

Article

Effects of Modified Biochar on the Mobility and Speciation Distribution of Cadmium in Contaminated Soil

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Abstract: Cadmium-contaminated soil poses a threat to the environment and human health. Biochar materials have received widespread attention as an in situ immobilizer for the efficient remediation of heavy-metal-contaminated soils. In this study, a modified biochar material (E-CBC) was developed for the immobilization of Cd in contaminated soil. E-CBC was characterized by XPS, SEM, BET, and FTIR. The effects of pristine biochar (BC) and E-CBC on soil physicochemical properties (pH and soil organic matter (SOM)), CaCl₂-extractable Cd, total characteristics leaching procedure (TCLP) Cd, and speciation distribution of Cd were studied by incubation experiments. The results showed that the application of BC and E-CBC increased soil pH slightly and SOM significantly. A 2% dosage BC and E-CBC treatment reduced CaCl₂-extractable Cd by 14.62% and 91.79%, and reduced TCLP Cd by 9.81% and 99.8%, respectively. E-CBC was shown to effectively induce the transition of Cd in the soil to a stable state. The application of a 0.25% dosage of E-CBC reduced the acid-extractable fraction of Cd from 58.06% to 10.66%. The functional groups increased after modification and may play an important role in the immobilization of Cd in the contaminated soil. In conclusion, E-CBC is a promising in situ immobilizer for the remediation of Cd-contaminated soil.

Keywords: biochar; Cd-contaminated soil; in situ immobilization; bioavailability; speciation



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1. Introduction

Heavy metals are discharged into the soil environment from industrial and agricultural activities, including mining, smelting, fertilizer application, and wastewater irrigation [1,2]. Heavy metals are nonbiodegradable and can accumulate in soils, which can influence soil quality, microbial activities, and agricultural productivity, and cause threats to ecosystems and public health [3,4]. Among heavy metals, Cd is recognized as a Group 1 hazardous carcinogen [5]. Soil Cd can be taken up by plants and accumulated; the Cd accumulated in the edible parts enters living organisms through the food chain, eventually threatening human health [6]. It causes a series of diseases, such as pulmonary emphysema, hypercalciuria, hypertension, kidney stones, and neurological disorders [7,8]. In situ immobilization technology has attracted attention in the treatment of heavy-metal-contaminated soil because of its high efficiency, no secondary pollution, and convenience of application [9–11]. Some researchers have developed various materials for the remediation of heavy-metal-contaminated soil such as lime [12], activated carbon [13], red mud [14], hydroxyapatites [15], kaolin [16], silicon [10], and microbial materials [17]. Although these materials have a remediation effect on heavy-metal-contaminated soils, the inefficiency, high cost, and secondary pollution limit their practical application.

Biochar is the solid product derived from pyrolysis of organic matter (e.g., agricultural and forestry residues, food waste, and manures) under oxygen-limited conditions. As a porous material, biochar can immobilize heavy metals in the soil and improve soil properties. Biochar has received extensive attention in soil environmental applications. Zhang et al. [18] reported that the application of rice-straw-derived biochar (10 t ha^{-1}) decreased Cd availability (EDTA-extraction) from 0.45 to 0.17 mg kg^{-1} and 0.85 to 0.57 mg kg^{-1} in two different soils. Zhang et al. [19] found that the leachability (TCLP-extraction) of Cd, Cu, Ni, Pb, and Zn were reduced by 47.81–78.0%, with 15% *Phyllostachys pubescens* biochar. Dai et al. [20] found that the acid-soluble fractions of Cu, Zn, As, and Cd were reduced and the residual fractions increased after the application of rice-straw-derived biochar (10–50% ratio). However, the addition ratio of biochar in these studies all exceeds 10%, which is not conducive to the practical application and also brings certain risks [21].

