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Sorption of humic acid to functionalized multi-walled carbon nanotubes

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ARTICLE INFO

ABSTRACT

The environmental behavior of carbon nanotubes (CNTs) and humic acid (HA) is a prominent concern, but effect of functionalities on their sorption is not clear yet. Functionalized multi-walled CNTs (MCNT15) and HA were used to study their sorption behavior. Sorption rate of HA to MCNTs was dominantly controlled by its diffusion from liquid-MCNT boundary to MCNT surfaces. The sorption is in the sequence of MCNT15 > MCNT15-NH$_2$ > MCNT15-OH > MCNT15-COOH > MCNT15-Ni, which was dependent on their surface area and meso- and macro-pore volume. The functionalities of MCNTs regulated the sorption by affecting their interaction mechanisms (i.e., H-bonding, π–π, and hydrophobic interaction). Additionally, the amount of these functionalities on the MCNT surface reduced indirectly the sorption sites due to the steric hindrance. Electrostatic repulsion deceased the sorption of HA by MCNTs with increasing pH. This study demonstrated the importance of functionalities on the MCNTs for the sorption of HA.

1. Introduction

Carbon nanotubes (CNTs) with unique structure of extensive sp^2 carbon atoms arranged in fused benzene rings keep attracting a great deal of research attention. Their structures give them exceptional electrical, chemical, and physical properties, which are utilized in various applications, e.g., sorbent, polymeric materials, medical products (Petersen et al., 2011). With increasing production and potentially wide use, CNTs will be inevitably released into the environment and then generate potential ecological risk. Some previous studies provide estimated releases of CNTs into various media (i.e., air, water, soil, and sediment), and the consequent risks to various ecological receptors (Gottschalk et al., 2009, 2010; Zhao et al., 2012). Therefore, the understanding of the environmental behavior of CNTs is an important issue for evaluating environmental and health impact of CNTs.

Dissolved organic matter (DOM) is ubiquitous in the environment. Once CNTs are released into the environment, they will interact with DOM (Hyung and Kim, 2008). As a consequence of the interaction, the environmental behavior would alter. Pristine MCNT could be stabilized (suspended) in the aqueous phase by DOM

which might provide sterically and electrostatically stable surfaces to MCNTs after sorption to MCNTs (Hyung et al., 2007). This result suggested that the dispersion of CNTs might occur to some extent in the natural aquatic environment. In this case, the sorption of organic contaminants by CNTs would be changed. For example, the physical form and surface properties of DOM (humic acid)-coated MCNT dramatically were altered, but the coating did not make striking changes on sorption of phenanthrene, naphthalene and 1-naphthol by MCNT (Wang et al., 2008). Additionally, phenanthrene sorption by nano-TiO$_2$ and nano-ZnO particles was enhanced significantly by coated humic acids (HAs), which was contributed to different functional groups of HA (i.e., phenolic OH with nano-TiO$_2$, while COOH with nano-ZnO) (Yang and Xing, 2009b). These various findings illustrate that the obvious differences may be due to the functionalities of nanoparticles. Because the various functional groups affect the sorption between sorbents and sorbates by changing the intensity of H-bond, π–π, and hydrophobic interaction, the functionalities of nanoparticles would regulate the overall sorption as a main factor except for the surface area.

Up to now, many studies were focused on the sorption of various organic matters to different carbonaceous nanoparticles. The surface area and sum of meso- and macro-porosity-normalized sorption coefficient values of a given HA by MCNTs increased with increasing outer diameters of MCNTs (10–20, 40–60, and 60–100 nm), because MCNTs with larger outer diameter were more

