2 cm thick dry quartz sand were laid on the upper and lower ends of the soil column to ensure the maintenance of soil particles and the outflow of the solution, and evenly distribute the leachate without being splashed out. When filling the soil column, attention should be paid to compact the soil at the edge of the soil column wall, to ensure no wall seepage and avoid the edge effects as much as possible.

Before the start of leaching, 120 mL deionized water was added to reach the maximum field water holding capacity. The leaching test was started after the saturation of 24 h. To get closer to the natural precipitation process, the intermittent leaching method was used to make the soil have a certain reaction time. The soil column was leached once every 48 h and collected once, each time the leachate was 150 mL, and the controlled leaching rate was 3 mL min^{-1} for 6 times. The leaching capacity was 900 mL (the annual average rainfall of Rizhao area is 870 mm, according to the cross-section of the soil column, the annual precipitation is about 1.7 L, which is equivalent to the half annual average rainfall). The pH value of the leachate and the Cd(II) content in the leachate was determined.

2.4. Data analysis

According to formula (1), the Cd(II) adsorption amount in different soil samples was calculated.

$$q_e = \frac{\left(C_0 - C_e\right)\times V}{m} \tag{1}$$

where q_e (mg g^{-1}) is the Cd(II) equilibrium adsorption capacity; C_0 (mg L^{-1}) and C_e (mg L^{-1}) are the Cd(II) concentration at the initial time and adsorption equilibrium, respectively; V (L) is the volume of the solution; m (g) is the soil mass.

The Cd(II) adsorption data on soil samples with different biochars were analyzed by the Freundlich isotherm adsorption model. The equation of Freundlich is shown in Eq. (2).

$$q_e = K_F + C_e^{1/n} \tag{2}$$

where K_F is the Freundlich model parameter, reflecting the adsorption capacity of the adsorbent. The larger the K_F value, the greater the adsorption capacity. The $1/n$ is the nonlinear index, reflecting the characteristics of the adsorbent adsorption site in the energy distribution. The smaller $1/n$ is the stronger adsorption strength.

3. Results and discussion

3.1. Effect of biochar from different sources and its application ratios on the Cd(II) adsorption

The fitting results of the Freundlich isotherm adsorption model for the Cd(II) adsorption are shown in Table 3 and Fig. 1. As seen from Table 3, the Freundlich isotherm model could well fit the Cd(II) adsorption (R^2 > 0.9528), indicating that the Cd(II) adsorption was multi-layer adsorption on heterogeneous surface, and the adsorption capacity would continue to increase at high concentrations.

Table 3 showed that the application of the two types of biochar could significantly increase the adsorption capacity of tea garden soil for Cd(II), and the adsorption capacity gradually increases with the increase of the biochar

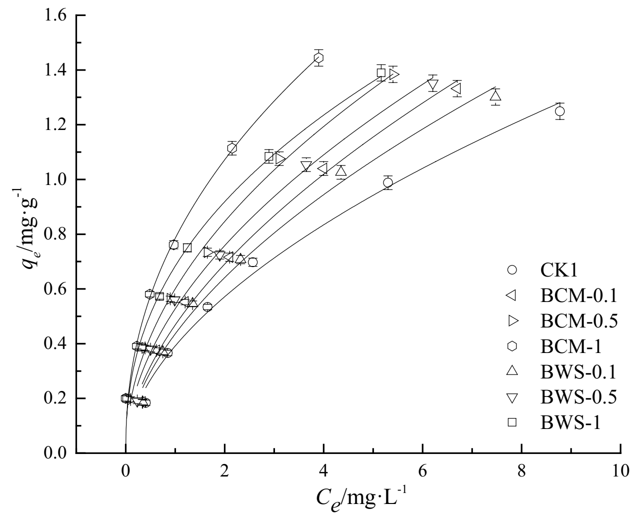

Fig. 1. Cd(II) adsorption isotherms in tea garden soils amended with biochar.

