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The kinetic and thermodynamic sorption and stabilization of multiwalled carbon nanotubes in natural organic matter surrogate solutions: The effect of surrogate molecular weight

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ABSTRACT

Styrene sulfonate (SS) and polystyrene sulfonates (PSSs) were used as surrogates of natural organic matter to study the effect of molecular weight (from 206.2 to 70,000 Da) on their sorption by a multiwalled carbon nanotube (MWCNT) and an activated carbon (AC) and on their stabilization of MWCNT suspension. Results indicate that surface-diffusion through the liquid-sorbent boundary was the rate-controlling step of the kinetic sorption of both MWCNTs and AC, and surface-occupying and pore-filling mechanisms respectively dominated the thermodynamic sorption of MWCNTs and AC. Sorption rates and capacities of MWCNTs and AC in molecular concentration of SS and PSS decreased with increasing molecular weight. The PSSs but not SS facilitated the stabilization of MWCNT suspension because of the increased electrosteric repulsion. The PSSs with more monomers had greater capabilities to stabilize the MWCNT suspension, but the capabilities were comparable after being normalized by the total monomer number.

1. Introduction

Carbon nanotubes (CNTs) are promising nanomaterials that are being increasingly used in a variety of industrial areas (Baughman et al., 2002; Mauter and Elimelech, 2008), which may result in their exposure to the aquatic environment (Petersen et al., 2011; Wiesner et al., 2006). An increasing number of studies have observed hazardous effects of CNTs on cells, tissues, and various organisms (Helland et al., 2007; Johnston et al., 2010; Long et al., 2012), which raises concerns over the environmental behavior and ecological effects of CNTs. Pristine CNTs are highly hydrophobic and can readily aggregate and precipitate in water, and thus their transport is restricted (Lin et al., 2010b). However, ubiquitous natural organic matter (NOM) can adsorb on the hydrophobic CNTs, thus promoting their aqueous stabilization and transport (Hyung et al., 2007; Hyung and Kim, 2008; Lin and Xing, 2008a; Lin et al., 2009, 2010a, 2012; Saleh et al., 2010; Schwyzer et al., 2012; Smith et al., 2012; Zhou et al., 2012) and influencing their ecotoxicity (Edgington et al., 2010). Hence, CNT-NOM interactions are receiving more and more attention from researchers (Lin et al., 2010b; Petersen et al., 2011).

The underlying mechanism of the CNT-NOM interaction is becoming obvious. NOM can adsorb on CNTs mainly through hydrophobic interactions (Wang et al., 2011), $\pi-\pi$ interactions (Hyung and Kim, 2008; Lin and Xing, 2008a), hydrogen bonding, and/or electrostatic interactions (Lin et al., 2009). The adsorbed NOM can more or less disperse and form stable suspension of the CNTs via electrostatic repulsion, steric repulsion, and/or solvation (Hyung et al., 2007; Lin and Xing, 2008b; Lin et al., 2012; Saleh et al., 2010; Zhou et al., 2012). However, NOM is a highly heterogeneous mixture, and the interaction of the specific components of NOM with CNTs is still being studied (Liu et al., 2012, 2013; Louie et al., 2013) and merits more specific investigations.

It was reported that the NOM adsorption on CNTs varied greatly with the type of NOM and was proportional to the aromatic carbon content of the NOM, and that the concentration of the CNT suspension depended on the amount of NOM adsorbed per unit mass of CNTs (Hyung and Kim, 2008). Our previous study investigated the interaction between CNTs and humic acids (a typical NOM analogue) and found that the humic acid adsorption on CNTs increased with decreasing polarity of the humic acids, whereas the capability of the CNT-adsorbed humic acids for the CNT stabilization increased with increasing polarity of the humic acids (Lin et al.,

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2012). The molecular weight or size of the NOM components can play an important role in their interaction with nanoparticles (Louie et al., 2013). However, limited studies have specifically examined the effect of the molecular weight or size of the NOM on its sorption on CNTs. Hyung and Kim (2008) observed that the high-molecular weight fractions of NOM could be preferentially adsorbed by CNTs. The higher adsorption capacity of CNTs for high-molecular weight NOM was also reported in a study by employing tannic acid and gallic acid as high- and low-molecular weight NOM analogues, respectively (Liu et al., 2012). Furthermore, to the best of our knowledge, no study has specifically investigated the effect of the molecular weight or size of NOM on the stabilization of CNTs.

