



Contents lists available at ScienceDirect

Environmental Pollution

journal homepage: www.elsevier.com/locate/envpol

Insights into the attenuated sorption of organic compounds on black carbon aged in soil[☆]

Lei Luo^{a,*}, Jitao Lv^a, Zien Chen^a, Rixiang Huang^b, Shuzhen Zhang^a

^a State Key Laboratory of Environmental Chemistry and Ecotoxicology, Research Center for Eco-Environmental Sciences, The Chinese Academy of Sciences, Beijing, 100085, China

^b School of Earth and Atmospheric Sciences, Georgia Institute of Technology, Atlanta, 30332, USA

ARTICLE INFO

Article history:

Received 9 June 2017

Received in revised form

28 August 2017

Accepted 6 September 2017

Available online xxx

Keywords:

Biochar

Sorption

Surface functionality

Surface porosity

Organic compound

ABSTRACT

Sorption of organic compounds on fresh black carbons (BCs) can be greatly attenuated in soil over time. We examined herein the changes in surface properties of maize straw-derived BCs (biochars) after aged in a black soil and their effects on the sorptive behaviors of naphthalene, phenanthrene and 1,3-dinitrobenzene. Dissolved fulvic and humic acids extracted from the soil were used to explore the role of dissolved organic carbon (DOC) in the aging of biochars. Chromatography analysis indicated that DOC molecules with relatively large molecular weight were preferentially adsorbed on the biochars during the aging processes. DOC sorption led to blockage of the biochar's micropores according to N₂ and CO₂ adsorption analyses. Surface chemistry of the biochars was also substantially modified, with more O-rich functional groups on the aged biochars compared to the original biochars, as evidenced by Near-edge X-ray absorption fine structure (NEXAFS) spectroscopy and X-ray photoelectron spectroscopy (XPS) analyses. The changes in both the physical and chemical surface properties of biochars by DOC led to significant attenuation of the sorption capacity and nonlinearity of the nonionic organic compounds on the aged biochars. Among the tested organic compounds, phenanthrene was the most attenuated in its sorption by the aging treatments, possibly because of its relatively large molecular size and hydrophobicity. The information can help gain a mechanistic understanding of interactions between BCs and organic compounds in soil environment.

© 2017 Elsevier Ltd. All rights reserved.

1. Introduction

Black carbons (BCs) from natural and anthropogenic sources are an important carbon pool and involved in important biogeochemical processes in soil, including the immobilization of inorganic and organic pollutants because of their excellent sorption property (Lohmann et al., 2005; Ghosh et al., 2011; Hale et al., 2011). Many studies have noticed that the sorption of organic compounds, particularly nonionic ones, on BCs was greatly attenuated in soils and sediments over time (Ghosh et al., 2011; Hale et al., 2011; Oen et al., 2012; Khorram et al., 2017). The attenuation presents a fundamental challenge for assessing the effectiveness of BCs in contaminant immobilization, because evaluation based solely on the physicochemical properties of pristine BCs may be inaccurate

(Oen et al., 2012; Teixidó et al., 2013). Therefore, understanding the attenuated sorption mechanisms is critical for predicting the fates of nonionic organic compounds (NOCs) in soil environment with BCs presence.

The surface area and pore size distribution of carbonaceous materials are an important property that affects their sorption of organic compounds (Zhu et al., 2005). Several studies demonstrated that the presence of dissolved organic carbon (DOC) could cause significant reduction in the surface area and pore volume of activated carbons and BCs and their sorption capacity for organic compounds (Kilduff and Wigton, 1999; Pignatello et al., 2006; Xiao et al., 2012). Researchers also observed that aged BCs exhibited obviously decreased sorption capacity for organic compounds in contaminated soil because of the competition for sorption sites between the contaminants and soil organic matter (Cornelissen and Gustafsson, 2006; Nguyen et al., 2007; Oen et al., 2012). These evidences suggest that blockage/filling of pores and reactive sites on BCs' surface contribute to the attenuated organic compound sorption on aged BCs in the environment (Kilduff and

[☆] This paper has been recommended for acceptance by Dr. Yong Sik Ok.

* Corresponding author.

E-mail address: leiluo@rcees.ac.cn (L. Luo).

Wigton, 1999; Oen et al., 2012; Wang et al., 2017).

However, some studies showed BCs with relatively low surface area and porosity do not necessarily have small sorption capacity for organic compounds, suggesting that surface area and porosity are not the only factor controlling the sorption property of BCs (Nguyen et al., 2007; Chen et al., 2008; Mohan et al., 2014; Wang et al., 2017). Surface functionality also plays an important role in organic compound sorption on carbonaceous materials (Zhu et al., 2005; Chen et al., 2008). Recent studies indicated that soil organic matter including DOC can modify the surface chemical composition of soil and affect the sorption of NOCs in soil (Luo et al., 2010; Mitchell and Simpson, 2013). Surface functionality of BCs in the environment can also be modified by DOC (Cheng and Lehmann, 2009) since BCs were believed to have strong affinity for DOC (Kasozzi et al., 2010; Xiao et al., 2012). We thus hypothesize that soil DOC can modify both the physical and chemical properties of BC surfaces and affect their sorption of NOCs. The process remained poorly understood (Zhang et al., 2016) because of the technical challenges in the characterization of BC surface properties. An in-depth understanding of the mechanisms underlying aged BCs' attenuated sorption of organic compounds necessitates a systematic characterization of BCs using advanced environmental molecular techniques, since macroscopic measurements alone cannot probe the detailed molecular processes.