Table 3
Freundlich parameters of the Cd(II) adsorption in tea garden soils amended with biochar

Treatment	K_F/(mg g^{-1}) (mg L^{-1})$^{-n}$	$1/n$	R^2
CK1	0.40 ± 0.02	0.53 ± 0.03	0.9901
BWS-0.1	0.44 ± 0.02	0.55 ± 0.03	0.9906
BWS-0.5	0.53 ± 0.02	0.52 ± 0.02	0.9929
BWS-1	0.68 ± 0.02	0.43 ± 0.02	0.9917
ABWS-1	0.53 ± 0.01	0.53 ± 0.02	0.9955
BCM-0.1	0.47 ± 0.02	0.55 ± 0.03	0.9903
BCM-0.5	0.60 ± 0.01	0.50 ± 0.01	0.9975
BCM-1	0.78 ± 0.05	0.45 ± 0.06	0.9528
ABCM-1	0.67 ± 0.01	0.51 ± 0.01	0.9985

BWS-0.1, BWS-0.5, and BWS-1 represent the tea garden soils amended with BWS by 0.1, 0.5, and 1 WT%, respectively; BCM-0.1, BCM-0.5, and BCM-1 represent the tea garden soils amended with BCM by 0.1, 0.5, and 1, respectively; ABWS-1and ABCM-1 represent the tea garden soils amended with aged BWS and BCM by 1 WT%.

application ratios. After applying different ratios (0.1, 0.5, and 1 WT%) of wheat-straw-derived biochar (BWS) in tea garden soil, its K_F value increased from 0.40 to 0.44, 0.53 and 0.68, and its adsorption capacity for Cd(II) increased by 10%, 32%, and 70%, respectively compared with CK1. After applying different ratios (0.1, 0.5, and 1 WT%) of chicken-manure-derived biochar (BCM) in tea garden soil, its K_F value increased from 0.40 to 0.47, 0.60 and 0.78, and its adsorption capacity for Cd(II) increased by 17.5%, 50%, and 95%, respectively compared with CK1. In addition, the increase of the Cd(II) adsorption capacity in tea garden soil is closely related to the biochar type. The adsorption effect of tea garden soil amended with BCM on Cd(II) was better than that of tea garden soil amended with an equal amount of BWS, indicating that the biochar from livestock and poultry manure showed a more pronounced adsorption effect on Cd(II) than the biochar from plant residue. The biochar prepared by different raw materials has different physicochemical properties such as elemental composition, pore structure, and surface functional groups, etc. which affected the adsorption of heavy metal ions by biochar [21–23].

Biochar could precipitate heavy metal ions in the soil by forming carbonate or phosphate. The higher the pH value of biochar, the stronger ability of adsorption and fixation of heavy metal ions by precipitation [24,25]. In this study, the reason why the adsorption capacity of the biochar from livestock and poultry manure for Cd(II) was better than that of the biochar from plant residue might also be that its pH value and ash content were higher than that of BWS (Table 1).

3.2. Effect of biochar aging on the Cd(II) adsorption

The Freundlich isotherm model can well fit the Cd(II) adsorption isotherm on tea garden soil amended with aged biochar ($R^2 > 0.9955$). The fitting parameters and curves are shown in Table 3 and Fig. 2, respectively. As seen from Table 3, the Cd(II) adsorption capacity and intensity of tea garden soils amended with 1 WT% aged biochar were significantly lower than those with 1 WT% fresh biochar. Compared with the tea garden soil amended with the fresh BWS, the K_F value with the aged biochar decreased from 0.68 to 0.53, and the adsorption capacity decreased by 22%. The parameter $1/n$ increased from 0.43 to 0.53, and the adsorption strength decreased by 23%. Compared with the tea garden soil amended with the fresh BCM, the K_F value with the aged biochar decreased from 0.78 to 0.67, and the adsorption capacity decreased by 14%. $1/n$ increased from 0.45 to 0.51, and the adsorption strength decreased by 13%. The above results indicated that the aging treatment affected the Cd(II) adsorption by the biochar type. In addition, the Cd(II) adsorption capacity in the tea garden soil after the application of 1 WT% aged BWS and BCM still increased by 32.5% and 67.5% compared with that of CK1, respectively. As seen in Fig. 2, the Cd(II) adsorption capacity in tea garden soil amended with aged biochar was significantly higher than that in blank control soil.