Therefore, polystyrene sulfonates (PSSs) with different molecular weights were used in this study as NOM surrogates, in particular, as the aromatic fraction of NOM, to investigate the effect of the molecular weight or size of NOM on its sorption by a type of CNT and the stabilization of the CNTs. PSSs with aromatic rings and oxygen-containing functional groups have been widely used as NOM surrogates (Muller et al., 2000; Kawasaki et al., 2011; Ando et al., 2010; Karanfil et al., 1996; Li et al., 2003; Revchuk and Suffet, 2009) and to suspend CNTs (Huang et al., 2011; Li and Adronov, 2007; O'Connell et al., 2001). An activated carbon (AC) having a similar elemental composition but a different pore structure and morphology as the CNTs was chosen as an alternative sorbent to explore the sorption mechanism and compare the results. The results of this study are expected to promote an understanding of the CNT-NOM interaction and help the evaluation of the environmental behavior and ecological effects of CNTs.

2. Materials and methods

2.1. Materials

Multi-walled carbon nanotubes (MWCNTs) with outer diameters of 60–100 nm were purchased from Shenzhen Nanotech Port Co., China. AC powders were obtained from Sinopharm Group, Shanghai, China. The length and outer diameter of the MWCNTs was measured with the aid of a transmission electron microscope (TEM, JEM-1230, JEOL, Japan). The specific surface areas and total pore volumes of the MWCNTs and AC were calculated from the adsorption–desorption isotherm of N_2 at 77 K by the multipoint Brunauer–Emmett–Teller (BET) method, and the mesopore and micropore volumes were calculated by the Barrett–Joyner–Halenda (BJH) and Dubinin–Ashtakhov (DA) methods, respectively. The ash contents were measured by heating the MWCNTs and AC at 900 °C for 10 h. The dry weight-based C, H, and N contents of the MWCNTs were determined using an elemental analyzer (Flash EA 1112, ThermoFinnigan, Italy). The oxygen content of the MWCNTs was calculated by the mass differences.

Styrene sulfonate (SS, $C_8H_7O_3S.Na$) and PSS $(C_8H_7O_3S.Na)_x$ with molecular weights of 4300, 6800, 10,000, 17,000, and 70,000 Da were purchased from Sigma–Aldrich Co. The structures and sizes of the SS and SS monomer in the PSS molecules were modeled by the Molecular Operating Environment (MOE) Software (2009). A 0.01 mol L^{-1} NaCl solution at pH 7, representing the typical ionic strength and pH of natural surface water, was used as the background solution in the following kinetic and thermodynamic sorption and stabilization experiments.

2.2. Kinetic sorption experiment

The kinetic sorptions of SS and the PSSs by the MWCNTs and AC were studied using a batch experiment in screw cap vials at 25 ± 1 °C. Eight milliliters of the SS or PSS solutions (20 mg L^{-1}) were added into the screw cap vials containing certain amounts of the MWCNTs and AC (Table S1 in the Supporting Information). All vials were shaken in a thermostat shaker (110 rpm) for 1, 2, 3, 4, 5, 10, 20, 40, 60, 120, 180, 360, 720, 1080, and 1440 min. Each point in time was sampled, including blanks (i.e., without MWCNTs and AC), and was run in duplicate. After separating the MWCNTs and AC from the sorptive solution using a 0.2-μm filter membrane (Millipore, PTFE), the residual SS and PSSs were quantified with a UV–vis spectrometer (Shimadzu, UV-2540) at 255 and 225 nm because they had marked absorption peaks at these wavelengths, respectively. A negligible mass loss of SS and the PSSs was observed in the sorption and filtration processes. The adsorbed amounts of SS and PSSs by the MWCNTs and AC were then calculated by the mass differences.

