

퇴적물내 Black Carbon에 대한 Naphthalene과 Phenanthrene의 수착 및 탈착동력학

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Sorption and Desorption Kinetics of Naphthalene and Phenanthrene on Black Carbon in Sediment

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ABSTRACT

Black carbon (BC), a kind of high surface area carbonaceous material (HSACM), was isolated from Andong lake sediment. Sorption and desorption kinetics of naphthalene (Naph) and phenanthrene (Phen) in organic carbon (OC) and BC in the Andong lake sediment were investigated. Several kinetic models such as one-site mass transfer model (OSMTM), two-compartment first-order kinetic model (TCFOKM), and a newly proposed modified two-compartment first-order kinetic model (MTCFOKM) were used to describe the sorption and desorption kinetics. The MTCFOKM was the best fitting model. The MTCFOKM for sorption kinetics showed that i) the sorbed amounts of PAHs onto BC were higher than those onto OC, consistent with BET surface area; ii) the equilibration time for sorption onto BC was longer than those onto OC due to smaller size of micropore (11.67 Å) of BC than OC (38.18 Å); iii) initial sorption velocity of BC was higher than OC; and iv) the slow sorption velocity in BC caused the later equilibrium time than OC even though the fast sorption velocity was early completed in both BC and OC. The MTCFOKM also described the desorption of PAHs from the OC and BC well. After desorption, the remaining fractions of PAHs in BC were higher than those in OC due to stronger PAHs-BC binding. The remaining fractions increased with aging for both BC and OC.

Key words : Black carbon, Sorption/Desorption Kinetics, Naphthalene, Phenanthrene, Organic carbon

1. Introduction

As sorption and desorption of polycyclic aromatic hydrocarbons (PAHs) by sediments are dominated by their distribution, fate and transport in environment, their interaction mechanisms have been studied in numerous studies (Agarwal and Bucheli, 2011; Cornellison et al., 2004, 2005; Jonker and Koelmans, 2001, 2002). However, it is difficult to clearly identify all the factors controlling sorption and desorption of contaminants in sediments because of the

heterogeneous nature of sediments, specifically rendered by the presence of high surface area carbonaceous material (HSACM) such as soot, black carbon (BC), coal and kerogen in sediments (Agarwal and Bucheli, 2011).

Sorption of hydrophobic organic compounds (HOCs) onto organic carbon (OC) has received considerable attention as the most important process controlling interaction between HOCs and soils or sediments. Therefore, the organic carbon content (f_{oc}) is one of the most important parameters for the sorption/desorption and,

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in an extensive point, fate and transport of these compounds in soils and sediments (Agarwal and Bucheli, 2011; Brusseau, 1995; Chiou et al., 1998; Pignatello and Xing, 1996).

Among organic carbons in sediment, the black carbon (BC) with the high surface area serves as a strong sorbent in spite of very small fraction of BC in soil or sediment (Agarwal and Bucheli, 2011; Bucheli and Gustafsson, 2001; Cornelissen et al., 2005; Jonker and Koelmans, 2002). Lambert et al. (2011) reported that the sorption of HOCs in complex matrix composed of minerals and organic matters was dominated by sorption onto OC and preferential sorption of HOCs onto BC can increase the distribution onto the solid phase by 1-3 orders of magnitude. However, still there are not much information on sorption/desorption kinetics of PAHs occurring in macro- (> 50 nm), meso- (2-50 nm), or micro-pores (< 2 nm) (Rockne et al., 2000). Therefore, it is expected that the PAHs sorption and desorption in BC take longer time depending on the pore size.

For sorption and desorption kinetics in BC, a fast initial uptake or release followed by a very slow sustained approach to apparent equilibrium over time scales of weeks to years has been commonly accepted (Cornelissen et al., 1997; Jonker et al., 2005). To explain slow desorptive phenomena, Ball and Roberts (1991a; b) interpreted the slow diffusion in terms of retarded sorbate diffusion by steric hindrance in narrow soil pores. Cornelissen et al. (1997) further reported that slow and extremely slow desorption were caused by both a combination of slow release from strongly sorbing high-energy sites in the organic matter and slow diffusion.

In this work, the sorption and desorption kinetics of naphthalene (Naph) and phenanthrene (Phen) in OC and BC in sediment were analyzed by several kinetics models including the one-site mass transfer model (OSMTM), the two-compartment first-order kinetic model (TCFOKM) and the modified two-compartment first-order kinetic model (MTCFKOM) in order to compare between the kinetic characteristics of the sorption and desorption onto OC and BC. The newly derived MTCFKOM was analyzed in detail in terms of the equilibration time, the sorbed or desorbed amounts of PAHs at equilibration time, and the slow and

fast sorption and desorption velocities. In addition, the effects of aging on desorption behaviors were also evaluated.

2. Materials and methods

2.1. Sediments sources

Sediment sample was obtained from the Andong reservoir in Korea, oven-dried at 60°C for 48 h, ground using a mortar and passed through a 212 μm sieve (No. 70) to remove debris, shell and so on, and then stored in sealed containers at room temperature.

2.2. Isolation and Quantification of Black Carbon

The BC from the sediment was isolated by an acid and chemical treatment method suggested by Lim and Cachier (1996). In short, 40 g of dried sediment samples were treated with 200 mL of 3 M HCl by ultrasonic (3210R-DTH, Branson[®], USA) for 5-15 min and left the reaction over 24 h to remove carbonate from the sediments. Following repeated centrifuge and rinsing (3-6 times) with deionized water, 200 mL of 10 M HF/1 M HCl was added to the residue and tumbled at room temperature for 24 h to liberate any superficial carbonaceous material which may be trapped between the silicate sheets (Lim and Cachier, 1996). After centrifugation and rinsing (3-6 times) until pH in the rinse water become 4-5, the samples were treated by 10 M HCl for 24 h, dried at 60°C, and chemically oxidized with 200 mL of 0.1 M $\text{K}_2\text{Cr}_2\text{O}_7$ /2 M H_2SO_4 . The oxidized samples were further treated by sonication in an ultrasonic bath at 40°C for 10 min to break up aggregates and to ensure rapid contact of the sediment with the oxidant and then transferred to a water bath at $55 \pm 1^\circ\text{C}$ for 60 h. After the reaction, the samples were washed with deionized water for 3-6 times and dried at 60°C. The chemically treated sediment (CTS) contains BC and some refractory kerogen depending on the extent of oxidation (Lim and Cachier, 1996).

The organic carbon contents (%) in the sediment and CTS were measured by the elemental analyzer (Elementar, vario MACRO CHNS, Germany) to obtain the OC (f_{OC}) and BC contents (f_{BC}), respectively.

2.3. Methods for Analysis of Sorbent Characterization

To investigate the characteristics of sediment and its black carbon, scanning electron microscopy (SEM), Brunauer-Emmett-Teller (BET) surface area and X-ray diffraction (XRD) analyses were conducted. SEM (Hitachi S-4300, Japan) analysis was used to investigate the shapes, sizes and morphologies of the sediment and BC. The BET surface area and pore size distribution (microporosity) were analyzed by a specific surface area and pore size analyzer (NAVA 2000 & Autosorb-1-C) with relative pressures in the range of 10^{-6} to 10^0 and at 77 K to obtain the nitrogen gas adsorption isotherms. Mineral compositions of sediment were identified by an X-ray diffractometer (XRD, Rigaku, D/Max-2500) to estimate non-removed mineral species during demineralization.

2.4. Sorbate and Chemicals.

Naph (Aldrich Chemical Co., 99+%) and Phen (Sigma Chemical Co., 96+% HPLC grade) were used as sorbates. The radio-labeled [^{14}C] Naph (American Radiolabeled Chemicals, Inc. (ARC), 50 mCi/mmol) and [^{14}C] Phen (ARC, 55 mCi/mmol) were used as radio-tracers. The ^{14}C -Naph and -Phen were further diluted with unlabeled ^{12}C stock solution (1000 mg/L of Naph and Phen in methanol) to prepare ^{14}C stock solution for desired concentrations. Thus, the ^{14}C stock solutions of the Naph and Phen contained both labeled ^{14}C - and unlabeled ^{12}C -Naph and -Phen, respectively.

Buffer solution (pH 8.0) was prepared as a background solution before each sorption experiment using the ^{14}C stock solution and electrolyte solution including 1 mM $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ (Duksan Pure Chemical Co. Korea, 70%), 0.5 mM $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ (Duksan Pure Chemical Co. Korea, 98%) and 0.5 mM $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ (Sigma Chemical Co., 99.5-105.0%). 200 mg/L of NaN_3 (Duksan Pure Chemical Co., 97%) was used as a bacterial inhibitor.

