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Research article

Effects of biochars derived from chicken manure and rape straw on speciation and phytoavailability of Cd to maize in artificially contaminated loess soil

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A B S T R A C T

While biochar can reduce the bioavailability of heavy metals in acidic soils and reduce their risk of entering the food chain, conditions for alkaline soils such as loess soils with high pH values, high carbonate content and low organic matter content remain unclear. Pot experiments were conducted to assess the effects of four rates (1%, 5%, 10%, and 15% w/w) of biochars prepared at 600 °C from chicken manure and rape straw (CBC and RBC) on soil properties, Cd speciation and phytoavailability, and plant growth in Cd contaminated (20 mg kg^{-1}) light sierozem using maize (*Zea mays* L.) as an indicator plant. Biochar additions significantly ($P < 0.05$) increased soil pH values, cation exchange capacity (CEC) and soil organic matter (OM). The results showed that Cd speciation turned somewhat into stable state as biochar application increased. When CBC and RBC was applied at the rate of 15%, the content of acid-extractable Cd decreased only by 16.3% and 11.64%, respectively. The uptake of Cd by maize shoots scarcely decreased with CBC and RBC amendment at the rate of 1% and 5%, respectively. Although it seemed that additions of more than 5% CBC or RBC significantly ($P < 0.05$) reduced Cd contents in maize shoots, maize growth was largely inhibited due to the high value of soil pH. These results could provide different implications for immobilization remediation of loess soils (e.g., light sierozem) contaminated with Cd.

1. Introduction

As a consequence of anthropogenic activities, concentrations of heavy metals in soils have increased worldwide (Alloway, 2013). In China, over 16.76% of farmland soils are reported to be contaminated with heavy metals, in which Cd contamination is more severe (Song et al., 2013). For example, concentrations of Cd in farmland around Baiyin City, which is the largest nonferrous metal base in northwestern China, are even 20-fold higher than the average value for Toyama County in Japan, where an outbreak of 'Itai-Itai' disease had occurred (Zhao and Wang, 2010). Stabilization/immobilization soil remediation technologies are simple, inexpensive and environmentally friendly and are considered to be some of the most ideal techniques for the remediation of heavy metal contaminated soils (Mahar et al., 2015). The key to this technology is to find a remediation agent that is capable of immobilizing heavy metals while also being environmentally friendly.

Biochar (BC) is the by-product of biomass that has been pyrolyzed under limited oxygen supplies (Lehmann, 2007). Due to its prominent properties, biochar is proven to be an innovative and promising method for mitigating climate change, improving soil properties and enhancing crop yields (Ladygina and Rinceau, 2013; Lehmann et al., 2011). Recently, it has been reported that biochar could serve as an *in-situ* alternative material for remediating soils contaminated with heavy metals through immobilization due to its capability to enhance soil pH values (resulting in the precipitation of heavy metals), and the capability of adsorbing heavy metals owing to its porous structure, negatively charged surface and large number of functional groups on its surface, thus reducing the phytoavailability of heavy metals (Beesley et al., 2011; Mahar et al., 2015).

Recently, several studies (Bian et al., 2013, 2014; Houben et al., 2013a; Jin et al., 2011; Li et al., 2016; Lu et al., 2014; Mohamed et al., 2015; Niu et al., 2015) show that the addition of biochar to

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acidic soils can significantly enhance soil capacities to adsorb and immobilize heavy metals such as Cd, thereby reducing the bioavailability of heavy metals. Even a low biochar rate amendment could positively affect soil properties, the bioavailability of heavy metals and crop yields. These results also indicate that a change in soil properties, and especially in pH values, could serve as a main reason for the immobilization of Cd in biochar-treated soils. Loess soils are spreading extensively throughout the world, covering the one-tenth of the global land area. Generally speaking, loess soils are loose in structure, present high porosity and water permeability and have a low agglomerating force and organic matter (Zhu et al., 1983) and thus differ from acidic soils. However, few studies have examined the effects of biochar on the immobilization and bioavailability of heavy metals in loess soils (calcareous soils). Meanwhile, few studies have reported on suitable levels of biochar application in alkaline soils (Al-Wabel et al., 2015), to our knowledge.

Two biochars were prepared at 600 °C from chicken manure and rape straw (CBC and RBC). Pot experiments were conducted to study the effects of CBC and RBC on the soil properties, the distribution of Cd in soil, the uptake of Cd in maize, and maize growth in Cd spiked loess soil. The aims were to identify the feasibility of applying biochars as an alternative for Cd contaminated loess soil. These research results may have various implications for immobilization and remediation using biochars for heavy metal contaminated loess soils.

2. Materials and methods

2.1. Chemicals and materials

Analytical grade $Cd(NO_3)_2$ was purchased from Shanghai Chemical Co., China. Deionized water was used in all of the experiments.

