**Micropore Clogging by Dissolved Black 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 dissolved BC (DBC) fraction with deionized water and 0.5 M NaOH (accounting for 0.61% and 9.04% of total organic carbon, respectively), 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. DBC removal also accelerated sorption kinetics and reduced sorption irreversibility. These observations were attributed to increased accessibility of BC micropores initially clogged by DBC. 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 DBC. 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 DBC (i.e., micropore clogging) in the nonideal sorption of organic contaminants to BC.

41 **Capsule:** Removal of dissolved black carbon accelerated sorption kinetics and reduced sorption
42 irreversibility of organic contaminants to bulk rice residue-derived black carbon.
43 **Keywords:** black carbon (BC); dissolved black carbon (DBC); sorption kinetics; sorption
44 irreversibility; pore clogging
45

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 is typically produced from thermal decomposition of biomass and fossil fuel under oxygen-limited conditions, and consists of a broad continuum of carbonaceous materials with varying aromaticity, recalcitrance, and pore structures (Bird et al., 2015; Keiluweit et al., 2010). The major global BC pool is estimated to be 54–109 Pg in top 1-m soils, 480–1,440 Pg in ocean sediments, and 26–145 Pg in marine water (Bird et al., 2015), and is thus considered an important component in the global carbon cycle. Moreover, biochar (an engineered BC) has gained increasing attention as a promising soil amendment to increase soil carbon storage, soil quality, nutrient and water retention, and contaminant immobilization (Cornelissen et al., 2005; Lehmann, 2007). 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 BC-amended soils, 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), high sorption irreversibility (Braida et al., 2003), and slow sorption kinetics (Vrind et al., 2006; Xiao et al., 2004). The strong sorption affinity of 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 (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 reported that loading of humic acid on charcoal could change the sorbent pore size and surface property, which in turn impeded desorption kinetics of PAHs and increased their sorption irreversibility. 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 humic substances, 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 dissolved BC (DBC), the water soluble fraction of BC (operationally defined as the < 0.45 or $0.7 \mu\text{m}$ 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). DBC 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; Wang et al., 2013b). This underscores the significant role of DBC 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 DBC 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 DBC release 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 DBC-removed BC with detailed chemical, microscopic, and spectroscopic characterizations. To simulate the reversal of the BC washing (i.e., BC pore clogging by DBC), a template-synthesized mesoporous carbon (CMK3) 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 DBC 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 DBC fraction, 10 g of BC was mixed with 500 mL of deionized (DI) water or 0.5 M sodium hydroxide (NaOH) in a 1-L beaker, and the suspension was purged with nitrogen (N₂) and stirred at 200 rpm using an overhead stirrer at room temperature for 24 h. After quiescent settling of about 30 min, the suspension was 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 DBC.

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 N₂ sorption/desorption isotherms at -196 °C (77 K) using a Micrometrics ASAP 2020 system (Micromeritics Instrument Co., Norcross, GA, USA). To assess the effect of atrazine sorption on pore size distribution, atrazine-loaded sorbents were measured along with the atrazine-free sorbents. Prior to N₂ sorption, the sorbents were activated at 300 °C under vacuum for 3 h, and the atrazine-loaded sorbents were activated at 100 °C under vacuum for 3 h. The activation procedure presumably removed the sorbed water residues completely without decomposing the sorbed atrazine molecules if presented. Surface elemental compositions were determined by X-ray photoelectron spectroscopy (XPS) (Perkin Elmer PHI 550 ESCA/SAM, USA). Elemental analysis was performed on a Vario EL cube (Elementar, Germany). Transmission electron microscope (TEM) images were collected on a Hitachi H-800 TEM (Hitachi, Japan), and

scanning electron microscope (SEM) images on an EMAX Energy EX-250 SEM (Hitachi). X-ray diffraction (XRD) patterns were recorded on a Rigaku D/max-RA powder diffractometer (Rigaku, Tokyo, Japan) using Cu K α radiation. Mineral compositions of BC sorbents were determined by X-ray fluorescence (XRF) spectroscopy (ARL 9800XP+, Switzerland). TOC analysis was measured using a Shimadzu 5000A TOC analyzer (Japan).

