The role of ash content on bisphenol A sorption to biochars derived from different agricultural wastes

Jing Li, Ni Liang, Xiuqi Jin, Dandan Zhou, Hao Li, Min Wu, Bo Pan[*]

Faculty of Environmental Science & Engineering, Kunming University of Science & Technology, Kunming 650500, Yunnan, China

HIGHLIGHTS

- Oxalates and KCl formed at low temperature, while carbonates at high temperature.
- Insoluble crystals and the dissolved salts do not alter BPA sorption.
- BPA interacts with surface functional groups when ash blocks inner pores.
- Acid treatment exposes more sorption sites, and increases BPA sorption.
- Biochar sorption can be increased when enhancing the accessibility of inner pores.

ARTICLE INFO

ABSTRACT

Inorganic minerals are important compositions in biochars, but their roles in biochar functions are investigated limitedly, which restricted our understanding on biochar applications. This study applied different biomasses to produce biochars. Their properties as well as sorption to bisphenol A (BPA) were studied, with a major focus on the role of inorganic compositions. Oxalates, carbonates, as well as KCl crystals were observed in the produced biochars depending on the feedstocks and temperatures. Oxalates and KCl formed at relatively low temperature (200–300 °C), while carbonates generally formed at pyrolysis temperature above 400 °C. The separated insoluble crystal particles and the dissolved salts have limited contribution to the apparent BPA sorption, but ash content removal altered BPA sorption. The potential impact of inorganic composition to BPA sorption should be resulted from biochar properties. Based on biochar characterization and sorption comparison before and after ash removal, we proposed that the formation of inorganic mineral compositions in biochar particles may have blocked the inner pores, which limited the significance of these sorption sites. As a result, the interactions of BPA and biochars were mostly determined by biochar surface functional groups. The acid treatment removed most of the inorganic compositions, and exposed more sorption sites, which consequently increased BPA sorption. Biochar sorption capacity may be further increased if the accessibility of the inner pores could be enhanced.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

Biochars refer to carbon-rich solid particles produced from biomass under oxygen-limited pyrolysis at a relatively low temperature (<700 °C) (Lehmann, 2007; Chen et al., 2008). In recent years, increasing attention for biochars is ascribed to the benefit of using biochars in carbon sequestration, climate change mitigation, soil amendment and contaminant removal (Mohan et al., 2014; Tan et al., 2015).

Many studies have reported that biochars exhibited high sorption to diverse contaminants such as organic pollutants and heavy metals from aqueous solutions (Tan et al., 2015). Among them, most researches used low-mineral biochars or deashed biochars (treated using HCl or HCl/HF) to investigate their surface property and porous structure in relation to their sorption characteristics. The investigators tried to establish relationship between specific surface area, pore distribution, or surface functional groups and sorption parameters (Chen et al., 2008; Sun et al., 2011). However, it should be noted that with the increased pyrolysis temperature, ash content can account up to over 80% of the biochar mass (Sun

et al., 2013). Inorganic fractions are present as part of biochars when they are applied to soil or used as a sorbent. It may be improper to predict biochar environmental roles based on experiments using de-ashed biochars. However, the effect of inorganic fraction on pollutant sorption has been usually neglected except for a limited number of studies (Cao et al., 2009; Cao and Harris, 2010; Sun et al., 2013; Zheng et al., 2013). Cao and his coworkers (Cao et al., 2009) have systematically determined the impact of mineral compositions on pollutant sorption, but mostly focused on heavy metals. Zheng et al. studied the importance of inorganic fractions to the sorption of ionic organic contaminants on biochars, without identifying the types of mineral crystals (Zheng et al., 2013).

The roles of inorganic moieties in natural geosorbents for contaminant sorption have been studied extensively (Keiluweit and Kleber, 2009; Yang et al., 2011), but the properties and functions of inorganic fraction in biochars and their influence on the fate of organic contaminants has seldom been studied. Compared with activated carbon and other carbonaceous materials, cheap and abundant feedstocks make biochars a new potential low-cost and sustainable adsorbent (Cao et al., 2009; Zheng et al., 2010). Many kinds of biomasses, including agricultural residues, livestock manure, sawdust and sewage sludge have been utilized to produce biochars. Biochars derived from these materials may have quite different compositions, especially inorganic fraction. How the amount and type of inorganic fractions affect organic contaminant sorption is a question that needs to be systematically investigated. This line of study will guide the proper application of biochars. In this work, four types of biomass were chosen to produce biochars, and BPA was selected as a representative organic pollutant. The major focus was on the role of inorganic fraction to the apparent BPA sorption.

2. Experimental section

2.1. Adsorbate

Bisphenol A (BPA, pKa = 9.59) was selected as a relatively hydrophobic organic contaminant, which do not dissociate at experimental pH < 9.59. Its solubility is 380 mg L^{-1}, and log K_{OW} value is 0.9. BPA was from Sinopharm Chemical Reagent Co. Ltd (purity > 98%).

