Science of the Total Environment 586 (2017) 738–745

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Bound and unbound humic acids perform different roles in the aggregation and deposition of multi-walled carbon nanotubes

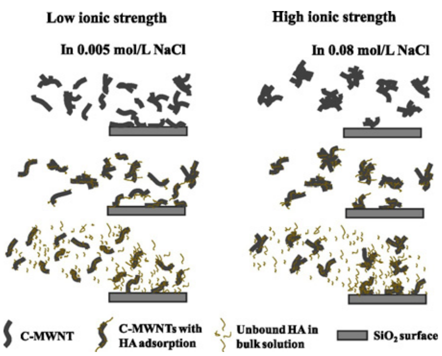
Xuezhi Yang [a], Qi Wang [a], Xiaolei Qu [b], Wei Jiang [a,*]

[a] Environment Research Institute, Shandong University, Jinan 250100, China
[b] State Key Laboratory of Pollution Control and Resource Reuse, School of the Environment, Nanjing University, Jiangsu 210093, China

HIGHLIGHTS

- Unbound HA mitigates CNT aggregation due to the additional adsorption with cations.
- Bound HA changes the CNT surface groups and their interaction with SiO_2.
- Bound HA affects the deposition on SiO_2 more remarkably than unbound HA.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 24 October 2016
Received in revised form 3 February 2017
Accepted 6 February 2017
Available online 13 February 2017

Editor: Jay Gan

Keyword:
Carbon nanotubes
Aggregation
Deposition
Humic acid
Silica surface

ABSTRACT

Natural organic matter influences the carbon nanotube transport in aqueous environments. The role of bound humic acid (HA) on carbon nanotubes and unbound HA in bulk solution in the aggregation and deposition of carboxylated multi-walled carbon nanotubes (C-MWNTs) was examined in NaCl and $CaCl_2$ electrolyte solution. Time-resolved dynamic light scattering and quartz crystal microbalance with dissipation monitoring were employed to investigate the C-MWNT aggregation and deposition kinetics, respectively. The critical coagulation concentration (CCC) of C-MWNTs is 30 mM in NaCl and 3 mM in $CaCl_2$. The bound HA results in CCCs of 32 mM in NaCl and 2.9 mM in $CaCl_2$. However, the existing unbound HA causes much slower aggregation in both NaCl and $CaCl_2$ electrolytes and results in CCCs of 86 mM in NaCl and 5.8 mM in $CaCl_2$. The HA adsorption experiment confirms the additional adsorption of unbound HA in the presence of cations, which can increase the steric effect between C-MWNTs. The more negative charge of C-MWNTs in the presence of unbound HA also stabilizes the suspension. In contrast, the bound HA on C-MWNTs has a more remarkable effect on the deposition rate on the SiO_2 surface than the unbound HA. Bound HA changes the C-MWNT surface functional groups, leading to differences in the interaction between C-MWNTs and the SiO_2 surface. Hence, the C-MWNTs dispersed by their covalently bonded oxygen-containing groups on the carbon framework and dispersed by the bound HA show nearly the same aggregation rates but quite different deposition rates. The additional unbound HA adsorption does not change the surface functional groups or the changing trend of the CNT deposition rate. Distinguishing the role of bound and unbound HA in the aggregation and deposition of carbon nanomaterials is important to predict their transport in various natural waters.

---

* Corresponding author.
E-mail address: jiangw@sdu.edu.cn (W. Jiang).

http://dx.doi.org/10.1016/j.scitotenv.2017.02.050

1. Introduction

Due to their unique mechanical, electronic, thermal and optical properties, carbon nanotubes (CNTs) have attracted considerable attention since their discovery in 1991 (Iijima, 1991). Currently, CNTs are widely used in electronic, catalytic, biomedical, pharmaceutical, hydrogen storage and environmental applications (Baughman et al., 2002; Hendren et al., 2011; Park et al., 2013), and their release into the environment is inevitable through various pathways (Petersen et al., 2011). Moreover, CNTs have been reported to exhibit toxic effects on organisms and human beings and possibly accumulate through the food chain when taken up by organisms (Helland et al., 2008; Migliore et al., 2010; Petersen and Henry, 2012; Ryman-Rasmussen et al., 2009). All of the above-mentioned reasons raise concerns as to the fate and transport of CNTs in natural aquatic systems.

Carbon nanotubes with perfect surface structure are extremely hydrophobic and prone to aggregation through van der Waals forces along their length axis. They are not readily dispersed in aqueous solutions (Wang et al., 2008). There are two main mechanisms that can increase the CNT surface hydrophilicity, allowing CNTs to be stably suspended in natural waters. The first is to covalently bond enough hydrophilic groups to the carbon framework, such as oxygen-containing groups (Hyung et al., 2007). The other way is to cover the CNTs with hydrophilic molecules through non-covalent adsorption. Natural organic matter (NOM) is the most possible coating because it is ubiquitous in nature. NOM adsorption disperses CNTs not only through increased hydrophilic and charged groups but also by steric effects (Lin et al., 2012; Yi and Chen, 2011). The suspended CNTs obtained from both methods will be stable for a period until a change occurs in the natural media.