2.4 Batch sorption and desorption experiment

Batch sorption experiment was conducted using a batch approach as described previously (Zhu and Pignatello, 2005a). Briefly, each 40-mL amber vial with polytetrafluoroethylene-lined screw cap received 10 mg of sorbent and 0.02 mol L⁻¹ sodium chloride (NaCl) background solution. The sorbent samples were pre-wetted for 12 h and then a pre-determined volume of sorbate stock solution (prepared in methanol for nitrobenzene and naphthalene, and in 0.02 mol L⁻¹ NaCl solution for atrazine) was added to achieve an initial concentration range of 0.005–0.220 mmol L⁻¹ for nitrobenzene, 0.020–0.155 mmol L⁻¹ for naphthalene, and 0.0003–0.142 mmol L⁻¹ for atrazine. The volume percentage of methanol, if applied, was kept below 0.1% (v/v) to minimize the cosolvent effect. The samples were then filled with 0.02 mol L⁻¹ NaCl, wrapped with aluminum foil, and tumbled at 6 rpm and 25 $\pm$ 1 °C for 3 d. This duration was sufficient to reach apparent sorption equilibrium (no further uptake of sorbate) according to sorption kinetics data as discussed later. Afterwards, the samples were centrifuged at 3000 rpm for 10 min, and the supernatant was analyzed for solute concentrations using high performance liquid chromatography (HPLC) equipped with an ultraviolet detector as described in SI. Sorption isotherms of naphthalene and atrazine to water extracted DBC were also collected using a dialysis bag method combined with solid-phase microextraction (details described in SI). To take into account any potential sorbate loss to experimental apparatus (e.g., glassware and

septum) or through volatilization during the experiments, calibration curves were obtained from the control treatments that underwent the same experimental procedure without any sorbent added. Calibration curves included at least 6 standard concentration levels to cover the test concentration range, and were used in the HPLC analysis of aqueous-phase sorbate concentrations. The sorbed mass of sorbate was calculated from the difference between initial and final aqueous-phase masses. Following the sorption experiment, desorption experiment was conducted using a single-step, centrifuge-withdraw-refill method as described in our previous study (Ji et al., 2009).

Single batch experiment was conducted to assess sorption/desorption kinetics with repeated sampling (< 0.5 ml aliquot each time for HPLC analysis) using 60-mL vials. Calibration curves were obtained separately from sorbent-free controls receiving repeated sampling during the same time interval. The sample pH was adjusted by hydrochloric acid or NaOH and was at 6.0 ± 0.2 as measured by the end of the batch experiment. Triplicate samples were run for the kinetic experiments, and duplicate for all other experiments.

3. Results and Discussion

3.1 Characterization of sorbents

Surface elemental compositions, specific surface area, and pore volume parameters of sorbents are provided in Table 1, and their elemental and mineral compositions in Table S2. The BC surfaces contained mainly C (67.0–75.6%) and O (20.9–26.8%) with minor amount of Si and N. After the removal of DBC, the change of specific surface area was negligible (< 1.4%), while total pore volumes and micropore volumes increased significantly by up to 12.7% and 60%, respectively, with a larger increase observed for BC-B (Table 1). These results suggested that the accessibility of BC pores, specifically micropores, increased via the removal of DBC. TOC

measurements indicate that DI water and NaOH extractions could remove 0.61% and 9.04% of organic carbon from bulk BC, respectively. In addition to organic carbon content, the extraction treatment (especially with NaOH) pronouncedly lowered the content of SiO₂ and K₂O in the bulk BC as supported by the XRF analysis (Table S2).

The surfaces of CMK3 and CMK3-NH₂ composed mainly of carbon (> 87.7%) and oxygen to a lesser extent (< 8.77%). The N content on the surface of CMK3-NH₂ was 3.59%, suggesting successful grafting of alkylamino groups. The loading of humic acid led to increased O content but decreased C content on CMK3-NH₂-HA as compared with CMK3-NH₂. CMK3 had the largest specific surface area (972.5 m² g⁻¹), followed by CMK3-NH₂ (680.9 m² g⁻¹) and CMK3-NH₂-HA (709.6 m² g⁻¹). Similar trends were observed on total pore volume and micropore volume of the three CMK3 sorbents. Surprisingly, CMK3-NH₂-HA exhibited higher surface area and higher pore volume than CMK3-NH₂, despite the fairly high loading level of humic acid (24.80 mg C g⁻¹). This could be probably due to the specific Lewis acid-base and/or electrostatic interactions between alkylamino groups and carboxylic groups of humic acid (Tao et al., 2010), which might help anchor and stretch out the twined alkylamino groups, resulting in slightly enhanced pore opening of CMK3-NH₂-HA than that of CMK3-NH₂.