strongly dispersed by HAs thereby making more sorption sites exposed for HA sorption. The hydroxyl/amino functional groups of the sorbates (2,4-dichlorophenol, 2-naphthol, 1,3-dichlorobenzene, and naphthalene) and the surface properties of the sorbents (untreated, lightly oxidized, highly oxidized single-walled CNTs, and graphite) played a combinational role in determining the significance of the nonhydrophobic sorptive interactions. These above studies illustrated that the sorption of sorbate-sorbent system is depend on sorbate properties (i.e., polarity, type of functionalities, surface area). Nowadays, due to the specific demand for various applications, different types of CNTs with variety of functionalities are produced. Hence, it is important to further investigate environmental behavior of different types of CNTs. One study reported that the sorption of sulfamethoxazole by functionalized CNTs was in the order of hydroxylized > graphitized > carboxylized via hydrophobic and electron-donor—acceptor interactions (Zhang et al., 2010). Because limited work has been done on DOM sorption by functionalized CNTs, the importance of the functionalities and porosity of CNTs still remain largely unknown.

The specific objectives of this work, therefore, were to 1) determine and compare the sorption rate of a humic acid (HA) by functionalized MCNTs; 2) identify the main driving force and mechanism that regulate sorption of HA by MCNTs; and 3) examine the effect of pH on the sorption. To achieve these aims, the functionalized MCNTs are from a same origin MCNT15 to keep the same graphene structure. Therefore, it would be clear to examine the impact of various type of functionalities on the sorption of HA for better understanding the environmental behavior of CNTs.

2. Materials and methods

2.1. Materials and characterization

Five MCNTs with outer diameter of 8–15 nm were used and abbreviated as MCNT15, MCNT15-OH, MCNT15-COOH, MCNT15-NH$_2$ and MCNT15-Ni, respectively. They were purchased from Chengdu Organic Chemistry Co. The synthesis method of MCNTs was shown in Supplementary materials. Their surface area and pore volume (Table S1) were calculated from the multipoint Brunauer—Emmett—Teller (BET) method. Functional groups of the MCNTs were analyzed by diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) using a Perkin—Elmer spectrum one spectrometer with DRIFTS accessory (NICOLET6700, Thermo SCIENTIFIC). Zeta potentials (ZetaPlus, Brookhaven Instruments Corporation) of these MCNTs were determined as well.

Aldrich humic acid (HA) was purchased from Aldrich Chemical Co, and further purified using 0.1 M Na$_4$P$_2$O$_7$. It was then de-ashed using 0.1 M HCl/0.3 M HF solution, rinsed five times with deionized water, and freeze-dried. Finally, the HA was ground to pass through a 250 μm sieve and stored for further experiments (Pan et al., 2007; Wang et al., 2008). The main characterization of HA was shown in Supplementary materials, and performed as described elsewhere (Pan et al., 2007). All reagents were analytical-grade and were used as received. Deionized distilled water was used in all experiments.

2.2. Equilibrium sorption of HA

Sorption isotherms of HA by MCNTs were obtained using batch experiments in 20 ml screw cap vials. To prepare HA stock solutions, 100 mg HA was dissolved in 5 ml 0.1 mol NaOH solution and mixed constantly on a magnetic stirring stand for 30 min, then diluted in 1 L background solution, and followed by adjusting pH to 7.0 by 0.1 mol/L NaOH or HCl. The background solution contained 0.02 mol NaCl in deionized distilled water with 200 mg/L NaN$_3$ to inhibit biodegradation. The solution was filtered through 0.22 μm poly(tetrafluoroethylene) (PTFE) filter (Wang et al., 2009). The final DOM solution was analyzed with a high-temperature TOC instrument and a concentration of 96 mg/L was obtained. This stock HA solution was stored in dark at 4 °C before use.

