



Short Communication

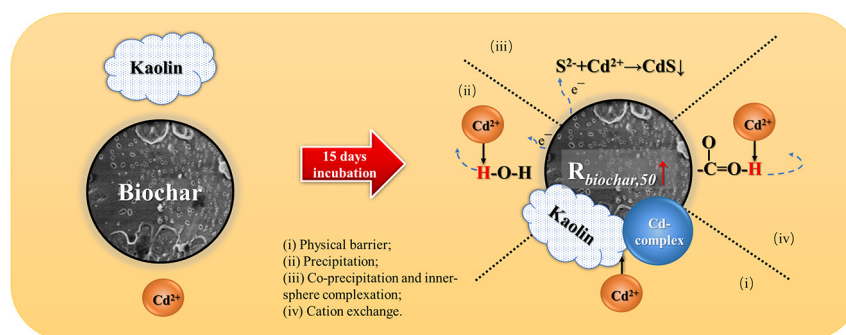
A study of cadmium remediation and mechanisms: Improvements in the stability of walnut shell-derived biochar

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HIGHLIGHTS

- Walnut shell derived biochar is promising for cadmium remediation of soil.
- Walnut shell derived biochar could reduce the mobility of cadmium.
- Both Cd and kaolin could increase the stability of biochar after incubation.
- Mechanisms of stability improvement of biochar were investigated.

GRAPHICAL ABSTRACT



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ABSTRACT

Biochar has been recognized as an efficient soil amendment for cadmium remediation in recent years. In the present study, biochar was prepared using walnut shell, and it was incubated in $\text{Cd}(\text{NO}_3)_2$ and kaolin for 15 days. Different chemical forms of cadmium in kaolin and biochar were determined, and the stability of biochar was evaluated by R_{50} using TGA analysis. It was found that walnut shell derived biochar could reduce the mobility of cadmium. After incubation, the $R_{50, \text{biochar}}$ value increased from 61.31% to 69.57%–72.24%, indicating that the stability of biochar was improved. The mechanisms that initiated improvements in biochar stability were investigated by XPS, XRD and SEM-EDS analysis. The result showed that the enhanced biochar stability is likely due to physical isolation and the formation of precipitates and complexes, formed on the surface or interior of the biochar. The results suggested that walnut shell-derived biochar can be used as a cadmium sorbent for soil remediation.

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1. Introduction

Cadmium is one of the most important contaminants on Earth; it possesses significant toxicity and jeopardizes soil. Traditional methods

for the remediation of Cd contaminated soil, including solidification, bioremediation, stabilization, thermal desorption, electro remediation techniques, soil vapor extraction, soil washing and flushing, have been widely investigated in both laboratory-controlled and field experiments (El-Naggar et al., 2018; Makino et al., 2007; Makino et al., 2006; Makino et al., 2008; Serencam et al., 2008; Tang et al., 2018). Among these techniques, in situ contaminant stabilization using organic amendments, such as lime, biosolid compost and biochar, which could reduce Cd uptake by remodeling the soluble/exchangeable portion into an organic

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bond fraction (Ozdes et al., 2009), exhibited great potential because of cost-effective performance and strong agro-environmental compatibility (Tang et al., 2017).

Walnut shell is a low-cost raw material with a high fixed carbon content (Song et al., 2017). Walnut shell-derived biochar possesses high basicity, large pore volume and surface area, and can easily be separated. Modified walnut shell biochar has been used as a catalyst to remove organic sulfur and arsenic (Song et al., 2017). However, there is a limited amount of research available that focuses on cadmium remediation using walnut shell-derived biochar methods. It was reported that Cd could be immobilized due to the precipitation and formation of anions (such as OH^- , CO_3^{2-} , PO_4^{3-} and SO_4^{2-}) under alkaline conditions (Inyang et al., 2016; Xu et al., 2011). Thus, walnut shell-derived biochar is a promising amendment for the remediation of Cd-contaminated soil.

The stability of biochar was affected by various reactions between soil components and microbes being added to the soil, thus leading to inefficient carbon sequestration processes (Wang et al., 2013). Nevertheless, Clough and Skjemstad (2000) found that organic material was more antioxidant in calcareous soils than in noncalcareous soils, regardless of whether calcium was added to the soil as an amendment or occurred naturally (Clough and Skjemstad, 2000). $\text{Fe}_8\text{O}_8(\text{OH})_8\text{C}_{11.35}$ and $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ were newly formed in biochar, and these compounds could enhance biochar's resistance to oxidation after incubating with FeCl_3 and AlCl_3 for three months (Yang et al., 2016). Thus, it was suggested that the stability of biochar could be improved with soil encapsulation, and its combination with soil minerals facilitated long-term carbon sequestration.

In the present study, walnut shell-derived biochar was incubated with Cd-contaminated soil for 15 d. The stability of biochar was determined by Thermogravimetric Analysis (TGA). The morphology and chemical changes among biochar, Cd and soil were detected by X-ray photoelectron spectroscopy (XPS), X-ray diffractometer (XRD) and energy dispersive spectrometer with scanning electron microscopy (SEM-EDS).

