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Micropore clogging by leachable pyrogenic organic carbon: A new perspective on sorption irreversibility and kinetics of hydrophobic organic contaminants to black carbon[☆]

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ABSTRACT

Black carbon (BC) plays a crucial role in sequestering hydrophobic organic contaminants in the environment. This study investigated key factors and mechanisms controlling nonideal sorption (e.g., sorption irreversibility and slow kinetics) of model hydrophobic organic contaminants (nitrobenzene, naphthalene, and atrazine) by rice-straw-derived BC. After removing the fraction of leachable pyrogenic organic carbon (LPyOC) (referring to composites of dissoluble non-condensed organic carbon and associated mineral components) with deionized water or 0.5 M NaOH, sorption of these sorbates to BC was enhanced. The sorption enhancement was positively correlated with sorbate molecular size in the order of atrazine > naphthalene > nitrobenzene. The removal of LPyOC also accelerated sorption kinetics and reduced sorption irreversibility. These observations were attributed to increased accessibility of BC micropores initially clogged by the LPyOC. Comparison of BC pore size distributions before and after atrazine sorption further suggested that the sorbate molecules preferred to access the micropores that were more open, and the micropore accessibility was enhanced by the removal of LPyOC. Consistently, the sorption of nitrobenzene and atrazine to template-synthesized mesoporous carbon (CMK3), a model sorbent with homogeneous pore structures, showed decreased kinetics, but increased irreversibility by impregnating sorbent pores with surface-grafted alkylamino groups and by subsequent loading of humic acid. These findings indicated an important and previously unrecognized role of LPyOC (i.e., micropore clogging) in the nonideal sorption of organic contaminants to BC.

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1. Introduction

Black carbon (BC) is a collective term referring to relatively recalcitrant carbonaceous materials ubiquitously present in soils, sediments, waterbodies, and the atmosphere (Schmidt and Noack, 2000). BC has strong sorption affinities for many organic contaminants such as polycyclic aromatic hydrocarbons (PAHs), pesticides, and pharmaceuticals (Chen et al., 2008; Liu et al., 2016; Loganathan et al., 2009; Sander and Pignatello, 2005). For instance, BC was reported to exhibit 10–100 times greater sorption of phenanthrene

than soil amorphous organic matter (e.g., humic substances) (Cornelissen and Gustafsson, 2004; Cornelissen et al., 2005; Nam et al., 2008). As BC can account for 2–15% of total organic carbon (TOC) in natural soils (Cornelissen et al., 2005), and its concentration would be even greater in soils amended with biochar (an engineered BC), BC is considered as one of key soil constituents controlling the fate and transport of organic contaminants in soils (Vrind et al., 2006).

A large effort has been dedicated to understanding complex sorption properties of BC toward apolar organic contaminants (e.g., benzene, chlorinated benzenes, and PAHs), including strong sorption affinity (Accardi-Dey and Gschwend, 2002; Chen and Yuan, 2010; Cornelissen et al., 2005; Lattao et al., 2014), high sorption irreversibility (Braidat et al., 2003), and slow sorption kinetics (Vrind et al., 2006; Xiao et al., 2004). The strong sorption affinity of

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organic contaminants to BC has been attributed to hydrophobic effect (Chun et al., 2004; Zhu and Pignatello, 2005b), π - π electron coupling between graphitized BC moieties and π -electron-bearing compounds (Lattao et al., 2014; Wang et al., 2014; Zhu et al., 2005), and/or filling of micropores (Nguyen et al., 2007). As BC typically has a highly disordered microporous structure (Harris and Tsang, 1997; Palotás et al., 1996), micropore filling and size exclusion could prevail in sorption processes, depending on molecular size and geometry of sorbates. It has been shown that micropore filling enhanced sorption of small-sized sorbates (e.g., naphthalene and low-substituted monoaromatics) to charcoal on a unit surface area basis as compared with nonporous graphite (Zhu and Pignatello, 2005b). Conversely, the bulky tetracycline manifested lower sorption to BC due to the size-exclusion effect (Ji et al., 2011). Additionally, it was reported that pore fouling by humic substances could result in pore blockage and sorption competition, and consequently decreased sorption of organic contaminants to carbonaceous sorbents (Kilduff and Wigton, 1999; Kwon and Pignatello, 2005; Pignatello et al., 2006).

The pore structure of carbonaceous sorbents has a pronounced influence on sorption irreversibility. Our previous study demonstrated that sorption of phenol was fully reversible to template-synthesized microporous carbon with a rigid, regular-shaped, and interconnected open pore structure (Ji et al., 2009). Similarly, Yu et al. (2010) found that sorption irreversibility of pyrimethanil to biochar was relieved by increase in pore size, presumably due to facilitated pore entrance and escape of sorbate molecules. Zhou et al. (2010) also proposed that loading of humic acid on charcoal could change the sorbent pore size and surface property, leading to impeded desorption kinetics of PAHs and increased sorption irreversibility. However, it is still unclear how and to what extent the coated humic acid would affect the sorbent pore structure, partially due to the hard entrance of humic acid macromolecules into the micro-sized pores of BC. Alternatively, Braida et al. (2003) attributed the irreversible sorption of benzene to BC to pore deformation characterized by internal pore expansion in response to the presence of the sorbate.