Previous study indicated that biochar can immobilize heavy metals owing to its unique properties, such as porous structure, large surface area, and surface functional groups [22]. Therefore, improving the performance of biochar helps to enhance its ability to immobilize heavy metals in the soil while reducing the application dosage. Many methods have been used to modify biochar, such as acid or base treatment, steam or gas purging, load minerals, and magnetic modification [23]. Recently, organic modification has received more attention from researchers. Tang et al. [24] developed polyethyleneimine (PEI) modified biochar for the remediation of Cd-contaminated yellow brown soil, and the research showed that PEI-modified biochar could immobilize Cd better and improve the soil quality more significantly than ordinary biochar. Fan et al. [25] prepared the thiol-modified biochar to remediate the Cd- and Pb-contaminated soil and successfully reduced the available Cd by 34.8–39.2% and Pb by 8.6–11.1%. These studies have shown that numerous functional groups have been grafted onto the surface of the modified biochar, which is involved in the immobilization of heavy metals.

In a previous study, we synthesized chitosan–EDTA-modified magnetic biochar, which had an excellent adsorption capacity for Pb in an aqueous solution [26]. We hypothesized that the chitosan–EDTA-modified biochar can be effectively applied to remediate Cd-contaminated soil. The objectives of this research were to synthesize and characterize the modified biochar, evaluate the immobilization of modified biochar on Cd in soil, and investigate the effect of modified biochar on Cd speciation distribution.

2. Material and Methods

2.1. Preparation of Cd-Contaminated Soil

The surface soil (0–20 cm) sample was collected from the East District of Shandong Academy of Sciences, Jinan, China. The soil was air-dried, ground, and sieved through a 2 mm mesh for further use. An artificially Cd-contaminated soil was prepared by spraying a cadmium nitrate ($\text{Cd}(\text{NO}_3)_2$) solution into the homogenized soil. The contaminated soil was then aged for 15 days. The physicochemical properties of the soil are presented in Table 1.

Table 1. The physicochemical properties of the soil.

pH	SOM (g kg^{-1})	Total Cd Concentration (mg kg^{-1})	CaCl_2 -Extractable Cd Concentration (mg kg^{-1})	TCLP-Extractable Cd Concentration (mg kg^{-1})
7.57	13.3	0.18	0.05	0.07

2.2. Preparation of Chitosan–EDTA-Modified Biochar

Pristine biochar (BC) was purchased from Senmiao Energy Saving Technology Co., Ltd. Nanyang, China. It is produced from peanut shells at 500°C for 2 h under oxygen-limited conditions. The chitosan–EDTA-modified biochar was synthesized according to the previous method [26]. Briefly, 3.0 g sieved (100-mesh) biochar, 3.0 g chitosan, and 300 mL

2% acetic acid were stirred for 2 h; the mixture was then adjusted to pH 10 and reacted overnight. The biochar was separated and washed with deionized water, oven-dried, and sieved (100 mesh). Next, 1.0 g of separated biochar, equal quality EDTA, and 100 mL deionized water were stirred for 4 h at 60 °C. The mixture was cooled to 40 °C, and 5 mL 1 mol L⁻¹ NaOH and 0.96 g EDAC were added sequentially. The reaction was allowed to continue for 2 h and then the mixture was stirred at room temperature overnight. Finally, the filtered solid was washed with deionized water, oven-dried, and sieved (100 mesh). This final product is labeled E-CBC herein.

2.3. Characterization

The pH of the soil sample was determined in a water solution at 1:2.5 (*w/v*), and measured by a multiparameter meter (Mettler–Toledo, Zurich, Switzerland) after shaking at 180 rpm for 30 min. Soil organic matter (SOM) was determined by the potassium dichromate oxidation spectrophotometric method [27].

The surface area, pore parameters, surface morphology, chemical composition, and functional groups of BC and E-CBC were measured by the Brunauer–Emmett–Teller (BET) surface area and porosity analyzer (Quantachrome, Boynton Beach, FL, USA), scanning electron microscopy (SEM) (Zeiss, Oberkochen, Germany), X-ray photoelectron spectroscopy (XPS) (Thermo, Waltham, MA, USA), and Fourier transform infrared spectroscopy (FTIR) (Thermo, Waltham, MA, USA).

2.4. Soil Incubation Experiment

The incubation experiments were carried out with 1000 g Cd-contaminated soil in plastic boxes at room temperature. BC and E-CBC were thoroughly mixed with the Cd-contaminated soil at a rate of 0, 0.25%, 0.5%, 1.0%, and 2.0%. During the incubation period, deionized water was added to maintain 60% of maximum water-holding capacity, and mixed to achieve homogeneity each day. Soil samples were collected from each box on the 5th, 10th, 30th, 60th, and 90th day, air-dried, and ground to pass through a 2 mm mesh for the next analysis. All treatments were replicated three times.

