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Effect of silkworm excrement biochar on the chemical properties of paddy soil and the speciation of cadmium

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Abstract: In order to make better use of silkworm excrement (SE) resources, the soil incubation experiments were conducted in this study to investigate the effects of SE and silkworm excrement biochar (SB) on the chemical properties of paddy soil. The sequential extraction procedure (SEP) was applied to analyze the chemical forms of cadmium (Cd), and the stability and mobility of Cd in paddy soil was also evaluated by leaching test. Results showed that SE and SB could significantly ($p < 0.05$) increase the soil pH, cation exchange capacity (CEC) and reduce the content of the extractable Cd, especially at 10% application rate, than that in the untreated soil. The SEP elucidated that SE decreased the ratio of exchangeable fraction (F1), increased the ratio of carbonated-bound fraction (F2), Fe-Mn oxides fraction (F3) and complexed with organic matter (F4), compared with the control. However, SB reduced the ratio of F1 and F2, increased the ratio of F3, F4 and residual fraction (F5). The 10% SB treatment reduced the concentration of phytoavailable Cd by 85.5% compared to the control. The results indicated that the SB could immobilize the Cd effectively, reducing its mobilization and phytoavailability in soils.

Keywords: passivation, silkworm excrement, biochar, cadmium, chemical form

1. Introduction

With the rapid development of industry, croplands contaminated by heavy metals has turned into a worldwide environmental issue [1]. In China, there was about 2.0×10^7 ha of ploughland has been polluted by heavy metals, especially in paddy soils, capturing 19.4% of the whole cultivated land [2]. Cadmium (Cd) is an unnecessary component for the organs of the human body and it is an extremely harmful environmental chemical pollutant to plants and animals, which is one of the most ordinary contaminants in the soils of China and can be mostly discharged from the mining, ceramics, metallurgy and electroplating industry into the environment [3,4].

A tremendous amount of work has been done on innovating effective and reasonable treatment solutions for the treatment of heavy metals polluted soils. So far, the main remediation methods for contaminated soil contain chemical immobilization [5,6], chemical washing [7,8], soil replacement [9], phytoremediation [10-15] and microorganism remediation [16,17]. Chemical immobilization has been proved to be a good choice for its easiness, low investment and high efficiency [18-20]. Chemical immobilization could decrease the phytoavailability and mobility of heavy metals by adding some organic or inorganic conditioners into soil. These amendments could react with the heavy metals through adsorption, complexation, ion exchange and precipitation, *etc*. to affect the behavior of metal [6,20]. To date, a lot of innovative materials have been found as immobilization agents, such as phosphates-containing materials, biochar materials, clay minerals, furnace slag, Si-rich minerals, and so on [18,19,21,22]. Biochar material is mainly gained through the pyrolysis process of sewage sludge and agricultural residue in an oxygen-limited atmosphere [2,23]. It could be utilized to confiscate carbon, repair polluted wastewater and soils, and also could be a useful soil amendment in agriculture for its porous structure, specific surface area, maintained surface functional groups and abundant mineral matters. Application of biochar could significantly increase soil pH and porosity [2,24], improve plant growth [25,26], reduce greenhouse gas emissions [18,27] and the extractable heavy metals concentrations of soils [2,24]. Silkworm excrement (SE) is the main by-product of sericulture industry. In China, there would be over 4.5 million tons SE every year [28]. Fresh SE contains solid excrement, as well as some residual mulberry leaf, lime powder and bedding [25,28]. SE has been mainly used as composting material due to its richness in organic matter (OM), nitrogen (N), phosphorus (P) and potassium (K) [28,29]. Also, there are some studies reported that the SE could be utilized to prepare carbon materials, such as nanosheets for high-performance supercapacitors [29], biochar for adsorption of bisphenol A [30], porous carbon for the continuous emission of the pesticide [31], compost for remediation the heavy metals [25].

Currently, there are few studies investigated the SE biochar (SB) on the chemical properties of paddy soils and associated the speciation of Cd. In order to better reflect the reactions between the SE biochar and Cd in soil, batch experiments were conducted in this study to investigate the effects of SB prepared at 450 ℃ under limited oxygen on the natural Cd contaminated paddy soil properties and chemical forms of Cd, which has been incubated for 1 year. And the extractable Cd was also examined at the end of the incubation.

