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Interaction mechanism of benzene and phenanthrene in condensed organic matter: Importance of adsorption (nanopore-filling)

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ABSTRACT

Although microporosity and surface area of natural organic matter (NOM) are crucial to mechanistic evaluation of the sorption process for nonpolar organic contaminants (NOCs), they have wrongly been estimated by the N_2 adsorption technique. Nuclear magnetic resonance spectroscopy (^{13}C NMR), and benzene, carbon dioxide, and nitrogen adsorption techniques were used to characterize structural and surface properties for different condensed NOM samples, which were related to the sorption behavior of phenanthrene (Phen). It was found that the revised Freundlich model by taking the chemical activity into account can well describe the isotherms for benzene and Phen. The benzene and Phen adsorption volumes for the coal samples are similar to or lower than the CO_2-nanopore volumes. Adsorption volumes of both benzene and Phen are significantly related to the aliphatic carbon structure, and their correlation lines are nearly overlapped, suggesting that the nanopore filling for Phen and benzene on the investigated samples is the dominating mechanism, and also is not affected by water molecules. The entrapment of benzene and/or the pore deformation in the NOM nanopore are likely responsible for the observed hysteresis of benzene. The above results demonstrate that Phen and benzene adsorption on the condensed NOM is closely associated with the aliphatic carbon structure of the investigated samples.

1. Introduction

Sorption and sequestration of nonpolar organic chemicals (NOCs) by natural organic matter (NOM) associated with aquifers, soils, sediments (geosorbents) control bioavailability, risk, and biodegradation of NOCs (Brusseau et al., 1991; Chefetz and Xing, 2009; Pignatello and Xing, 1996). Many investigations during the last three decades identified that the organic matter types and microporosity are important for the sorption of NOCs (Chefetz and Xing, 2009; Chen and Xing, 2005; Grathwohl, 1990; Plaza et al., 2009; Salloum et al., 2002; Senesi, 1992). However, the physicochemical mechanisms of sorption/desorption and reduced bioavailability are limited.

The chemical and structural properties of NOM strongly affect the sorption and desorption of NOCs in soils and sediments (Chefetz and Xing, 2009; Pignatello and Xing, 1996; Weber et al., 1992). Previous investigations indicated that various types of bulk SOM with high aliphatic carbon showed strong sorption for phenanthrene and pyrene (Chefetz et al., 2000; Mao et al., 2002). NOM has been characterized as comprising dual domains or components that exhibit distinctly different sorption reactivity (Grathwohl, 1990; Kleineidam et al., 2002; Ran et al., 2004; Weber et al., 1992; Xing and Pignatello, 1997). Depending on parental sources and diagenetic alteration histories, NOM may comprise different types of organic materials ranging from biopolymer, humus, kerogen and coal materials, and black carbon. Condensed organic carbons such as kerogen, coal, and black carbon can substantially contribute to NOM in soils and sediments (Cornelissen et al., 2005; Ran et al., 2002, 2007; Weber et al., 1992). It is noted that NMR spectroscopy has been increasingly used to provide a basis for inferring the molecular structure in these organic matter (Chefetz et al., 2000; Filimonova et al., 2004; Kögel-Knabner, 1997; Ran et al., 2002, 2007; Salloum et al., 2002).

Surface and geometric heterogeneity in NOM could be very important for the sorption mechanism of NOCs on NOM. The surface area of NOM is crucial to the mechanistic interpretation of sorption process. N_2 adsorption was recommended as the standard method to measure the surface area of soils/sediments (Gregg and Sing, 1982). However, large discrepancies were reported between NOM surface areas derived from CO_2 adsorption and N_2 adsorption, primarily because of the activated diffusion phenomenon (Aochi and Farmer, 2005; de Jonge and Mittelmeijer-Hazeleger, 1996; Li and Werth, 2001; Ran et al., 2013; Ravikovitch et al., 2005; Xing and Pignatello, 1997). Carbon dioxide at 273 K and benzene at 295 K have been used as alternative gases for probing the surface properties of carbonaceous materials (Corley et al., 1996;

