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A settling curve modeling method for quantitative description of the dispersion stability of carbon nanotubes in aquatic environments

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ABSTRACT

Understanding the aggregation and deposition behavior of carbon nanotubes (CNTs) is of great significance in terms of their fate and transport in the environment. Attachment efficiency is a widely used index for well-dispersed CNT solutions. However, in natural waters, CNTs are usually heterogeneous in particle size. The attachment efficiency method is not applicable to such systems. Describing the dispersion stability of CNTs in natural aquatic systems is still a challenge. In this work, a settling curve modeling (SCM) method was developed for the description of the aggregation and deposition behavior of CNTs in aqueous solutions. The effects of water chemistry (natural organic matter, pH, and ionic strength) on the aggregation and deposition behavior of pristine and surface-functionalized multi-walled carbon nanotubes (MWCNTs) were systematically studied to evaluate the reliability of the SCM method. The results showed that, as compared to particle size and optical density, the centrifugal sedimentation rate constant (k_s) from the settling curve profile is a practical, useful and reliable index for the description of heterogeneous CNT suspensions. The SCM method was successfully applied to MWCNT in three natural waters. The constituents in water, especially organic matter, determine the dispersion stability of MWCNTs in natural water bodies.

Introduction

Carbon nanotubes (CNTs) are allotropes of carbon with a cylindrical nanostructure having extraordinarily high length-to-diameter ratios. As a new class of nanomaterials, the unique physicochemical properties of CNTs make them widely applicable in many fields, such as microelectronics (Rosen et al., 2000), energy storage materials (Che et al., 1998), composites (Ajayan et al., 1994), nanoprobes and sensors (Baughman et al., 1999). The ever-rising demand and decreasing cost make their release into the atmosphere, soil and natural waters inevitable.

Due to their nanoscale, CNTs easily go through the skin and penetrate the cell membrane of biological tissues, incurring an inflammatory response (Klaine et al., 2008). Once entering a water body, CNTs, with their strong hydrophobicity and large specific surface area, readily associate with organic matter in water, and eventually enter the human body by the food chain (Klaine et al., 2008). Toxicological studies have proved that the toxicity of nanoparticles depends largely on their size (Limbach et al., 2005; Zhu et al., 2008; Panessa-Warren et al., 2009; Keller et al., 2010; Manna and Rana, 2012). Because of van der Waals and electrostatic forces between the walls, CNTs are extremely prone to aggregate spontaneously in agglomerates or bundles. Natural organic matter (NOM), which is ubiquitous in natural waters, can cause surface modification of CNTs and change their aggregation behavior. The dispersion stability of CNTs can greatly influence their bioavailability and sedimentation in natural waters. Thus, understanding the aggregation and deposition behavior of CNTs

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is of great significance in terms of their fate and transport in aquatic environments.

The size distribution of CNT aggregates is an index of their dispersion stability. Currently, time-resolved dynamic light scattering (DLS) is the most widely used experimental technique to detect the size distribution profiles of CNT particles in aqueous solutions. Since small particles in solutions undergo Brownian motion, the distance between the particles in solution is constantly changing with time. Thus, a time-dependent fluctuation in the scattering intensity can be observed. The DLS technique is useful in well-dispersed systems. For DLS determination, a standard protocol is to sonicate CNT suspensions for a certain time interval, and then take the stable supernatant for further analysis (Bhabak and Mugesh, 2010; Krause et al., 2010; Saleh et al., 2010; Shi et al., 2010). In this way, a reliable time-dependent particle size profile can be obtained. Attachment efficiency (α) is used to reflect the dispersion stability of CNTs. A fast aggregation rate constant (k) can be determined from the slope of the initial change of the hydrodynamic diameter with time (Chen et al., 2006; Chen and Elimelech, 2007):

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

where N_0 is the initial CNT particle concentration; D_h is the hydrodynamic diameter.

By normalizing k in a given solution, an empirical α can be obtained:

$$\alpha = \frac{\frac{1}{N_0}\left(\frac{dD_h}{dt}\right)_{t\to 0}}{\frac{1}{N_{0,fav}}\left(\frac{dD_h}{dt}\right)_{t\to 0,fav}} = \frac{k}{k_{fav}} \quad (2)$$

where, the subscript 'fav' refers to diffusion-limited (favorable) aggregation conditions.

