



Effects of humic acid and heavy metals on the sorption of polar and apolar organic pollutants onto biochars[☆]



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ARTICLE INFO

Article history:

Received 4 May 2017

Received in revised form

18 July 2017

Accepted 6 August 2017

Keywords:

Sorption

Biochar

Humic acid

Heavy metal

Naphthalene

ABSTRACT

The effects of humic acid (HA) and heavy metals (Cu^{2+} and Ag^+) on the sorption of polar and apolar organic pollutants onto biochars that were produced at temperatures of 200 °C (BC200) and 700 °C (BC700) were studied. Due to the plentiful polar functional groups on BC200, cationic propranolol exhibited higher levels of sorption than naphthalene on BC200 while naphthalene and propranolol showed similar sorption capacities on BC700. HA changed the characteristics of biochars and generally inhibited the sorption of target organic pollutants on biochars; however, enhancement occurred in some cases depending on the pollutants involved and their concentrations, biochars used and the addition sequences and concentrations of HA. On BC200, HA modifications mainly influenced sorption by decreasing its polarity and increasing its aromaticity, while on BC700, the surface area and pore volume greatly decreased due to the pore-blocking effects of HA. Residue dissolved HA in solution may also contribute to sorption inhibition. Complexation between polar functional groups on BC200 and heavy metals slightly enhanced the sorption of neutral naphthalene and significantly enhanced that of anionic 4-nitro-1-naphthol, while limited the sorption of cationic propranolol. Heavy metals together with their associated water molecules decreased the sorption of target chemicals on BC700 via pore-filling or pore-mouth-covering. Inhibition of heavy metals for 4-nitro-1-naphthol was found to be the weakest due to the bridge effects of heavy metals between 4-nitro-1-naphthol and BC700. The higher polarizability of Ag^+ led to the increase of its sorption on biochars in the presence of organic aromatic pollutants. The results of the present study shed light on the sorption mechanisms of bi-solute systems and enable us to select suitable biochar sorbents when chemicals co-exist.

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1. Introduction

Biochars are materials obtained by pyrolyzing biomass at relatively low temperatures (<700 °C) with little to no oxygen (Marris, 2006). Due to their high sorption capacities for organic pollutants, biochars have been proposed to act as promising sorbents for soil remediation and wastewater treatments and play an important role in governing the fate of organic pollutants in the environment (Ahmed et al., 2017; Kołtowski et al., 2017). However, in real

environment and treatment systems, the sorption efficiency of organic pollutants by biochars is influenced by multiple factors. For instance, dissolved organic matter (DOM) and heavy metals extensively found in the environment and in treatment systems can exert great effects as revealed through studies on the sorption of organic pollutants by other sorbents (Cao et al., 2009; Andreu et al., 2016; Sun et al., 2016).

DOM is widely found in the natural environment, and humic acid (HA) is a major component of DOM (Hyung and Kim, 2008; Pignatello, 2012). Unique characteristics of HA, e.g., the presence of multiple functional groups, such as carboxylic, phenolic and aromatic groups linked to aryl rings and alkyl chains (Klavins and Purmalis, 2009) and varied conformations formed under different water chemistry conditions (Pignatello et al., 2006; Armanious

[☆] This paper has been recommended for acceptance by Baoshan Xing.

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et al., 2014), make it be able to combine with different types of materials through different interactions, thus affecting the sorption behaviors of organic pollutants on sorbents (Kwon and Pignatello, 2005). It has been reported that HA can be adsorbed on the surfaces of high temperature biochars via hydrophobic and π - π electron donor-acceptor (EDA) interactions (Pignatello et al., 2006; Kasozi et al., 2010) and on low temperature biochars through hydrophilic interactions such as hydrogen bonds (Sun et al., 2010; Ji et al., 2011).

Different effects have been reported about the co-existence of HA on the sorption of organic pollutants. It has been reported that HA prohibits the sorption of hydrophobic organic compounds (HOCs) on the surfaces of carbonaceous materials by competing for surface sorption sites or through pore-blocking (Koelmans et al., 2009; Lian et al., 2015; Zhang et al., 2015a). Koelmans et al. (2009) reported that the sorption inhibition of HA is more pronounced for sorbates of stronger sorption affinities. Pignatello et al. (2006) proposed that influences of HA on the sorption of organic chemicals are in proportion to their molecular volumes. Meanwhile, it has also been reported that the addition of HA does not affect the sorption of phenanthrene on black carbon (Cornelissen and Gustafsson, 2006). Wang et al. (2013) showed that HA enhances polychlorinated biphenyls (PCBs) sorption on biochars because adsorbed HA provides new sorption sites for PCBs. Regarding the sorption of polar organic pollutants, the presence of HA may have different effects as compared to HOCs due to that the two types of organic pollutants have different sorption mechanisms. It has been reported that the loading of tannic acid reduces the sorption of polar pesticides on black carbon (Qiu et al., 2009) while HA coating boosts the sorption of sulfamethoxazole but inhibits that of sulfanilamide on biochars (Lian et al., 2015). Such contradictory conclusions can be ascribed to the fact that sorption mechanisms change with sorbent and pollutant properties. Thus, a systematic investigation of the effects of HA on the sorption of organic pollutants onto different biochars is further needed.