2.5. Analytical Methods

The bioavailable Cd concentration in soil samples was measured using the procedure of Meng et al. [22]. Briefly, a 1.0 g soil sample and 10 mL 0.1 mol L⁻¹ CaCl₂ solution were shaken in a 15 mL centrifuge tube at 200 rpm for 2 h, then centrifuged at 4000 rpm for 20 min. The supernatant liquid was filtered with a 0.45 µm membrane, and then measured by inductively coupled plasma optical emission spectroscopy (ICP–OES) (Perkin Elmer, Waltham, MA, USA).

The toxicity characteristic leaching procedure (TCLP) of Cd in soil samples was carried out by following the Environmental Protection Industry Standard of China (HJ/T 300–2007). Briefly, 1.0 g soil sample and 20 mL glacial acetic acid solution (pH = 2.8) were shaken in a centrifuge tube at 120 rpm for 20 h. The mixture was centrifuged at 4000 rpm for 20 min, filtered with a 0.45 µm membrane, and then measured by ICP–OES.

Various chemical speciation of Cd in soil samples were determined by modified Tessier procedures [28]. Briefly, five sequential extractions were conducted. Step 1: 1 mol L⁻¹ MgCl₂ (pH 7.0) was added to the soil sample to extract exchangeable form; Step 2: 1 mol L⁻¹ NaOAc (pH 5.0) was added to the residue of Step 1 to extract carbonate-bound form; Step 3: 0.04 mol L⁻¹ NH₂OH·HCl in 25% HOAc (pH 2.0) was added to the residue of Step 2 to extract the Fe–Mn-oxides-bound form; Step 4: 0.02 mol L⁻¹ HNO₃ in 30% H₂O₂ (pH 2.0) and 3.2 mol L⁻¹ NH₄OAc in 20% HNO₃ (pH 2.0) was added to the residue of Step 3 to extract organic-matter-bound form; HF, HNO₃, and HClO₄ were added to the residue of Step 4 to extract the residual form. All the extracts were centrifuged at 4000 rpm for 20 min, filtered with a 0.45 µm membrane, and then measured by ICP–OES.

2.6. Statistical Analysis

All experiments were conducted at least in triplicate. The statistical analysis was carried out using Microsoft Excel 2016 (Microsoft Corporation, Redmond, WA, USA). The variability of data was expressed as standard deviation ($p < 0.05$). All figures were produced using the Origin Pro software version 2016 (OriginLab, Northampton, MA, USA).

3. Results and Discussion

3.1. Physicochemical Properties of Biochars

The physicochemical properties of BC and E-CBC are shown in Table 2. The elemental composition changed significantly after modification. The percentage of C1s in E-CBC decreased from 83.9% to 65.33%, and the contents of N1s and O1s increased from 2.72% to 6.77% and 13.38% to 27.9%, respectively. This indicates that the coating of chitosan and EDTA modification was successful [26]. Figure 1 shows the surface morphology of BC and E-CBC. The structure of the BC surface was smooth and porous. The surface of E-CBC became rough and many pores were blocked, which is consistent with the result of BET [29]. The FTIR spectra of BC and E-CBC are shown in Figure 2. The bands around 3430 cm^{-1} (O–H stretching), and 1632 cm^{-1} (C=O stretching) were observed from BC, and intensified bands were observed from E-CBC at the corresponding wavenumber. This indicated that the functional groups on the surface of E-CBC increased after medication.

Table 2. Physicochemical properties of BC and E-CBC.

	pH	Pore Diameter (nm)	Pore Volume (cc g^{-1})	Surface Area ($\text{m}^2\text{ g}^{-1}$)	Element Content		
					C (%)	N (%)	O (%)
BC	9.44	5.35	0.044	49.26	83.9	2.72	13.38
E-CBC	8.17	12.38	0.017	6.06	65.33	6.77	27.9