The biochar surface inevitably undergoes biological or abiotic degradation processes. The changes in surface physicochemical properties based on biochar aging will ineluctably affect its effect of adsorption and immobilization on heavy metal pollutants in tea garden soil [26,27]. At present, the mechanism of biochar aging has not been determined yet. In this study, the adsorption capacity of the two types of biochar on Cd(II) decreased after aging treatment. On the one hand, it may be due to the decrease of the pH value and ash content of biochar during the aging process; On the other hand, it can be attributed to the changes of functional groups on the surface of biochar. The decrease of aromatization degree and alkaline groups during the aging process resulted in a decrease of its adsorption capacity for Cd(II) [28]. Martin et al. [29] also demonstrated that the aging process could cause partial breakage of biochar, which may cause the biochar adsorption site to be blocked, thus affecting its adsorption capacity for Cd(II). In addition, studies have shown that although the biochar aging caused the changes in its surface properties and the decrease of its stability, the stability of the remaining biochar in the

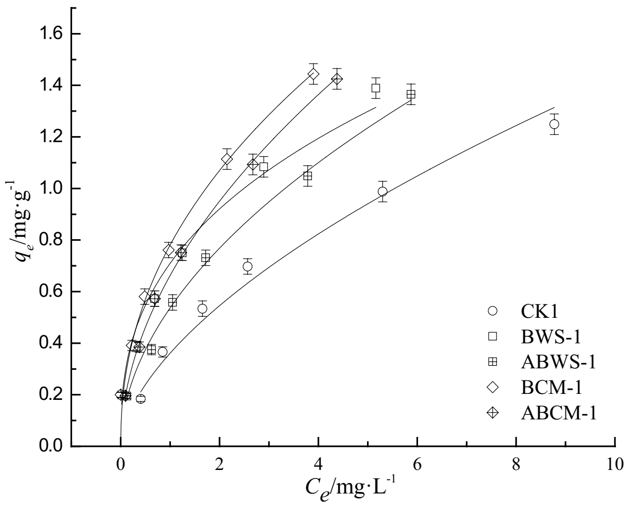

Fig. 2. Cd(II) adsorption isotherms in tea garden soils amended with aged biochar.

biochar particles would remain for a long time [30,31]. On the whole, although the adsorption capacity of the biochar for Cd(II) was reduced after the aging process, the two types of biochar can still be used as alternative amendments for remediation of heavy metal contaminated soil, considering that they can remain stable in the soil for a long time and can significantly improve the adsorption capacity of tea garden soil for Cd(II).

3.3. Effect of biochar application on the pH of soil leachate

The changes in the pH value in soil leachate are shown in Fig. 3 during the leaching process of the simulated rainfall. Compared with CK2, the biochar application could significantly increase the pH value of soil leachate, indicating that the biochar application could improve the buffering performance of tea garden soil. The pH value of the leachate in the CK2 and biochar-treated tea garden soil increased first, reached the maximum value, and then decreased with an increase of leaching times. At the 5th leaching, the pH value of the leachate of CK2, CBWS-1, and CBCM-1 reached the highest value, which of CK2 was 7.55, and which of CBWS-1 and CBCM-1 increased by 3.17% and 6.22%, respectively compared with CK2.

This was mainly due to the biochar prepared by high-temperature pyrolysis containing a large amount of alkaline ash, and the K, Ca, Na, Mg and other ions in the ash were mostly present in the form of the carbonate, which made the pH value of the leachate increase. Furthermore, the pH value of the leachate (deionized water) was higher, which made the pH value of soil leachate rise in a certain range. However, with the increase of leaching times, the salt-based ions in tea garden soil were continuously leached out, and the soil salinity saturation decreased, which made the pH value of soil leachate begin to decline. In addition, the pH value of soil leachate applied with BCM was higher than that of soil leachate with BWS, which was due to the higher ash content and pH value of BCM than BWS (Table 2), indicating that the biochar from livestock and poultry manure had better effect in alleviating soil acidity than that from plant residue.