2.2. Preparation and characterization of biochars

Four biomasses, including corncob, pomelo peel, eucalyptus globulus, and silkworm excrement, were collected as raw materials, and were referred to as CC, PP, EG, and SE, respectively. These materials were washed several times to remove dusts, then air-dried for days and subsequently oven-dried for 12 h at 70–80 °C. Biochars were produced at various temperatures (200–500 °C) in a muffle furnace via pyrolyzing under oxygen-limited conditions. The muffle furnace was provided with continuously flowing N$_2$ during the whole heating process. After 4-h charring process, N$_2$ was kept continuously flowing until the temperature decreased to room temperature. The resulted charred residues were gently ground and then passed through a 75 μm sieve. All the biochars were named by a combination of their resource and pyrolytic temperatures (200, 300, 400, and 500 °C were indicated by a suffix number of 2, 3, 4 and 5, respectively). For example, CC2 refers to corncob biochar pyrolyzed at 200 °C. The others can be deduced by analogy. SE biochars were deashed by 1 M HCl solution (solid-to-liquid ratio: 1:20) three times (Chun et al., 2004; Chen et al., 2008), then washed to neutral using deionised water, hereafter referred to as SEH biochars.

The bulk C, H, N, S and O contents of the biochars were determined by an elemental analyzer (MicroCube, Elementar, Germany). Ash contents of the biochars were measured by heating samples at 1000 °C in the presence of O$_2$ for 4 h. Their functional groups were characterized using Fourier transform infrared spectrometer (Varian 640-IR, USA). The surface area, total pore volume and pore size distribution were measured using N$_2$ (Autosorb-1C, Quantachrome). The inorganic components of biochars were determined by X-ray diffraction (XRD) patterns which were obtained with a Rigaku D/MAX2200 X-ray diffractometer (Japan) equipped with Cu Kα radiation source.

2.3. Sorption experiments

Batch sorption experiments were conducted for BPA on all the biochars. Stock solutions (64 mg L^{-1} for BPA, dissolved in background solution containing 0.01 M CaCl$_2$ to maintain a constant ionic strength and 200 mg L^{-1} NaN$_3$ as a biocide) were diluted by the background solution to nine different concentrations ranged between 1 and 64 mg L^{-1}. The aqueous/solid ratio in the sorption experiment was 800:1 to ensure 20–80% uptake of initial sorbates concentration at equilibrium. All the sorption experiments were conducted in 4 ml glass vials capped with Teflon-lined screw, and were shaken on an air-bath shaker in dark at 25 °C for 7 d. Headspace was kept minimal to reduce solute vapor loss. All the vials were then centrifuged at 3000 g for 15 min. The supernatants were sampled for adsorbate quantification on a high performance liquid chromatography (HPLC). All adsorption data points were run in duplicate and reference samples were set without biochars. The concentrations on solid-phase were calculated by the difference between initial concentration references and the corresponding equilibrium aqueous-phase concentrations.

The biochar supernatants were prepared with the same aqueous/solid ratio for every SE biochars for 7 d. The supernatants were added in the corresponding SHE biochars (after acid treatment) to illustrate the potential impact of the dissolved chemicals.

2.4. Detection of BPA

The concentrations of BPA in the supernatants were quantified by an HPLC (Agilent Technologies 1200) equipped with a reversed-phase C8 column (5 mm, 4.6–150 mm) and an UV detector. BPA was quantified at 280 nm. The mobile phase was 40:60 (v: v) of acetonitrile and deionized water. The flow rate was 1 mL min^{-1}. The detection limits was 0.1 mg L^{-1}.

2.5. Data analysis

The Freundlich and the Dual-mode models were selected as sorption isotherms fitted with Sigmaplot 11.0. Freundlich model (FM) is expressed as:

$$\log Q_e = \log K_F + N \log C_e \tag{1}$$

where Q_e (mg kg^{-1}) and C_e (mg L^{-1}) are equilibrium solid and liquid phase concentrations, respectively. K_F [(mg kg^{-1})/(mg L^{-1})^N] is the Freundlich adsorption coefficient, and N is the indicator of isotherm nonlinearity.

Dual-model (DM) distinguishes adsorption and partitioning as:

$$Q_e = Q_{ad} + Q_p = Q^0 C_e/(a + C_e) + K_p C_e \tag{2}$$

where Q_{ad} (mg kg^{-1}) is the adsorption fraction, and Q_p (mg kg^{-1}) is the partition fraction; Q^0 (mg kg^{-1}) is the adsorption capacity; a (kg L^{-1}) is the affinity coefficient, and K_p (L kg^{-1}) is the partitioning