The objectives of this study are to systematically characterize the surface properties (porosity and functionality) of BCs aged in soil under abiotic conditions, and to explore the mechanism underlying the attenuated sorptive behaviors of BCs toward organic compounds during the aging processes. Specifically, we hope to elucidate (i) how soil DOC affects the pore size distribution of BCs, (ii) how functional groups on BC surfaces change after aged in soil, and (iii) how these changes relate to the attenuated sorption of organic compounds on BCs. To this end, X-ray photoelectron spectroscopy (XPS) and synchrotron radiation-based C 1s near-edge X-ray absorption fine structure (NEXAFS) spectroscopies were used, because they are sensitive to a sample depth of approximately 10 nm and therefore ideal to probe the surface functionality information (Cheng et al., 2006; Mukome et al., 2014). Two biochar samples, produced at 300 °C and 500 °C using maize straw as the feedstock, were used as model BCs because of their dramatic differences in porosity and functional group composition (Luo et al., 2015). Three NOCs, namely naphthalene (NAP), phenanthrene (PHE) and 1,3-dinitrobenzene (DNB), were selected as model organic compounds to reveal the effects of molecular properties (polarity and size) on the sorption.

2. Materials and methods

2.1. Materials

Two biochar samples, prepared from maize (*Zea mays* L) straw by pyrolysis for 1 h under N₂ atmosphere at 300 °C and 500 °C, respectively, as described previously (Luo et al., 2015), were used as sorbents. The samples are hereafter referred to as B300 and B500. A black soil (Mollisol), with organic carbon and DOC contents (extracted with deionized water at a soil-to-water ratio of 1:20) of 2.62% and 851 mg/kg, respectively, was used for aging treatments. Fulvic acid (FA) and humic acid (HA), extracted from the black soil according to the standard procedures recommended by the International Humic Substance Society, were used as DOC. Naphthalene (NAP, >99%), phenanthrene (PHE, >98%) and 1,3-dinitrobenzene (DNB, >98%) were obtained from Acros Organics and used as received.

To examine the effect of DOC on the surface properties of biochars during aging, the produced biochar particles were treated as

follows. (i) DOC removal: B300 or B500 was washed repeatedly with deionized water at a solid-to-solution ratio of 10.0 g biochar/L, constantly stirred for 6 h each time and then separated through 0.45-μm mixed cellulose acetate filters until the authigenic DOC in the biochars was below 10 mg/kg. After the washing, the biochar samples collected from the filters were freeze-dried, and subsequently equilibrated in deionized water with 100 mg/L NaN₃ (used to inhibit microbial activity) for 30 days. (ii) Aging in FA/HA: the B300 and B500 were equilibrated with the soil-extracted FA or HA at a concentration of 100 mg C/L with 100 mg/L NaN₃ at a solid-to-solution ratio of 10.0 g biochar/L for 30 days at pH 6.5 and then separated via filtration. The supernate was analyzed for DOC content and molecular weight distribution using Phoenix 8000 TOC analyzer (Tekmar-Dohrmann, USA) and high performance size exclusion chromatography (Zhou et al., 2000), respectively. (iii) Aging in soil and OC-removed soil with 30% H₂O₂ (Luo et al., 2008): biochar particles (0.25–1.0 mm) were added (at 0.5% w/w) to the black soil and H₂O₂-treated black soil (pass through 0.25 mm sieve to allow the separation of biochar particles from the soil through sieving after the aging) and aged at 25 °C and 75% of water holding capacity for 30 days. The original soil was not specifically sterilized and 100 mg/L NaN₃ was added during the aging. After the aging incubation in the dark, the separated biochar particles were rinsed with deionized water and then freeze-dried for following characterization and sorption experiments.

2.2. Carbon 1s NEXAFS spectroscopy

Carbon 1s NEXAFS spectroscopy analysis for biochar samples as well as FA, HA standards was conducted at the beamline 08U1A at Shanghai Synchrotron Radiation Facility and the beamline 4B7B at Beijing Synchrotron Radiation Facility. Samples were mixed in water at 5 wt%, then loaded on gilded silicon wafers and air-dried to fix the samples onto the wafers. All C 1s NEXAFS spectra in total electron yield detection mode were recorded in the energy range of 275–330 eV. The spectra were normalized to unity around 300 eV position to prevent spectral dependence on the total C content (Mukome et al., 2014). In order to compare the functional groups of biochars under the effect of aging treatments, a least-squares fitting scheme was applied to semi-quantitatively deconvolute the normalized spectra in the range 284–290 eV. The scheme was based on six Gaussian peaks (at ~284.3, ~285.1, ~286.3, ~287.2, ~288.2, and ~289.3 eV) with full width at half maximum set at 0.4 eV (Tables S1 and S2 in the Supplementary Information (SI) for the assignment) and an arctangent function for the ionization step at 290.5 eV (full width at half maximum set at 1 eV). Only the discrete part of the spectra (284–290 eV) was utilized in the spectral deconvolution due to peak broadening and overlapping that occurs beyond 290 eV. The sum of total areas under the Gaussian peaks was set to 100%. The error in the relative proportion of various functional groups derived from the Gaussian function was <3% using the procedure.

2.3. X-ray photoelectron spectroscopy

XPS was used to compare the surface functionality of biochars following different aging treatments. Particularly, biochars aged in soil were analyzed in two forms: unaltered and finely-grounded, with the first presenting mostly the surface groups and the latter exposing both exterior and interior surface groups (Cheng et al., 2006). XPS analysis was conducted using an Axis Ultra Imaging X-ray Photoelectron Spectrometer (Kratos, UK) with monochromatic Al K α radiation (1486.7 eV) operated at 180 W. High energy resolution scan spectra of C1s and O1s were recorded in 0.1 eV steps with a pass energy of 40 eV. A nonlinear least-squares

Download English Version:

<https://daneshyari.com/en/article/8857688>

Download Persian Version:

<https://daneshyari.com/article/8857688>

[Daneshyari.com](https://daneshyari.com)