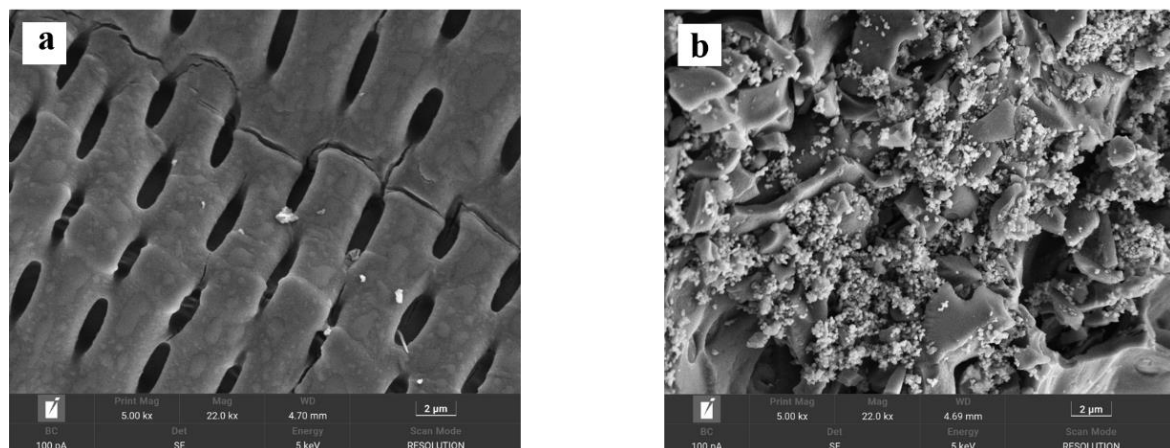


Figure 1. SEM images of BC (a) and E-CBC (b).

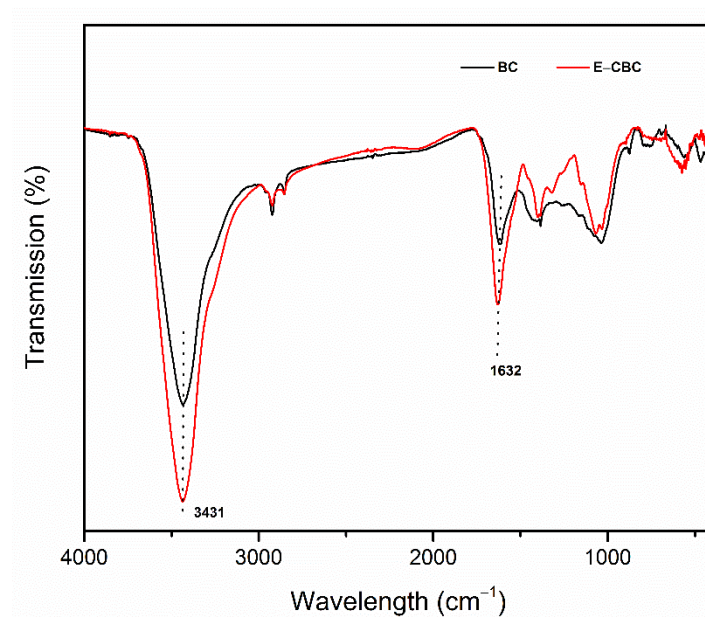


Figure 2. FTIR spectra of BC and E-CBC.

3.2. Effects of Modified Biochar on Soil pH and SOM

The pH is a key parameter of soil physicochemical properties and has an important influence on the mobility and speciation of heavy metals [24]. Generally, adding biochar material to the heavy-metal-contaminated soil tends to increase pH because biochar material is alkaline [30]. The type and dosage of biochar materials may have a great effect on soil pH. Meng et al. [22] employed biochar produced from rice straw and swine manure to contaminated soil and found the pH increased by 0.68–1.08 units after 150 days of incubation with a 3% dosage. In this laboratory incubation experiment, the soil pH values of different biochar treatments at different times are given in Figure 3a. The soil pH of the different treatments increased gradually with time during the incubation period. Compared with the treatments at 5 days, the pH increased by 0.05, 0.1, and 0.13 units, respectively, in the soils that were untreated (CK), and treated with BC and E-CBC with a 2% dosage, at an incubation of 90 days. The soil pH slightly increased with the increasing proportion of BC and E-CBC. Addition of 0.25%, 0.5%, 1%, and 2% BC resulted in soil pH increases of 0.12, 0.14, 0.2, and 0.29, respectively, at the end of incubation. Addition of 0.25%, 0.5%, 1%, and 2% E-CBC resulted in soil pH increases of 0.12, 0.12, 0.15, and 0.16, respectively, at the end of incubation. The results show that BC is a more effective means to improve soil pH because it is more alkaline than E-CBC. Liu et al. [31] observed that higher pH favors immobilization of heavy metals in soil. However, a relatively low dosage of biochar material has little effect on soil pH, as reported by the previous study [16].

