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Adsorption and desorption of dissolved organic matter by carbon nanotubes: Effects of solution chemistry☆

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ABSTRACT

Increasing use of carbon nanotubes (CNTs) has led to their introduction into the environment where they can interact with dissolved organic matter (DOM). This study focuses on solution chemistry effects on DOM adsorption/desorption processes by single-walled CNTs (SWCNTs). Our data show that DOM adsorption is controlled by the attachment of DOM molecules to the SWCNTs, and that the initial adsorption rate is dependent on solution parameters. Adsorbed amount of DOM at high ionic strength was limited, possibly due to alterations in SWCNT bundling. Desorption of DOM performed at low pH resulted in additional DOM adsorption, whereas at high pH, adsorbed DOM amount decreased. The extent of desorption conducted at increased ionic strength was dependent on pre-adsorbed DOM concentration: low DOM loading stimulated additional adsorption of DOM, whereas high DOM loading facilitated release of adsorbed DOM. Elevated ionic strength and increased adsorbed amount of DOM reduced the oxidation temperature of the SWCNTs, suggesting that changes in the assembly of the SWCNTs had occurred. Moreover, DOM-coated SWCNTs at increased ionic strength provided fewer sites for atrazine adsorption. This study enhances our understanding of DOM–SWCNT interactions in aqueous systems influenced by rapid changes in salinity, and facilitates potential use of SWCNTs in water-purification technologies.

1. Introduction

Carbon nanotubes (CNTs) are one of the most widely manufactured nanoparticles (Iijima, 1991). CNTs exhibit high tensile strength (Niyogi et al., 2002) and intriguing magnetic behavior (Meng et al., 2012), and they are considered extremely good adsorbents. They are therefore being extensively examined for their use in biomedicine (Meng et al., 2012), composite materials (De Volder et al., 2013) and water treatment (Upadhyayula et al., 2009). CNTs are introduced into the environment during their synthesis, application and disposal (Pan et al., 2010). In the aquatic environment, CNTs can interact with various substances, such as organic/inorganic pollutants (Pan and Xing, 2008), and dissolved organic matter (DOM) (Furman et al., 2013).

DOM is a complex mixture of soluble organic compounds that pass through a 0.45-μm filter (Bolan et al., 2011). DOM is ubiquitous in the environment, playing a significant role in many biogeochemical processes (Bolan et al., 2011; Mackowiak et al., 2001), where its concentrations vary from 0.5 mg C L^{-1} in the oceans (Nebbioso and Piccolo, 2013) to 1.5 mg C L^{-1} in lakes and rivers (Imai et al., 2001), and up to 40 mg C L^{-1} in streams receiving wastewater effluents (Borisover et al., 2011; Imai et al., 2002; Baghoth et al., 2011). The presence of DOM affects water quality and may have negative impacts, such as promotion of bacterial growth and increased levels of pollutants (Matilainen et al., 2010). The properties and composition of DOM vary with its origin, concentration and surrounding conditions (Leenheer and Croue, 2003).

The interactions proposed responsible for DOM adsorption by CNTs are Van der Waals forces, H-bonding, cation bridging and $\pi-\pi$ interactions (Li and Huang, 2010; Wang et al., 2013; Yang and Xing, 2010). Thus, different functionalities of multi-walled CNTs (MWCNTs) were found to affect the adsorption of humic acid (Wang et al., 2013). The adsorption of natural organic matter by oxidized MWCNTs was reported to decrease as their oxygen content increased because the MWCNTs were less prone to form $\pi-\pi$ interactions and in light of increased electrostatic repulsion (Smith

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et al., 2012). Studies have reported preferential adsorption of higher molecular weight fractions of natural organic matter (Hyung and Kim, 2008) and aromatic-rich polar fulvic acid fractions (Yang and Xing, 2009) by CNTs. Similarly, fractionation of DOM by CNTs has been observed (Engel and Chefetz, 2015), suggesting that the nanotubes facilitate preferential adsorption of the hydrophobic acidic moieties of DOM and consequently affect the composition of the non-adsorbed DOM. The impact of solution chemistry on DOM adsorption by CNTs has also been investigated (Hyung and Kim, 2008). High values of pH were shown to decrease DOM adsorption by CNTs owing to increased electrostatic repulsion between the two. In contrast, increasing ionic strength ultimately decreases electrostatic repulsion between DOM and CNTs due to enhanced double-layer compression (Hyung and Kim, 2008; Lin et al., 2009).

Although adsorption of DOM by CNTs has been well characterized, information on its desorption is lacking, including knowledge of the effects of varying solution conditions on the CNTs' DOM-desorption capability. This information is essential to fully assess the environmental behavior of CNTs and to accurately evaluate the ability to use CNTs as adsorbing agents. To the best of our knowledge, the influence of changing solution parameters between the adsorption and desorption phases on DOM adsorbed amounts has not been addressed. Moreover, kinetics experiments are frequently given little attention and the possible effects of varying solution conditions on equilibrium time are disregarded with no suitable verification. Therefore, the main objective of this study was to evaluate the effects of solution chemistry on adsorption/desorption of DOM by CNTs. We hypothesized that DOM adsorption by CNTs is dependent on DOM conformation (i.e., the spatial arrangement of molecules in solution) and availability, which in turn is dependent on solution conditions. Non-functionalized single-walled CNTs (SWCNTs) were chosen as adsorbents in this study in light of their superior adsorptive capabilities and potential introduction into the environment (Petersen et al., 2011; Yu et al., 2014).

