



Isolation and characterization of biochar-derived organic matter fractions and their phenanthrene sorption[☆]

Jie Jin^{a, b}, Ke Sun^{b, *}, Wei Liu^a, Shiwei Li^a, Xianqiang Peng^a, Yan Yang^b, Lanfang Han^b, Ziwèn Du^c, Xiangke Wang^a

^a College of Environmental Science and Engineering, North China Electric Power University, Beijing, 102206, China

^b State Key Laboratory of Water Environment Simulation, School of Environment, Beijing Normal University, Beijing, 100875, China

^c College of Environmental Science and Engineering, Beijing Forestry University, Beijing, 100083, China

ARTICLE INFO

Article history:

Received 10 November 2017

Received in revised form

26 January 2018

Accepted 5 February 2018

Keywords:

Biochar

Biochar-derived organic matter

Sorption

Phenanthrene

ABSTRACT

Chemical composition and pollutant sorption of biochar-derived organic matter fractions (BDOMs) are critical for understanding the long-term environmental significance of biochar. Phenanthrene (PHE) sorption by the humic acid-like (HAL) fractions isolated from plant straw- (PLABs) and animal manure-based (ANIBs) biochars, and the residue materials (RES) after HAL extraction was investigated. The HAL fraction comprised approximately 50% of organic carbon (OC) of the original biochars. Results of XPS and ¹³C NMR demonstrated that the biochar-derived HAL fractions mainly consisted of aromatic clusters substituted by carboxylic groups. The CO₂ cumulative surface area of BDOMs excluding PLAB-derived RES fractions was obviously lower than that of corresponding biochars. The sorption nonlinearity of PHE by the fresh biochars was significantly stronger than that of the BDOM fractions, implying that the BDOM fractions were more chemically homogeneous. The BDOMs generally exhibited comparable or higher OC-normalized distribution coefficients (K_{OC}) of PHE than the original biochars. The PHE $\log K_{OC}$ values of the fresh biochars correlated negatively with the micropore volumes due to steric hindrance effect. In contrast, a positive relationship between the sorption coefficients (K_d) of BDOMs and the micropore volumes was observed in this study, suggesting that pore filling could dominate PHE sorption by the BDOMs. The positive correlation between the PHE $\log K_{OC}$ values of the HAL fractions and the aromatic C contents indicates that PHE sorption by the HAL fractions was regulated by aromatic domains. The findings of this study improve our knowledge of the evolution of biochar properties after application and its potential environmental impacts.

© 2018 Elsevier Ltd. All rights reserved.

1. Introduction

Recently, soil application of biochar has attracted great attention in agricultural practices to improve soil fertility and to mitigate climate change through soil C sequestration (Lehmann, 2007; Reisser et al., 2016; Rombolà et al., 2015; Yoshizawa, 2016). With the increasing recognition of biochar as a potential means for soil remediation, there is an urgent need to examine the fate of biochar after application, as it would play vital roles in the biogeochemical cycle of soil organic carbon (OC) as well as the environmental behaviors of nutrients and contaminants in soils and aquatic systems

(Gibson et al., 2016; Harvey et al., 2016; Jin et al., 2017b; Qu et al., 2016).

In evaluating the long-term environmental significance of biochar in soil, it is crucial to have an understanding of the evolution of its physicochemical properties after application (Harvey et al., 2016). There is a general consensus that physicochemical heterogeneity of fresh biochar is mainly controlled by source material and the production conditions (Ahmad et al., 2014; Jin et al., 2014; Lehmann and Joseph, 2015). Once it has been applied into soils, biochar would undergo alterations in physicochemical properties with time (Hale et al., 2011; Rechberger et al., 2017). Many previous studies have detected such alterations of biochar, such as fragmentation to smaller particles, deposition of minerals and natural organic matter (NOM), decrease in pore availability and poly-aromatic ring size, and concentration of polar groups (Cheng et al., 2008; Ghaffar et al., 2015; Rechberger et al., 2017; Shi et al., 2015;

[☆] This paper has been recommended for acceptance by B. Nowack.

* Corresponding author.

E-mail address: sunke@bnu.edu.cn (K. Sun).

Singh et al., 2012). These studies examined the evolution of biochar's physicochemical properties by considering biochar materials as integral particles. However, with weathering, biochar will release fulvic acid-like (FAL) as well as poly aromatic humic acid-like (HAL) molecules (Hiemstra et al., 2013; Mao et al., 2012; Shindo and Nishimura, 2016). This indicates that biochar materials can be actively involved in the pedogenic process and can eventually become components of soil organic matter (SOM) (Knicker, 2011). Using the classic fractionation method of SOM recommended by the International Humic Substances Society (IHSS) to obtain fulvic acid (FA) and humic acid (HA) fractions, not only geologically formed NOM fractions but also biochar-derived organic matter (BDOM) fractions can be isolated from soils (Hiemstra et al., 2013; Mao et al., 2012). Specifically, in Japanese Andosols, the contribution of pyrogenic HA derived from charred plant residues to HA in the whole soils was in the range of 12–44% (Shindo and Nishimura, 2016). Any consideration of the environmental behaviors and impacts of biochar must consider the physicochemical properties of these BDOM fractions, which, however, are still largely unknown.

Moreover, biochar is well known as an effective environmental sorbent to retain hydrophobic organic compounds (HOCs) (Cornelissen et al., 2005; Hale et al., 2011; Jin et al., 2017a). The aforementioned incorporation of BDOMs into soils requires insight into the BDOMs-HOC interactions. Derived from biochar, BDOM fractions may show sorption properties for HOCs similar to biochar. It is generally accepted that biochar's very high affinity and capacity for sorbing HOCs is primarily due to its hydrophobic and nanoporous character (Ahmad et al., 2014; Lehmann and Joseph, 2015). Previous studies also found that the aromatic moieties of biochar made significant contributions to the overall sorption of HOCs (Ahmad et al., 2014; Sander and Pignatello, 2005; Zhu and Pignatello, 2005). Therefore, it is reasonable to assume that the micropores and aromatic components of BDOM fractions will regulate their sorption of HOCs.