The changes of SOM in the soil incubation experiment are shown in Figure 3b. The addition of biochar materials significantly improved the SOM content. Yan et al. [32] had the same finding. Increasing the application dosage of biochar materials resulted in higher SOM content in this study. Compared to CK, the SOM content of the sample with the 2% addition of BC and E-CBC increased by 67.54–84.67% and 88.32–95.30%, respectively. The results showed that adding E-CBC could more effectively increase the content of SOM. The SOM content increased with time in the first 30 days of the incubation experiment, and then leveled off. The increase in SOM by biochar material may remain for a long time [33], which enhances soil fertility [34] and affects the stability of Cd [17].

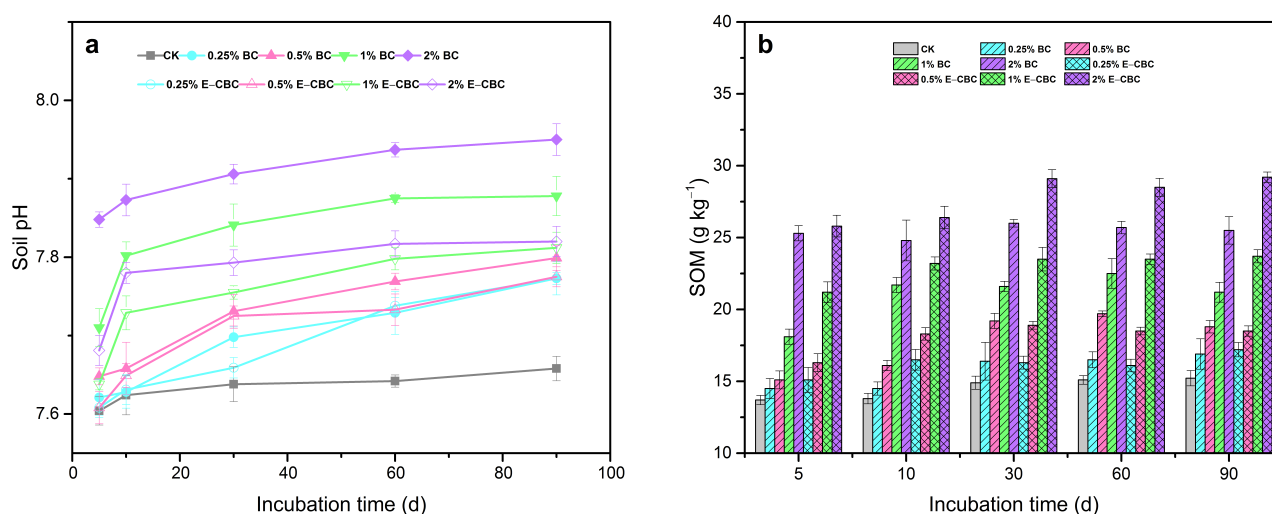


Figure 3. Effects of BC and E-CBC on soil pH (a) and SOM (b).