2. Experimental section

2.1. Materials and characterization

Pristine SWCNTs (outer diameter 1–2 nm, length 5–30 μm) were purchased from Chengdu Organic Chemistry Co. Ltd. (Chengdu, China). The purity (94%) and oxidation temperature of the SWCNTs were evaluated using thermal gravimetric analysis (TGA Q500, TA Instruments, New Castle, DE, USA) performed at a constant temperature ramp of 10 °C min^{-1} (room temperature to 900 °C) in the presence of oxygen (representative thermograms are presented in Fig. S1). Surface area, mesopore, and micropore volumes of the SWCNTs were determined from N_2 adsorption–desorption isotherms at 77 K (Quantachrome Instruments, Boynton Beach, FL, USA). The surface elemental composition of the SWCNTs was examined by X-ray electron spectroscopy (Axis Ultra, Kratos Analytical, Manchester, UK).

DOM was extracted from composted biosolids (1:10 g:mL solid-to-water ratio) by overnight agitation (250 rpm, 25 °C) as previously described (Engel and Chefetz, 2015). The suspension was then centrifuged (12,000g, 20 min) and filtered through a 0.45-μm Acrodisc Supor membrane (PALL Corp., Ann Arbor, MI, USA). Carbon concentration of DOM (i.e., dissolved organic carbon—DOC) was determined using a V_{CSH} total organic carbon analyzer (Shimadzu, Japan). Limit of quantification for the DOC was 0.5 mg C L^{-1}. The ionic composition of the DOM extract was measured by inductively coupled plasma atomic emission spectrometry (Acros-EOP, Spectro, Kleve, Germany) after digestion of the DOM solution with 65% HNO_3 and 35% HCl at 150 °C for 2 h. The surface tension of DOM was measured with a contact angle goniometer (DSA20E, Krüss, Hamburg, Germany). Elemental composition of the DOM was determined with a Flash EA 1112 CHN analyzer (Thermo Fisher Scientific Inc., Breda, The Netherlands). UV–vis absorbance was measured with an Evolution 300 spectrophotometer (Thermo Scientific, Waltham, MA, USA). Zeta potentials of the DOM and SWCNTs and DOM conductivity were measured using a Zetasizer Nano ZS (Malvern Instruments, Southborough, MA, USA). Images of the dried DOM and SWCNTs were obtained by transmission electron microscopy (Tecnai T12 G2 Spirit, FEI Company) operated at 120 kV. The herbicide atrazine (1-Chloro-3-ethylamino-5-isopropylamino-2,4,6-triazine, 90% purity) was obtained from Agan Chemicals (Ashdod, Israel). Deionized water and analytical grade solvents (Sigma–Aldrich, Rehovot, Israel) were used in all experiments.

2.2. Adsorption experiments

A batch-equilibration technique was used for all adsorption trials. DOM was diluted to a series of initial concentrations and introduced into 20-mL Pyrex vials with Teflon screw caps containing 4 mg of SWCNTs (1:4 mg:mL solid-to-water ratio). All experiments were conducted in a background solution with a constant ionic composition which simulated the composition of the DOM extract (Ca^{2+}, 4.4 mg L^{-1}; Mg^{2+}, 3.8 mg L^{-1}; Na^{+}, 12.5 mg L^{-1} and K^{+}, 28.8 mg L^{-1}). NaN_3 (100 mg L^{-1}) was added to all solutions to inhibit biodegradation (Skipper and Westermann, 1973). The final ionic strength of the background solution was 4 mM. The samples were agitated (200 rpm, 25 °C) for 2 days according to adsorption kinetics experiments (Fig. 1). At the end of the equilibration time, supernatants were passed through a 0.45-μm filter and DOC concentrations were measured. Complete removal of the SWCNTs by filtration was confirmed by measuring the absorbance at 800 nm (Smith et al., 2012; Hyung et al., 2007). Adsorption trials were performed at seven DOC concentrations (triplicates); for each concentration, controls (i.e., DOM without SWCNTs) were included. The amount of DOM adsorbed to the SWCNTs was calculated by mass differences; mass losses for control samples were negligible (<1%).

Adsorption experiments (shown schematically in Fig. S2A) were performed at pH 4, 7 and 10 (25 °C). These pH values were chosen to examine different protonation degrees of the DOM (i.e., the carboxylic and phenolic groups). pH was adjusted by addition of either NaOH or HCl (variations in ionic strength between pH values were negligible). pH was measured at the beginning and end of the experiment. The effect of temperature on adsorption was evaluated by conducting the experiments at 10, 25 and 40 °C. The impact of ionic strength was tested by adding different percentages of simulated seawater (conforming to US Environmental Protection Agency guidelines (U.S. EPA, 2002)) to the background solution. Simulated seawater (100%) exhibited an ionic strength of 617 mM.

Adsorption of atrazine by SWCNTs was evaluated at the same solid-to-water ratio as that used for the adsorption of DOM. SWCNTs were primarily shaken in solutions of different ionic strengths with or without DOM for 2 days, then filtered and dried. Solutions of atrazine (at a constant initial concentration of 13 mg L^{-1}) were prepared at the corresponding ionic strengths and introduced into vials containing either the bare (non-coated) or DOM-coated SWCNTs. Concentration of atrazine was determined using a Waters HPLC system (e2695, Waters, Milford, MA, USA), equipped with a reversed-phase C-18 column (LiCrospher® 100 RP-18, 25 cm × 4.6 mm, 5 μm) and a photodiode array detector. Atrazine was eluted from the column at a constant flow rate of 1 mL/min at 35 °C using an isocratic program of 70% acetonitrile and 30% double-distilled water according to absorption at 222 nm.