3.4. Effect of biochar application on the Cd(II) leaching

The Cd(II) leaching characteristics in the leachate of biochar-treated contaminated tea garden soil during the simulated rainfall are shown in Fig. 4, and the Cd(II) leaching amount in the leachate is shown in Table 4. From the charts, the Cd(II) leaching loss in the CK2 and the contaminated soil treated with the two types of biochar was the highest at the beginning of leaching, and the first leaching loss accounted for 88.65%~92.23% of the cumulative leaching loss. The Cd(II) leaching loss decreased rapidly in the second

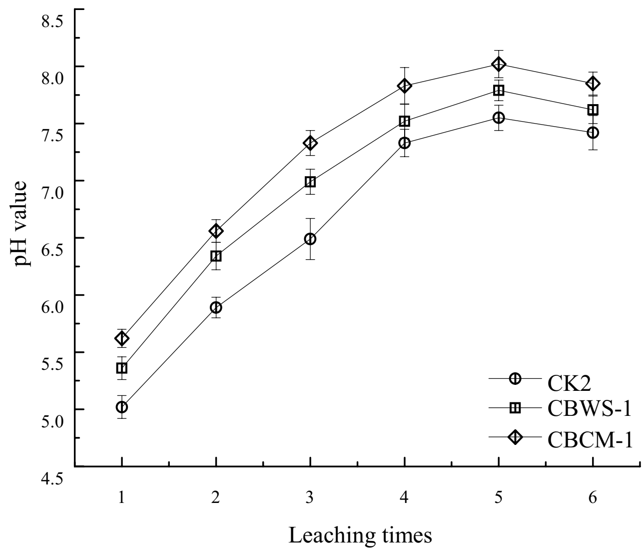

Fig. 3. Changes of pH with leaching times in leachate.

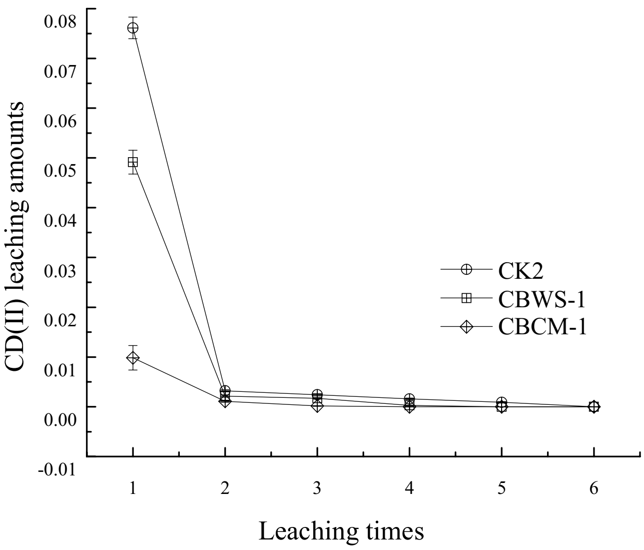

Fig. 4. Cd(II) leaching characteristics in the contaminated tea garden soils amended with biochar.

Table 4
Cd(II) leaching amounts in contaminated tea garden soil by the application of biochar

Treatment	Leaching amounts (mg^{-1})						
	1	2	3	4	5	6	Accumulation amounts
CK2	0.07612 ± 0.00216	0.00322 ± 0.00022	0.00242 ± 0.00021	0.00160 ± 0.00016	0.00089 ± 0.00015	0.00000 ± 0.00001	0.08425 ± 0.00291
CBWS-1	0.04915 ± 0.00239	0.00215 ± 0.00024	0.00171 ± 0.00018	0.00028 ± 0.00006	0.00000 ± 0.00002	0.00000 ± 0.00001	0.05329 ± 0.00290
CBCM-1	0.00985 ± 0.00246	0.00110 ± 0.00022	0.00016 ± 0.00007	0.00000 ± 0.00003	0.00000 ± 0.00002	0.00000 ± 0.00001	0.01111 ± 0.00281

CBWS-1 and CBCM-1 represent contaminated tea garden soils amended with BWS and BCM by 1 WT%, respectively.