2.5. Sorption Kinetic Study

Sorption kinetic studies were conducted in batch mode using 40 mL amber glass vials (Fisher Co.) with Teflon-faced silicone septa. Control experiments conducted to investigate sorption of chemicals on the surface of the glassware showed that adsorption of Naph and Phen on the

glass surfaces was negligible. 1.0 g of the sediment or 0.5 g of the BC was placed into the vials and then Naph solution (= 3 mg/L, initial radioactivity = 2,000 cpm/mL) or Phen solution (= 1 mg/L, initial radioactivity = 2,000 cpm/mL) was carefully added minimizing the headspace of the vials. The vials were placed in a tumbler and completely mixed at 20°C and 1 rpm.

After predetermined time intervals (30 min to 14 day), the vials were collected and centrifuged in a centrifuge (Hanil, MF6100) for 20 min at 2,000 rpm. 1 mL of the supernatant was mixed with 8 mL of scintillation cocktail (Ecolite(+)TM, MP Biochemicals) and the radioactivity was analyzed via scintillation counting (LSC, EG&G Wallac Co., 1220 Quantulus). The solid phase equilibrium concentrations were calculated by assuming that all concentration changes in solution were caused by sorption onto the solid phase. All experiments were conducted in duplicate.

The sorbed amounts of PAHs onto OC (= q_{OC}) and BC (= q_{BC}) were calculated by the following equation:

$$q(t)_{OC(\text{or } BC)} = q(t)f_{OC(\text{or } BC)} = (C_0 - C(t)) \frac{V/W}{f_{OC(\text{or } BC)}} \quad (1)$$

where $q(t)_{OC(\text{or } BC)}$ is the sorbed amount of PAH onto OC or BC (mg/kg-OC or -BC) at time t (day), f_{OC} and f_{BC} are the OC content in the sediment and the BC content in CTS, respectively (-), C_0 and $C(t)$ are the sorbate concentrations (mg/L) in the solution at initial and at time t , respectively, V (L) is the volume of solution, and W (g) is the mass of sorbent.

2.6. Desorption Kinetic Study

Effect of aging on the desorption kinetics of Naph and Phen from OC in the sediment and BC in the CTS was investigated. Desorption kinetic experiment was conducted using the solute-loaded sorbents after sorption for 7, 30 and 100 d. After centrifugation, approximately 95% of the supernatant was replaced with fresh solute-free electrolyte solution. The exact amount of the supernatant removed was gravimetrically determined and nonzero initial concentration of the aqueous solution in the desorption stage was computed from the mass balance accordingly. The vials were placed and completely mixed in a tumbler at 20°C and 1 rpm. After predetermined time intervals (30 min to 21

day), the sorbent was separated from the solution by centrifuging for 20 min at 2,000 rpm. The equilibrium concentrations of Naph in the supernatant were determined via scintillation counting. The solid phase equilibrium concentrations were calculated by assuming all concentration changes in solution phase resulted from desorption from the solid phase. All experiments were run in duplicate.

3. Sorption and Desorption Kinetic Models

3.1. One-Site Mass Transfer Model (OSMTM)

The OSMTM for sorption rate was proposed by Nzungung et al. (1997). Basically, the sorption kinetics were represented as the first-order equation as follows:

$$\frac{VdC}{Wdt} = k_s(q - K_{p,s}C) = k_s\left(q_0 + \frac{V}{W}(C_0 - C) - K_{p,s}C\right)$$

with $C = C_0$ at $t = 0$ (2)

where k_s is the mass transfer coefficient (1/day) for sorption between the solution and solid phase and $K_{p,s}$ represents the partition coefficient for sorption (L/kg). Subscript 0 denotes initial concentration in each phase. Eq. (2) leads to $q_e = K_{p,s}C_e$ at sorption equilibrium, where the subscript e denotes equilibrium concentration in each phase. Assuming fresh sorbent (i.e., $q_0 = 0$), Eq. (2) can be rewritten as follows (Oh and Shin, 2010):

$$\frac{C(t)}{C_0} = \frac{C_e}{C_0} + \left(1 - \frac{C_e}{C_0}\right) \exp\left[-\left(\frac{C_0}{C_e}k_s\right)t\right]$$
 (3)

To estimate the sorption kinetics of Naph and Phen onto OC or BC, the Eq. (3) was changed using $W(q - q_0) = V(C_0 - C)$ as follows:

$$q(t) = q_e \left[1 - \exp\left(-\frac{C_0}{C_e}k_s t\right) \right] = q_e \left[1 - \exp\left(-\frac{k_s}{1 - \frac{Wq_e}{VC_0}}t\right) \right]$$
 (4)

We assumed that most of Naph and Phen sorption reactions are affected by f_{OC} and f_{BC} . The amount of Naph and Phen sorbed onto OC and BC at equilibrium is defined as the $q_{e,OC}$ and $q_{e,BC}$, respectively. Considering the f_{OC} and f_{BC} conception as $W \cdot f_{OC(or BC)} \cdot q_{OC(or BC)} = V(C_0 - C)$ as the Eq. (4) was transformed to:

$$q(t)_{OC(or BC)} = q_{e,OC(or BC)} \left[1 - \exp\left(-\frac{k_s}{1 - \frac{W \cdot f_{OC(or BC)} q_{e,OC(or BC)}}{VC_0}}t\right) \right]$$
 (5)

where $q(t)_{OC}$ ($= q(t)/f_{OC}$, mg/kg-OC) or $q(t)_{BC}$ ($= q(t)/f_{BC}$, mg/kg-BC) and $q_{e,OC}$ ($= q_e/f_{OC}$, mg/kg-OC) or $q_{e,BC}$ ($= q_e/f_{BC}$, mg/kg-BC) are the concentrations of Naph and Phen sorbed onto OC (or BC) at time t and at equilibrium, respectively.

The OSMTM for desorption rate was derived (Kim et al., 2005) taking the same concept as Nzungung et al. (1997) did in their original derivation for sorption rate. After substituting the dq for dC in Eq. (2) using the $Wdq = -VdC$, the OSMTM for desorption rate was derived as:

$$\frac{VdC}{Wdt} = k_d(q - K_{p,d}C) \text{ or } -\frac{dq}{dt} = k_d\left(q - K_{p,d}\left[C_0 - \frac{W}{V}(q - q_0)\right]\right)$$

with $q = q_0$ at $t = 0$ (6)

where k_d and $K_{p,d}$ are the mass transfer coefficient (1/day) and partition coefficient for desorption (L/kg), respectively. Similarly, Eq. (6) is reduced to $q_e = K_{p,d}C_e$ at desorption equilibrium. We assumed that partition coefficients for sorption and desorption are different.

Since the initial concentration in the solution, C_0 is, in general, not exactly zero in desorption experiment, the solution of OSMTM for desorption can be written as follows:

$$\frac{q(t)}{q_0} = \frac{q_e}{q_0} + \left(1 - \frac{q_e}{q_0}\right) \exp\left[-\left(\frac{q_0 k'_d}{q_e}\right)t\right]$$

with $k'_d = k_d K_{p,d} \left(\frac{C_0}{q_0} + \frac{W}{V}\right)$ (7)

The main structure of Eq. (7) is very similar to Eq. (3) for sorption, except for the variable q in desorption instead of C in sorption. Furthermore, the desorption mass transfer coefficient, k_d should be determined from the apparent mass transfer coefficient for desorption (k'_d , 1/day) to compare with the sorption mass transfer coefficient k_s . In Eq. (7), $q(t)$ and q_e can be replaced by $q(t)_{OC}$ (or BC) and $q_{e,OC}$ (or BC), respectively.

