



# Sorption of four hydrophobic organic contaminants by biochars derived from maize straw, wood dust and swine manure at different pyrolytic temperatures



Ziying Wang<sup>a</sup>, Lanfang Han<sup>a</sup>, Ke Sun<sup>a,\*</sup>, Jie Jin<sup>a</sup>, Kyoung S. Ro<sup>b</sup>, Judy A. Libra<sup>c</sup>, Xitao Liu<sup>a</sup>, Baoshan Xing<sup>d</sup>

<sup>a</sup> State Key Laboratory of Water Environment Simulation, School of Environment, Beijing Normal University, Beijing, 100875, China

<sup>b</sup> Coastal Plains Soil, Water, and Plant Research Center, Agricultural Research Service, U.S. Department of Agriculture, 2611 West Lucas Street, Florence, SC, 29501, USA

<sup>c</sup> Leibniz Institute for Agricultural Engineering, Max-Eyth-Allee 100, 14469 Potsdam-Bornim, Germany

<sup>d</sup> Stockbridge School of Agriculture, University of Massachusetts, Amherst, MA, 01003, USA

## HIGHLIGHTS

- Swine manure biochars had higher sorption capacity, due to its higher ash content.
- Pore filling could dominate the sorption of tested biochars.
- Surface polarity and aliphatic C affect sorption of low temperature wood biochars.
- Aromatic C may regulate the sorption of biochars produced at high temperatures.

## ARTICLE INFO

### Article history:

Received 1 February 2015

Received in revised form

21 July 2015

Accepted 11 August 2015

Available online xxx

### Keywords:

Biochar

CO<sub>2</sub>-surface area

Surface polarity

Sorption

Minerals

## ABSTRACT

Sorption behavior of acetochlor (ACE), dibutyl phthalate (DBP), 17 $\alpha$ -Ethinyl estradiol (EE2) and phenanthrene (PHE) with biochars produced from three feedstocks (maize straw (MABs), pine wood dust (WDBs) and swine manure (SWBs)) at seven heat treatment temperatures (HTTs) was evaluated. The bulk polarity of these biochars declined with increasing HTT while the aromaticity and CO<sub>2</sub>-surface area (CO<sub>2</sub>-SA) rose. The surface OC contents of biochars were generally higher than bulk OC contents. The organic carbon (OC)-normalized CO<sub>2</sub>-SA (CO<sub>2</sub>-SA/OC) of biochars significantly correlated with the sorption coefficients ( $n$  and  $\log K_{oc}$ ), suggesting that pore filling could dominate the sorption of tested sorbates. SWBs had higher  $\log K_{oc}$  values compared to MABs and WDBs, due to their higher ash contents. Additionally, the  $\log K_{oc}$  values for MABs was relatively greater than that for WDBs at low HTTs ( $\leq 400$  °C), probably resulting from the higher CO<sub>2</sub>-SA/OC, ash contents and aromaticity of MABs. Surface polarity and the aliphatic C may dominate the sorption of WDBs obtained at relatively low HTTs ( $\leq 400$  °C), while aromatic C affects the sorption of biochars at high HTTs. Results of this work aid to deepen our understanding of the sorption mechanisms, which is pivotal to wise utilization of biochars as sorbents for hazardous organic compounds.

© 2015 Elsevier Ltd. All rights reserved.

## 1. Introduction

Biochars, which are products of the pyrolytic processing of biomass materials (Chun et al., 2004; Chen et al., 2008), has attracted increasing interest since their application to soil could act as effective sorbents for organic pollutants (Chun et al., 2004; Chen

et al., 2008), may enhance the sequestration of atmospheric carbon dioxide (Lehmann et al., 2006), and simultaneously improve soil fertility (Sohi et al., 2010). Studies have shown that the physicochemical properties of biochars, which would govern their sorption capacity for hydrophobic organic compounds (HOCs) (Chen et al., 2008; Sun et al., 2011a, 2012), vary remarkable with feedstock sources and pyrolysis process conditions, among which heat treatment temperature (HTT) is a key factor (Chen et al., 2008; Keiluweit et al., 2010; Sun et al., 2012). Generally, biochars produced at lower HTTs (250–400 °C) are not fully carbonized, but

\* Corresponding author.

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

have higher yields and contain more diversified organic structures, including aliphatic and cellulose structures (Novak et al., 2009). While those made at relatively high HTTs (400–700 °C) are well carbonized with large amounts of condensed aromatic C structures (Keiluweit et al., 2010) and exhibit rigid surfaces along with considerable pores for nonlinear adsorption of HOCs (Chen et al., 2008, 2012; Sun et al., 2011a). The question on how these different physicochemical properties can be correlated to the difference in sorption capacity for HOCs has been the subject of much recent work.

For biochars produced at various HTTs from chitin and cellulose, the sorption capacity (e.g., organic carbon (OC)-normalized distribution coefficient ( $K_{oc}$ )) for phenanthrene (PHE) and naphthalene (NAPH) was enhanced as the aromatic domains and surface area (SA) of the chars increased with increasing HTTs (Wang and Xing, 2007). In contrast, the sorption of polar phthalic acid esters (PAEs) was found to be controlled by the aliphatic and polar domains within biochars derived from both high and low HTTs (Sun et al., 2012). Furthermore, there is emerging evidence to indicate that chars appeared to have a higher surface capacity for a polar sorbate than for a nonpolar sorbate (Chun et al., 2004; Sun et al., 2012). Based on these, it can be reasonably assumed that due to the hydrophobicity and structure difference of sorbates, dissimilar sorption mechanisms would take place between different sorbates and biochars. Moreover, with respect to the same sorbate, sorption mechanisms also possibly vary with the HTT at which biochars were produced. In order to systematically probe the mechanism underlying the interactions between HOCs and biochars, biochars produced at a set of HTTs were used as sorbents, acetochlor (ACE), dibutyl phthalate (DBP), 17 $\alpha$ -Ethinyl estradiol (EE2) and PHE were selected as sorbates owing to their different polarity, element composition, electron polarizability and aromaticity.