The slow kinetics observed in sorption/desorption of many organic contaminants (e.g., chlorinated benzenes and PAHs) to soils and sediments could be also related with the micropore structure of BC constituents (Pignatello and Xing, 1996; Vrind et al., 2006; Xiao et al., 2004). Compared with amorphous organic matter, diffusion of organic solutes within the microporous network of BC is expected to be much slower, therefore leading to slowed sorption/desorption kinetics. For example, Kleineidam et al. found that some large grain fractions of aquifer sands/gravels and fresh rock fragments exhibited very slow sorption/desorption kinetics of phenanthrene (>1000 d to reach the apparent equilibrium) (Kleineidam et al., 2004), which was mainly attributed to the long-range and sorption-retarded diffusion of the sorbate within the micropores of BC.

It has recently been reported that leachable pyrogenic organic carbon (LPyOC) makes an important fraction of BC (up to 2–3% on the basis of organic carbon) (Liu et al., 2015; Mukherjee and Zimmerman, 2013). Notably, dissolved LPyOC (operationally defined as the <0.45 or 0.7 μm fraction) (Bird et al., 2015; Major et al., 2010; Qu et al., 2016) is an important constituent of natural dissolved organic carbon (DOC), accounting for approximately 10% of DOC in natural surface waters (Jaffe et al., 2013). LPyOC can be readily released from bulk BC by infiltration and surface runoff (Jaffe et al., 2013), and has significant mobility in surface and subsurface environments as shown in column studies (Wang et al., 2013a, 2013b). This underscores the significant role of LPyOC in affecting the carbon cycle and the fate and transport of contaminants (Aiken et al., 2011; Jaffe et al., 2013; Qu et al., 2016). On the

other hand, the release of endogenic LPyOC might change the structural and chemical properties of bulk BC, which in turn affects its sorption properties for organic contaminants. However, to our best knowledge, no relevant studies have been conducted thus far.

This study is aimed to investigate the impact of releasing endogenic LPyOC on sorption behaviors of organic contaminants to bulk BC, particularly from the perspective of sorption irreversibility and kinetics. Batch sorption isotherms and kinetics of three sorbates (nitrobenzene, naphthalene, and atrazine) with varying molecular size were examined for pristine bulk BC and LPyOC-removed BC with detailed chemical, microscopic, and spectroscopic characterizations. To simulate the reversal of the BC washing (i.e., BC pore clogging by LPyOC), a template-synthesized mesoporous carbon (CMK3) with homogeneous, three-dimensional and open access pore structure was impregnated with surface-grafted alkylamino groups and subsequently loaded with humic acid. These materials were used as additional sorbents. The findings were further discussed to elucidate the role of LPyOC in nonideal sorption of hydrophobic organic contaminants to BC.

2. Experimental

2.1. Chemicals

Three test sorbates were nitrobenzene (99.5%, Fluka, Switzerland), naphthalene (98%, Sigma-Aldrich, USA), and atrazine (97%, J&K Chemical, China). Their selected physicochemical properties are listed in Table S1 of the Supporting Information (SI). Humic acid (technical grade) was purchased from Sigma-Aldrich.

2.2. Preparation of sorbents

BC used in this study was prepared by pyrolyzing pulverized rice straw (Nantong, Jiangsu Province, China) at 400 °C as described in our previous study (Qu et al., 2016). To remove the LPyOC fraction, 10 g of BC was mixed with 500 mL of deionized (DI) water or 0.5 M NaOH in a 1-L beaker, and the suspension was purged with nitrogen (N_2) and stirred at 200 rpm using an overhead stirrer at room temperature for 24 h. After quiescent settling of about 30 min, the settled fraction and the remaining suspension were combined and filtered through a 0.45- μm mixed cellulose acetate membrane (Anpel Scientific Instrument, China). The BC retained on the filter membrane under the NaOH treatment was continuously rinsed with DI water until reaching a neutral solution pH in the filtrate. The BC samples collected from the membrane were then dried at 60 °C overnight in a vacuum oven and designated as BC washed with DI water (BC-W) and BC washed with base (BC-B). The filtrates were freeze-dried and designated as LPyOC.

CMK3 was purchased from XFNANO Materials Tech Co. Ltd (Nanjing, China). Alkylamino-functionalized CMK3 was prepared using a previously developed method (Wang et al., 2010). In brief, CMK3 was first oxidized by nitric acid to introduce surface carboxyl functional groups, followed by covalent grafting of (3-aminopropyl) trimethoxysilane, and the resultant material was referred to as CMK3-NH₂. Another CMK3-derived sorbent was prepared by sorbing humic acid to CMK3-NH₂ using a batch technique, and was designated as CMK3-NH₂-HA. More details on sorbent preparation are presented in SI.

2.3. Characterization of sorbents

Specific surface areas and pore structure parameters of sorbents were measured from N_2 sorption/desorption isotherms at -196 °C (77 K) using a Micromeritics ASAP 2020 system (Micromeritics Instrument Co., Norcross, GA, USA). To assess the effect of atrazine

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