The TEM images of BC sorbents (Figure S1) revealed that the removal of DBC made BC-W and BC-B less opaque, indicating plausibly more open pore structures than that of BC. This was also supported by the SEM images with successively increasing pore openness among BC, BC-W, and BC-B (Figure S2). Similarly, it was observed that the original CMK3 manifested highly ordered and open hexagonal pore structures, whereas the pores of CMK3-NH₂ and CMK3-NH₂-HA were partially clogged, but to a lower degree for CMK3-NH₂-HA (Figure S3).

The broad XRD peaks at 24.4° observed for BC sorbents (Figure S4) indicated the presence

of ordered graphitic structure (Wang et al., 2009). The peak intensities of both BC-W and BC-B were stronger than that of BC, reflecting higher degree of ordered graphitic structure after the removal of DBC. The small angle XRD patterns of the three CMK3 sorbents were also compared in Figure S4. The distinct diffraction peak at 1° (100) suggested an ordered hexagonal mesopore structure (Jun et al., 2000). Compared with CMK3, the much lower peak intensities observed for CMK3-NH₂ and CMK3-NH₂-HA suggested the occurrence of pore clogging.

3.2 Sorption isotherm

Sorption isotherms of different sorbate/sorbent combinations are presented in Figure 1. The sorption isotherms were fitted with the Freundlich model, $q = K_F C_e^n$, where q (mmol kg⁻¹) is the sorbed solid-phase concentration, C_e (mmol L⁻¹) is the equilibrium aqueous-phase concentration, K_F (mmol¹⁻ⁿ Lⁿ kg⁻¹) is the Freundlich affinity coefficient, and n (dimensionless) is the Freundlich linearity index. The fitting parameters are presented in Table S3, and the Freundlich model fitted the isotherm data well ($R^2 > 0.97$). Clearly, sorption of nitrobenzene, naphthalene, and atrazine to BC was enhanced by the removal of DBC, following the same increasing order of sorbent micropore volume (BC < BC-W < BC-B). Furthermore, for a given BC sorbent the sorption enhancement by the removal of DBC was positively correlated with sorbate molecular size (atrazine > naphthalene > nitrobenzene). The enhanced sorption was likely caused by increased accessibility of BC micropores that were initially clogged by DBC. Apparently, the removal of pore-clogging would be more effective in enhancing sorption for larger-sized sorbate molecules (e.g., atrazine) than for smaller-sized sorbate molecules (e.g., nitrobenzene). The sorbate size-dependent pore-clogging mechanism was explored earlier to explain the suppressed sorption of organic solutes to charcoal by pre-sorbed humic acid (Pignatello et al., 2006). It is noteworthy that DBC made negligible contribution to the overall sorption to bulk BC, as justified

by comparing the sorption isotherms of naphthalene and atrazine between DBC and BC (Figure S5). Thus, DBC influenced sorption of organic solutes to bulk BC by acting as a pore clog rather than as a separated individual sorbing phase.

The pore-clogging mechanism proposed for BC can be further illustrated by comparing the sorption data of nitrobenzene and atrazine among the three CMK3 sorbents (Figure 1d and 1e). For these two test sorbates, sorption to CMK3-NH₂ and sorption to CMK3-NH₂-HA were very close, but they were both tremendously lower than sorption to CMK3. This was because the grafting of alkylamino groups and subsequent loading of humic acid pronouncedly clogged CMK3 pores, and hence led to pronounced sorption suppression to CMK3-NH₂ and to CMK3-NH₂-HA.

3.3 Pore size distributions of sorbents

Figure 2 compares the pore size distributions within the range of 0–5 nm for each test sorbent before and after atrazine loading. Clearly, the removal of DBC created more pore volume, particularly for micropores (< 2 nm), while the surface grafting of alkylamino groups and subsequent loading of humic acid on CMK3 markedly lowered the pore volume. For all sorbents, the pore size distribution profiles were substantially attenuated by atrazine sorption; however, a detailed examination indicated that the micropore volume was more attenuated than the mesopore volume with the exception of BC (Table 1). In fact, the micropore volumes of BC-W and BC-B (initially 0.017 and 0.024 cm³ g⁻¹) almost completely vanished after atrazine sorption (0.005 and 0.003 cm³ g⁻¹). Consistently, for CMK3 sorbents the micropore volumes decreased by ~66% after atrazine sorption, whereas the mesopore volumes decreased by only 20–31%. These results illustrated that the sorbate molecules preferred the open, exposed micropores, likely due to their higher adsorption energies and easy access.