time, which was 88.83%~95.76% lower than the first leaching loss. Then the leaching loss gradually decreased. In the CK2, no Cd(II) was detected in the leachate at the 6th leaching, while no Cd(II) was detected in the leachate of the tea garden soil treated with the two types of biochar at the 5th and 4th leaching, respectively. As for the cumulative leaching loss, the biochar application reduced the Cd(II) leaching loss in contaminated tea gardens soil to varying degrees. Compared with CK2, the Cd(II) cumulative leaching loss in the contaminated tea garden soil treated with BWS and BCM decreased by 36.75% and 86.81%, respectively. This suggested that the biochar application could significantly improve the Cd(II) adsorption and fixation ability and reduce the Cd(II) migration activity in tea garden soil. At the same time, the application effect of the BCM on adsorbing and fixing Cd(II) in tea garden soil is better than that of the BWS. This is consistent with the previous study [21].

Current studies have demonstrated that the biochar application in the soil increased the amount of adsorption and non-linear adsorption, slowed the desorption of heavy metal pollutants, reduced the mobility, bioavailability, and toxicity of heavy metal pollutants in the soil environment, and lowed the heavy metal concentration in agricultural products [32–34]. Biochar passivates and fixes heavy metal contaminants in the soil mainly through the following three ways: the first is electrostatic action. The electrostatic potential of biochar itself is negative. After biochar applied to soil, the cation exchangeability of soil can be improved by increasing the negative charge groups on its surface, thus increasing the electrostatic attraction between soil and heavy metals. As a result, heavy metals are firmly adsorbed on the soil surface, and their mobility decreases [35]. The second is precipitation. The biochar is generally alkaline, and after applied to the soil, it will increase the pH value of the soil, promote the precipitation reaction of heavy metal ions in the soil, and produce insoluble metal oxides, metal phosphates, and carbonates, etc. [36]; the third is cation-π action, biochar has highly aromatic and heterocyclic structure. After applied to soil, its aromatic structure can act as an electron donor to bond with heavy metal ions in the soil, thereby adsorbing and fixing heavy metal ions and reducing their mobility [37].

4. Conclusion

The application of BWS and BCM could significantly improve the adsorption capacity of the tea garden soil for Cd(II), and which increased with the increase of biochar application ratios. In addition, the Cd(II) adsorption effect in tea garden soil amended with BCM was significantly better than that of the same amount of BWS. The Cd(II) adsorption capacity and adsorption strength in the tea garden soil treated with the aged biochar decreased significantly. However, its adsorption capacity for Cd(II) was still significantly higher than that of tea garden soil without biochar. The biochar application increased the pH value of soils leachate and decreased the Cd(II) leaching loss in contaminated tea garden soils. The application of both types of biochar could significantly improve the buffering performance of tea garden soil and the Cd(II) retention ability, especially the effect of the biochar from livestock and poultry manure was more obvious than the biochar from plant residue.

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References

[1] MEP, MLR, National Soil Pollution Survey Bulletin, The Ministry of Environmental Protection and The Ministry of Land and Resources, 2014. Available at: http://www.mee.gov.cn/gkml/sthjbgw/qt/201404/t20140417_270670.htm.

[2] J.S. Lu, Z.L. Zhang, L.Y. Yang, Sources identification and hazardous risk delineation of heavy metals contamination in Rizhao City, Acta Geogr. Sin., 67 (2012) 971–984.

[3] H.L. Cao, F.Y. Cai, W.B. Jiao, C. Liu, N. Zhang, H.Y. Qiu, C. Rensing, J. Lu, Assessment of tea garden soils at An'xi County in southeast China reveals a mild threat from contamination of potentially harmful elements, R. Soc. Open Sci., 5 (2018) 180050.

[4] X. Cao, W. Harris, Properties of dairy-manure-derived biochar pertinent to its potential use in remediation, Bioresour. Technol., 101 (2010) 5222–5228.

