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Short Communication

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

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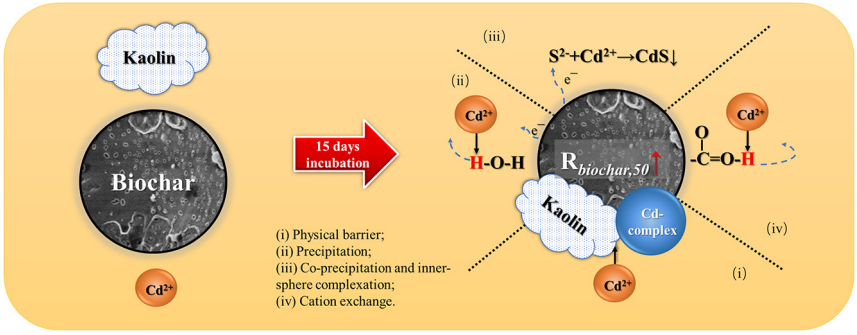
HIGHLIGHTS

- 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 $Cd(NO_3)_2$ 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 $R_{50,\ biochar}$ 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.

1. Introduction

Cadmium is one of the most important contaminates 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). $Fe_8O_8(OH)_8C_{11.35}$ and $AlCl_3 \cdot 6H_2O$ 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 Thermos Gravimetric 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 ($Al2O_3 \cdot 2SiO_2 \cdot 2H_2O$) and Cadmium (II) nitrate ($Cd(NO_3)_2$) 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) $Cd(NO_3)_2$ solutions mixed with 2.5 g biochar; (C) $Cd(NO_3)_2$ solutions mixed with 50 g kaolin; (D) $Cd(NO_3)_2$ 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).

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

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

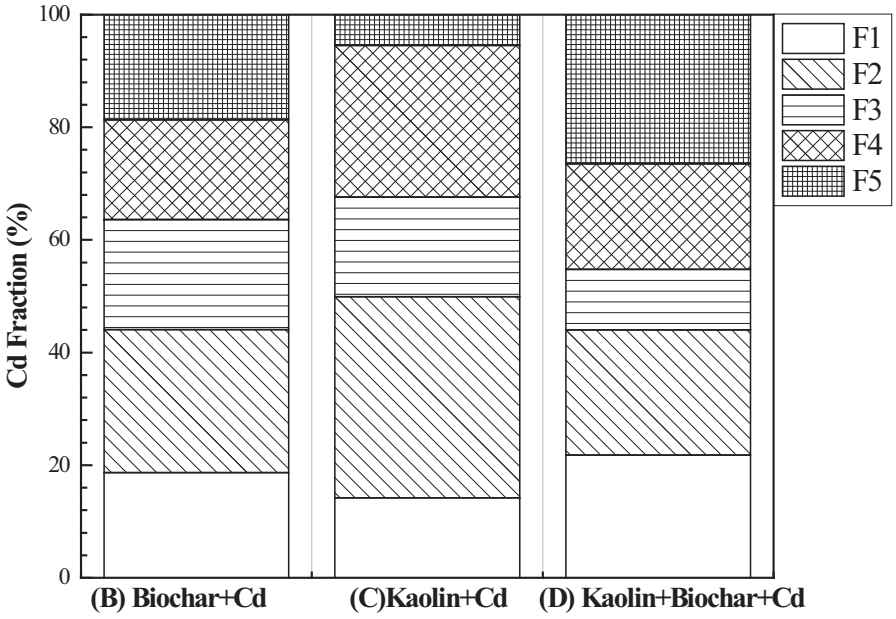


Fig. 1. Speciation of Cd in kaolin and biochar after incubation.

et al., 2017). Although fraction F4 degraded, resulting in Cd release, this process is time-consuming. The residual solid (F5) retains Cd within the crystal structure after the first four fractions (F1, F2, F3 and F4) have been removed.