2. Materials and methods

2.1. Materials

Biochar was prepared by walnut shell through slow pyrolysis. The walnut particles were ground to <2 mm and pyrolyzed at 500 °C under an atmosphere of N_2 for 2 h. Elements of C, H, N and S in the biochar were determined by Elemental Analyzer (VARIO MICRO CUBE, Germany). The pH value of biochar was measured by pH detector (EUTECH pH 510, USA) with a solid to water ratio of 1:20 (w/v). The specific surface area and pore size distribution of the biochar was determined by Gas Sorption Analyzer (24/Autosorb-IQ3, China). The properties of walnut shell-derived biochar are listed in Table A.1.

Kaolin ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$) and Cadmium (II) nitrate ($\text{Cd}(\text{NO}_3)_2$) were purchased from Sinopharm Chemical Reagent Company, and kaolin was chosen to represent soil.

2.2. Incubation experiment

The preliminary incubation experiment was conducted in darkened glass containers (with an internal diameter of 66 mm and a height of 90 mm) for a 3-month period at 25 ± 1 °C. It was found that all the results kept stable after 15 d. Thus, in order to observe the short-term potential of biochar a formal incubation experiment was conducted over 15 days. Four different groups were set for incubation: (A) 2.5 g biochar; (B) $\text{Cd}(\text{NO}_3)_2$ solutions mixed with 2.5 g biochar; (C) $\text{Cd}(\text{NO}_3)_2$ solutions mixed with 50 g kaolin; (D) $\text{Cd}(\text{NO}_3)_2$ solutions mixed with 2.5 g biochar and 50 g kaolin. The proportion (5%) of biochar to kaolin was chosen according to an appropriate additive proportion of biochar and the range of actual soil minerals (Li et al., 2013). 20 mL 100 mg/L cadmium nitrate solution was added in group (B), (C) and (D), which

amounted to 16 mg cadmium/kg soil in group (C) and (D). We maintained the moisture content at a 100% maximum water holding capacity by adding deionized water to compensate for daily water loss. Incubation experiments were replicated three times for each group, and the mean values were used for calculations. After incubation, biochar particles were carefully separated by centrifuging at 4000 rpm for 10 min and ultra-sonification.

2.3. Biochar stability measurements

"Stability" is the ability of biochar to resist decomposition when applied to a soil environment. In this study, biochar stability was evaluated by R_{50} during TGA analysis, as proposed by Harvey (Harvey OR, 2012).

$$R_{50, \text{biochar}} = \frac{T_{50, \text{biochar}}}{T_{50, \text{graphite}}} \times 100\%$$

where $T_{50, \text{biochar}}$ and $T_{50, \text{graphite}}$ are the temperatures at which there is a 50% weight loss of biochar and graphite via oxidation, respectively. $T_{50, \text{graphite}}$ is a fixed value, which is 886 °C.

The R_{50} values for biochar, which represent the recalcitrance/carbon sequestration capacity, are divided into Class A ($R_{50} \geq 0.70$), Class B ($0.50 \leq R_{50} < 0.70$) and Class C ($R_{50} < 0.50$) (Gómez et al., 2016).

2.4. Analytical methods

Different chemical forms of cadmium in kaolin and biochar, which include the exchangeable fraction (F1), the carbonate fraction (F2), the iron and manganese oxide fraction (F3), the organic matter fraction (F4) and the residual fraction (F5), were determined following Tessier's method (Tessier et al., 1979).

XPS (AXIS Ultra DLD, Japan) was used to analyze changes in the surface composition of biochar. Calibration of the spectra binding energies was performed with the C1s aliphatic carbon peak at 284.8 eV. XRD (Bruker D8 Advance, Germany) was used to determine the occurrence and properties of crystal mineral formation within the biochar. SEM-EDS (Hitachi S-4800, Japan) was used to determine the morphology and chemical compositions of biochar.

3. Results and discussion

3.1. Effects of kaolin and biochar on the speciation of Cd

Fig. 1 shows the speciation of Cd in group (B), (C) and (D) after a 15-day incubation period. Fractions F1 + F2 + F3 represent the toxic Cd, and fractions F4 + F5 represent the stable state of Cd. Group (D) possesses the lowest F1 + F2 + F3 content and the highest F4 + F5 content, indicating that adding biochar to soil is likely to increase cadmium stability and decrease its toxicity. We propose that biochar is an effective amendment for the remediation of Cd contaminated soil.

Exchangeable forms of Cd (F1) demonstrate sorption-desorption behaviors and processes, which are affected by the ionic composition of water. The percentage of F1 in group (B) and (D) is higher (18.7% and 21.8%) than that in group (C) (14.2%), due to the possibility that cadmium was bound to biochar via surface adsorption and ion exchange (Ren et al., 2017). The carbonate-bound fraction (F2) is susceptible to changes in pH. Due to kaolinite's high buffering capacity, group (C) contained the largest amount of the carbonate-bound fraction. These two forms of Cd (F1 and F2) are both biologically available and easily converted to other forms (Zhang et al., 2017). The Fe/Mn oxyhydroxide phase (F3) controls the bio-availability. Fraction (F3) has an oxide coating, which is thermodynamically active in anoxic environments (Tessier et al., 1979). Group (B) has the highest proportion (25.4%) of fraction F3, whereas group (C) has the lowest proportion (17.7%). This dynamic may exist because phosphates and carbonates in kaolinite curbed the complexation between Cd and Cd oxides (Ren

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