



## Single-solute and bi-solute sorption of phenanthrene and dibutyl phthalate by plant- and manure-derived biochars



Jie Jin <sup>a</sup>, Ke Sun <sup>a,\*</sup>, Fengchang Wu <sup>b</sup>, Bo Gao <sup>c</sup>, Ziyang Wang <sup>a</sup>, Mingjie Kang <sup>a</sup>, Yingcheng Bai <sup>c</sup>, Ye Zhao <sup>a</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> State Key Laboratory of Environmental Criteria and Risk Assessment, Chinese Research Academy of Environmental Sciences, Beijing 100012, China

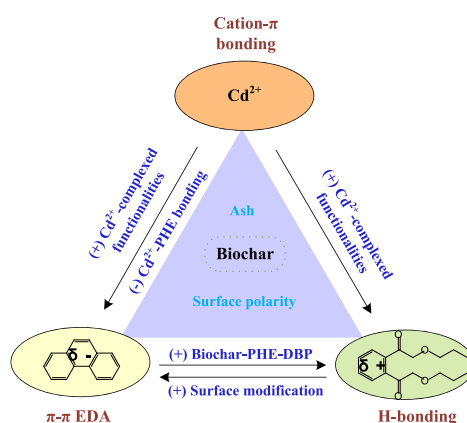
<sup>c</sup> State Key Laboratory of Simulation and Regulation of Water Cycle in River Basin, China Institute of Water Resources and Hydropower Research, Beijing 100038, China

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

### HIGHLIGHTS

- Sorption of DBP and PHE in single and binary systems was studied.
- PHE and DBP sorption by the biochars was influenced by their surface polarity.
- PHE could increase DBP adsorption on biochars.
- Increased PHE adsorption by Cd<sup>2+</sup> depends on the amount of sorbed Cd<sup>2+</sup> by biochars.

### GRAPHICAL ABSTRACT



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### ABSTRACT

The spatial arrangement of biochar and the exact underlying interaction mechanisms of biochar and hydrophobic organic compounds both remain largely unknown. The sorption of dibutyl phthalate (DBP) and phenanthrene (PHE) to plant- and manure-derived biochars in both single- and bi-solute systems was investigated. The significant positive relation between surface polarity and ash content suggests that minerals benefit the external distribution of polar groups on particle surfaces. PHE and DBP sorption by the biochars was regulated by their surface polarity. The PHE generally displayed a pronounced enhancement of DBP sorption, likely resulting from the formation of biochar-PHE-DBP complexes, suggesting that DBP and PHE had different sorption sites on the biochars. The enhancement of Cd<sup>2+</sup> (a soft Lewis acid) on DBP sorption implied that π-π interactions should not dominate DBP sorption by biochars. The influence of Cd<sup>2+</sup> on PHE sorption by biochars would depend on the balance between suppressive sorption by Cd<sup>2+</sup>-PHE bonding and enhanced sorption by Cd<sup>2+</sup>-complexed functionalities, and the amounts of Cd<sup>2+</sup> adsorbed by biochars determined the relative role of increased sorption by Cd<sup>2+</sup> in the overall PHE sorption.

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\* Corresponding author. Tel./fax: +86 10 58807493.

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

## 1. Introduction

Biochar is a charcoal-like material produced by the thermochemical pyrolysis of biomass materials. Biochar has great potential to sequester carbon in soil, improve soil fertility, and remediate groundwater and soil contamination (Barrow, 2012; Laird, 2008). In addition to these promising applications, much of the attention towards biochars is directed to their physicochemical diversity and strong affinity for organic pollutants (Cao et al., 2009; Keiluweit et al., 2010).

There is a general consensus that the physicochemical heterogeneity of biochars is controlled by the sources of biomass feedstocks (e.g., wood, crop residues, and poultry litter) and combustion conditions (Keiluweit et al., 2010; Sun et al., 2012; Zheng et al., 2013a, 2013b). It is well established that the progressive thermal alteration of biomass across a charring temperature gradient yields biochars with a dynamic molecular structure from predominantly amorphous carbon to turbostratic crystallites (Keiluweit et al., 2010). At the same time, stacks of graphene (which are polycyclic aromatic) grow into larger sheets, enabling biochars to acquire the ability to engage in  $\pi$ - $\pi$  electron donor-acceptor (EDA) interactions. The aromatic sheet is expected to be polarizable and may act as an electron donor, acceptor, or possibly show amphoteric properties towards sorbates. Biochars generated at low or intermediate energy input levels are expected to retain a significant number of electron-withdrawing functional groups and may be bipolar; aromatic rings ( $\pi$ -acceptor) in the center of a given sheet are electron deficient, and carbon rings closer to the edges ( $\pi$ -donor) are left electron rich (Sun et al., 2012; Zhu and Pignatello, 2005). Nevertheless, the ways in which aromatic compounds interact with the biochar aromatic core and edge functionality is not clear. Moreover, research on molecular variations among different biochar categories, differences in their organic sorption, and associated underlying mechanisms is still in its infancy.

The sorption of hydrophobic organic compounds (HOCs) to biochars has been demonstrated to be strong and nonlinear (Sun et al., 2012; Wang and Xing, 2007). Previous studies attributed the adsorption of aromatic contaminants on chars to  $\pi$ - $\pi$  EDA interactions, pore-filling processes, hydrophobic driving forces, and H-bonding mechanisms (Sun et al., 2012; Wang and Xing, 2007; Zhu et al., 2005). Furthermore, the bonding strengths of EDA interactions have been demonstrated to be larger than the H-bonding and hydrophobic effects (Keiluweit and Kleber, 2009). However, the contribution of  $\pi$ - $\pi$  EDA interactions to the overall interactions has not yet been confirmed. The elucidation of major molecular-level interactions that control the sorption of aromatic compounds and the influence of solution-phase compositions (such as coexisting organic compounds and ions) on sorption by biochar properties is of considerable theoretical and practical importance.