The Lagergren pseudo first-order (Eq. (1)) and second-order (Eq. (2)) models and the Weber-Morris model (Eq. (3)) were employed to fit the kinetic sorption data (Ho and Mckay, 1999; Svilovic et al., 2010; Wang et al., 2011).

$$Q_t = Q_e\left(1 - e^{-K_1 t}\right) \tag{1}$$

$$\frac{1}{Q_t} = \frac{1}{K_2}\cdot\frac{1}{Q_e^2}\cdot\frac{1}{t} + \frac{1}{Q_e} = \frac{1}{V_0}\cdot\frac{1}{t} + \frac{1}{Q_e} \tag{2}$$

$$Q_t = A + K_a t^{0.5} \tag{3}$$

where Q_t and Q_e are the sorbed amounts of sorbate by sorbent at time point t and equilibrium (mg g^{-1}), respectively; K_1 and K_2 are the Lagergren sorption rate constants of the pseudo first-order (h^{-1}) and second-order (g mg^{-1} h^{-1}) kinetics models, respectively; t is the contact time (h); V_0 is the initial sorption rate (mg g^{-1} h^{-1}); A is the intercept of the vertical axis (mg g^{-1}); K_a is the overall diffusion constant for sorption (mg (g $h^{0.5}$)$^{-1}$).

2.3. Thermodynamic sorption experiment

Sorption isotherms of SS and the PSSs by the MWCNTs and AC were also obtained using a batch experiment in screw cap vials. The MWCNTs and AC were added into 8 mL of the sorbate solutions with initial sorbate concentrations of 0, 5, 10, 15, 20, 40, 60, 80, and 100 mg L^{-1}. Each concentration point, including blanks (i.e., without MWCNTs and AC), was run in duplicate. The mixtures were equilibrated in a thermostat shaker (110 rpm) for 24 h. The kinetic adsorption experiments indicated that the apparent sorption equilibrium was reached within 12 h. The equilibrium dissolved and the sorbed concentrations of the sorbates were determined as in the kinetic sorption experiments.

The Langmuir model (Eq. (4)) was employed to fit the equilibrium sorption data (Lin and Xing, 2008b; Wang et al., 2011):

$$q_e = \frac{q_0 b C_e}{1 + b C_e} \tag{4}$$

where q_e (mg g^{-1}) is the amount of sorbate, which is sorbed per unit mass of the sorbent, C_e (mg L^{-1}) is the sorbate concentration at equilibrium, q_0 (mg g^{-1}) is the sorption capacity of the sorbent, and b (L mg^{-1}) is the constant related to the molar heat of adsorption.

2.4. Suspending experiment

The suspending kinetics of the MWCNTs in the SS and PSS solutions were carried out as a function of the sonication time at room temperature. Four mg of the MWCNTs were added into 20 mL of a 20 mg L^{-1} SS or PSS solution. The mixtures were sonicated (600 W, 50 kHz) for 0, 5, 10, 20, 40, 60, 90, 120, and 180 min and were then centrifuged at 3000 g for 15 min. The concentrations of the stabilized MWCNTs in the resultant supernatants were measured by UV–vis spectrometry at 800 nm. Samples from each point in time were run in triplicate. The absorbance at 800 nm was calibrated with the MWCNT concentration measured by a total organic carbon analyzer (TOC analyzer, Shimadzu, TOC-VCPH) to quantify the stabilized MWCNTs (Lin et al., 2010a, 2012).

The thermodynamic suspending experiment of the MWCNTs in the SS and PSS solutions was conducted by sonicating (600 W, 50 kHz) mixtures of 4 mg of the MWCNTs and 20 mL of the SS and PSS solutions with concentrations of 0, 0.1, 0.5, 1.0, 1.5, 2.0, 2.5, 5, 10, 20, and 40 mg L^{-1} for 3 h. Each concentration point, including the blanks (i.e., without MWCNTs), was run in triplicate. The suspensions were then centrifuged at 3000 g for 15 min. The stabilized MWCNTs in the resultant supernatants were then quantified. The zeta potentials of the suspended MWCNTs were measured by a zetasizer (Nano ZS90, Malvern Instrument, UK).

3. Results and discussion

3.1. Properties of the sorbents and sorbates

Selected properties of the MWCNTs and AC are summarized in Table 1. The pore size distributions of the MWCNTs and AC are shown in Fig. S1 in the Supporting Information. The specific surface area and the total pore, mesopore, and micropore volumes of the AC were much greater than those of the MWCNTs. The AC had an abundant pore structure with a large amount of micropores. The structure of the MWCNTs was mainly mesoporous.

The three-dimensional molecular structure diagrams of SS and the repeating SS monomer of PSS are shown in Fig S2. The molecular size of SS is approximately 6.026–8.430 Å. The molecular sizes of the PSSs were not measured by the MOE Software owing to the complex spatial molecular structures.