3.2. Two-Compartment First-Order Kinetic Model (TCFOKM)

The overall sorption (or desorption) in the TCFOKM was

assumed to consist of the sum of the two first-order sorption (or desorption) rates in the fast and slow compartments (Brusseau and Rao, 1991; Cornellison et al., 1997; Opdyke and Loehr, 1999):

$$\frac{C(t)}{C_0} \left(\text{or } \frac{q(t)}{q_0} \right) = f_1 e^{-k_1 t} + (1-f_1) e^{-k_2 t} \quad (8)$$

where f_1 and $f_2 (= 1 - f_1)$ are the fast and slow sorption (or desorption) compartments, respectively, and k_1 and k_2 are the sorption (or desorption) rate constants in the fast and slow compartments (1/day), respectively. However, the TCFOKM is mathematically wrong because both exponential terms in the right-hand side of Eq. (8) becomes 0 as $t \rightarrow \infty$ (i.e., $e^{-\infty} = 0$) and thus left-hand side term also becomes 0 (i.e., $C(t)/C_0 \rightarrow 0$ for sorption or $q(t)/q_0 \rightarrow 0$ for desorption) (Oh and Shin, 2009). Eq. (8) can be rewritten considering f_{OC} and f_{BC} using the assumption of $W \cdot f_{OC} \cdot q_{OC}$ (or $W \cdot f_{BC} \cdot q_{BC}$) = $V(C_0 - C)$ as follows:

$$q(t)_{OC(\text{or } BC)} = \frac{V}{W f_{OC(\text{or } BC)}} C_0 [1 - f_1 e^{-k_1 t} - (1-f_1) e^{-k_2 t}] \quad (9)$$

3.3. Modified Two-Compartment First-Order Kinetic Model (MTCFOKM)

To overcome the mathematical limitation of the TCFOKM, a modified TCFOKM (MTCFOKM) for sorption is proposed:

$$\frac{q_e - q(t)}{q_e - q_0} = f'_{1,s} e^{-k'_{1,s} t} + (1-f'_{1,s}) e^{-k'_{2,s} t} \quad (10)$$

where $f'_{1,s}$ and $f'_{2,s}$ are the fast and slow sorption fractions (-), respectively, and $k'_{1,s}$ and $k'_{2,s}$ are the sorption rate constants in the fast and slow fractions (1/day), respectively. In Eq. (10), $q(t)$ becomes $q_0 (= 0$ for fresh sediment) at $t \rightarrow 0$ and $q(t)$ approaches to q_e with increasing time (t). Eq. (10) also can be rearranged as follows:

$$\begin{aligned} \frac{q(t)}{q_e} &= 1 - f'_{1,s} e^{-k'_{1,s} t} - (1-f'_{1,s}) e^{-k'_{2,s} t} \quad \text{or} \\ q(t) &= q_e \left[1 - f'_{1,s} e^{-k'_{1,s} t} - (1-f'_{1,s}) e^{-k'_{2,s} t} \right] \end{aligned} \quad (11)$$

Eq. (11) can be rewritten considering PAHs sorption on OC and BC:

$$\begin{aligned} q(t)_{OC(\text{or } BC)} &= q_{e,OC(\text{or } BC)} \left[1 - f'_{1,s} e^{-k'_{1,s} t} - (1-f'_{1,s}) e^{-k'_{2,s} t} \right] \\ &= q_{e,OC(\text{or } BC)} \left[f'_{1,s} \left(1 - e^{-k'_{1,s} t} \right) + (1-f'_{1,s}) \left(1 - e^{-k'_{2,s} t} \right) \right] \end{aligned} \quad (12)$$

where $q(t)_{OC} = q(t)/f_{OC}$ or $q(t)_{BC} = q(t)/f_{BC}$ and $q_{e,OC} = q_e/f_{OC}$ or $q_{e,BC} = q_e/f_{BC}$.

Eq. (12) is divided into the fast and slow sorption rate formulas:

$$q(t)_{OC(\text{or } BC),fast} = q_{e,OC(\text{or } BC)} f'_{1,s} \left(1 - e^{-k'_{1,s} t} \right) \quad (13)$$

$$q(t)_{OC(\text{or } BC),slow} = q_{e,OC(\text{or } BC)} (1-f'_{1,s}) \left(1 - e^{-k'_{2,s} t} \right) \quad (14)$$

Using the mass balance, $W(q - q_0) = V(C_0 - C)$, following equations are obtained:

$$\frac{C(t) - C_e}{C_0 - C_e} = f'_{1,s} e^{-k'_{1,s} t} + (1-f'_{1,s}) e^{-k'_{2,s} t} \quad (15)$$

$$\text{or } \frac{C(t)}{C_0} = \frac{C_e}{C_0} + \left(1 - \frac{C_e}{C_0} \right) \left[f'_{1,s} e^{-k'_{1,s} t} + (1-f'_{1,s}) e^{-k'_{2,s} t} \right] \quad (16)$$

In Eqs. (15) and (16), $C(t) \rightarrow C_0$ as $t \rightarrow 0$ and $C(t) \rightarrow C_e$ as $t \rightarrow \infty$.

Eqs. (11) to (16) are the transformed formulas from Eq. (10) which is also similar to Eq. (8), but Eq. (10) includes q_e in the numerator and denominator of the left-hand side of the equations.

Similarly, the MTCFOKM for desorption can be derived using the mass balance, $W(q - q_0) = V(C_0 - C)$:

$$\frac{q(t)}{q_0} = \frac{q_e}{q_0} + \left(1 - \frac{q_e}{q_0} \right) \left[f'_{1,d} e^{-k'_{1,d} t} + (1-f'_{1,d}) e^{-k'_{2,d} t} \right] \quad (17)$$

where $f'_{1,d}$ and $f'_{2,d}$ are the fast and slow sorption fractions, respectively, and $k'_{1,d}$ and $k'_{2,d}$ are the desorption rate constants in the fast and slow compartments (1/day), respectively. In Eq. (17), $q(t) \rightarrow q_0$ as $t \rightarrow 0$ and $q(t) \rightarrow q_e$ as $t \rightarrow \infty$. In terms of f_{OC} and f_{BC} , Eq. (17) can be rewritten as:

$$\begin{aligned} \left(\frac{q(t)}{q_0} \right)_{OC(\text{or } BC)} &= \left(\frac{q_e}{q_0} \right)_{OC(\text{or } BC)} + \\ &\left[1 - \left(\frac{q_e}{q_0} \right)_{OC(\text{or } BC)} \right] \left[f'_{1,d} e^{-k'_{1,d} t} + (1-f'_{1,d}) e^{-k'_{2,d} t} \right] \end{aligned} \quad (18)$$

3.4. Intraparticle Diffusion Model

The intraparticle diffusion model was used to analyze the slow sorption and desorption processes on OC and BC. The mathematical dependence of uptake, $q(t)$, of sorbates on $t^{1/2}$ is obtained if the sorption process is considered to be influenced by diffusion in the spherical sorbent and by convective diffusion in the sorbate solution (Valderrama et al., 2008). This dependence is given by the following equation (Weber and Morris, 1963):

$$q(t) = K_{di}\sqrt{t} + A \quad (19)$$

where K_{di} is the intraparticle diffusion rate constant ($\text{mg/g}/\text{min}^{1/2}$) and A (mg/g) is a constant that gives an indication of the thickness of the boundary layer.

All model parameters were estimated by non-linear regression using a commercial software package, Table Curve 2D (Version 5.1, SYSTAT Software, Inc.).

4. Results and discussion

4.1. Sorbent Characteristics

The SEM images of the sediment and BC at $\times 10\text{k}$ magnification scale are depicted in Fig. 1. The morphology and size of BC was clearly different from the sediment. Compared to the sediment, the higher surface area of BC was attributed to the smaller particle size of BC. Jonker and Koelmans (2002) reported that various sizes of the traffic soot and oil soot were observed in the BC particles and the most aciniform agglomerates in BCs were less than $50\ \mu\text{m}$

in size. In our study, the particles looking like the ‘bunches of grapes’ were not observed in BC (Fig. 1b), indicating it could not be decided whether the aciniform particles were

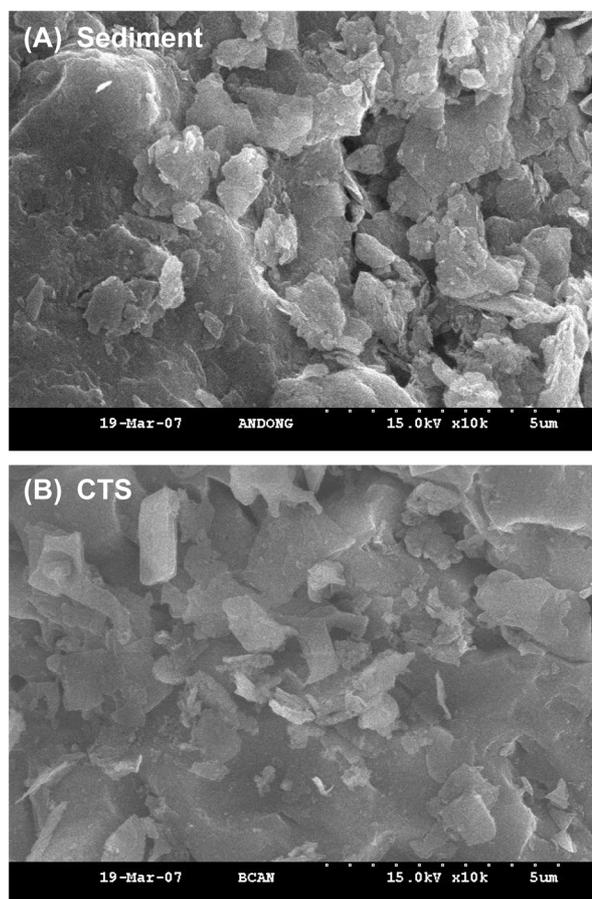


Fig. 1. Scanning electron microscopy (SEM) images of the sorbents: (a) sediment and (b) the chemical-treated sediment (CTS).