Phthalate acid esters (PAEs) are plasticizers that are widely used to induce flexibility and workability in polymeric materials. They are prevalent in various media, including surface water, sediments, soil and food (Lin et al., 2003; Zhu et al., 2006). Previous studies demonstrated that PAEs could interfere with normal hormone-regulated processes in humans and wildlife (Liu et al., 2009), and they are categorized as endocrine disruption compounds (EDCs) and priority pollutants by the US EPA and European Union. Because of their widespread presence and adverse health effects, PAE contamination and behavior have become major concerns. Although the sorption of other HOCs such as polycyclic aromatic hydrocarbons (PAHs) (Wang and Xing, 2007; Zhu and Pignatello, 2005) has been extensively investigated, few studies have been performed to illustrate the sorption mechanism of PAEs by biochars. PAHs can behave as donors towards  $\pi$ -acceptor sites in biochars, and PAEs may act as acceptors because of their ester functional group (Sun et al., 2012; Zhu and Pignatello, 2005). Taken together with prior reports indicating that the aromatic sheets in chars were capable of engaging in EDA interactions with both  $\pi$ -donors and  $\pi$ -acceptors, we hypothesize that if  $\pi$ - $\pi$  EDA interactions control PAH and PAE sorption onto biochars, they should have no or negligible influence on mutual

sorption in a bi-solute sorption system. Additionally, the hypothesis can be further tested by investigating the effects of  $\text{Cd}^{2+}$  addition. It has been reported that  $\text{Cd}^{2+}$  is a soft Lewis acid and can occupy electron-rich sites on biochar via cation- $\pi$  bonding (Harvey et al., 2011). Thus, it could be expected that the addition of  $\text{Cd}^{2+}$  should lessen the PAEs sorption by the biochars via competition of the same electron-rich sites of the biochar and have no or negligible effect on the PAHs sorption due to no competition of sorption sites of the biochars.

Therefore, phenanthrene (PHE) and dibutyl phthalate (DBP) were chosen as a representative PAH and PAE. We investigated the sorption of PHE and DBP by five biochars produced from feedstock sources including grass, wood and animal manure in single-solute and bi-solute systems.  $\text{Cd}^{2+}$  was introduced as a competitor to elucidate its effect on the sorption of PHE and DBP. The major objectives were as follows: 1) to examine property variations among different biochar categories and their impacts on the sorption of PHE and DBP; and 2) to discuss the contribution of  $\pi$ - $\pi$  EDA interactions to the overall sorption of PHE and DBP onto biochars.

## 2. Methods

### 2.1. Sorbents and sorbates

Biochar preparation was described elsewhere (Chen et al., 2008). In brief, the five biochars used in this study were produced from grass (soybean, rice, and cotton) straw, wood dust and swine manure at 450 °C for 2 h after being charred at 200 °C for 2 h in a closed container under  $\text{N}_2$  conditions. The biochars were further demineralized with 0.1 M HCl. The residues were subsequently separated from the supernatant by centrifugation, washed with deionized (DI) water, freeze-dried, milled to pass a 0.25-mm sieve and stored for further use. Here, the biochars were classified as WB (wood biochar), GB (grass biochar) and AB (animal waste biochar) according to the feedstock sources. For example, soybean, rice, cotton, wood dust, and swine manure were referred to as GSB, GRB, GCB, WWB, and ASB, respectively.

DBP (99 + %) and PHE (98 + %) were purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany) and Sigma-Aldrich Chemical Co., respectively. The hexadecane-water partition coefficient ( $\log K_{\text{HW}}$ ) of PHE and DBP are 4.74 and 3.81, respectively (Abraham et al., 1994; Wang et al., 2010).  $\text{Cd}^{2+}$  was applied as a nitrate salt in this study.

### 2.2. Biochar characterization

The physicochemical properties of biochar were determined through elemental analysis, bulk and surface functional group characterization, crystallization (X-ray diffraction, XRD), and  $\text{CO}_2$  surface area ( $\text{SA-CO}_2$ ). For elemental analysis, the C, H, N and O contents were measured with an Elementar Vario EL Elemental Analyzer. Ash contents were measured by heating samples at 750 °C for 4 h. Surface chemistry was evaluated with an FTIR spectrophotometer and an X-ray photoelectron spectroscope (XPS). The FTIR spectrum was collected on a Nexus 670 FTIR spectrophotometer (Thermo Nicolet Corporation, US) using KBr pellets (1–2 mg of sample dispersed in 100 mg of KBr) from 4000 to 400  $\text{cm}^{-1}$  with a resolution of 4  $\text{cm}^{-1}$ . XPS was performed on a Thermo Scientific ESCALAB 250 XPS with a Kratos Axis Ultra electron spectrometer using monochromatic Al K $\alpha$  radiation operated at 225 W. The  $\text{C}_{1s}$  binding energy levels were assigned as follows: 284.9 eV to C–C, 286.5 eV to C–O, 287.9 eV to C=O, and 289.4 eV to COO. To obtain information on the chemical composition of biochars, their 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) operating at a  $^{13}\text{C}$  frequency of 75 MHz and a magic angle spinning rate of 12 kHz. XRD patterns were obtained on an X'Pert PRO MPD

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