3.2. Biochar stability improvements

The water and ash content-corrected TGA patterns of biochar, after incubation with Cd and kaolin, are presented in Fig. 2. Temperatures correspond to a loss of biochar (50% weight) via oxidation ($T_{50,\ biochar}$). At the beginning of weight loss processes, there were no obvious differences between groups (A), (B) and (D). We observed large differences between these groups once the hydrolysis temperature rose above 500 °C. The results showed that the $T_{50,\ biochar}$ values for groups (A), (B) and (D) are 543.17 °C, 618.73 °C and 640.05 °C, respectively. R_{50} represented the capacity of recalcitrance (Harvey OR, 2012). Biochar with higher R_{50} values indicated a higher environmental recalcitrance and a higher capacity for carbon sequestration. These biochar samples required a significantly higher input of energy to oxidize a unit of mass. The $R_{50,\ biochar}$ values for group (B) and (D) increased from 61.31% (Class B) to 69.83% (Class B) and 72.24% (Class A), after adding Cd and Cd + kaolin, respectively. The results indicate that the walnut shell-derived biochar is resistant to oxidation. Long-term oxidation resistance was highly enhanced after incubating with Cd and kaolin together.

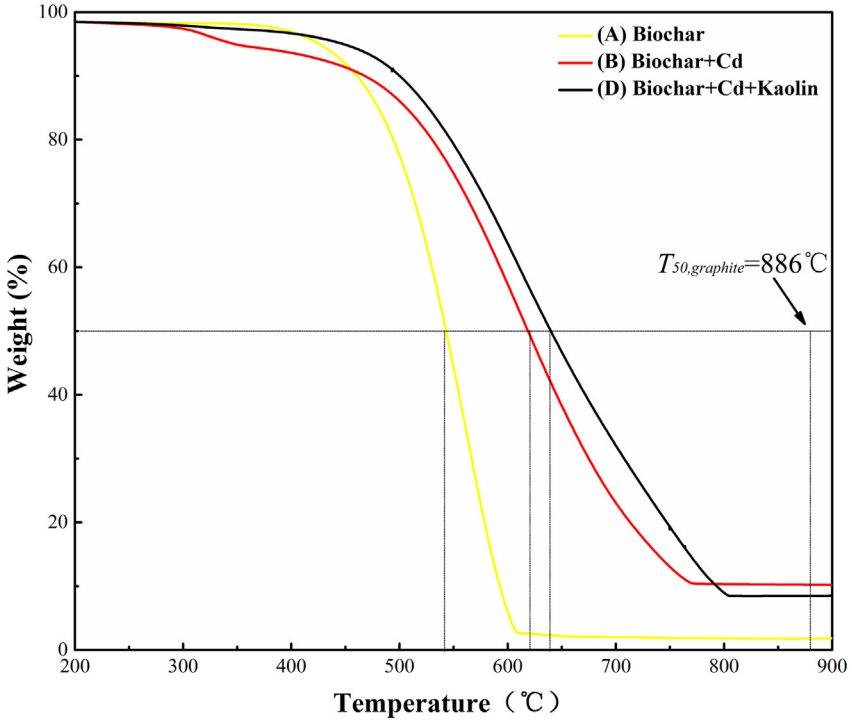


Fig. 2. The thermogravimetric patterns of biochar after incubation.

Obviously, both Cd and kaolin could in turn increase the stability of biochar.

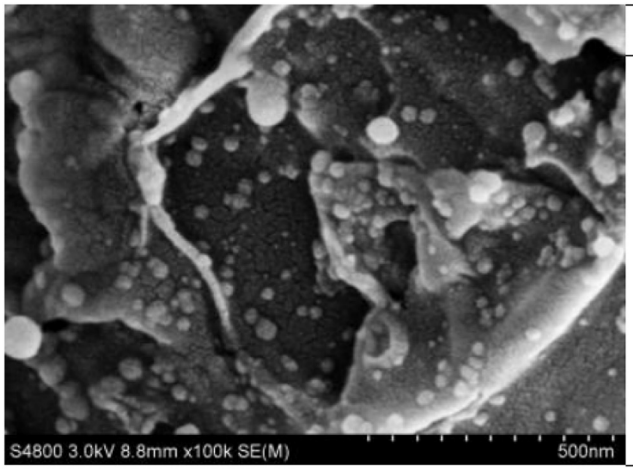
3.3. Mechanisms of the enhanced stability of biochar in soil

SEM images of group (D) (Fig. 3) showed that kaolin surfaces were completely covered by biochar to avoid oxidation. It was reported that new-born complexes would work as a strong obstacle which could keep O_2 from penetrating the interior of the biochar (Li et al., 2014). Thus, synergistic effects between kaolin and biochar could facilitate the efficient remediation of soils affected by Cd pollution.