A recent study found that minerals within biochars may exert an influence upon the organic matter (OM) spatial arrangement within biochars, thereby influencing the sorption of HOCs by biochars (Sun et al., 2013). While the focus of most current studies has been on sorption with low-mineral plant residue-derived biochars (PLABs), the sorption properties of high-mineral animal waste-derived biochar (ANIBs) have rarely been investigated. Therefore, it is necessary to further probe the characteristics of high-mineral biochars along with their sorption behavior.

Thus, the major works of this study were to 1) systematically examine the bulk and surface characteristics of biochars produced from feedstock materials with different mineral levels, including the maize straw, pine sawdust and swine manure at different HTTs; 2) investigate the sorption characteristics of ACE, DBP, EE2 and PHE by tested biochars; and 3) further test the roles of biochars characteristics (i.e., minerals, polarity, aromaticity and SA) in HOCs sorption.

## 2. Materials and methods

### 2.1. Sorbates

ACE (98 + %), a non-ionic and non-volatile herbicide, and DBP (99 + %), one of the most widely used PAEs, were purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany). EE2 (98 + %), one of the most frequently studied endocrine disrupting chemicals (EDCs) in environmental research, was obtained from Aldrich Co. (Milwaukee, WI). PHE (98 + %), which is a ubiquitous polycyclic aromatic hydrocarbon (PAHs) in the environment, was purchased from Sigma–Aldrich Chemical Co. Selected physicochemical properties of ACE, DBP, EE2 and PHE are presented in Table S1, Supplementary data.

### 2.2. Sorbents

The specific processes of biochar preparation were reported in a previous study (Sun et al., 2013). Briefly, maize straw (Henan Province, China), pine sawdust (Heilongjiang Province, China) and dewatered swine manure (Beijing, China) samples were obtained and air-dried at room temperature. Maize straw and pine wood dust were washed with deionized water (DI water) before use. Then all dried feedstock materials were ground to obtain a particle size of less than 1.5 mm and then pyrolyzed for 1 h at seven HTTs (i.e., 250, 300, 350, 400, 450, 500, and 600 °C) under oxygen-limited conditions in a muffle furnace. Next, the biochars were treated with 0.1 M HCl to decrease pH values of biochars and remove some nutrients (soluble salts and potassium compounds), carbonates, and dissolved organic matter (DOM) as well, which could prevent other factors mainly including pH values and DOM of biochars from impacting HOCs sorption by biochars. After the supernatants were removed by centrifugation, the residues were washed with DI water until the aqueous phase became nearly neutral and then dried at 105 °C. Subsequently, the biochars were gently milled to pass a 0.25 mm sieve (60 meshes) for further analysis. According to their feedstocks and HTTs, the 21 biochars are hereafter referred to as: MAXXX (maize straw), WDXXX (pine wood dust) and SWXXX (swine manure), with XXX indicating the charring temperature (250–600 °C). For comparison, samples of the feedstock, MA0, WD0 and SW0, were also analyzed. Here, the biochars were classified to PLABs (maize biochars (MABs) and wood dust biochars (WDBs)) and ANIBs (swine biochars (SWBs)) according to the feedstock sources. The biochars produced at low temperatures and high temperatures were named as LTBs and HTBs, respectively.

### 2.3. Biochar characterization

The bulk organic carbon (OC, the carbonate-free basis), H, N, and O contents of all the biochars were measured using an Elemental Vario ELIII elemental analyzer via complete combustion. Ash contents of the biochars were determined by heating samples at 750 °C for 4 h. To get more information on the chemical composition of biochars, solid-state cross-polarization magic angle spinning  $^{13}\text{C}$  nuclear magnetic resonance ( $^{13}\text{C}$  NMR) spectra were obtained using a Bruker Avance 300 NMR spectrometer (Karlsruhe, Germany) operated at a  $^{13}\text{C}$  frequency of 75 MHz and a magic angle spinning rate of 12 KHz. Surface area ( $\text{CO}_2$ -SA) using  $\text{CO}_2$  isotherm at 273 K was detected by gas adsorption using an Autosorb-1 gas analyzer (Quantachrome Instrument Corp., Boynton Beach, FL) and calculated using nonlocal density functional theory (NLDFT) (Braidia et al., 2003). The surface functionalities and domain spatial arrangement of samples were determined using X-ray photoelectron spectra (XPS) with a Kratos Axis Ultra electron spectrometer using monochromated Al K $\alpha$  source operated at 225 W, and more detailed information of XPS characterization was described elsewhere (Yang et al., 2011; Sun et al., 2013). (The  $\text{C}_{1s}$  binding energy levels were assigned as following: 284.9 eV for C–C, 286.5 eV for C–O, 287.9 eV for C=O, and 289.4 eV for COO.)

### 2.4. Sorption experiments

The sorption isotherms were obtained by a batch equilibration of biochar samples in glass vials with Teflon-lined screw caps. For the sorption of ACE, 8 mL glass vials were used for all the sorbents; for DBP and EE2, 15 mL glass vials were used for biochars produced at 500 and 600 °C, and 8 mL glass vials for the rest sorbents; and for PHE, 8 mL were used for feedstock samples, 40 mL for the biochars produced at 250–350 °C, and the 60 mL for the rest sorbents. The background solution contained 0.01 M  $\text{CaCl}_2$  to maintain a constant

Download English Version:

<https://daneshyari.com/en/article/6307162>

Download Persian Version:

<https://daneshyari.com/article/6307162>

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