[5] X. Qin, Y. Liu, Q. Huang, Y. Liu, L. Zhao, Y. Xu, In-situ remediation of cadmium and atrazine contaminated acid red soil of South China using sepiolite and biochar, Bull. Environ. Contam. Toxicol., 102 (2018) 128–133.

[6] C.S. Zhang, L. Liu, M.H. Zhao, H.W. Rong, Y. Xu, The environmental characteristics and applications of biochar, Environ. Sci. Pollut. Res., 25 (2018) 21525–21534.

[7] H.L. Lu, W.H. Zhang, Y.X. Yang, X.F. Huang, S.Z. Wang, R.L. Qiu, Relative distribution of Pb^{2+} sorption mechanisms by sludge-derived biochar, Water Res., 46 (2012) 854–862.

[8] L. Huang, C. Liu, X. Liu, Z. Chen, Immobilization of heavy metals in e-waste contaminated soils by combined application of biochar and phosphate fertilizer, Water Air Soil Pollut., 230 (2019) 26.

[9] Z. Mahdi, Q.J. Yu, A. El Hanandeh, Competitive adsorption of heavy metal ions (Pb^{2+}, Cu^{2+}, and Ni^{2+}) onto date seed biochar: batch and fixed bed experiments, Sep. Sci. Technol., 54 (2019) 888–901.

[10] Y.J. Sun, T. Tian, N. He, Effects of freeze-thaw on soil characters and arsenate adsorption and desorption, Ecol. Environ., 25 (2016) 724–728

[11] S.E. Hale, K. Hanley, J. Lehmann, A.R. Zimmerman, G. Cornelissen, Effects of chemical, biological, and physical aging as well as soil addition on the sorption of pyrene to activated carbon and biochar, Environ. Sci. Technol., 45 (2011) 10445–10453.

[12] W.L. Ju, Y.D. Jing, Effect of aging treatment on physicochemical characteristics of cotton straw biochar, Acta Sci. Circum., 37 (2017) 3853–3861.

[13] A. Venegas, A. Rigol, M. Vidal, Effect of ageing on the availability of heavy metals in soils amended with compost and biochar: evaluation of changes in soil and amendment properties, Environ. Sci. Pollut. Res., 23 (2016) 20619–20627.

[14] F.F. Sui, J. Zuo, D. Chen, L.Q. Li, G.X. Pan, D.E. Crowley, Biochar effects on uptake of cadmium and lead by wheat in relation to annual precipitation: a 3-year field study, Environ. Sci. Pollut. Res., 25 (2018) 3368–3377.

[15] H. Deng, M.S. Li, Y.C. Zhou, Soil metal contamination and fractionation of tea plantations: case studies in a normal tea garden and in a restored mineland tea stand, Pol. J. Environ. Stud., 21 (2012) 1223–1228.

[16] Y. Liu, Z. Ma, J. Lv, J. Bi, Identifying sources and hazardous risks of heavy metals in topsoils of rapidly urbanizing East China, J. Geogr. Sci., 26 (2016) 735–749.

[17] S. Bao, R. Jiang, C. Yang, Measurement of Organic Matter Content in Soil, Chinese Agricultural Science and Technology Press, Beijing, 1999.

[18] L. Shen, Y. Jing, X. Sun, H. Hao, Y. Cao, Cd^{2+} adsorption characteristics of animal-waste-and-plant-derived biochars in water, J. Ecol. Rural Environ., 34 (2018) 363–370.

[19] W. Miao, Aging Effect of Biochar on Soil Nutrients and Growth of Rice, Shengyang Agricultural University, Shenyang, China, 2014.

[20] W.J. Tian, X.Q. Wang, D. Li, Release and vertical migration of polycyclic aromatic hydrocarbons in red soil under simulated acid rain, J. Agro-Environ. Sci., 33 (2014) 1928–1932

[21] D.Y. Xu, Y. Zhao, K. Sun, B. Gao, Z.Y. Wang, J. Jin, Z.Y. Zhang, S.F. Wang, Y. Yu, X.T. Liu, Cadmium adsorption on plant- and manure-derived biochar and biochar-amended sandy soils: impact of bulk and surface properties, Chemosphere, 111 (2014) 320–326.