Table 1. The characteristics of the Andong sediment and CTS

Sorbents	pH	Total Carbon (%)	Organic Carbon (%)	CEC ^{a)} (meq/100g)	
Sediment	7.04	3.013	2.210	4.737	
CTS	2.68	2.983	2.097	1.467	
Sorbents	A_{BET}^b (m^2/g)	V_{total}^c (cm^3/g)	V_{micro}^d (cm^3/g)	Fraction of V_{micro} (%)	Pore Size (\AA)
Sediment	14.11	0.043	0.007	16.3	38.18
CTS	93.72	0.027	0.005	18.5	11.67
Sorbents	Elemental analysis				
	C %	H %	N %	S %	O %
Sediment	3.013	0.728	0.342	0.046	7.310
CTS	2.983	0.257	0.103	0.124	2.758

^{a)}CEC = meq as Na^+ /100g sediment

^{b)} A_{BET} = BET surface area (m^2/g)

^{c)} V_{total} = Total pore volume (cm^3/g)

^{d)} V_{micro} = micropore volume (cm^3/g)

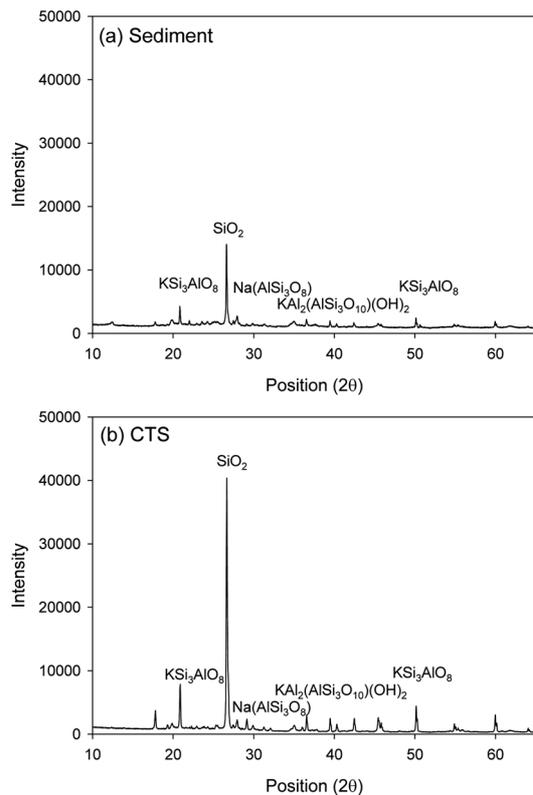


Fig. 2. XRD patterns of (a) sediment and (b) CTS.

present in BC or not.

Sorbent characterization employing N_2 gas adsorption isotherms at 77 K were presented in Table 1. In the Table, the observed N_2 BET surface areas (A_{BET}) of BC ($93.72 \text{ m}^2/\text{g}$) was much higher than that of the sediment ($14.11 \text{ m}^2/\text{g}$). Rockne et al. (2000) reported that over 90% of the total specific surface area (SSA) of BCs was composed of below 20 \AA -sized pores compared to 38 \AA for sediments. Therefore, these results are consistent with the previous study on the BC by Cornelissen et al. (2004) that reported the environmental BC has nanoporosity in less than $4\text{-}10 \text{ \AA}$ size range.

XRD patterns of sorbents presented in Fig. 2 showed that some mineral species such as quartz and albite were not digested in the acid treatment. The sharp peak of quartz was found at about 28° of 2θ in the spectra for both sediment and BC. In addition, BC samples originating from the sediment had higher peak height than the sediment.

4.2. Sorption kinetics of Naph and Phen onto organic carbon vs. black carbon

Sorption kinetics of Naph and Phen onto OC in the

Table 2. Model parameters for sorption kinetic of Naph ($C_0 = 3.0 \text{ mg/L}$) and Phen ($C_0 = 1.0 \text{ mg/L}$) onto OC and BC in Andong sediment

Model	Parameters	Naph		Phen	
		OC	BC	OC	BC
<i>OSMTM</i>	$q_{e,OC}$ or $q_{e,BC}$ (mg/kg-OC or -BC)	2,090	3,874	6,005	7,092
	C_e (mg/L)	1.898	2.046	0.367	0.294
	k_s (1/d)	57.31	74.08	26.65	27.36
	t_{eq} (d)	0.051	0.042	0.063	0.049
	R^2	0.955	0.961	0.965	0.989
<i>TCFOKM</i>	$f_{1,s}$	0.354	0.305	0.613	0.692
	$k_{1,s}$ (1/d)	109.3	139.5	81.88	102.0
	$f_{2,s}$	0.646	0.695	0.387	0.308
	$k_{2,s}$ (1/d)	0.0065	0.0057	0.0156	0.0149
	R^2	0.976	0.987	0.978	0.995
<i>MTCFOKM</i>	$q_{e,OC}$ or $q_{e,BC}$ (mg/kg-OC or -BC)	2,219	4,301	6,287	7,369
	$f'_{1,s}$	0.839	0.847	0.862	0.920
	$k'_{1,s}$ (1/d)	182.0	162.5	107.7	113.7
	$f'_{2,s}$	0.161	0.153	0.138	0.080
	$k'_{2,s}$ (1/d)	1.198	0.214	1.360	0.6051
	t'_{eq} (d)	2.317	12.76	1.933	3.445
	$v_{0,s}$ ($\times 10^3 \text{ mg/kg-OC}$ (or-BC)/day)	339.5	592.0	584.3	770.9
	R^2	0.991	0.991	0.988	0.998

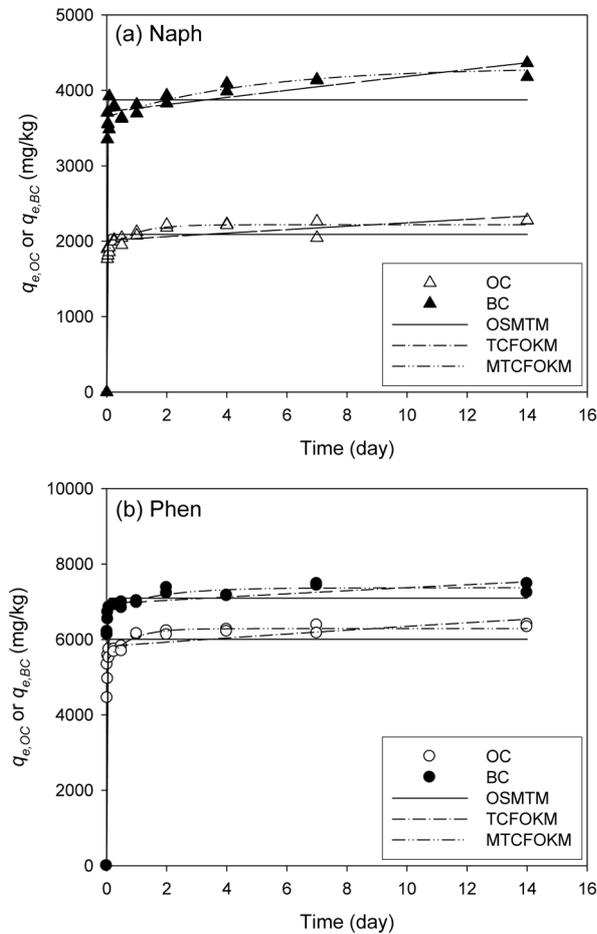


Fig. 3. Sorption kinetics of (a) Naph and (b) Phen onto OC and BC.

sediment and BC in the CTS were investigated and the data were fitted to the two-parameter OSMTM, three-parameter TCFOKM and four-parameter MTCFOKM. The sorption kinetic data and the model predictions are presented in Fig. 3 and the predicted model parameters are listed in Table 2. In terms of the coefficients of determinations (R^2), MTCFOKM was the best fitting model ($R^2 = 0.988 - 0.998$) as expected from the largest number of model parameters involved.

4.2.1. Sorbed amounts of Naph and Phen onto organic carbon and black carbon

We assumed that most of Naph and Phen were sorbed onto OC and BC in the sediment. The experimental sorption rate curves of Naph and Phen onto OC and BC sites are illustrated in Fig. 3a and 3b, respectively.

