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Application potential of biochar in environment: Insight from degradation of biochar-derived DOM and complexation of DOM with heavy metals

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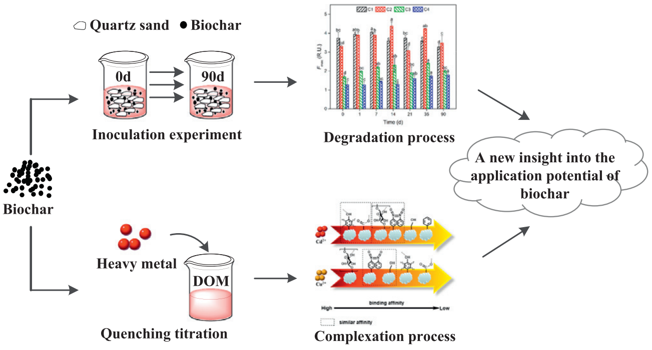
HIGHLIGHTS

- The biochar-derived DOM has a high aromaticity, stability, and resistance.
- Environmental risk of Cu cannot be neglected while using biochar in polluted soil.
- Binding behaviors of DOM with heavy metals was analyzed using 2DCOS of SF and FTIR.
- The work enhances the knowledge of behavior of Cd and Cu in biochar-amended soils.

GRAPHICAL ABSTRACT



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ABSTRACT

Biochar-derived dissolved organic matter (DOM) is important for determining the application potential of biochar in soil remediation. However, little is known about the degradation behavior of biochar-derived DOM and its interaction with heavy metals. Here, incubation experiments combined with quenching titration experiments, which analyzed by spectroscopic technology and chemometric method, were conducted to reveal such behaviors and mechanisms. Ultraviolet–visible (UV–Vis) spectra showed that high aromatic and hydrophobic fractions were enriched in biochar-derived DOM and enhanced during the cultivation process, thus the biochar-derived DOM may retain a high aromaticity, stability, and resistance. However, the environmental risk of Cu caused by the increase of DOM hydrophobicity cannot be overlooked while applying biochar to polluted soil. One fulvic-like (C1), one protein-like (C2) and two humic-like (C3, C4) substances were identified from biochar-derived DOM by using parallel factor analysis of excitation-emission matrix. Additionally, the fluorescence intensity variations of these components in DOM offered an additional interpretation for the observations from UV–Vis spectra. Two-dimensional correlation spectroscopy revealed that Cd binding to biochar-derived DOM first occurred in the protein- and fulvic-like fraction while protein- and humic-like substances had a stronger affinity for Cu. Furthermore, both phenolic and carboxyl groups firstly participated in the binding process of Cd with biochar-derived DOM, while polysaccharide gave the fastest response to Cu binding. These results clearly demonstrated the differences in specific heavy metal binding features of individual fluorescent substances and functional

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Abbreviations: DOM, dissolved organic matter; UV–Vis, ultraviolet–visible; EEM, excitation-emission matrix; $SUVA_{254}$, specific UV-absorbance values at 254 nm; $SUVA_{260}$, specific UV-absorbance values at 260 nm; PARAFAC, parallel factor; SF, synchronous fluorescence; FTIR, Fourier transform infrared; 2DCOS, two-dimensional correlation spectroscopy; DOC, dissolved organic carbon; Ex, excitation; Em, emission; R.U., Raman units; F_{max}, maximum fluorescence intensity; ANOVA, one-way analysis of variance.

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groups in biochar-derived DOM and contribute to improving the application effect of biochar in a multi-heavy metal polluted soil system.

1. Introduction

With the rapid development of industry and agriculture, soil heavy metal pollution has become a severe problem (Bolan et al., 2014; Zhao et al., 2015). The control and remediation of heavy metal pollution is utmost necessary. Biochar, a black carbon-rich material, is produced from the pyrolysis of organic biomasses (e.g. agricultural and forest residues) under limited oxygen supply (Lehmann, 2007; Lehmann et al., 2011). Recently, biochar has been recommended as a soil amendment to improve soil fertility and crop yields (Graber et al., 2010) and remediate heavy metal contaminated soil (Beesley et al., 2014; Zhai et al., 2018). Noteworthily, an increasing number of biochar-derived dissolved organic matter (DOM) will be taken into soil while gaining the above benefits of biochar application (Beesley et al., 2010), which may have significant influence in respect of the application potential of biochar in soil. One of the reasons is the interaction of biochar-derived DOM with heavy metals (Soja et al., 2018; Yuan et al., 2017). Biochar-derived DOM, the easily mineralizable and extractable carbon portion released from biochar, is a heterogeneous mixture of organic compounds with highly reactive functional group (Chen et al., 2013; Li et al., 2018; Li et al., 2017). It can directly participate in the complexation of heavy metals depending on its high aromatic compounds and abundant organic functional groups like carboxyl and phenol (Chen et al., 2015; Li et al., 2017; Soja et al., 2018). Through the process of complexation, biochar-derived DOM may influence metal speciation, thus changing the toxicity and bioavailability of heavy metals in soils (Soja et al., 2018). Therefore, focusing in depth on the interaction between biochar-derived DOM and heavy metals has important implications for the assessment of risks associated with the use of biochars.