Biochar was generally oxidized from the surface to interior structure (Spokas et al., 2014). Results from XPS (Table A.2) showed that oxygen-bearing functional groups were abundant in biochar. After biochar incubation, with Cd and kaolin, the relative content, of the group C—C/C═C/C—H, increased; however, the relative content of —COOH decreased. The minimum relative content of C—O was only 21.16%. These results indicated that the interactions between biochar, Cd and kaolin might inhibit the surface oxidation of biochar by preventing C—C/C═C/C—H groups from transforming to C—O and COOH functional groups.

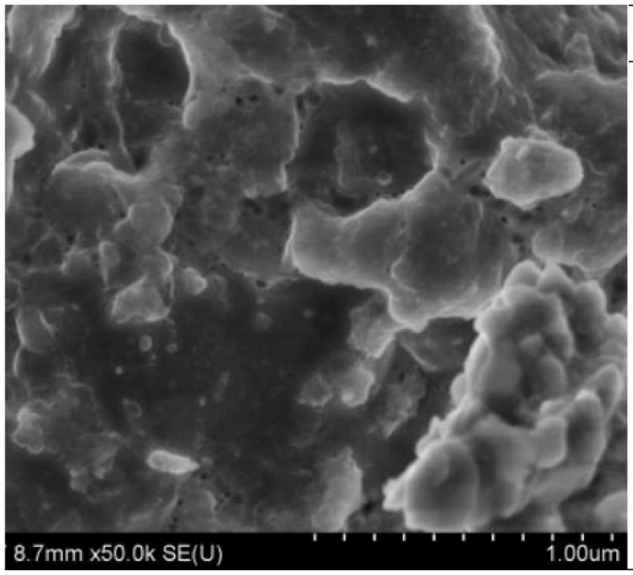
Moreover, the increases in biochar stability might be attributed to the preservation of a biochar-carbon outer layer formed by a soil and Cd complex (Zhao et al., 2014). It was reported that of organometallic complexes (such as Fe—O—C) were generated at the biochar-mineral interface to remove Cd (Shen et al., 2017). The SEM-EDS analysis (Fig. 3) and XRD results (Fig. A) showed that there are occurrences of cadmium carboxylate and cadmium hydroxide in groups (C) and (D). Occurrences of aluminum–cadmium–silicates, cadmium sulfides, cadmium carbonates and aluminum hydroxides were formed in group (D).

Four proposed possible mechanisms that occurred during the interaction between biochar, Cd and kaolin were presented: (i) physical barrier. The kaolinite minerals were physically covered on the biochar surface and were inserted into biochar pores and channels and blocked. (ii) Precipitation. It was reported that cadmium in soil might form hydroxide sediments, under alkaline conditions induced by biochar, confirming our results (Kim et al., 2013; Xu et al., 2017). In this study, pH value in soil solution is 8.121. Providing additional cation sorption sites is insufficient. However, Cd was possibly immobilized as $Cd(OH)_2$. (iii) Co-



Element	Wt (%)	Atomic (%)
C K	51.28	69.66
O K	25.92	26.44
Si K	0.16	0.09
Cl K	0.31	0.14
K K	1.09	0.45
Ca K	0.48	0.19
Cd L	20.76	3.01
Total	100	

(a)



Element	Wt (%)	Atomic (%)
C K	48.27	58.67
O K	38.69	35.3
Al K	5.66	3.06
Si K	4.9	2.55
Ca K	0.12	0.04
Ti K	0.23	0.07
Fe K	0.15	0.04
Cd L	1.99	0.26
Total	100	

(b)

Fig. 3. (a) SEM-EDS analysis of biochar in group (C) (scale bar = 500 nm). (b) SEM-EDS analysis of biochar in group (D) (scale bar = 1 μm).

precipitation and inner-sphere complexation. In soil, sulfur promoted the production of sulfhydryl protein, with the chelation of a portion of Cd (Zhang et al., 2014). This incited the precipitation of CdS. (iv) Cation exchange (e.g., cadmium carboxylate). The content of the functional group —COOH in the original biochar, was more than the incubated biochar, a possible consequence of Cd absorption to carboxylate functional groups.

4. Conclusion

As a sustainable, rapid and effective soil amendment for cadmium remediation, walnut shell-derived biochar showed its promising prospect. It could reduce the mobility of cadmium, whereas both Cd and kaolinite could in turn increase the stability of biochar after short periods of incubation. Physical barrier, precipitation, co-precipitation and inner-sphere complexation, and cation exchange might be the four main mechanisms that control improvements in the stability of walnut shell-derived biochar for soil remediation.

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2018.04.215.

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