Heteroaggregation of multiwalled carbon nanotubes with sediments

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ABSTRACT

In this study, the effect of ion type and concentration on the heteroaggregation and release of multiwalled carbon nanotubes (MWCNTs) and hydroxylated MWCNTs (OH-MWCNTs) with sediments is reported. Means of the first-order heteroaggregation rate constant (k_{het}) for MWCNTs and OH-MWCNTs and a freshwater sediment in 0.4 mM $CaCl_2$ (0.21 and 0.17 d^{-1}) are significantly higher than those in 10 mM NaCl (0.096 and 0.094 d^{-1}). All sediment-electrolyte combinations exhibit first-order heteroaggregation rates during the initial time period ($\leq$5 days) as evidenced by the linearity of the ln concentration vs time plots, and for some low ionic strength treatments heteroaggregation is first-order over the duration of the entire experimental period. However, faster heteroaggregation rate treatments deviate from linearity at longer time periods due to the formation of large, settleable aggregates (homoaggregation). Heteroaggregation attachment efficiency (α_{het}) values for both MWCNTs and OH-MWCNTs increase mostly linearly with ionic strength and are greater for the sediment higher in Al hydroxide content. Both nanotube heteroaggregation with sediments and deposition on model environmental surfaces is irreversible under constant background solution conditions. When background solution ionic strength is reduced, nanotube release from sediments and a model surface is dependent on the initial solution chemistry, with nanotubes deposited from NaCl solutions released much more readily than those deposited from $CaCl_2$ solutions. The lowest fractional release observed was for OH-MWCNTs deposited from $CaCl_2$ solutions indicating potential OH-Ca-NOM bridging effects.

1. Introduction

The unique electronic, mechanical, and structural properties (Baughman et al., 2002; Loiseau et al., 2006; Hu et al., 2007) of carbon nanotubes (CNTs), their potential in drug delivery and other biomedical applications (Bianco et al., 2005; Mahmood et al., 2009), as well as utilization in polymer composites (Clayton et al., 2005), has led to increased production of these versatile materials. More than 1600 hundred consumer products are reported to contain nanoscale materials, and the use of carbon-based nanomaterials (including fullerenes, CNTs, and graphene family materials) in these products trails only nano-scale silver and titanium (WWICS, 2013). Carbon-based nanomaterials are also referenced in 40% of the nano-technology patent applications submitted to the US Patent and Trademark Office from 1/2010–3/2011 (Leitch et al., 2012) and upper estimates for US CNTs production are in excess of 1000 tons per year (Hendren et al., 2011). Clearly, as more CNTs are produced and utilized in commerce, the potential for either permitted or accidental releases increases and the potential for human and ecological exposures increases concomitantly (Murayama et al., 2004; Wiesner et al., 2009). These potential exposures underscore the importance of understanding the processes that govern CNT transport and transformation in the environment.

Studies have investigated the effects of dispersion media (Lisetski et al., 2011) and aqueous solution parameters, primarily ionic strength and dissolved organic carbon (DOC) concentration, on CNT aggregation state (Hyung et al., 2007; Saleh et al., 2008; Bouchard et al., 2012) and deposition on model surfaces (Yi and Chen, 2011; Chang and Bouchard, 2013). General conclusions from these studies are that CNT aggregation follows Derjaguin–Landau–Verwey–Overbeek (DLVO) theory (Overbeek, 1999) and that dispersed CNTs may be quite stable at ionic strengths commonly observed in fresh waters, particularly at high DOC concentrations. In addition, one-dimensional transport of CNTs in porous media columns has indicated that CNTs are significantly retained in porous media under environmentally representative background solution conditions (Jaisi and Elimelech, 2009; Liu et al., 2009; Bouchard et al., 2013). Koelmans et al. (2009) estimated sediment concentrations for carbon-based nanoparticles and black carbon nanoparticles and concluded that the manufactured

materials will yield negligible concentrations relative to black carbon. In a later work however, the same group found that an in situ benthic community was more sensitive to multi-walled carbon nanotubes (MWCNTs) than to bulk activated carbon (Velzeboer et al., 2013).

As CNT exposure models are developed and applied, the types of data needed to parameterize these models, and model sensitivity to these parameters, is becoming clearer. A key exposure model parameter for quantifying CNT interactions with environmental surfaces, like the surfaces of sediments, is the CNT heteroaggregation attachment efficiency (α_{het}) which represents the fraction of CNT-surface collisions that result in attachment. In studying the heteroaggregation of MWCNTs and hematite nanoparticles (Huynh et al., 2012), and single walled carbon nanotubes and gold nanospheres (Afrooz et al., 2013), CNT–CNT aggregation values (homoaggregation, α_{hom}) could be determined but not α_{het} values. Unfortunately, while α_{hom} values are common in the literature, α_{het} values for the heteroaggregation of CNTs with naturally occurring particulate matter, such as sediments and particulate organic matter are quite rare.

It is clear that α_{het} is both important and rare (particularly for CNTs), and that a better understanding of the CNT, sediment, and solution parameters that determine α_{het} are needed to reduce uncertainty in CNT exposure modeling. Therefore, the objectives of this work are to measure important CNT characteristics such as size and charge for functionalized (OH-MWCNTs) and unfunctionalized MWCNTs over a range of background solution conditions. MWCNT–MWCNT and MWCNT-sediment interactions are investigated and α_{hom} and α_{het} values as a function of background solution conditions reported. Finally, the reversibility of MWCNT attachment to environmental surfaces is explored by measuring MWCNT release from sediment surfaces and from a model environmental surface.