As depicted in Fig. 3, the sorption kinetics approached

constant plateau at approximately 2 days when it reached to apparent equilibrium. The sorbed amounts of Naph and Phen onto BC were higher than those onto OC. The equilibrium sorption concentrations of Naph and Phen onto OC ($q_{e,OC}$) and onto BC ($q_{e,BC}$) were summarized in Table 2. According to MTCFOKM, the $q_{e,OC}$ and $q_{e,BC}$ for Naph were 2,219 mg/kg-OC and 4,301 mg/kg-BC and for Phen were 6,287 mg/kg-OC and 7,369 mg/kg-BC, respectively. This indicates that Naph and Phen sorption onto BC was higher than those onto OC (i.e., $q_{e,BC} > q_{e,OC}$) due to higher BET surface area of BC in CTS ($A_{BET} = 93.72 \text{ m}^2/\text{g}$) than OC in the sediment ($A_{BET} = 14.11 \text{ m}^2/\text{g}$). This result was consistent with the previous results reported by Van Noort (2003) and Cornelissen et al. (2004), which showed that the carbonaceous materials such char, soot and kerogen with high surface area resulted in high sorption quantity of PCBs.

4.2.2. Equilibration time of Naph and Phen sorption kinetics onto OC and BC

The equilibration time (t_{eq}), the time to reach the equilibrium condition, can be calculated from OSMTM and MTCFOKM, when $q(t)_{OC}$ or $q(t)_{BC}$ approached almost constant at $q_{e,OC}$ or $q_{e,BC}$ (i.e., $(q_e - q(t)) / q_e = 0.01$ for both OC and BC) for each sorption kinetics. OSMTM estimated that t_{eq} was less than 0.1 d for both sorbents, indicating that OSMTM under-estimated as compared to experimental data shown in Fig. 3. Therefore, the t_{eq} were calculated by the best-fitting model, MTCFOKM ($R^2 = 0.988 - 0.998$). The calculated t_{eq} values were 2.32 and 12.8 d for OC and BC for Naph and 1.93 and 3.45 d for Phen, respectively, visually matching well to the experimental data (see Fig. 3). The t_{eq} for sorptions of Naph and Phen onto BC was higher than that onto OC mainly due to micro-pores developed in BC. Lesage et al. (2010) reported that the slow sorption occurred for a very long time period due to the very slow diffusion in the micro-pores for the adsorption of toluene and naphthalene onto granular activated carbon (GAC). Therefore, pore diffusion and intra-particle diffusion are generally rate-limiting (El-Ashtouky et al., 2008). In this study, as shown in Table 1, the fraction of the micro-pore volume (V_{micro}) of BC (18.5%) was higher than that of the sediment (16.3%) and the average pore size of BC (11.67

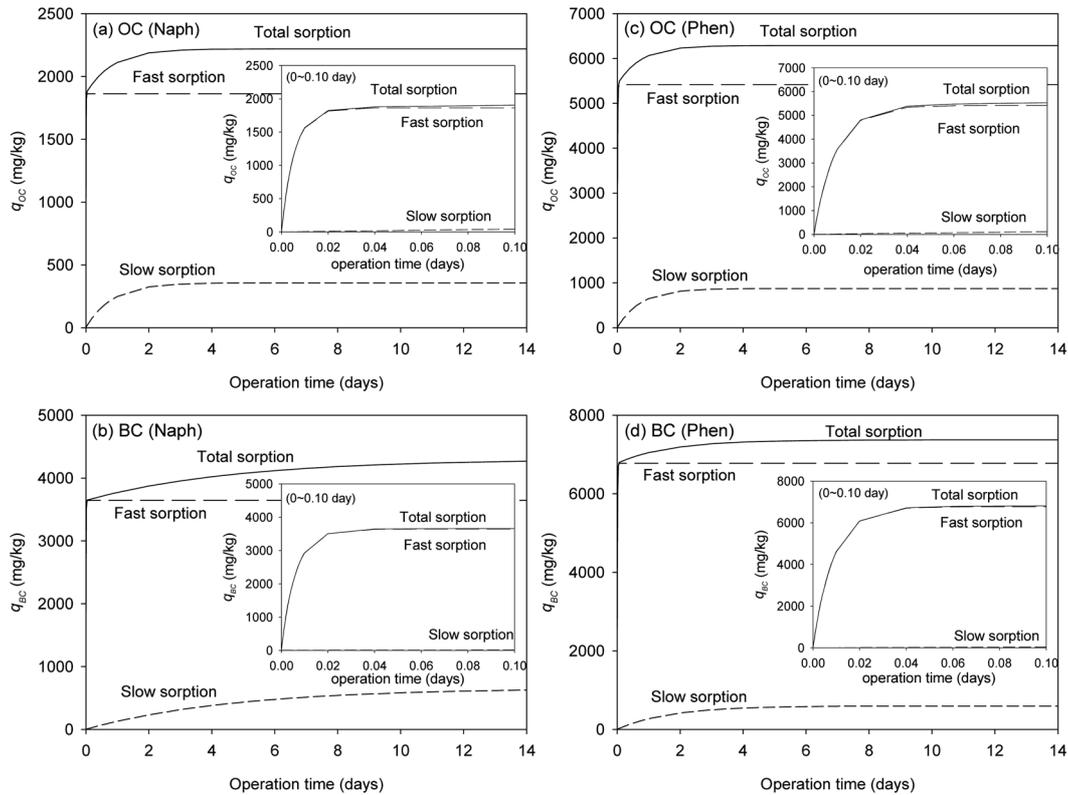


Fig. 4. The fast and slow sorption kinetics of (a) Naph on OC, (b) Naph on BC, (c) Phen on OC and (d) Phen on BC in MTCFOKM.

Å) was lower than that of the sediment (38.18 Å), indicating the higher chances of Naph and Phen sorptions onto micro-pores in BC.

4.2.3. Fast and slow sorption kinetics of Naph and Phen onto OC and BC

The profiles for the fast and slow sorption concentrations of Naph and Phen over time onto OC in sediment and BC in CTS from Eqs. (13) and (14), respectively, were described in Fig. 4. The fast sorptions reached to the equilibrium almost instantly, whereas the slow sorptions took several days. For determining the equilibration time for the fast and slow sorption kinetics, the sorption velocities for the fast and slow fractions were calculated by differentiation of the MTCFOKM equation. The differentiated equation from Eq. (12) becomes:

$$\begin{aligned} \left(\frac{dq(t)}{dt}\right)_{OC(or\ BC)} &= q_{e,OC(or\ BC)} [f'_{1,s} e^{-k_1 t} + (1-f'_{1,s})f'_{2,s} e^{-k_2 t}] \\ &= v_{fast} + v_{slow} \end{aligned} \tag{20}$$

where v_{fast} = fast sorption velocity (mg/kg-OC/day or mg/kg-BC/day) and v_{slow} = slow sorption velocity (mg/kg-OC/day or mg/kg-BC/day). The fast and slow sorption velocities of Naph and Phen onto OC and BC calculated by Eq. (20) are depicted in Fig. 5. In Fig. 5, the fast sorption curves of Naph and Phen onto BC were higher than those onto the OC, indicating that fast sorption fractions of Naph and Phen onto BC were faster than those onto OC. The end points of the fast and slow sorptions were estimated at the time when the fast or slow sorptions were almost completed, i.e., $(dq(t)/dt)_{OC}$ or $(dq(t)/dt)_{BC}$ approaches almost zero (= 0.01 mg/kg/day). As shown in Fig. 5, the fast sorptions of Naph and Phen onto OC and BC were completed around 0.1 d (for endpoint, Naph: 0.095 and 0.110 d; Phen: 0.166 and 0.160 d for OC and BC, respectively) when the fast sorptions were not independent on the total sorption velocities.

The slow sorption curves showed different patterns from the fast sorption. In all slow sorptions, the slow sorption velocities of both Naph and Phen for BC was lower but

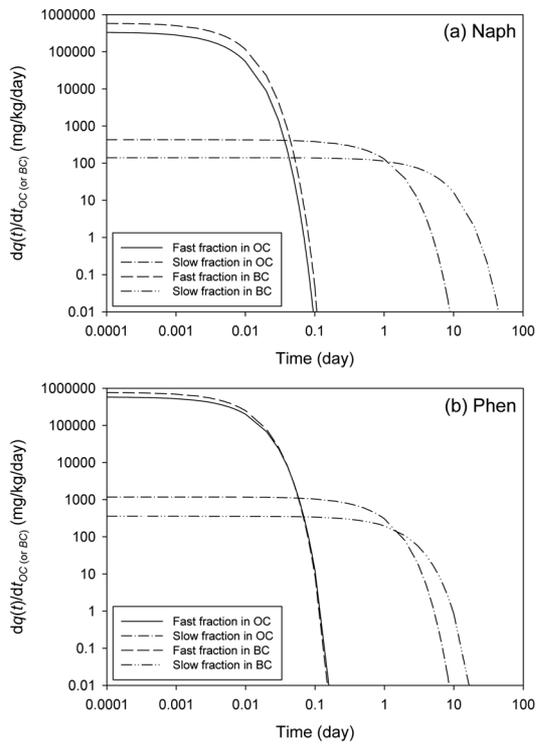


Fig. 5. The fast and slow sorption rates of (a) Naph and (b) Phen onto OC and BC (calculated from differentiating MTCFOKM).