2. Materials and methods

2.1. Soil, SE and SB

The soil was sampled from a farmland in a village (113°03′19″ E, 27°53′48″ N), which was located in Zhuzhou city, Hunan province, China. The topsoil (0~20 cm) was sampled and air-dried at room temperature, crushed to pass across a 2-mm sieve for further use. The SE was collected at the fifth star of silkworm from the Changsha branch of National Silkworm Improvement Center, in the Sericultural Research Institute of Hunan Province. After removing the impurities such as the broken leaves and lime particles from the silkworm excrement, it was dried in an oven at 70 ℃ to stable weight, and part of which was used to make SB. A tube furnace (OTF-1200X-80, Hefei Kejing Material Technology Co., LTD, China) was utilized to change these SE samples into SB. For each pyrolysis experiment, about 20 g of the dried SE was put into a quartz boat (6 cm diameter, 15 cm long) designed to fit the inside structure of the tube furnace. The nitrogen gas was passed through the chamber of tube furnace to keep the tube inert anaerobic atmosphere. Then the temperature was designed to 450 ℃ at an ascendant rate of 7 ℃ /min and held at 450 ℃ for 2 h before cooling down to room temperature [18]. The obtained SB was slightly grounded and passed across a 2-mm sieve, then stored in air-tight containers before use.

2.2. Soil incubation experiments

Thirty grams air-dried soil was put into each 50-mL plastic centrifuge tube. The SE was added into the soil at 0%, 5% and 10% (w/w, dry basis) and the SB was added at the rate of 0%, 1%, 3%, 5% and 10% (w/w, dry basis). The soil and SB or SE were blended absolutely and added the deionized water to reach 70% of field water-holding capacity of the soil. Each treatment was repeated 3 times. All tubes were covered with a plastic lid, and some little holes were made to enable gas exchange and limit moisture loss. Then the all tubes were incubated at 20 ±1 ℃ for 1 year in the dark atmosphere.

2.3. Characterization of SB and the SB treated soils

The selected basic physio-chemical properties of paddy soil were detected by the routine analytical methods [32]. The Elemental compositions (C, H, N, S, and O) of SB were determined through an elemental analyzer (3H-2000PM2, Best instrument technology (Beijing) Co., Ltd). Specific surface areas and total pore volume were determined a physical adsorption analyzer (MicroActive for ASAP 2460, Shanghai, China) in the N2 atmosphere by adsorption and desorption technique. The treatment and Cd concentrations analysis of the soil and plant samples were followed by a previous study [33]. The selected physical and chemical properties of soils, SE and SB were showed in Table 1.

Table 1. Some physical and chemical properties of soils, SE and SB.

	pH	OM（%）	CEC (cmol(+)/kg)	Mechanical compositions(%)					Cd concentration (mg/kg)
				sand		silt		clay	
Soil	5.44	2.38	8.72	20		36		40	0.94
SE	8.57	69.40	13.45	/		/		/	0.03
		Surface area (m^2/g)	Pore volume (cm^3/g)	C (%)	H (%)	O (%)	N (%)	S (%)	
SB	9.45	7.24	0.014	36.24	2.82	23.83	1.55	0.23	0.13

2.4. Sequential extraction process

For the speciation of Cd, 1 g (dry base) soil from each tube was sequentially extracted by the ways of Tessier method [34]. Heavy metal Cd in the extraction solutions was detected by Atomic Absorption Spectrometry (AAS) (Thermo Fisher ICE-3400, America) [33].

2.5. Leaching experiment

In order to investigate the stabilization of Cd in the paddy soil after the incubation experiment with SE and SB, the leaching tests were conducted [35]. Briefly, 5 g of paddy soil (dry) was put into 50-mL centrifuge tube and 25 mL of 0.1 M HCl was added, then the suspensions were shaken (100 rpm, 30 ℃) for 1 h in a shaking incubator (ZWY-200D, ZHCHENG, Shanghai, China). The solution in the tube was filtered by filter membrane (< 0.45 μm) and was analyzed using AAS.

2.6. Statistical analyses

Each treatment was conducted three replicates and all the data were showed as means ± SD (n=3). The SPSS software (version 17.0) was utilized for the data analysis and Duncan's multiple range test ($P < 0.05$) was used to contrast the significant differences among the mean values of different treatments.