Heavy metals and organic pollutants may co-exist in natural environments and treatment systems (Andreu et al., 2016). Heavy metals can be sorbed via cationic exchange or surface complexation, which can in turn affect the sorption of organic pollutants by changing surface chemical characteristics of carbonaceous materials (Sun et al., 2010; Wang et al., 2011b). Wang et al. (2013) found that metal cations boost PCBs sorption on biochars by cationic complexation with the aromatic rings of PCBs (cation- π EDA interaction). Kong et al. (2011) on the other hand found that Hg^{2+} decreases the removal efficiencies of phenanthrene in a bi-solute system by competing for biochars surface sorption sites. The co-existences of Pb^{2+} and Cr^{6+} suppress atrazine sorption on sludge-derived biochar, as the inner complex between heavy metal and hydroxyl groups on biochars inhibits the formation of hydrogen bonds with atrazine (Zhang et al., 2015b). While co-existing effects of heavy metals on the sorption of polycyclic aromatic hydrocarbons, PCBs and pesticides have been well-studied, effects of heavy metals on the sorption of different types of organic pollutants on biochars (especially on ionizable organic compounds, IOCs) have not been paid enough attention (Ding et al., 2014; Inyang et al., 2015).

To develop a comprehensive understanding of the effects of DOM and heavy metals on the sorption of different organic pollutants on biochars and the mechanisms involved, we selected two biochars produced by pyrolyzing corn straw at temperatures of 200 °C and 700 °C as sorbents and hydrophobic naphthalene, cationic propranolol and anionic 4-nitro-1-naphthol as sorbates. Effects of HA were studied via pre-coating and co-introducing and effects of divalent Cu^{2+} and monovalent Ag^{+} were compared.

2. Materials and methods

2.1. Materials and chemicals

Biochar preparation and characterization methods employed were the same as those employed in our previous study (Wang et al., 2016). In brief, biochars were made by pyrolyzing corn straw at temperatures of 200 °C and 700 °C for 4 h, marked as BC200 and BC700, respectively. Characterizations (elemental compositions, atomic ratios, surface area, pore volume distribution, surface functional groups, thermogravimetric and derivative thermogravimetric curves, scanning electron microscopy images, XRD spectra and Fourier transform infrared spectroscopy) of the biochars are shown in Table S1, Table S2, Fig. S1 and Fig. S2 of Supplementary Information (SI).

Humic acids (HA) were purchased from J&K Scientific (Beijing, China). $CuCl_2$ and $AgNO_3$ used were of analysis grade and were obtained from Tian Chemical Reagents Company (Tianjin, China).

Naphthalene ($\geq 98\%$), 4-nitro-1-naphthol ($\geq 98\%$) and propranolol (99%) were purchased from CNW Technologies (Germany). Related physical and chemical properties, including molecular structures, molecular weights, solubility, octanol-water partition coefficients, acidity coefficients and molecular volumes of the target chemicals are shown in Table S3.

2.2. Pre-coating of HA onto the biochars

HA purification was conducted following a previously developed method (Lin et al., 2012). In brief, 10 g HA was dissolved in 400 mL 0.1 mol/L NaOH for 18 h and was then centrifuged at 3500 rpm for 15 min. The supernatant was then collected. The solution pH was adjusted to 1–1.5 with 3 mol/L HCl, and then precipitation was collected after centrifugation at 3500 rpm for 15 min. The collected fraction was transferred to a 100 mL aqueous solution (0.5 mL HCl + 0.5 mL 48% HF + 99 mL H_2O) and then was shaken for 5 h and centrifuged at 3500 rpm for 15 min. The precipitation was rinsed twice with distilled water, centrifuged, and dried at 40 °C in a vacuum.

The biochar was mixed with the purified HA solution at concentrations of 0.4 g/L and 4 g/L with theoretical dry weight percentages of HA set to 1% and 10%, respectively, and it was then shaken in the dark at 20 ± 0.5 °C for 14 d. After centrifugation, the solid phase was freeze-dried and stored for use and was marked as HA-BC200s (1% HA-BC200 and 10% HA-BC200) and HA-BC700s (1% HA-BC700 and 10% HA-BC700). Residual HA concentrations in the supernatant were analyzed after they were passed through a 0.22 μm polytetrafluoroethylene membrane to determine the actual loading volume of HA.

2.3. Effects of HA on the sorption of polar and apolar organic pollutants

Effects of HA on the sorption of naphthalene and propranolol were studied through two experiments. First, the sorption of naphthalene and propranolol was studied on HA-coated biochars. To do so, 50 mg of BC200 and HA-BC200s, and 5 mg BC700 and HA-BC700s were weighed in 40 mL amber EPA vials. The background solution was an aqueous solution containing 0.01 mol/L $CaCl_2$ and 200 mg/L NaN_3 (bioinhibitor). The initial concentrations of naphthalene were in the range of 0.0234–0.234 mmol/L, and the initial concentration range of propranolol was set to 7.78–77.8 $\mu mol/L$ in the BC200 and HA-BC200s system. Initial concentration ranges of naphthalene and propranolol in the BC700 and HA-BC700s systems were set to 0.0234–0.234 mmol/L and 0.778–77.8 $\mu mol/L$, respectively. Methanol content levels were kept below 0.1% in

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