lasted longer than those for OC. The calculated end-points of slow sorption for OC and BC were 8.90 and 44.7 d for Naph and 8.59 and 17.3 d for Phen, respectively. These indicate that the slow sorption onto BC takes longer time than that onto OC because of very slow sorbate diffusion into micro-pores in BC due to very small pore size (11.67 Å). Rockne et al. (2000) defined the pore size less than 2 nm as the micro-pore in the analysis of pore structures of soot. In this study, to explain the effect of pore size on kinetics, the intraparticle diffusion model was used to fit the slow sorption part only to differentiate the diffusion of PAHs into the micro-pores in OC (Figs. 6a and 6c) and BC (Figs. 6b and 6d). Fig. 6 shows the slow sorption onto BC fitted well to the intraparticle diffusion model ($R^2 = 0.98$ for Naph and 0.85 for Phen, respectively). This indicates that the molecular diffusion mainly occurred in the micro-pores in BC causing the slow sorption. However, the intraparticle diffusion model fitted relatively poorly to the slow sorption in OC ($R^2 = 0.71$ for Naph and 0.69 for Phen), indicating that the molecular diffusion was not mainly responsible for the slow sorption.

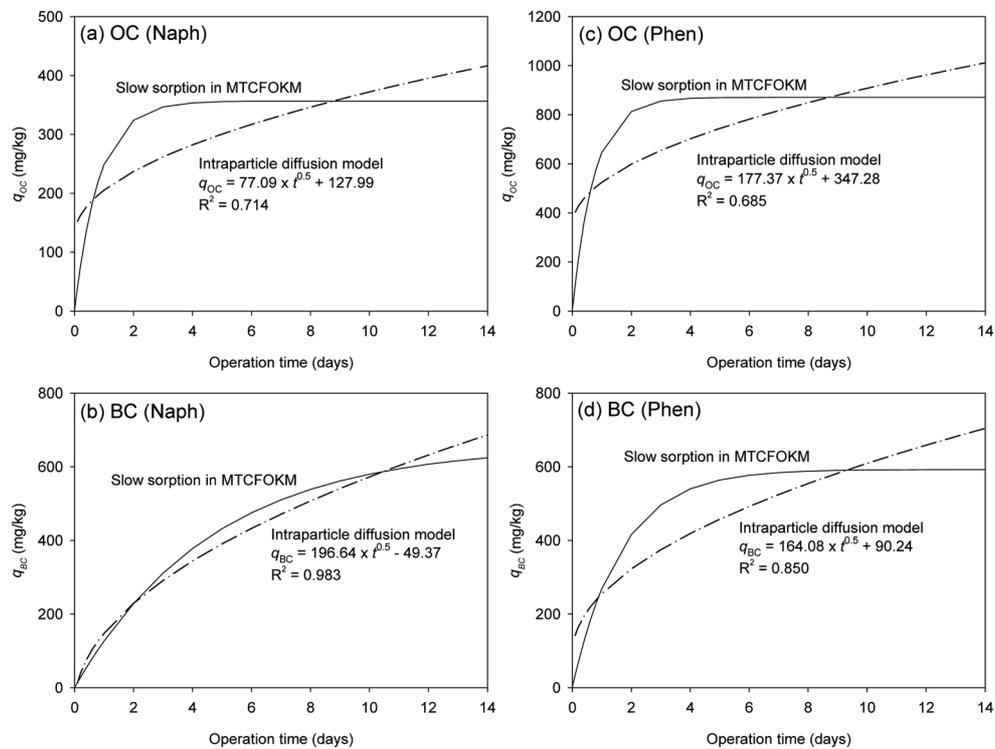


Fig. 6. Comparison of the slow sorption kinetics with the intraparticle diffusion model: (a) Naph on OC, (b) Naph on BC, (c) Phen on OC and (d) Phen on BC.

The initial sorption velocity ($v_{0,S}$) is very closely related to the fast sorption velocity and can be calculated from Eq. (20) at $t \rightarrow 0$:

$$v_{0,S} = \left(\frac{dq(t)}{dt} \right)_{OC(or BC)} \Big|_{t=0} = q_{e,OC(or BC)} f'_{1,s} k'_{1,s} + q_{e,OC(or BC)} (1-f'_{1,s}) k'_{2,s} = v_{0,fast} + v_{0,slow} \quad (21)$$

where $v_{0,S}$ = initial sorption velocity (g/kg-OC/day or g/kg-BC/day), $v_{0,fast}$ = initial sorption velocity for fast fraction (g/kg-OC/day or g/kg-BC/day) and $v_{0,slow}$ = initial sorption velocity for slow fraction (g/kg-OC/day or g/kg-BC/day).

The calculated $v_{0,S}$ values for Naph and Phen were 592.0 and 770.9 g/kg-BC/day and 339.5 and 584.3 g/kg-OC/day, respectively, which were consistent with the surface area (A_{BET}). In addition, the $v_{0,S}$ was dominated by the initial sorption velocity for fast fraction, $v_{0,fast}$. If $t \rightarrow 0$ in Eq. (21), the $v_{0,fast}$ values for Naph and Phen become 591.9 and 770.5 g/kg/day for BC and 339.0 and 583.1 g/kg/day for OC, respectively, which are almost the same as $v_{0,S}$ values. At the same time, the initial sorption velocities for slow fraction, $v_{0,slow}$, calculated from Eq. (21) for Naph and Phen were only 0.1405 and 0.3586 g/kg/day for BC and 0.427 and 1.1835 g/kg/day for OC, respectively, showing that $v_{0,slow}$ is much less than $v_{0,fast}$.

However, as time increases the slow sorption becomes more dominant in sorption mechanisms. For example, at $t = 0.1$ d the fast sorption velocities of both Naph and Phen for OC and BC were below 0.020 g/kg-OC/day (or g/kg-BC/day), whereas the slow sorption velocities for Naph and Phen were 0.1376 and 0.3376 g/kg-BC/day for BC and 0.3788 and 1.033 g/kg-OC/day for OC, respectively. This indicates that the fast sorption is dominating until 0.1 d followed by slow sorption.

4.3. Comparison of Naph and Phen desorption kinetics from OC and BC

4.3.1. Desorbed amounts of Naph and Phen from OC and BC

Desorption kinetic studies were conducted for OC and BC in sediment preloaded with equal amount of Naph and Phen after aging for 7 days. The desorbed fractions, $(q(t)/q_0)_{OC}$ and $(q(t)/q_0)_{BC}$, of Naph and Phen over time were fitted to OSMTM, TCFOKM and MTCFOKM using

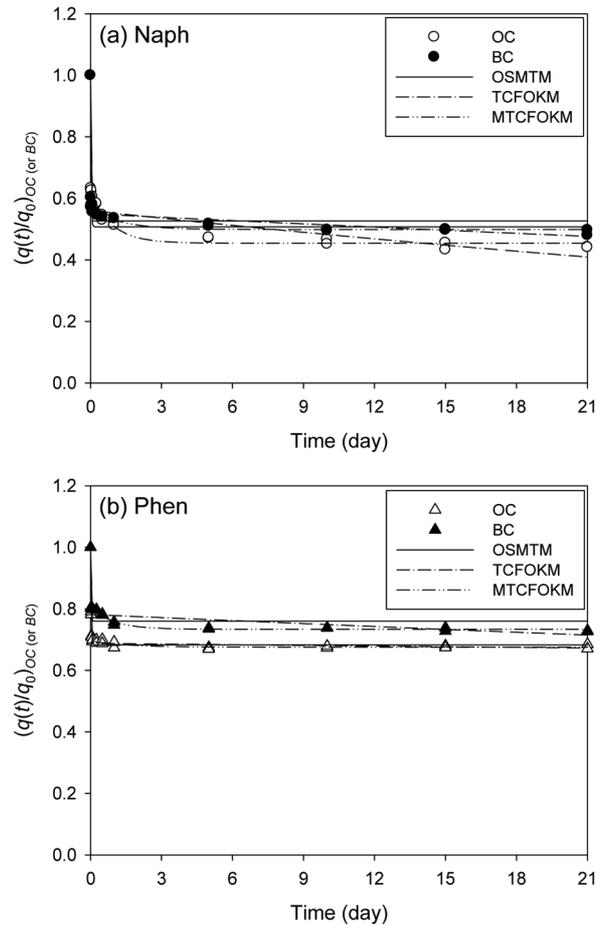


Fig. 7. Desorption kinetics of (a) Naph and (b) Phen from OC and BC.

nonlinear regression method as shown in Fig. 7. The model parameters are summarized in Table 3. Comparison of R^2 values showed that the MTCFOKM is the best fitting model ($R^2 > 0.995$) among the tested models due to the number of model parameters involved.