3. Results and discussion

3.1. Soil chemical properties

The soil pH is one of the particularly significant items in changing the soil surface electric charge and also the fractions of heavy metal in soil [36,37]. In this study, the SB increased the soil pH significantly ($P < 0.05$) and the pH values were increased with the increasing application rate of SB (Figure 1). The pH of the soil with 10% SB (m/m) was 8.99, 36.42% higher than the control group (Figure 1). During the production of biochar, the formation of -COO- and -O- functional groups makes the pH of biochar increase. Also, with the reduction of volatile component in the biomass, the content of organic matter decreased, the pH and CEC of biochar increased [38]. Once the pH of the soil expanded, the phenolic, hydroxyl and other acidic groups in the soil would be deprotonated, which made the soil particles be more negatively-charged. The more negatively-charged sites, the more attraction for Cd [37].

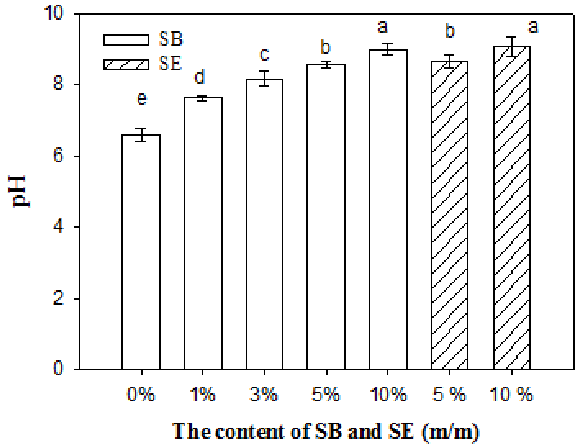

Figure 1. Effect of SB and SE on the pH of Cd-contaminated paddy soil.

Organic matter (OM) in soil is also another key item influencing the phytoavailability of heavy metals. OM includes lots of functional groups, which can interact with heavy metal ions through many physical chemistry reactions to influence the activity of heavy metals, such as adsorption, complexation, oxidation-reduction [36]. In this study, compared with the control, the soil OM differed without significant differences with the increase of SB (Figure 2). However, the SE (5% and 10%) increased the OM significantly for that SE is a good organic fertilizer containing lots of organic chemicals (Figure 2). The soil OM could decrease the phytoavailability of heavy metals in soils because the humic substances in soils could absorb the heavy metals and form stable complexes [39]. Meanwhile, some OM in the soil solution could combine with the heavy metals and increase its phytoavailability [40]. The soil OM increases or reduces the phytoavailability of Cd was determined by the type of OM. Dissolved organic matter (DOM) could generate explicable compounds with Cd, reduce the adsorption of Cd on soils and increase the availability of Cd, while particulate organic matter (POM) could increase the adsorption of Cd on soil and then decrease the mobility and bioavailability of Cd [36,37].

The cation exchange capacity (CEC) in soil is a valuable indicator for estimating the soil fertility [36]. In this paper, the CEC was significantly increased no matter application of SB or SE (Figure 3). When the SB content was 10%, the soil CEC was 10.8 cmol(+)/kg, significantly higher than that of 10% SE (Figure 3). Both SB and SE increased the soil CEC, indicating that the nutrient retention in the soil was increased [41]. The increase of CEC in SE treatments could be owed to the microbial degradation process, which formed the carboxyl and carboxylate functional groups. However, the increase of CEC in SB treatments could be attributed to the high surface area of SB [42]. In this study, the addition of SB (10%) increased the soil CEC significantly and resulted in an intense adsorption for Cd, which may decrease the Cd phytoavailability [37]. The soil incubation results indicated that soil pH, CEC increased significantly after the addition of SB, particularly at the application rate of 10%, reflecting the liming potential of SB.

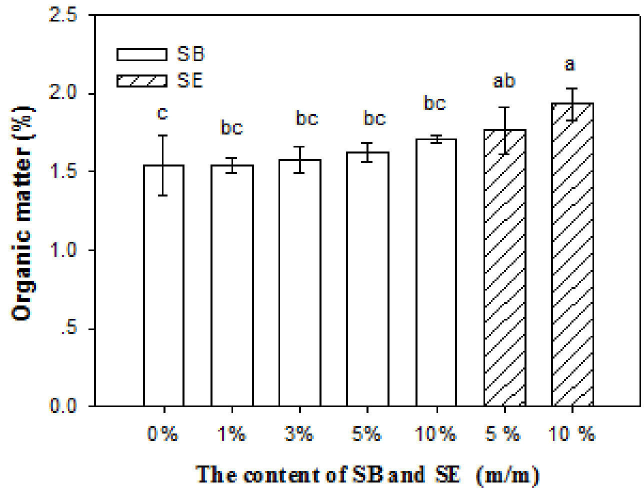

Figure 2. Effect of SB and SE on the organic matter content in the Cd-contaminated paddy soil.