The soil sample (0–20 cm) was collected from a hill on the Lanzhou Jiaotong University campus in China, where few low artemisia plants grow. The sandy loam soil was classified as light sierozem (Zhu et al., 1983). The soil was thoroughly mixed, air dried and strained through a 2 mm sieve. The pH value of the soil was determined as 1:2.5 ratio of soil mass (g) to water volume (mL) using a pH meter (PHS-3C, Electronic and Scientific Instrument Corporation, Shanghai, China). The concentration of background Cd in the soil was determined by HCl-HNO_3-HF-$HClO_4$ digestion and atomic absorbance spectrophotometry (AAS) (China GB/T 1249.3–1999) using Varian Spectrum AA 110/220 (USA). The cation exchange capacity (CEC) value of the soil was determined using a method designed for calcareous soil (China NY/T1121.5–2006). The content of organic matter (OM) was tested via potassium dichromate oxidation spectrophotometry (China HJ615-2011) using a UV-1800 spectrophotometer (Shanghai Spectrum Instrument Co. Ltd., China). The carbonate content in the soil was determined by the CO_2 volume method (China NY/T 86-1988). The soil texture was tested using the gravity meter method (China NY/T 112.3–2006). General properties of the soil studied are listed in Table 1.

Chicken manure and rape straw were collected from henneries and agricultural lands around the city of Lanzhou, respectively. The raw material was rinsed (chicken manure without cleaning) with tap water, dried at 80 °C for 12 h in a drier (Beijing Kewei Yongxing Instrument Co., China), and ground using a grinder (FW100, Tianjin Hauxing Instrument Company, China). The debris were passed through a 0.43 mm sieve and placed into a crucible. The samples were then placed in a muffle furnace (SX2, Shanghai Yuejin Medical Instrument Factory, China) at 600 °C for 4 h to pyrolyze the biomass. The obtained biochars are referred to as CBC and RBC. Their pH, CEC, OM and carbonate values were determined using the same methods as those applied for the soil sample described above. The ash content was tested using the standard method for wood based activated carbon (GB/T 12496.3–1999). An elemental analysis was completed using an elemental analyzer (Vario EL, Germany). C, H, N and S contents were determined directly, and O contents were determined by subtracting C, H, N, S and ash contents from the total biochar mass. The specific surface area was determined using a surface and porosity analyzer (Micromeritics ASAP 2020, USA). The main properties of CBC and RBC are listed in Table 1.

Table 1
Basic properties of soil and biochars.

	Soil	CBC	RBC
pH	8.23	10.16	9.98
CEC (cmol kg^{-1})	5.10	9.14	26.2
OM (g kg^{-1})	9.20	213.52	307.02
Carbonate (mg kg^{-1})	117.32	239.53	61.35
BET specific area (m^2 g^{-1})	8.0321	14.78	17.75
Cd (mg kg^{-1})	0.34		
Soil texture (%)	Grave 12		
	Silt 62.40		
	Clay 25.60		
Ash content (%)		47.85	22.28
Element analysis (%)		C 33.25	C 60.24
		H 0.69	H 1.31
		N 1.89	N 1.04
		S 0.64	S 0.76
		O 15.68	O 14.37
O/C ratio		0.472	0.239

2.2. Pot experiments

The natural soil was spiked using a $Cd(NO_3)_2$ solution, generating a final Cd(II) concentration of 20 mg kg^{-1}, which was chosen according to the occurrence of Cd contaminated loess farmland soils with this average concentration near the research site (Liu, 2005) and the need to examine clearly the effects of biochar on immobilization and bioavailability of heavy metals in soils. The simulated contaminated soil was incubated in the dark for 1 month, being irrigated with deionized water to 70% of the field water holding capacity, to obtain a stable state. The soil sample was then air-dried and strained through a 2 mm sieve. 1 kg of the Cd-contaminated soil was thoroughly mixed with 5 g of a slow-release fertilizer (N: P_2O_5: K_2O = 15: 15: 15) and with CBC or RBC at 1%, 5%, 10% and 15% (w/w) rates. The mixed soil was placed in a 130 mm × 116 mm (height x diameter) pot. A sample with no CBC or RBC addition was prepared as a blank control (CK). Three replicates were prepared per treatment.

The incubation experiments were conducted in a chamber under controlled conditions, i.e., a temperature of 25 °C, average humidity of 40% and 16 h d^{-1} light conditions. Two months later, 6 maize seeds (*Zea mays* L., Longyuan No. 3 obtained from Beijing Kenfeng Longyuan Seed Technology Co. Ltd., China) were sowed in each pot. After 1 week of germination, three seedlings were retained. After the plants had grown for one month, they were harvested and soil samples were collected. The harvested plants were thoroughly rinsed with deionized water; their heights were determined and then they were oven-dried in paper bags at 70 °C until constant weights were achieved. The dried plant samples were ground with a stainless steel mill and stored for chemical analysis. Soil from each pot was air-dried and thoroughly mixed. The air-dried soil was passed through a 2 mm sieve to remove any visible roots. The soil samples were then analyzed for pH, CEC, OM, carbonate and concentrations of Cd using the same methods described above for the nature soil. Soil Cd fractions were