2. Materials and methods

2.1. Materials

MWCNTs and hydroxylated MWCNTs (OH-MWCNTs) were purchased from CheapTubes Inc., (Brattleboro, VT) with reported 95% purity. Both materials have a reported outside diameter of 20-30 nm and length of 10–30 μm. OH-MWCNTs contain 1.6% OH groups by weight. Analytical grade sodium chloride (NaCl), calcium chloride ($CaCl_2$), and sodium dodecyl sulfate (SDS) were purchased from Thermo-Fisher (Fremont, CA). Suwannee River humic acid (SRHA, Standard II, International Humic Substances Society, St. Paul, MN) was used to model the natural organic matter (NOM) coating of environmental surfaces. All solutions were prepared with deionized water (DI) with a resistivity = 18.2 mΩ cm and the SHRA solution was filtered through a 0.45 μm cellulose acetate filter prior to use. The sediments used were Ottawa sand sediment obtained from Unimin Corporation (New Canaan, CT) and a freshwater sediment collected from Calls Creek near Athens, GA, USA. Both sediments were wet-sieved to yield 250–500 μm particle size fractions. Relevant physical-chemical data is contained in Table S1 and a more extensive characterization of these materials is reported elsewhere (Zhang et al., 2012).

2.2. Methods

2.2.1. Preparation and Characterization of MWCNTs and OH-MWCNTs Suspensions

Nanotubes in 0.001% w/v SDS solution (40 mL) were ultrasonicated with a probe sonicator (Sonic & Materials, Newton, CT) in an ice-water bath for 10 min at an average energy level of ∼32

Watts. The resulting mixture was centrifuged at 10,000 RCF at 4 °C (Beckman Coulter, Brea, CA) for 30 min and the supernatant nanotube concentrations determined using UV–vis absorbance at 500 nm (Enspire Multimode Reader 2300, PerkinElmer, MA) and pre-determined calibration curves (Chang and Bouchard, 2013). Electrophoretic mobility (EPM) was determined using phase analysis light scattering, and the intensity-averaged (Z-average) hydrodynamic diameter (D_h) and polydispersity index (PDI) were determined using dynamic light scattering (Nano Zeta-Sizer, Malvern Instruments, Worcestershire, U.K.; DynaPro Plate Reader II, Wyatt Technology, CA)]. Instrument performances were verified using NIST-traceable latex microsphere and polystyrene microsphere standards.

AFM imaging was performed using a Veeco Multimode Atomic Force Microscopy (AFM) with a Nanoscope V controller and an E-Scanner (Bruker AXC Inc., Madison, WI). MWCNTs deposited on PLL-coated surfaces (silica quartz crystal microbalance (QCM) sensors) were gently dried with nitrogen, and then mounted on 12 mm stainless steel discs. Images were taken under tapping mode with TESP cantilevers at the speed of 1.0 Hz and a resolution of 512 × 512 pixels.

Nanotubes homoaggregation was measured using time-resolved dynamic light scattering and a reported protocol (Chang and Bouchard, 2013):

$$k_a \propto \frac{1}{N_0}\left(\frac{dD_h(t)}{dt}\right)_{t\to 0} \tag{1}$$

where k_a is the aggregation rate during the initial aggregation period t_0, which is defined as the period from experiment initiation to when the D_h reaches 1.50 $Z_{ave,initial}$, and N_0 is the initial particle concentration. The homoaggregation attachment efficiency (α_{hom}) was defined as k_a normalized by the aggregation rate under diffusion-limited (fast) conditions:

$$\alpha_{hom} = \frac{k_a}{k_{a,fast}} = \frac{\frac{1}{N_0}\left(\frac{dD_h(t)}{dt}\right)_{t\to 0}}{\frac{1}{N_{0,fast}}\left(\frac{dD_h(t)}{dt}\right)_{t\to 0,fast}} \tag{2}$$

2.2.2. MWCNT and OH-MWCNT Heteroaggregation with Sediments

Nanotube heteroaggregation with Calls Creek and Ottawa sand sediments was measured in batch systems. 3 g of the sediments were placed in 20-mL glass vials and 6 mL of nanotube suspensions in 1, 5, 10, and 20 mM NaCl; or 0.1, 0.2, 0.4, 0.6 mM $CaCl_2$ were added. The vials were placed on an orbital shaker (100 rpm) and the supernatants were periodically subsampled after a 1-h settling time over the course of approximately 2 weeks. MWCNT and OH-MWCNT concentrations in the supernatant were determined by UV–vis absorbance. To account for the potential confounding effects of homoaggregation and subsequent aggregate precipitation on heteroaggregation determination, MWCNT and OH-MWCNT D_h was monitored in all samples for the duration of the experimental period.

Prior studies on heteroaggregation of CNTs and gold nanospheres demonstrated both reaction-limited and diffusion-limited regimes indicative of DLVO behavior (Afrooz et al., 2013). In addition, nanoparticle-microparticle heteroaggregation interaction energies have been observed to decrease with increasing ionic strength consistent with classic colloidal theory (Shen et al., 2014). Hence, a particle attachment approach for nanotube-sediment attachment was used to estimate heteroaggregation attachment efficiency (α_{het})

$$\alpha_{het} = \frac{k_{het}}{k_{coll} \cdot C_{particle}^{SPM}} \tag{3}$$