3.3. Effects of Modified Biochar on the Bioavailability of Cd

The bioavailability of Cd relates to where Cd can be bioabsorbed or organisms accumulated in the soil [35]. Previous studies have shown that the CaCl_2 solution extraction can reflect the bioavailability of heavy metals [36,37]. The changes of CaCl_2 -extractable Cd in different soil treatments are shown in Figure 4. The results showed that all the treatments reduced the content of the CaCl_2 -extractable Cd from the contaminated soil and the extractable content decreased with the increase in biochar material dosage. On the 5th day of treatment with 2% BC and E-CBC, the content of CaCl_2 -extractable Cd was 9.5% and 40.5%, respectively, lower than that with 0.25% dosage. Compared to CK, the content of CaCl_2 -extractable Cd in the BC and E-CBC treatments was reduced by 2.7–16.9% and 75.68–92.76%, respectively. The addition of E-CBC is more effective at immobilizing Cd in contaminated soil than that of BC. Even adding 0.25% E-CBC to the soil, the content of CaCl_2 -extractable Cd was markedly decreased. A large number of hydroxyl, amino, and carbonyl functional groups on the surface of E-CBC are the main reason for this decrease. Previous reports also indicated that those functional groups have excellent adsorption and immobilization ability for Cd [18,38,39]. In all treatments, the content of CaCl_2 -extractable Cd decreased gradually with incubation time. Adding 2% BC, the content of CaCl_2 -extractable Cd was 11.97% and 14.62%, lower than that of CK on the 5th and 90th days. For 2% E-CBC, it was 85.33% and 91.79% lower than that of CK. A similar trend was reported in previous studies [21,40].

3.4. Effects of Modified Biochar on the Leachability of Cd

The solubility and leachability of Cd were evaluated by TCLP in all samples. As shown in Figure 5, the content of TCLP-extractable Cd decreased with an increasing application rate of BC and E-CBC. The BC treatment had slight decrease in extractable Cd by 1.76%, 3.81%, 7.56%, and 9.66%, at the dosage of 0.25%, 0.5%, 1%, and 2% after 5 days of incubation. However, the content of extractable Cd in E-CBC treatment sharply decreased by 90.06%, 91.97%, 93.87%, and 94.39%, respectively, at the same conditions. In addition, the content of TCLP-extractable Cd decreased with incubation time. The content of extractable Cd decreased by 8.71% on the 5th day and by 9.81% at the end of the 2% BC treatment incubation. However, in the treatment with E-CBC, the content of extractable Cd decreased by 94.39% on the 5th day and decreased by 97.27% at the end of the 2% E-CBC treatment incubation. The results indicated that BC was not effective for immobilizing Cd in soil and the process was slow, as reported by Liu et al. [31]. Both the efficiency and speed of E-CBC immobilization of Cd in soil are higher than that of BC and previously reported biochar materials [41,42]. This may be because of the increase in the functional groups after

modification. Therefore, E-CBC can be used to reduce the leaching toxicity of Cd in soil and thus reduce ecological risks.

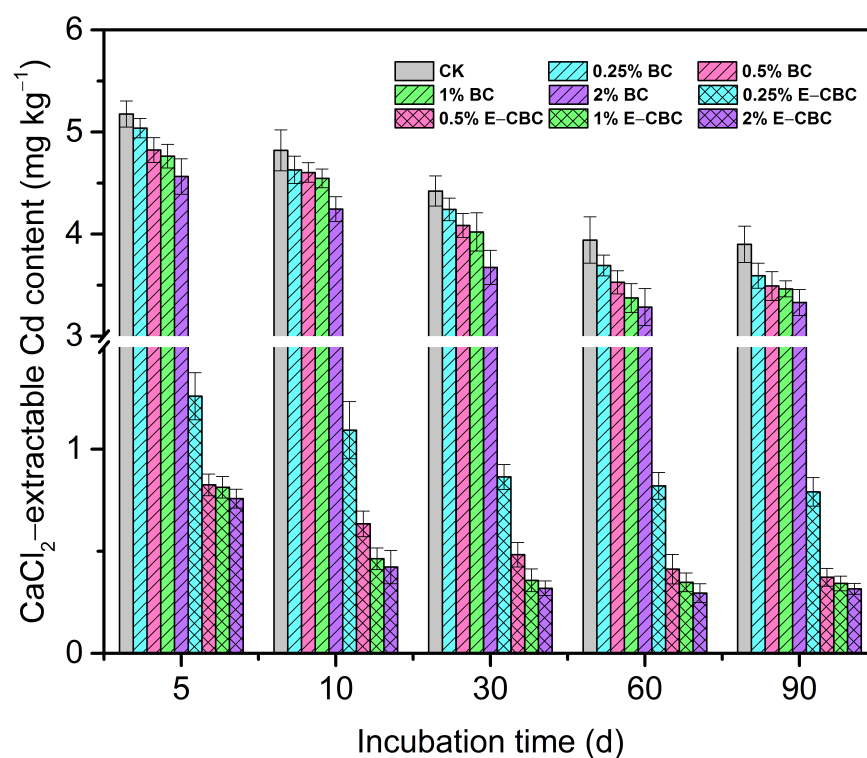


Figure 4. Effects of BC and E-CBC on the bioavailability of Cd in soil.