The interaction characteristics between heavy metals and DOM are highly dependent on the structure and composition of biochar-derived DOM which are closely related to the feedstock material, pyrolytic conditions (e.g., temperature and residence time) (Jamieson et al., 2014), and environmental conditions (e.g., pH and temperature) (Li et al., 2017). Besides, microbial degradation plays an important but still not well understood role in the compositional changes of biochar-derived DOM, although it strongly affects the fate of heavy metals. Interestingly, aromatic carbon is the dominant macromolecular structure in biochar, thus making it exists stably in soil for long periods (Warnock et al., 2007). It is still unclear whether DOM released from biochar also has a high aromaticity and stability, which makes it more resistant to degradation over time. To better understand the characteristic and degradation behavior of biochar-derived DOM, a series of incubation experiments were performed in this work. Furthermore, investigating the interaction mechanisms between heavy metals and DOM, combined with the knowledge of degradation process of biochar-derived DOM, may be a time- and labor-saving method to predict risk associated with the use of biochars. To date, studies mainly focused on the redox-mediated reactions between heavy metals and biochar-derived DOM, but not on the complexation mechanism (Dong et al., 2014; Yuan et al., 2017). Additionally, because of the extreme heterogeneity of DOM constituents (Abdulla et al., 2010; Xu et al., 2013), a more in-depth understanding of the complexation process of heavy metals with DOM remains a challenge.

Ultraviolet–visible (UV–Vis) absorption and excitation-emission matrix (EEM) spectroscopy would be a valid alternative to explore the heterogeneity of DOM composition (Jamieson et al., 2014; Tang et al., 2016). Ultraviolet-visible absorption is a valid alternative to explore the characterization of DOM by several spectra parameters (Gao et al., 2017). Specific UV-absorbance values at 254 nm ($SUVA_{254}$) value is especially related to C=O and C=C double bonds of aromatic C, which indicates the degree of aromaticity in DOM (Cerdán et al., 2016; Tang et al., 2016); specific UV–Vis absorption at 260 nm ($SUVA_{260}$) value allows for the estimation of the proportion of the hydrophobic components (Dilling and Kaiser, 2002). Additionally, EEM spectroscopy can quickly collect and provide general information regarding the fluorescence properties of DOM, however, clear peak overlapping problems in the original EEM spectra usually hamper the quantitative understanding of DOM composition (Bai et al., 2017; Sun et al., 2016). Parallel factor (PARAFAC) analysis can decompose the complex EEM spectra into separate fluorescence components and weaken the interference among fluorescent compounds, thus having become a sensitive and reliable approach for qualitatively and quantitatively describing the specific fluorescence information of DOM (Vera et al., 2017; Wu et al., 2012). For these appealing features, the characteristic changes of dominant fluorescent DOM components during cultivation of biochar can be obtained by combining EEM spectroscopy with PARAFAC analysis. To determine the binding behavior of heavy metals to DOM, optical spectroscopy technology combined with quenching titration has been recommended due to the different responses among different structures and components of DOM to metal interaction (Chen et al., 2015; Yamashita and Jaffé, 2008). Synchronous fluorescence (SF) and Fourier transform infrared (FTIR) spectroscopy can provide comprehensive insight into the fluorescent substances and functional groups in DOM, respectively (Chen et al., 2015; Li et al., 2014). However, due to highly overlapping responses from the extreme heterogeneity of DOM constituents, the availability of using traditional 1-dimensional techniques to probe the binding mechanisms of heavy metals with DOM is limited (Abdulla et al., 2010; Chen et al., 2015). Fortunately, two-dimensional correlation spectroscopy (2DCOS) analysis helps to resolve overlapped peaks and improve the spectral resolution by extending spectra in the second dimension and offering additional information on the sequencing of metal-induced peak changes (Li et al., 2017; Song et al., 2018). To our knowledge, 2DCOS analysis coupled with SF and FTIR spectroscopy has not been employed to quantify the heterogeneous binding characteristics between heavy metals and biochar-derived DOM.

Therefore, the objectives of this work are (1) to determine whether the biochar-derived DOM is too recalcitrant to be decomposed during cultivation of biochar; and (2) to provide an in-depth understanding of the interaction mechanisms of heavy metals with biochar-derived DOM regarding the binding capacities, binding sites, and binding order. Finally, this study will provide a new insight into cognition of the feasibility of biochar in possible environmental applications. For the above purposes, Cd and Cu, which are widely present in contaminated soil with high toxicity and widely studied, were selected as research objects (Wu et al., 2012; Zhang et al., 2017; Zhao et al., 2015).

2. Materials and methods

2.1. Material collection and biochar preparation

Rice straw, used for biochar preparation, was collected in paddy fields located in the outskirt of Changsha, China in the fall of 2015 (right after harvest). The straw was rinsed with tap and ultrapure Milli-Q water, air-dried, and ground to pass through a 60-mesh sieve. The ground rice straw was placed in a ceramic crucible with a lid and then pyrolyzed in a muffle furnace (Thermo Scientific, USA) under an N_2 atmosphere with the temperature rising to 450 °C at a rate of 6.5