In the present study, HAL fractions were extracted from biochars produced from plant straws and animal manures at different temperatures. The physicochemical properties of the HAL fractions and the residue (RES) materials after HAL extraction were investigated. The sorption of phenanthrene (PHE), a typical representative of HOCs, by these BDOM fractions was examined. The major objectives of this study were to (1) determine the physicochemical properties of biochar-derived HAL and RES fractions, (2) quantify the sorption coefficients of PHE to these BDOMs, and (3) investigate the underlying sorption mechanisms of BDOMs.

2. Material and methods

2.1. Chemicals and materials

Pure analytical grade (>98%) standards and radiochemicals (isotopic purity = 98%) of PHE were obtained from Sigma-Aldrich Chemical Co. (USA). Methanol was purchased from Merck Co. (Germany) in HPLC grade. All other reagents were obtained from Beijing Chemical Reagent Co. (China) in analytical grade. Five biomass input materials were selected to produce biochars: wheat straw, maize straw, swine manure, cow manure, and chicken manure. The feedstocks were oven-dried at 80 °C and ground to <1 mm. Subsequently, the ground feedstocks were placed in ceramic pots, covered with lids, and carbonized at specified temperatures (i.e., 300, 450, and 600 °C) for 1 h using a muffle furnace at 10 °C/min under oxygen-limited conditions. After cooling to

room temperature inside the furnace, the biochars were treated with 0.1 M of HCl to remove some soluble salts, carbonate, and dissolved organic matter. Next, the biochars were flushed by deionized water, freeze-dried, gently ground, and passed through a 0.25-mm sieve.

Chemical oxidation, which can provide an indication of hundreds to thousands of years of natural aging processes in soils (Hale et al., 2011), was used to artificially age biochars. The biochars were suspended in 25% HNO₃ (1:30, m/v) at a 1:30 solid/liquid ratio. The flasks containing the mixtures were heated under reflux at approximately 90 °C for 4 h (Shindo and Honma, 1998). After cooling, the HNO₃-treated residues of biochar were collected by centrifugation, washed thoroughly until neutral pH was attained, and freeze-dried for subsequent use. Next, the residues were mixed with 0.1 M of NaOH solution at a 1:10 solid/liquid ratio in a sealed flask under ambient conditions. After each flask had been shaken for 24 h, the suspension was centrifuged at 3000 g for 30 min. The supernatant was acidified (pH = 2 with 6 M of HCl) to separate the pyrogenic HAL precipitate from the soluble FAL fraction. The retained material after NaOH extraction was collected as the RES fraction. The isolated BDOM fractions were flushed five times with deionized water, freeze-dried, gently ground to pass through a 0.25-mm sieve, and stored until further use. The original biochars are hereafter referred to as SWH, SMA, MSW, MCW, and MCH according to the feedstock sources (wheat straw, maize straw, swine manure, cow manure, and chicken manure, respectively). Their BDOM fractions were named as SWH-HAL and SWH-RES, SMA-HAL and SMA-RES, MSW-HAL and MSW-RES, MCW-HAL and MCW-RES, and MCH-HAL and MCH-RES, respectively. The biochars produced from plant straws and animal manures were named as PLAB and ANIB, respectively.

2.2. Sorbent characterization

Bulk elemental C, N, H, and O abundances of the biochars and their BDOM fractions were determined using an Elemental Analyzer (Elementar Vario ELIII, Germany). Ash contents were measured by combustion at 750 °C for 4 h. X-ray photoelectron spectroscopy (XPS) was conducted using an ESCALAB 250 XPS (Thermo Scientific, USA) spectrometer with a monochromatic Al K α radiation source. Peak deconvolutions of high resolution C1s spectra were analyzed using the Gaussian–Lorentzian sum function (Avantage software, Thermo Scientific), and the resolved peaks were C-C at 284.9 eV, C-O at 286.5 eV, C=O at 287.9 eV, and COO at 289.4 eV. The contents of the surface acidic functional groups of the BDOM fractions were determined using Boehm's titration. Briefly, 0.1 g of BDOM sample was immersed into 20 mL 0.01 M NaHCO₃, Na₂CO₃, and NaOH solutions, respectively. The mixtures were shaken for 24 h to reach the equilibration and then carefully filtered. Next, 10 mL of aliquot from each filtrate was titrated with 0.01 M HCl solution to determine the contents of various acidic groups, including carboxylic, lactonic, and phenolic groups. The ¹³C nuclear magnetic resonance (NMR) spectra of the samples were obtained with an AVANCE 300 (Bruker, Germany) using the cross-polarization magic angle spinning (CP/MAS) technique, operated at a spin rate of 12 kHz and a ¹³C frequency of 75 MHz. For organic matter containing pores smaller than 0.5 nm, the surface area (SA) can be underestimated by the traditionally recommended N₂ adsorption techniques (Lattao et al., 2014; Ravikovitch et al., 2005; Xing and Pignatello, 1997). Accordingly, CO₂ at 273 K, which can enter the micropores (0–1.4 nm), has been used as an alternative gas for these materials (Xing and Pignatello, 1997). In this study,

Download English Version:

<https://daneshyari.com/en/article/8857073>

Download Persian Version:

<https://daneshyari.com/article/8857073>

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