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de Jonge and Mittelmeijer-Hazeleger, 1996; Gan et al., 1972; Kwon and Pignatello, 2005; Larsen et al., 1995; Ravikovitch et al., 2005; Reucroft and Sethuraman, 1987; Walker and Kini, 1965; Xing and Pignatello, 1997). Glassy forms of NOM including humin, kerogen and coals have internal microporosity that apparently is not accessed by N_2 at 77 K due to activation diffusion. Moreover, previous investigations demonstrated that the adsorption (hole-filling) mechanism is important for the sorption of hydrophobic organic contaminants by the isolated kerogen, Pahokee peat, and coals (Ran et al., 2002, 2004, 2013). However, how the microporosity measured by CO_2 and benzene gas molecules is related to the structure of NOMs and the aqueous sorption capacity for NOCs on various NOMs has not yet been systematically investigated.

This study investigates how the hydrophobic nanopore volumes measured with benzene vapor and CO_2 gas are related to the structure of NOM and the sorption capacity of phenanthrene (Phen) on a range of condensed NOM samples, and how the adsorption of aqueous Phen is related to that of gaseous benzene, and is affected by water molecules. We hypothesized that the hydrophobic nanopore in glassy NOM could be large enough for accommodating majority of NOCs. We used a wide range of condensed NOM ranging from nonhydrolyzable organic carbon (NHC) to black carbon (BC) and coals (Table 1) as sorbents, and Phen and benzene vapor as model sorbates to test this hypothesis.

2. Materials and methods

2.1. Sorbents and characterization

Two surface soil samples (HP04 and HP05) were collected to a depth of 20 cm in July 2002 from Hangpu district of Guangzhou city, China. Three surface sediment samples (C01, C03, and C08) (0–20 cm) were collected from the Pearl River Estuary (PRE) using a box sampler in August 2002. The water depth was 25 m for C01, 25 m for C03, and 69 m for C08. The soils and sediments were treated using an acid hydrolysis method and a combustion method at 375 °C for the separation of five nonhydrolyzable carbon (NHC) and one black carbon (BC) samples, respectively (Ran et al., 2007). Specifically, carbonates were first dissolved in 1 N HCl for 24 h. The residual fractions were treated with 1 N HCl and 10% HF for 5 days, which was repeated four times. Polysaccharides were released by trifluoroacetic acid (TFA) hydrolysis. Finally, the residual hydrolyzable organic matter was removed with 6 N HCl at 110 °C for 24 h. The residues (NHC) were obtained. An aliquot of NHC was heated at 375 °C for 24 h with sufficient air for the BC isolation. It is noted that that determining BC by heating at 375 °C is an accepted but somewhat arbitrary procedure. Many components of BC substrates vanish at lower temperatures, while at least portions of mineral-associated humic substances (not BC) resist to that temperature. In addition, Beulah-Zap lignite (BZ) was obtained from the American Argonne Premium coals. A lignite coal (JP), two bituminous coals (XW and XA), and an anthracite (YX), were collected from state-owned coal mines and covered a wide range of maturity with vitrinite reflectance (R_o) from 0.52% to 2.50% (Chen et al., 2005).

The C, H, O, and N contents were measured using an Elementar Vario ELIII or a Heraeus CHN-O-RAPID elemental analyzer. Specific surface areas (SSA) and microporosity were measured using the N_2-adsorption and CO_2-sorption techniques, at the normal boiling temperature (77 K) and at 273 K in a Micromeritics ASAP 2010 instrument and Autosorb-1 gas analyzer (Quantachrome Instrument Corp., Boynton Beach, FL), respectively (Ran et al., 2013). The ^{13}C CP/TOSS (cross polarization/total sideband suppression) NMR spectra for the five coals were obtained on a Bruker Avance-400 NMR spectrometer operated at a ^{13}C frequency of 100 MHz and at a magic-angle-spinning (MAS) rate of 6.0 kHz. Briefly, the solid coal samples were placed in a 4-mm diameter ZrO_2 rotor with a Kel-F cap. A 1.2-s recycle delay and a 1-ms contact time were used. Between 3500 and 4500 scans were collected. The physicochemical properties of the investigated samples are summarized in Table 1.