3.4 Sorption kinetics

Figure 3 compares sorption kinetics among varying sorbate/sorbent systems. For all test sorbates, the sorption kinetics was generally accelerated by the removal of DBC from BC, but impeded by the surface grafting of alkylamino groups on CMK3. These observations were in good agreement with the sorbent pore volume which is a description of pore exposure. Compared with the sorption kinetics (Figure 3), the desorption kinetics had much lower porosity dependency of sorbent (Figure S6). Interestingly, in contrast to nitrobenzene, atrazine exhibited faster sorption kinetics to CMK3-NH₂-HA than to CMK3-NH₂. As discussed earlier, the pore opening of CMK3-NH₂-HA could be slightly enhanced as compared with CMK3-NH₂ (Table 1); as a result, the sorption kinetics of the larger-sized atrazine to CMK3-NH₂-HA was more accelerated relative to the smaller-sized nitrobenzene.

The sorption kinetic data were described by an empirical biphasic pseudo-second order model consisting of a fast sorption phase and a slow sorption phase (Shi et al., 2011; Yang et al., 2008), expressed as:

$$q_t = q_{St} + q_{Ft} = t / (\frac{1}{k_S q_{Se}^2} + \frac{t}{q_{Se}}) + t / (\frac{1}{k_F q_{Fe}^2} + \frac{t}{q_{Fe}}) \quad (1)$$

where q_t is the total sorbed concentration, and q_{St} and q_{Ft} are the sorbed concentrations to the slow and fast sorption phases, respectively, at time t ; q_{Se} and q_{Fe} are the equilibrium sorbed concentrations by the two phases, and k_S and k_F are the rate constants for the slow and fast sorption phases, respectively. For BC sorbents, the fast sorption phase presumably corresponds to readily accessible sites on carbon surfaces and open, large-sized macro- and mesopores, while the slow sorption phase corresponds to less accessible sites of clogged, small-sized micropores. The model fitting results are presented in Figures S7-S9 and Table S4. For all test sorbates, k_S and k_F both increased by the removal of DBC from BC, but decreased dramatically by the

grafting of alkylamino groups on CMK3. Similar trends can be found for the ratio of q_{Se}/q_{Fe} (Table S4) which reflects the relative contributions of the two sorption phases. The contribution from the slow sorption phase consisting mainly of small-sized micropores increased after the removal of DBC from BC, but decreased after the grafting of alkylamino groups on CMK3. These results are in excellent agreement with the micropore-clogging mechanism.

3.5 Sorption irreversibility

Desorption isotherms of atrazine from different sorbents are presented in Figure 4, along with their respective sorption isotherms. The desorption data of nitrobenzene and naphthalene are shown in Figures S10-S11. It appeared that the degree of irreversible sorption varied among sorbents. To quantify the degree of irreversible sorption, a thermodynamic index of irreversibility (*III*) was calculated using a previously developed method (Sander et al., 2005),

$$III = \frac{\ln C^\gamma - \ln C^D}{\ln C^S - \ln C^D} \quad (2)$$

where C^S and C^D represent the aqueous concentrations of the sorption and desorption points, respectively, C^γ represents the concentration of the hypothetical reversible desorption state on the sorption isotherm with the same aqueous concentration as the desorption point. This index measures the molar free energy of sorption for creating a metastable sorbent state to cause irreversible sorption. The theoretical value of *III* varies between 0 and 1, corresponding to fully reversible sorption and fully irreversible sorption, respectively. The calculated *III* values are summarized in Table 2 for the different sorbate/sorbent combinations. Despite their relatively low content and negligible contribution to the overall sorption to BC (Figure S5), the presence of DBC markedly influenced the degree of irreversible sorption. Using atrazine as an example, the removal of DBC lowered *III* from 0.68 (BC) to 0.39 (BC-B).