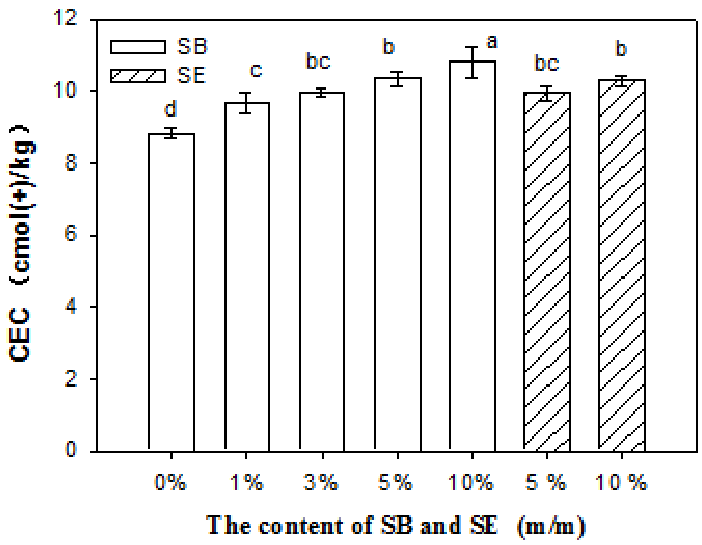

Figure 3. Effect of SB and SE on the soil CEC.

3.2. Cd speciation

The understanding the speciation of Cd is more important to know the environmental impacts of polluted soils. The total Cd in soil could be partitioned into five fractions: exchangeable, carbonated-bound, Fe-Mn oxides phase, complexed with organic matter, and residual by Tessier sequential extraction method [34]. In this study, the effects of SB and SE on the ratio of (F1) exchangeable, (F2) carbonate-bound, (F3) Fe-Mn oxide, (F4) organically bound, and (F5) residual fractions of Cd in the Cd-contaminated paddy soil were showed in Figure 4. For SB, compared with the control, the increasing SB significantly reduced the ratio of F1, slightly decreased the ratio of F2 (Figure 4). Meanwhile, the ratio of F5 with SB treatments were a little higher than that of control and the ratio of F3 and F4 were obviously increased with the increasing of SB, respectively (Figure 4). Though SE also decreased the ratio of F1, it increased the ratio of F2, F3 and F4 compared with the control group (Figure 4). Among the 5 geochemical fractions of Cd, F1 and F2 are more phytoavailable and toxic [12]. In this study, the content of F1 and F2 fractions in the control, SE (5%), SE (10%), SB (5%) and SB (10%) occupied the total soil Cd were 43.5%, 25.9%, 18.3%, 8.5% and 6.3%, respectively, suggesting that SB (10%) could reduce the phytoavailable Cd by 85.5% compared with the control (Figure 4). These results indicated that SB could reduce the phytoavailability of Cd effectively and the effect of SB was better than that of SE. The differences of pH could affect the speciation of Cd. When the pH value of soil increases, Cd could be gradually changed into a more stable and nonbioavailable form $Cd(OH)_2$, which becomes the main form when the soil pH > 8 [43]. In this study, the soil added with SB significantly increased the pH (from 6.59 to 7.65-8.99), indicating that the drop in the content of phytoavailable Cd was driven by changing the pH and promoting the precipitation of Cd. Also, the Cd in the soil could be absorbed by SB or soil colloids so that SB could be an effective way for the Cd stabilization [37].