[22] B. Sajjadi, J.W. Broome, W.Y. Chen, D.L. Mattern, N.O. Egiebor, N. Hammer, C.L. Smith, Urea functionalization of ultrasound-treated biochar: a feasible strategy for enhancing heavy metal adsorption capacity, Ultrason. Sonochem., 51 (2019) 20–30.

[23] M. Uchimiya, K.T. Klasson, L.H. Wartelle, I.M. Lima, Influence of soil properties on heavy metal sequestration by biochar amendment: 1. Copper sorption isotherms and the release of cations, Chemosphere, 82 (2011) 1431–1437.

[24] Z. Tan, Y. Wang, L. Zhang, Q. Huang, Study of the mechanism of remediation of Cd-contaminated soil by novel biochars, Environ. Sci. Pollut. Res. Int., 24 (2017) 24844–24855.

[25] Q. Wang, B. Wang, X.Q. Lee, J. Lehmann, B. Gao, Sorption and desorption of Pb(II) to biochar as affected by oxidation and pH, Sci. Total Environ., 634 (2018) 188–194.

[26] C.H. Cheng, T.P. Lin, J. Lehmann, L.J. Fang, Y.W. Yang, O.V. Menyailo, K.H. Chang, J.S. Lai, Sorption properties for black carbon (wood char) after long term exposure in soils, Org. Geochem., 70 (2014) 53–61.

[27] G. Abdul, G. Saikat, F.F. Li, X.D. Dong, D. Zhang, M. Wu, H. Li, B. Pan, Effect of biochar aging on surface characteristics and adsorption behavior of dialkyl phthalates, Environ. Pollut., 206 (2015) 502–509.

[28] Y. Guo, W. Tang, J.G. Wu, Z.Q. Huang, J.Y. Dai, Mechanism of Cu(II) adsorption inhibition on biochar by its aging process, J. Environ. Sci., 26 (2014) 2123–2130.

[29] S.M. Martin, R.S. Kookana, L. Van Zwieten, E. Krull, Marked changes in herbicide sorption-desorption upon ageing of biochars in soil, J. Hazard. Mater., 231–232 (2012) 70–78.

[30] M. Julie, L. Johannes, R. Marco, G. Christine, Fate of soil-applied black carbon: downward migration, leaching and soil respiration, Global Change Biol., 16 (2010) 1366–1379.

[31] J. Lehmann, J. Gaunt, M. Rondon, Bio-char sequestration in terrestrial ecosystems–a review, Mitigation Adapt. Strategies Global Change, 11 (2006) 403–427.

[32] L. Beesley, E. Moreno-Jimenez, J.L. Gomez-Eyles, Effects of biochar and green waste compost amendments on mobility, bioavailability, and toxicity of inorganic and organic contaminants in a multi-element polluted soil, Environ. Pollut., 158 (2010) 2282–2287.

[33] R.J. Bian, D. Chen, X.Y. Liu, L.Q. Cui, L.Q. Li, G.X. Pan, D. Xie, J.W. Zheng, X.H. Zhang, J.F. Zheng, A. Chang, Biochar soil amendment as a solution to prevent Cd-tainted rice from China: results from a cross-site field experiment, Ecol. Eng., 58 (2013) 378–383.

[34] J. Jiang, R.K. Xu, T.Y. Jiang, Z. Li, Immobilization of Cu(II), Pb(II) and Cd(II) by the addition of rice straw derived biochar to a simulated polluted Ultisol, J. Hazard. Mater., 229–230 (2012) 145–150.

[35] M. Uchimiya, W. Lynda H, K. Klasson, F. Chanel A, L. Isabel M, Influence of pyrolysis temperature on biochar property and function as a heavy metal sorbent in soil, J. Agric. Food Chem., 59 (2011) 2501–2510.

[36] H. Mousavi, A. Hosseinifar, V. Jahed, Removal of Cu(II) from wastewater by waste tire rubber ash, J. Serb. Chem. Soc., 75 (2010) 845–853.

[37] Dougherty, A. Dennis, The cation−π interaction, Chem. Rev., 97 (1997) 1303–1324.