The DBC-dependent irreversible sorption to BC sorbents can be explained by the micropore

deformation mechanism. As demonstrated in our previous study (Qu et al., 2016), the organic component of DBC comprised primarily of small aromatic clusters substituted by carboxylic groups, and by phenolic groups to a less extent. These structures are much more flexible than the highly rigid graphitized carbons contained in BC sorbents. The microporous interstices formed between DBC and graphitized carbons could be deformed to some extent (on the DBC side) by interactions with sorbate molecules, and irreversible sorption might occur due to incomplete relaxation of pore deformation (metastate). Accordingly, the irreversible sorption to BC would be alleviated by the removal of DBC. Consistent with this hypothesis, our previous study showed that sorption of monoaromatic compounds to template-synthesized microporous carbons was fully reversible because the sorbent had completely rigid and ordered open pore structures that could not be deformed (Ji et al., 2009).

An alternative explanation could be the ink-tank effect induced by micropore clogging. It can be imagined that DBC at or near the pore mouth could partially block the inside pore volumes via forming ink-tank pore structures. The activation energies for sorbate molecules to escape from the ink-tank pores are much greater than the energies for them to enter the pore (Pignatello and Xing, 1996). Therefore, sorption and desorption would undergo hysteretic pathways, consequently leading to sorption/desorption hysteresis. Notably, the irreversible sorption induced by either micropore deformation mechanism or ink-tank effect became more pronounced as the pore size decreased. This helps explain why the degree of irreversible sorption was negatively correlated with sorbent micropore volume (i.e., BC-B > BC-W > BC).

The surface grafting of alkylamino groups led to strong irreversible sorption to CMK3 (see the *TII* values in Table 2). For example, the *TII* value of nitrobenzene was only 0.08 for CMK3, but increased to 0.90 for CMK3-NH₂. Similar to the effect of DBC on BC, the surface grafted

alkylamino groups could induce pore deformation as well as ink-tank effect. However, the loading of humic acid on CMK3-NH₂ led to opposite hysteresis effects for nitrobenzene and atrazine, similar to their kinetic patterns (Figure 3). Upon loading of humic acid, the *T_{III}* value kept nearly constant (0.90 and 0.94) for nitrobenzene, but was pronouncedly decreased from 0.88 to 0.50 for atrazine. These contrasting results can be reconciled by the difference in sorbate molecular size. The irreversible sorption of the larger-sized atrazine by the slightly enhanced micropore volume of sorbents would be more relieved relative to the smaller-sized nitrobenzene (see sorbent pore volumes in Table 1).

4. Conclusion

The present study shows that removal of the DBC fraction from a rice residue-derived BC with DI water or 0.5 M NaOH solution could pronouncedly accelerated sorption kinetics and reduced sorption irreversibility of three probe sorbate molecules (nitrobenzene, naphthalene, and atrazine) to the BC. The observations were attributed to increased accessibility of BC micropores initially clogged by DBC and the key influence of DBC on the micropore structures of BC. The proposed DBC-induced pore effects can be well modeled and described by comparing the sorption-desorption properties of the CMK3 sorbents. Consistently, sorption kinetics to CMK3 sorbents was substantially decreased whereas the sorption irreversibility was increased by impregnating sorbent pores with surface-grafted alkylamino groups and by subsequent loading of humic acid. Findings of this study indicate that, in spite of the relatively low contents, the presence of DBC can effectively affect the sorption irreversibility and kinetics of hydrophobic organic contaminants to bulk BC. Intriguingly, DBC plays an important and previously unrecognized role in sorption-desorption processes of organic contaminants to BC, and thus may have significant implications on the environmental fate of organic contaminants. From a practical

standpoint, the findings in this study imply that the biochar application in agriculture may influence the mobility of organic compounds differently overtime when DBC is released from biochar during weathering and aging processes. On one hand, the increase in sorption capacity and kinetic rate could enhance the immobilization of organic contaminants; on another hand, the decrease in sorption irreversibility could lead to more release of organic contaminants to water.

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Table 1. Surface Elemental Composition, Specific Surface Area, and Pore Volume Parameters for Different Sorbents.