In Table 3, the desorbed amounts of Naph and Phen for BC (1,858 and 587.2 mg/kg-BC) were higher than those for OC (716.0 and 430.4 mg/kg-OC) due to higher initial sorbed amounts of PAHs in BC ($q_{e,d,BC}$) compared to in OC ($q_{e,d,OC}$). In order to compare the remaining fractions of Naph and Phen in BC to those in OC after desorption, the $q_{e,d,OC}/q_{0,OC}$ ratio for OC and the $q_{e,d,BC}/q_{0,BC}$ ratios for BC were calculated. The $q_{e,d,BC}/q_{0,BC}$ ratios of Naph (0.499) and Phen (0.732) were higher than the $q_{e,d,OC}/q_{0,OC}$ ratios of Naph (0.454) and Phen (0.676). This is probably due to strong sorption ability of BC (Cornelissen et al., 2005; Qi et

Table 3. Model parameters for desorption kinetic of Naph and Phen from OC and BC after aging (7, 30 and 100 days)

Model	Naph						Phen	
	OC in sediment			BC in CTS			OC in sediment	BC in CTS
	7 d	30 d	100 d	7 d	30 d	100 d	7 d	7 d
$q_{0,OC}$ (or BC) (mg/kg-OC or -BC)	1,576	2,174	3,229	3,724	4,841	5,458	637.1	802.0
OSMTM $q_{e,d,OC}$ (or BC) (mg/kg-OC or -BC)	799.8	1,299	2,158	1,963	3,179	3,990	435.1	609.3
$k'_{1,d}$ (1/d)	24.79	59.92	81.18	47.23	67.79	87.60	37.18	50.37
t_{eq} (d)	0.094	0.046	0.038	0.051	0.045	0.038	0.085	0.070
R^2	0.871	0.935	0.981	0.962	0.976	0.985	0.991	0.876
TCFOKM $f_{1,d}$	0.440	0.377	0.320	0.450	0.330	0.261	0.312	0.219
$k'_{1,d}$ (1/d)	75.16	152.5	154.9	112.9	128.1	144.3	56.70	100.5
$f_{2,d}$	0.560	0.623	0.680	0.550	0.670	0.739	0.688	0.781
$k'_{2,d}$	0.0150	0.0070	0.0029	0.0068	0.0033	0.0017	0.0011	0.0042
R^2	0.958	0.985	0.998	0.989	0.996	0.997	0.989	0.952
MTCFOKM $q_{e,d,OC}$ (or BC) (mg/kg-OC or -BC)	716.0	1,209	2,069	1,858	3,021	3,931	430.4	587.2
$q_{e,d,OC}$ (or BC) / $q_{0,OC}$ (or BC)	0.454	0.556	0.641	0.499	0.624	0.720	0.676	0.732
$f'_{1,d}$	0.690	0.824	0.885	0.857	0.871	0.912	0.940	0.716
$k'_{1,d}$ (1/d)	162.0	220.9	164.7	148.4	133.7	173.8	60.1	8,439
$f'_{2,d}$	0.310	0.176	0.115	0.143	0.129	0.088	0.060	0.284
$k'_{2,d}$ (1/d)	1.131	0.255	0.103	0.815	0.093	0.574	0.684	1.097
t_{eq} (d)	3.036	11.22	23.65	3.263	27.43	3.779	2.622	3.049
$v_{0,d}$ ($\times 10^3$, mg/kg-OC (or-BC)/day)	96.50	175.9	169.1	237.7	212.0	242.3	11.69	1,293
R^2	0.995	0.994	0.998	0.995	0.996	0.999	0.996	0.996

al., 2011) and irreversible pore deformation by the sorbate (Braida et al., 2003; Luo et al., 2011). Cornelissen et al. (2005) showed that the aromaticity of BC and the planarity of PAHs molecules could play an important role in the strong sorption. Luo et al. (2011) also reported that the irreversible capacity of BC with high surface area and porosity was also high.

4.3.2. Equilibration time of Naph and Phen desorption kinetics

The t_{eq} for desorption kinetics was estimated from OSMTM and MTCFOKM when $q(t)_{OC}$ (or BC) approached to constant plateau at $q_{e,OC}$ (or BC) (i.e., at $\{(q(t) - q_e) / (q_0 - q_e)\}_{OC}$ (or BC) = 0.01). Since R^2 values for MTCFOKM were above 0.995, the MTCFOKM was selected to estimate the t_{eq} for the desorption kinetics. The calculated t_{eq} values for Naph and Phen were 3.04 and 2.62 d for OC and 3.26 and 3.05 d for BC, respectively (Table 3), indicating that t_{eq}

values for BC were higher than those for OC. Cornellison et al. (2005) reported that the majority of BC-bound PAHs was observed to desorb over a time scale of decades to centuries and that slowly desorbing sorbate fractions demonstrated nonlinear sorption to BC due to geometric factors such as tortuous diffusion, or the high activation energy needed to overcome the partial phase transition and the strong dispersive interactions between BC and sorbate.

4.3.3. Fast and slow desorption velocities of Naph and Phen

MTCFOKM includes the fast and slow desorption fractions and thus the initial fast and slow desorption velocities can be calculated by differentiating Eq. (12):

$$v_{0,d} = -\left(\frac{dq(t)}{dt}\right)_{OC(or BC)} = (q_{0,OC(or BC)} - q_{e,OC(or BC)}) \left[f'_{1,d} k'_{1,d} e^{-k'_{1,d}t} + (1 - f'_{1,d}) k'_{2,d} e^{-k'_{2,d}t} \right] = v_{0,d,fast} + v_{0,d,slow} \quad (22)$$

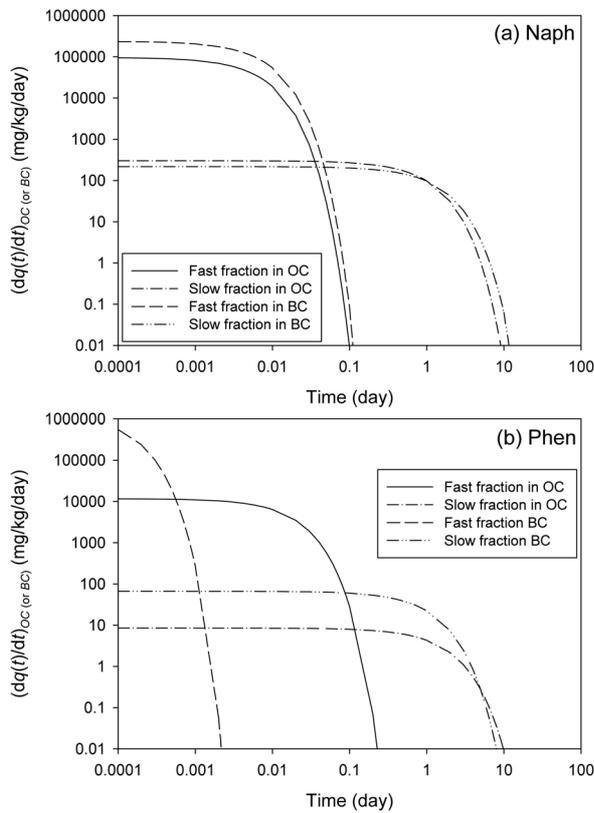


Fig. 8. The fast and slow desorption rates of (a) Naph and (b) Phen from OC and BC (calculated from differentiating MTCFOKM).

where $v_{0,d}$ = initial desorption velocity (mg/kg-OC/day or mg/kg-BC/day), $v_{0,d,fast}$ = initial desorption velocity (mg/kg-OC/day or mg/kg-BC/day) for fast fraction and $v_{0,d,slow}$ = initial desorption velocity (mg/kg-OC/day or mg/kg-BC/day) for slow fraction, respectively.

As shown in Table 3, MTCFOKM shows that the fast desorption fraction, $f'_{1,d}$, of Naph for BC (0.857) was higher than that for OC (0.690) and the fast desorption rate constant, $k'_{1,d}$, for BC (148.4 d⁻¹) was lower than that for OC (162.0 d⁻¹). On the other hand, $f'_{1,d}$ of Phen for BC (0.940) was lower than that for OC (0.716) whereas $k'_{1,d}$ for BC (8,440 d⁻¹) was even higher than that for OC (60.1 d⁻¹). Therefore, the fast desorption kinetics might be Naph- and Phen-specific, not affected by OC and BC.