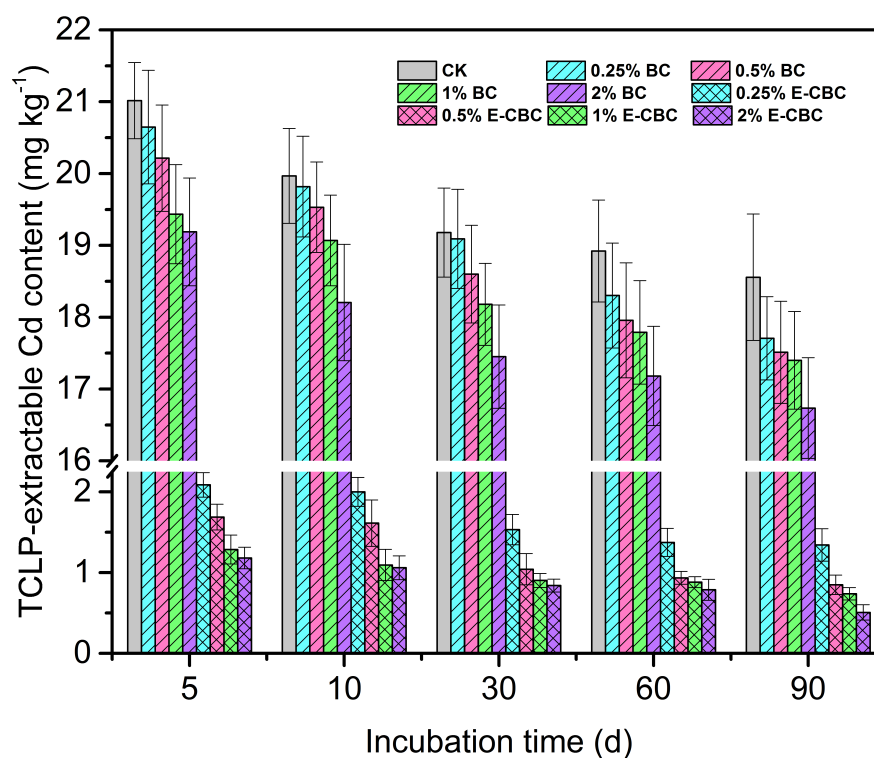


Figure 5. Effects of BC and E-CBC on the leachability of Cd in soil.

3.5. Effects of Modified Biochar on Speciation of Cd

The total content of heavy metals in polluted soil cannot accurately reflect the level of pollution, because heavy metals exist in the soil in different chemical speciation, and each speciation has a different impact on the environment [43]. The Tessier sequential extraction method separates heavy metals in soil into the acid-extractable form (F1), carbonate-bound form (F2), Fe–Mn-oxides-bound form (F3), organic-matter-bound form (F4), and residue form (F5) [18]. Among them, the acid-extractable form is soluble and most easily utilized by organisms to produce ecological toxicity. The residue form mainly exists in the crystal structure of the rocks and minerals, which is the most stable and not available for organisms in nature. The other three forms can be converted under specific conditions, which may produce ecological toxicity.

The Tessier sequential extraction method was applied to analyze the proportion of chemical speciation of Cd at the end of incubation. As shown in Figure 6, the application of BC and E–CBC affected the speciation distribution of Cd in the soil. With the increase in the BC application rate, the acid-extractable Cd in the soil was converted to the other four relatively stable forms. Compared with the CK, the acid-extractable form was decreased by 0.79%, 3.81%, 7.73%, and 9.33%, at the addition rate of 0.25%, 0.5%, 1%, and 2%, respectively. Correspondingly, the carbonate-bound form increased by 0.82%, 2.62%, 4.5%, and 6.22%. The percentage of the other three forms also increased very slightly. The effect of E–CBC on the distribution of Cd speciation in soil was significantly different from that of BC. The acid-extractable Cd and carbonate-bound Cd content in the soil significantly decreased with the application of E–CBC, with the former slightly affected by the dosage of E–CBC. The carbonate-bound form decreased by 11.78%, 15.77%, 26.38%, and 27.83%, at the addition rate of 0.25%, 0.5%, 1%, and 2%, respectively. The application of E–CBC increased the Fe–Mn-oxides-bound Cd, but the proportion of the Fe–Mn-oxides-bound Cd decreased from 60.59% to 44.91% with the increase in the E–CBC application rate. The organic-matter-bound Cd and residual Cd percentage in the soil increased with the application rate of E–CBC, the former proportion increased to 43.59% at 2% addition.