Sorbent	Surface elemental composition ^a				Specific Surface area ^b (m ² g ⁻¹)	V _{mic} ^c (cm ³ g ⁻¹)	V _{mes} ^d (cm ³ g ⁻¹)	V _t ^e (cm ³ g ⁻¹)	V _{mic} /V _t	Sorbed-Specific Surface area ^{b,f} (m ² g ⁻¹)	Sorbed -V _{mic} ^{c,f} (cm ³ g ⁻¹)	Sorbed -V _{mes} ^{d,f} (cm ³ g ⁻¹)	Sorbed -V _t ^{e,f} (cm ³ g ⁻¹)
	C%	O%	Si%	N%									
BC	67.02	26.78	4.13	2.06	58.32	0.015	0.048	0.063	0.23	28.15	0.011	0.025	0.036
BC-W	67.49	26.24	4.07	2.21	57.48	0.017	0.052	0.069	0.24	25.01	0.005	0.024	0.029
BC-B	75.63	20.90	0.68	2.79	57.43	0.024	0.047	0.071	0.33	24.10	0.003	0.025	0.028
CMK3	96.41	3.59	BDL ^g	BDL	972.50	0.350	0.640	0.990	0.35	703.40	0.117	0.513	0.630
CMK3-NH ₂	87.65	8.77	BDL	3.59	680.90	0.250	0.480	0.730	0.34	505.70	0.084	0.329	0.413
CMK3-NH ₂ -HA	81.04	15.35	BDL	3.61	709.60	0.270	0.540	0.810	0.33	554.90	0.097	0.413	0.520

^aDetermined by X-ray photoelectron spectroscopy (XPS).^bDetermined by N₂ sorption using the Brunauer-Emmett-Teller (BET) method.^cMicropore volume, calculated using the Dubinin-Astakhov method.^dMesopore volume, calculated by V_t-V_{micro}.^eTotal pore volume, determined at P/P₀ =0.99.^fMeasured for sorbents with pre-sorbed atrazine.^gBelow detectable level.

Table 2. Thermodynamic Index of Irreversibility (*TII*) for Different Sorbate/Sorbent Combinations.

Sorbate	<i>TII</i>					
	BC	BC-W	BC-B	CMK3	CMK3-NH₂	CMK3-NH₂-HA
Nitrobenzene	0.47±0.08	0.42±0.07	0.33±0.09	0.08±0.08	0.90±0.10	0.94±0.08
Naphthalene	0.74±0.07	0.73±0.07	0.66±0.09	ND ^a	ND	ND
Atrazine	0.68±0.07	0.65±0.07	0.39±0.09	0.30±0.09	0.88±0.20	0.50±0.25

^aNot determined.

Figure 1. Sorption isotherms plotted as sorbed-phase concentration (q) vs. aqueous-phase concentration (C_e) at equilibrium for different sorbate/sorbent combinations. (a) Nitrobenzene with BC sorbents. (b) Naphthalene with BC sorbents. (c) Atrazine with BC sorbents. (d) Nitrobenzene with CMK3 sorbents. (e) Atrazine with CMK3 sorbents.

Figure 2. Pore size distributions of sorbents before and after sorption of atrazine: (a) BC; (b) BC-W; (c) BC-B; (d) CMK3; (e) CMK3-NH₂; (f) CMK3-NH₂-HA. The pore size distribution profile was calculated by the slit Density Function Theory (DFT) method for the BC sorbents and by the Barrett-Joyner-Halenda (BJH) method for the CMK3 sorbents. The sorbed concentrations of atrazine were determined to be 14.3, 15.0, 15.2, 200, 183, and 174 mmol kg⁻¹ for BC, BC-W, BC-B, CMK3, CMK3-NH₂, and CMK3-NH₂-HA, respectively.

Figure 3. Sorption kinetics plotted as sorbed-phase concentration (q_t) to equilibrium sorbed concentration (q_e) vs. time (t , h) for different sorbate/sorbent combinations. (a) Nitrobenzene with BC sorbents. (b) Naphthalene with BC sorbents. (c) Atrazine with BC sorbents. (d) Nitrobenzene with CMK3 sorbents. (e) Atrazine with CMK3 sorbents. Error bars, in most cases smaller than the symbols, represent standard deviations calculated from triplicates.

Figure 4. Sorption and single-step desorption data plotted as solid-phase concentration (q) vs. aqueous-phase concentration (C_e) at equilibrium for atrazine to different sorbents. (a) BC. (b) BC-W. (c) BC-B. (d) CMK3. (e) CMK3-NH₂. (f) CMK3-NH₂-HA.

Graphical abstract