Aggregation and deposition of CNTs are important to estimate their fate and transport in natural waters, which have been widely studied and have been confirmed to be qualitatively consistent with the classic Derjaguin-Landau-Verwey-Overbeek (DLVO) theory (Derjaguin and Landau, 1993; Verwey et al., 1999). Plenty of studies have been performed on CNT aggregation and deposition processes, and some common viewpoints have been achieved. CNT aggregation will be accelerated by increased ionic strength, compressed electric double layers (Saleh et al., 2008), and the formation of cation bridges (Li and Huang, 2010; Saleh et al., 2010). However, the presence of NOM makes the system more complicated. The increased surface hydrophilicity (Smith et al., 2009) and steric effects caused by NOM adsorption will slow down the CNT aggregation rate (Lin et al., 2012; Yi and Chen, 2011). CNT deposition on natural surfaces also depends on the DLVO interactions between CNT and surfaces (Chang and Bouchard, 2013; Yi and Chen, 2011). Surface oxidation can increase the surface charge density of the CNTs and can thus affect their deposition properties in monovalent and divalent electrolytes (Yi and Chen, 2011). In addition to the electrostatic forces, the surface coating and dispersion methods also influence the CNT deposition (Chang and Bouchard, 2013; Chang et al., 2015).

When CNTs are dispersed by NOM adsorption, NOM will simultaneously exist as bound (adsorbed on CNTs) and unbound (in the bulk solution) NOM in the system. Although it has been well reported that NOM can stabilize CNT suspensions, the roles of bound and unbound NOM in CNT aggregation and deposition have not been studied separately. The common view is that the bound NOM perform the role. A study on silver nanoparticles (NPs) reported that NP aggregation and deposition were further reduced in the presence of unbound HA, which indicated that the unbound HA also stabilized NP suspension (Furman et al., 2013). However, it is unclear how the unbound HA in the system affects the stability of NPs. Moreover, aggregation and deposition are two related processes in CNT transport. A change in CNT aggregation may induce differences in their deposition on a natural surface. Bound and unbound NOM possibly perform related and/or different tasks in the two processes, which is worth further investigation. For CNTs, no experiments have been conducted to compare the effects of bound and unbound NOM.

Recognizing the role of bound and unbound HA is important to predict the behavior and fate of CNTs dispersed in different ways as well as their transport in an NOM-rich or NOM-free aqueous environment. Therefore, in this study, HA is the selected NOM to examine its role in the stability of carboxylated multi-walled carbon nanotubes (C-MWNTs) in natural aquatic systems. The objective of this paper is to investigate the effects of bound and unbound HA on the aggregation and deposition of the C-MWNTs in the presence of monovalent and divalent electrolytes. The aggregation and deposition kinetics of CNTs were monitored by time-resolved dynamic light scattering (DLS) and quartz crystal microbalance with dissipation monitoring (QCM-D).

2. Materials and methods

2.1. Materials and characterization

C-MWNTs (purity >95%; carboxyl content >3.85% by mass) were purchased from Chengdu Organic Chemistry Co., Ltd., Chinese Academy of Sciences. The specific surface area of the C-MWNTs is 161 m^2/g. It was calculated using the multi-point Brunauer-Emmett-Teller method from the N_2 adsorption isotherms at 77 K (NOVA 2000e, Quantachrome, USA). The C-MWNTs contain 94.0% carbon and 6.0% oxygen on the surface, determined using X-ray photoelectron spectroscopy with an Al Kα X-ray source (XPS, ESCALAB 250, Thermo Fisher Scientific, USA). The morphologies and length distributions of the C-MWNTs were imaged using transmission electron microscopy (TEM, JEM-1011, JEOL, Japan) at the electron emission of 100 kV. The degree of C-MWNT structural defects was measured by a Raman spectrometer (LabRAMHR 800, HORIBA Jobin Yvon, France) in our previous research (Jiang et al., 2017), indicating the high degree of surface defects. The metal impurity of the C-MWNTs was 0.59%, as measured by an inductively coupled plasma mass (ICP-MS) spectrometer (Agilent 8800, Santa Clara, CA, USA). The individual metal content is listed in supporting information (SI) Table S1.

Humic acid (HA) was purchased from Aladdin Chemistry Co, and was extracted from leonardite with a purity >90%. It contains 40.2% C, 3.76% H, 49.1% O, 0.99% N, and 0.86% S, as measured in our previous research (Hu et al., 2014). The metal impurity was approximately 2.7% in total, as measured by ICP-MS (Table S1). The distribution of HA carbon moieties was investigated by solid state ^{13}C nuclear magnetic resonance (^{13}C NMR) spectroscopy (Fig. S1) (Hu et al., 2014). The high content of aromatic groups (aromaticity: 47.9%) and carboxylic groups was reflected by the ^{13}C NMR spectrum (Fig. S1). The infrared spectra of HA, C-MWNTs and C-MWNTs with bound HA were scanned using a JASCO Fourier transform infrared (FTIR) spectrometer (Fig. S2). A large amount of hydroxyl and carboxylic acid groups was also revealed in HA by FTIR.

2.2. Preparation of HA and C-MWNT suspensions

To prepare the HA solution, 55 mg HA powder was dissolved in 500 mL deionized (DI) water and sonicated for 30 min (40 kHz, 20 °C). The solution was then filtered through 0.22 μm filters (one filter for every 100 mL) to remove any undissolved substance. The mass loss after filtration was <1.5%, as measured by weighing the mass increase on the filters. The HA stock solution was adjusted to 100 mg/L and stored in the dark at 4 °C. To rapidly quantify the HA concentration, the HA standard curve was made with the filtered solution using a UV–visible Spectrometer at 210 nm (Fig. S3a).

The C-MWNT stock suspension in the absence of HA (S-CNT) was prepared through successive sonication (Saleh et al., 2008). A total of 80 mg C-MWNTs was sonicated in 400 mL DI water for 30 min and then allowed to settle for 10 min to collect the upper suspension. The collected suspension was sonicated again to collect the newly formed upper suspension after standing. Such a cycle was repeated four more times, and the final stable suspension was collected as S-CNT. S-CNT