2.2. Sorption and desorption experiments

Adsorption isotherms of benzene vapor were recorded at 23 °C with an intelligent gravimetric analyzer (IGA supplied by Hidden Analytical Ltd). Benzene isotherms were obtained by setting pressure intervals relative to saturation vapor pressure (p/p_o) at 298 K. Prior to the measurements, the adsorbent was outgassed in situ until constant weight was achieved at a temperature of 373 K. About 70 mg of a given sample was loaded for each run. HPLC grade benzene was used as adsorbate. Pressure steps in the range of p/p_o values 0–0.94 were used to obtain the isotherm. The equilibrium time for each point of the sorption isotherms ranged from tens of minutes to several hours.

The completely mixed batch reactor (CMBR) systems were employed for the Phen sorption isotherms at room temperature (23 °C). The equilibrium time is four weeks. Flame-sealed glass ampules (50 ml) were used as the CMBRs. The experiments consisted of preliminary tests and final equilibrium tests. The average concentrations of Phen detected in the control reactors were within 98–102% of the initial concentrations. No correction for solute loss was made during the reduction of sorption data. Solute concentrations of the initial aqueous solutions and equilibrated aqueous solutions were analyzed on a reversed-phase HPLC (Hewlett-Packard model 1100, ODS, 5 μm, 2.1 × 250 mm C-18 column) with both diode array UV

Table 1
Physicochemical properties for the samples[a,b].

Samples	C %	H %	N %	O %	O/C	H/C	N_2-SSA m^2/g	N_2-V_o μl/g	CO_2-SSA m^2/g	CO_2-V_o μl/g	Ash %	R_o %
C01	36.9	2.49	0.38	9.26	0.19	0.81	13.3	nd[c]	nd	nd	50.97	nd
C03	23.2	1.82	0.23	7.49	0.24	0.94	7.93	nd	nd	nd	67.26	nd
C08	34.4	2.71	0.46	8.80	0.19	0.94	15.8	nd	nd	nd	53.63	nd
HP04	50.7	2.45	0.32	13.6	0.20	0.58	4.28	nd	nd	nd	32.93	nd
HP05	52.3	3.72	0.56	16.7	0.24	0.85	6.71	17	133	55.0	26.72	nd
HP05BC	17.3	0.77	0.18	3.09	0.13	0.12	16.7	nd	nd	nd	78.66	nd
BZ	68.1	4.51	1.07	19.0	0.21	0.79	1.74	6.0	206	85.0	6.59	0.50
JP	68.6	4.35	3.85	14.9	0.16	0.76	4.91	10	169	73.0	8.10	0.52
XA	73.2	3.62	4.14	3.63	0.04	0.59	1.61	6.0	146	48.7	13.91	1.70
XW	48.7	3.17	3.19	6.34	0.10	0.78	6.92	19	85.0	26.3	38.10	1.12
YX	82.5	3.22	0.53	1.75	0.02	0.47	2.57	10	253	84.0	8.93	2.50

[a] R_o, vitrinite reflectance; N_2-SSA, N_2-derived specific surface area; CO_2-SSA, CO_2-derived specific surface area; N_2-Vo, N_2-derived micropore volume; CO_2-V_o, CO_2-derived internal hydrophobic microporosity.

[b] The elemental compositions and reflectance (R_o %) were cited for the JP, XA, XW, and YX coals from Chen et al. (2005), for the BZ lignite from Larsen et al. (1995), and for the NHC (C01, C03, C08, HP04, and HP05) and BC (HP05BC) samples from Ran et al. (2007).

[c] nd, not determined.