Solid to solution ratio was adjusted to obtain 20–80% solute uptake by MCNTs. The obtained HA solution was diluted to give a series of initial HA concentration (3.0, 4.0, 6.0, 9.0, 13, 18, 27, 40, 55, and 80 mg/L) by the background solution. The vials containing 20 ml test solution of HA at various concentrations with MCNTs of about 2.0 mg were sealed with Teflon-screw caps and placed on a rotary shaker to mix for 3 days at room temperature (25 ± 1 °C). After mixing, the vials were centrifuged at 3000 rpm for 30 min, and the HA concentration in the supernatant were measured using a UV—visible spectrometer (UV-1800, Shimadzu, Kyoto, Japan) at 254 nm in a 1 cm quartz cell (Baken et al., 2011). The UV data could well relate with the TOC data

through the pre-experiments. Meanwhile, the standard curve between concentration of HA and UV intensity was good with $r^2 = 0.999$ (Fig. S1). All samples including blanks were run in duplicate. Sorption of HA by MCNTs was calculated by mass difference because their mass loss was negligible for blank samples. pH effects on sorption was conducted at an initial HA concentration of 18 mg/L, where the solution pH was adjusted by NaOH or HCl and the final pH of the supernatant after centrifugation was recorded. Sorbed HA was calculated by mass difference in TOC. The description of HA solution were presented in Supplementary materials.

2.3. HA sorption kinetics

Sorption kinetics of HA by MCNTs was also performed using batch experiments in screw cap vials. The concentration of HA was 18 mg/L. The solid to solution ratio and sample centrifugation at each time point were identical to those for the equilibrium sorption systems as aforementioned. Duplicate samples with the same condition were prepared at each sampling time point to avoid changing the solid to solution ratio of the kinetic sorption system.

2.4. Kinetic and equilibrium sorption data fitting

The Lagergren pseudo first- (1), second-order models (2) and Weber—Morris models (3) have widely been used to describe sorption kinetics of sorbates (e.g., DOMs and organic chemicals) from liquid to sorbents (Wang et al., 2011). Lagergren pseudo first- and second-order models are reaction-based models, and Weber—Morris model is diffusion-based model.

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{1}$$

$$\frac{1}{q_t} = \frac{1}{k_2 q_e^2} \cdot \frac{1}{t} + \frac{1}{q_e} = \frac{1}{v_0} \cdot \frac{1}{t} + \frac{1}{q_e} \tag{2}$$

where k_1 (h^{-1}) and k_2 (g mg^{-1} h^{-1}) are the rate constants for the pseudo first-order and pseudo second-order models, respectively, q_e (mg/g) and q_t (mg/g) are the amounts of solute adsorbed per unit sorbent at equilibrium and at time t (h), respectively. Herein, the initial adsorption rate (v_0) is calculated as: $v_0 = kq_e^2$ for the pseudo second-order model.

Weber—Morris model:

$$q_t = A + k_a t^{0.5} \tag{3}$$

where A is the intercept of the vertical axis (mg/g), and k_a is the overall diffusion constant for sorption (mg/(g h$^{0.5}$)).

The Langmuir and Freundlich models were employed to fit the equilibrium sorption data of HA by MCNTs.

Langmuir model:

$$q_e = \frac{q_{max} K_L C_e}{1 + K_L C_e} \tag{4}$$

where q_e and q_{max} are sorbed amount of HA to MCNTs at equilibrium and the maximum sorption capacity of HA (mg/g), respectively. K_L is the affinity parameter (mL/mg). C_e is the HA concentration in aqueous phase at equilibrium (mg/L).

Freundlich model:

$$q_e = K_f \cdot C_e^n \tag{5}$$

where K_f is the sorption coefficient ((mg/g)/(mg/L)^n), and n is a constant often used as an indicator of isotherm nonlinearity. Sorption coefficient (K_d) of HA by MCNTs was calculated with the equation $K_d = q_e/C_e$ (L/g).

3. Results and discussion

3.1. Characterization of MCNTs

Characteristics of the MCNTs are listed in Table S1. Lengths and outer diameters of the MCNTs are identical. The surface area and pore volume are distinct, but the differences are not large (Fig. S2). Meanwhile, these MCNTs contain various functional groups, i.e. −OH, −COOH, −NH$_2$, −Ni and impurities (ash). In addition, DRIFTS spectra show that MCNTs contains C=O, C−O as well (Fig. 1). These polar moieties could be introduced in the purification process due to oxidation.