Undoubtedly, study of the behavior of CNTs in well-dispersed solution is helpful for us to understand their transport in aquatic environments. However, in most cases, the CNTs released to water bodies are heterogeneous in particle size. The fate of CNTs in natural water largely depends on hetero-aggregation (Chen et al., 2010). For CNT suspensions of wide particle distribution and large particle size, it is difficult to get reliable data from DLS. Comparatively, the static light scattering (SLS) method has a much larger detection range than that of DLS. It can detect particles of size ranging from nanometers to microns. However, since SLS is a static method, it cannot track the aggregation behavior of particles. Describing the dispersion stability of CNTs in natural waters is still a technical challenge in the investigation of their fate and transport in aquatic environments.

Centrifugation is a useful process in preparative or analytical study of CNTs (Lu et al., 2006; Arnold et al., 2008; Azoubel and Magdassi, 2010; Bonaccorso et al., 2010; Rashmi et al., 2011; Harel et al., 2013). For example, density gradient ultracentrifugation can be used for the separation or density measurement of CNTs (Bonaccorso et al., 2010). By recording the variation of light transmission of centrifugally homogenized CNT suspensions as a function of settling time or as a function of liquid depth, the temporal or spatial distribution of CNT particles can be obtained (Azoubel and Magdassi, 2010; Rashmi et al., 2011; Harel et al., 2013). Such an analysis can provide a full view of the aggregation and deposition behavior of CNTs. Both the diffusion and sedimentation parameters of CNTs can be obtained from the collected data. However, such an analysis is only suitable for a supernatant without insoluble aggregates. In addition to an expensive ultracentrifuge, high-end instruments are needed for real-time and *in situ* monitoring.

The objective of this work is to develop a facile settling curve modeling method for quantitative description of the aggregation and deposition behavior of CNTs in aquatic environments. Pristine and surface-functionalized multi-walled CNTs, labeled as MWCNT, MWCNT–OH, MWCNT–COOH, were employed as the target CNTs. Settling curves of these CNTs, *i.e.*, absorbance of CNT suspension *versus* relative centrifugal force profiles, were collected. Compared with the results from laser particle size analysis, the obtained centrifugal sedimentation rate constants from the settling curves were used as indices for the dispersion stability of CNTs in aquatic systems. The effects of water chemistry, including NOM, solution pH, and ionic strength, on the stability of CNTs were systematically investigated. Moreover, the dispersion stability of the CNTs in three surface waters was studied to explore the aggregation and deposition of CNTs, if released into aquatic environments.

1. Materials and methods

1.1. Materials

Three commercially available CNTs, *i.e.*, MWCNT, MWCNT–OH, MWCNT–COOH, were purchased from Chengdu Organic Chemicals Co., Ltd., Chinese Academy of Sciences and used as received without any pretreatment. These CNTs were synthesized by chemical vapor deposition (CVD) from a CH_4/H_2 mixture using Ni as a catalyst, and purified by mixed H_2SO_4/HNO_3 solutions to remove the catalyst and amorphous carbon. Functionalized MWCNTs were prepared by oxidizing the pristine MWCNT in a $KMnO_4$ solution. The specific surface areas of these MWCNTs were measured with a Micromeritics ASAP 2020 analyzer (Micromeritics, USA) by using the Brunauer–Emmett–Teller (BET) model. Contents of functional groups were determined with a potentiometric titrator (Mettler Toledo T50, Switzerland). Some physicochemical properties of the studied CNTs are summarized in Table 1.

Table 1 – Properties of the studied MWCNTs.

CNT	OD [a] (nm)	Purity (wt.%)	Length (μm)	Bulk density (g/cm^3)	S_{BET} [b] (m^2/g)	CFG [c] (mM/g)
MWCNT	10–20	>95	10–30	0.22	153.3	N.D. [d]
MWCNT–OH	10–20	>95	10–30	0.22	180.2	0.098
MWCNT–COOH	10–20	>95	10–30	0.22	206.6	0.014

[a] Outer diameter, measured by transmission electron microscopy, n = 100.
[b] Specific surface area, calculated with the BET model.
[c] Content of surface functional groups, determined by the potentiometric titration.
[d] Not detectable.