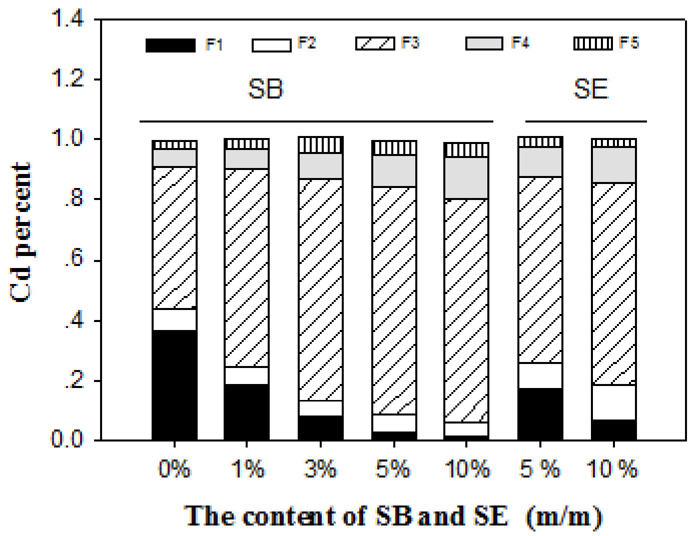

Figure 4. Effect of SB and SE on the ratio of (F1) exchangeable, (F2) carbonate-bound, (F3) Fe-Mn oxide, (F4) organically bound, and (F5) residual fractions of Cd in the polluted paddy soil.

3.3. Cd stabilization

The effects of SE and SB amendments on the concentrations of extractable Cd were very apparent, and the results were showed in Figure 5. The extractable Cd content for the control was 0.32 mg/kg. Among all the treatments, the treatment with 10% SB reduced the Cd leachability significantly, which got a 52.2% reduction than that of the control. And the concentrations of the extractable Cd were decreased with the increasing application of SB (Figure 5). In the case of SE, though the SE reduced the Cd leachability significantly compared with the control, the Cd stabilization effect was worse than that of application the same amount of SB. The reason for the higher leachability of Cd in the control soil may be that the bioavailable heavy metals, including the exchangeable fraction and the carbonate-bound fraction, were extracted under the slightly acidic conditions [35]. A significant decrease in the Cd concentration was showed in the soil samples incubated with SB (Figure 5). This was probably because that the SB treated soil buffered the leaching solution, so causing the inhibition of the carbonate dissolution [35]. These results suggested that SB could be effective as a potential immobilization agent for the stabilization of Cd in polluted soil. In fact, mulberry has become one of the representative plants for treatment and utilizing heavy metals polluted farmland. It is not only possible to use mulberry trees to repair contaminated soil, but also to increase farmers' income by planting mulberry and raising silkworms. What are the properties, functions, environmental risk and resource utilization of SB containing heavy metals is the next research focus.

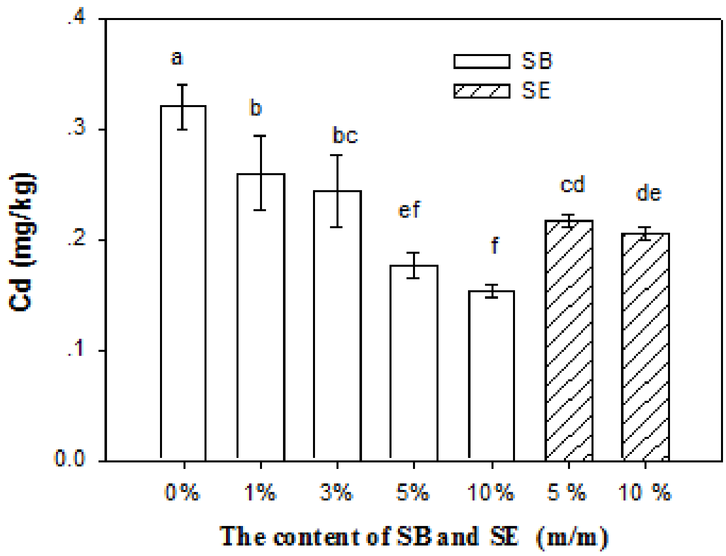

Figure 5. Effect of SB and SE on the extractable Cd concentrations in the Cd-contaminated paddy soil.

4. Conclusion

A soil incubation experiment was conducted to evaluate the immobilization efficiency of Cd by SE or SB. Results showed that the application of SB could significantly increase the soil pH and CEC. Compared with the control, though SE decreased the ratio of F1, increased the ratio of F2, F3 and F4, the SB could significantly reduced the ratio of F1, slightly decreased the ratio of F2, obviously increase the ratio of F3 and F4 and slightly increase the ratio of F5. Also, SB (10%) could reduce the extractable Cd by 52.2% compared with the control. These results indicated that SB could reduce the phytoavailability of Cd effectively and SB could be a potential immobilization agent to stabilize the Cd in polluted soil.

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Conflicts of interests

The authors declare no conflicts of interests.

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