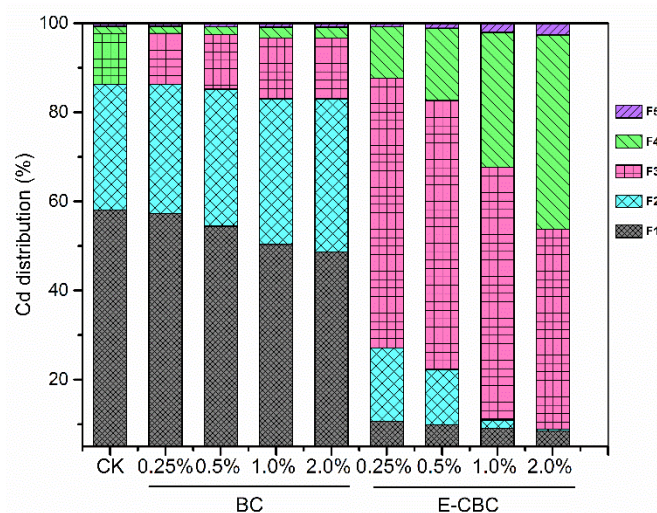


Figure 6. Effects of BC and E–CBC on speciation distribution of Cd in soil.

These results show that E–CBC can better induce the transformation of Cd in the soil to less toxic stable forms than BC. The reason for this difference may be related to the remediation material and soil physicochemical properties (pH, SOM, etc.) [20]. In the present research, the same dosage of BC made the soil pH higher than E–CBC, but the immobilization effect of Cd was the opposite. This suggests that the effect of pH is not the main reason for the difference. The SOM content was higher after E–CBC treatment, which affected the Cd speciation distribution. Zhang et al. [18] indicated that the increase in SOM content enables more Cd in the soil to be converted to a highly stable state. Moreover,

the modification process moved the functional groups to the E-CBC surface, which may play a key role in the Cd speciation distribution. Muhammad et al. [44] indicated that the functional groups (–OH, –COOH, –CONH–, etc.) combine with Cd to form complexes, which affects the adsorption and biomineralization of Cd. At the end of incubation, 0.25% E-CBC treatment soil had lower pH and SOM than that of 2% BC treatment; however, the immobilization of Cd was more effective. This indicates that the increased functional groups on the E-CBC surface may play a primary role in Cd immobilization.

4. Conclusions

Chitosan-EDTA-modified biochar (E-CBC) was successfully prepared by chemical grafting as amendment for Cd-contaminated soil. The effects of BC and E-CBC treatment on the soil pH and SOM, bioavailability, and leaching toxicity of Cd were investigated by incubation experiments. The results showed that both pH and SOM content of the soil increased with a dosage of the biochar materials and incubation time. BC was more effective in increasing soil pH, and E-CBC was more effective in increasing SOM, both of which were beneficial for Cd immobilization in soil. The application of E-CBC significantly reduced the bioavailability and leachability of Cd. At the end of incubation, the Cd bioavailability and leaching toxicity of the soil treated with 2% E-CBC were reduced by 91.79% and 97.27% compared with the CK, whereas those with 2% BC treatment were reduced by 14.62% and 9.81%. E-CBC treatment induced the transformation of Cd to stable form more effectively than BC treatment. The percentage of the acid-extractable form of Cd decreased from 58.06% to 10.66% after 0.25% E-CBC application; however, the data show only a decrease to 48.67% even with 2% BC application. The increased surface functional groups might be the reason for the sharply increased immobilization efficiency of E-CBC to Cd. These results indicate that E-CBC has a promising application prospect as an efficient in situ immobilizer for Cd-contaminated soil.

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