The initial desorption velocities ($v_{0,d}$) were 237.7 (Naph) and 1,293 g/kg/day (Phen) for BC and 96.50 (Naph) and 11.69 g/kg/day (Phen) for OC, respectively. The $v_{0,d}$ for BC were much higher than those for OC because higher amount of sorbates initially present on the external surfaces and

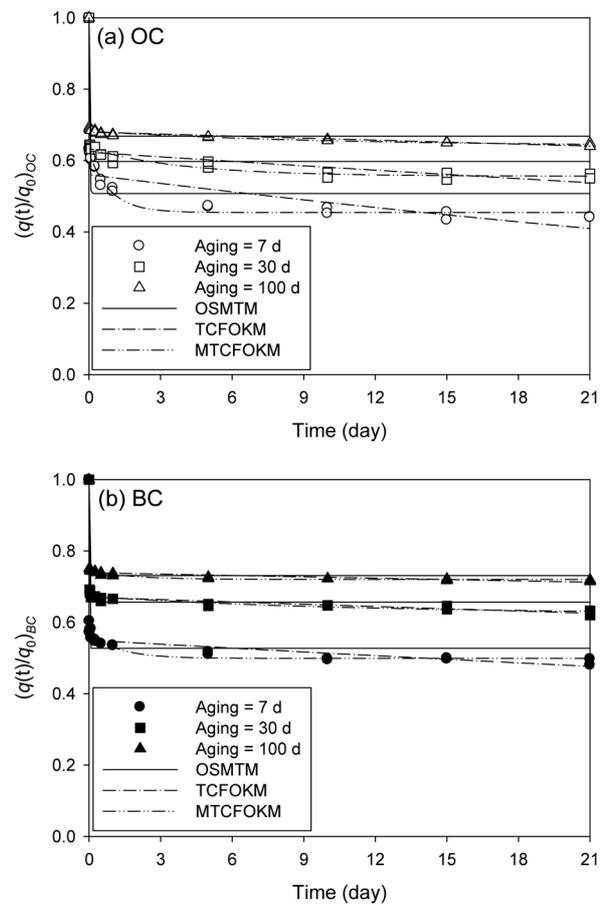


Fig. 9. Effect of aging time on the desorption kinetics of Naph from (a) OC and (b) BC.

macropores in BC were desorbed within very short time (Cornellison et al., 2005), and therefore this is related to the fast desorption fraction ($f'_{1,d}$).

The initial fast and slow desorption velocities of Naph and Phen from OC and BC were calculated from Eq. (20). The calculated $v_{0,d,fast}$ of Naph and Phen were 237.5 and 1,292 g/kg-BC/day for BC and 96.20 and 11.68 g/kg-OC/day for OC, respectively. This explains that the initial fast desorption is dominating the initial desorption kinetic velocity ($v_{0,d}$). The initial slow desorption velocities, $v_{0,d,slow}$, were relatively very low; only 0.2173 and 0.0665 g/kg/day for BC and 0.3010 and 0.0085 g/kg/day for OC, respectively. This indicates that initial slow desorption velocity is relatively negligible.

Similar to sorption, the importance of the slow desorption for the total desorption also increased over time. At $t = 0.2$ d, for example, the fast desorption velocities of Naph and

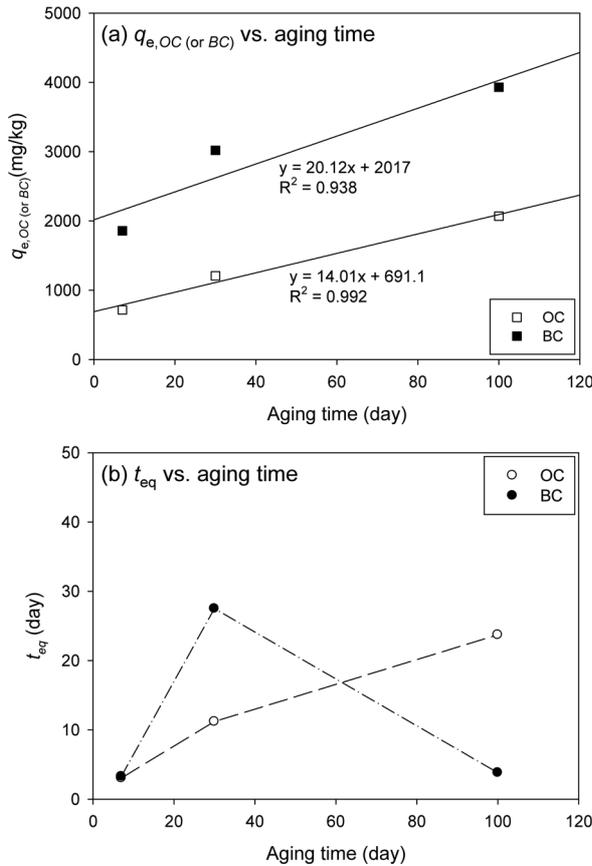


Fig. 10. Effect of aging time on (a) the equilibration concentrations of Naph ($q_{e,OC}$ or $q_{e,BC}$) and (b) the equilibration time (t_{eq}) for Naph desorption kinetics from OC and BC.

Phen for both OC and BC became negligible when the slow desorption velocities for Naph and Phen increased to range of 0.0074 to 0.2401 g/kg-OC (or -BC)/day, indicating that the slow desorption was dominant in the desorption after 0.2 d.

4.4. Effect of aging on desorption kinetics of Naph

In this study, the effect of aging (7, 30 and 100 d) on the Naph desorption kinetics were investigated by the three kinetic models. The desorption kinetics at different aging for OC and BC were plotted in Fig. 9 and the model parameters are summarized in Table 3. The MTCFOKM results show that the equilibrium concentration ($q_{e,d,OC}$ or $q_{e,d,BC}$) was affected by aging.

The effect of the aging on t_{eq} and $q_{e,d,OC}$ (or $q_{e,d,BC}$) were presented in Fig. 10. As shown in Fig. 10a, the $q_{e,d,OC}$ (or $q_{e,d,BC}$) increased with aging for both OC and BC. As shown

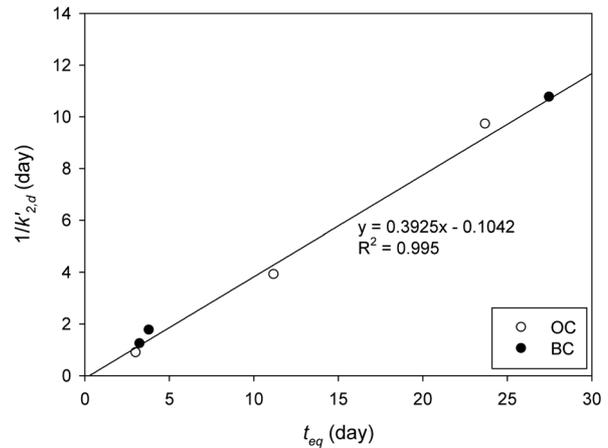


Fig. 11. The relationship between t_{eq} and slow desorption kinetics ($k'_{2,d}$) in MTCFOKM.

in Table 3 and Fig. 10b, the equilibration time (t_{eq}) was in the range of 3.04 to 23.7 d for OC and 3.27 to 27.5 d for BC, respectively; however, there was no correlations between t_{eq} and aging even though there was a positive relationship between $q_{e,OC}$ (or $q_{e,BC}$) and aging. In addition, t_{eq} was linearly related with $1/k'_{2,d}$ ($R^2=0.995$) in MTCFOKM (Fig. 11). This means the equilibration time was directly dependent on the slow desorption kinetics.

5. Conclusions

This study was conducted to evaluate the sorption and desorption kinetics of Naph and Phen onto/from OC and black carbon BC in a lake sediment. The kinetics data were analyzed by three kinetic models such as OSMTM, TCFOKM and MTCFOKM. Among these models, four-parameter MTCFOKM was the best fitting to the experimental kinetic data. The BC had higher BET surface area (A_{BET}) and smaller sized micro-pores than its original sediment and thus it could sorb or desorb higher amount of Naph and Phen and take longer equilibration time (t_{eq}). The fast and slow fractions of the sorption and desorption kinetics were also analyzed. The fast sorption and desorption were apparently completed within a very short time (about less than 0.1 d) for both sorbates and sorbents. The slow sorption of Naph and Phen onto BC took longer time than that onto OC due to the presence of micropore with small pore size in BC.

In terms of R^2 values, MTCFOKM was the best fitting in both sorption and desorption kinetics. The contribution of initial concentration on the sorption and desorption of Naph and Phen was evaluated. Sorption and desorption kinetics decreased as initial concentration increased. Effect of aging time on desorption kinetics on OC and BC in sediment was also investigated. The $q_{0,OC}$ (or BC) and $q_{e,OC}$ (or BC) increased with aging time. However, the relationship between aging time and fast and slow desorption kinetics is still not clear and further research is needed for more detailed mechanical explanations.

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