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Suspension stability and aggregation of multi-walled carbon nanotubes as affected by dissolved organic matters extracted from agricultural wastes☆

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ABSTRACT

Dissolved organic matters (DOMs) extracted from wheat straw (SDOM) and cow manure (MDOM) were used to investigate their effects on the suspension stability and aggregation of multi-walled carbon nanotubes (MWCNTs). Two types of DOM can effectively disperse and stabilize the MWCNTs. At initial MWCNT concentration of 500 mg/L, suspended MWCNT concentration ranged from 8.0 to 17.9 mg/L as DOM were varied from 50 to 200 mg/L dissolved organic carbon (DOC). The critical coagulation concentration (CCC) values were estimated to be 41.4 mM NaCl and 5.3 mM $CaCl_2$ in the absence of DOM. The presence of SDOM and MDOM significantly retarded the aggregation rate of MWCNTs. The CCC values increased to 120 mM NaCl and 14.8 mM $CaCl_2$ at SDOM concentration of 20 mg/L DOC. Due to its higher aromaticity and molecular weight, MDOM showed higher ability to stabilize MWCNTs, with CCC values of 201 mM and 15.8 mM at 20 mg/L DOC. These findings revealed that DOMs originated from agricultural wastes will have great impact on the dispersion and stabilization of MWCNTs, thus their fate in the aquatic environment.

1. Introduction

Carbon nanotubes (CNTs) have been increasingly used in a wide range of industrial applications and consumer products due to their exceptional electronic, mechanical, structural properties and potential in drug delivery (Bouchard et al., 2012; Köhler et al., 2008). With the widespread production and use of CNTs, it is inevitable that some of CNTs will be released into the environment (Hou et al., 2013; Zhang et al., 2012). It has been demonstrated that CNTs have strong affinities toward a variety of organic pollutants (Hou et al., 2013; Lerman et al., 2013; Li et al., 2014a; Zaib et al., 2012), their occurrence in the water environment would significantly affect the fate and transport of these contaminants, thus the associated toxicity and risks (Oleszczuk and Xing, 2011).

CNTs may be released into the aquatic environment as large aggregates and/or in dispersed form (Köhler et al., 2008; Zhang et al., 2012). Due to their amply exposed surface area, suspended CNTs would have greater environmental impact than aggregated ones. Pan et al. (2013) found that suspended CNTs contributed 20% to sulfamethoxazole adsorption with a mass percent less than 1%. To some extent, it is the dispersion state of CNTs that determines their environmental behavior and impact. Therefore, understanding the factors related to the dispersion and aggregation of CNTs is prerequisite for evaluating their environmental and health risk.

After their release, the dispersion state of CNTs will be further affected by the interaction with the substances present in the environment. Since dissolved organic matters (DOM) are ubiquitous in nature, the coexistence of CNTs and DOM could widely occur in the environment. DOMs will adsorb onto CNTs via hydrophobic effect, π–π stacking, hydrogen bonding and electrostatic

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interactions (Wang et al., 2011; Zhou et al., 2012). It has been reported that DOM could effectively facilitate the dispersion of CNTs through adsorption, which might decrease the hydrophobicity of CNTs (Hyung et al., 2006) and increase electrostatic repulsion and steric hindrance (Hyung et al., 2006; Kim et al., 2009). Most studies used DOM isolates rather than bulk-extracted DOMs. Suwannee River humic and fulvic acid are the commonly used DOM surrogates to investigate their effect on the suspension and stability of CNTs (Hyung and Kim, 2008; Schwyzer et al., 2013; Zhang et al., 2012). However, DOM consists of a highly heterogeneous mixture of components with various molecular weights and chemical properties and its composition is a function of source materials and biogeochemical processes (Aiken et al., 2011; Louie et al., 2013). It still remains unclear how some specific DOMs (e.g. DOMs extracted from agricultural wastes) will affect the behavior of CNTs in natural aquatic environments. DOM from wheat straw represents a pristine DOM without experiencing any decomposition processes while DOM from cow manure underwent decomposition and fermentation in the cow bodies. The two DOMs will differ from those aquatic DOMs and soil humic substances in molecular weights, aromaticity and polarity, thus likely their ability to suspend CNTs.

Straw incorporation and application of animal manures are common farmland management practices in China and many other countries around the world. DOMs originated from wheat straw and cow manure will be released into water environments along with farmland drainage or runoff. Studies have demonstrated that these DOMs can affect the adsorption, mobility, bioavailability and consequently the fate of organic pollutants in soils (Chen et al., 2010; Gao et al., 2007; Schnitzler et al., 2007; Song et al., 2010). To our knowledge, no information is available regarding the effects of these DOMs on the dispersion and stabilization of CNTs in aquatic environments.

Moreover, several commonly used surfactants/DOMs were selected for comparison. Triton X-100 (TX100), sodium dodecyl sulfate (SDS), sodium dodecyl benzene sulphonate (SDBS) and hexadecyltrimethylam monium bromide (CTAB) are the most commonly used surfactants for preparing stable suspension of CNTs and will be released into the natural environment along with CNTs. Tannic acid (TA) is widely used as a surrogate or model compound of DOM in environmental studies (Lin and Xing, 2008). Gallic acid (GA), the monomer of TA, is usually used as a surrogate of low-molecular weight DOM (Li et al., 2014b).

The specific objectives of this work, therefore, were to (1) investigate whether DOMs extracted from wheat straw and cow manure can facilitate the dispersion and stabilization of CNTs; and (2) compare the effects of these two DOMs with some commonly used surfactants in stabilizing CNT suspension.

2. Materials and methods

2.1. Materials

Multi-walled carbon nanotubes (MWCNTs) were obtained from Shenzhen Nanotech Co., (Shenzhen, China) with purity over 95% by wt. and outer diameter of 60–100 nm. The CNTs were synthesized by chemical vapor deposition from the CH_4/H_2 mixture at 700 °C with Ni particles as a catalyst, and purified by mixed HNO_3 and H_2SO_4 solution to remove the catalyst and amorphous carbon. Detailed properties of the CNTs were reported by Lin and Xing (2008) previously.

TA was purchased from Alfa Aesar (Massachusetts, USA). Gallic acid monohydrate was obtained from MP Biomedicals (Ohio, USA). Sodium chloride (NaCl), calcium chloride dihydrate ($CaCl_2 \cdot 2H_2O$) and SDS were purchased from Fisher Scientific. TX100, SDBS and CTAB were obtained from Acros (New Jersey, USA). Selected characteristics of the surfactants/DOMs are listed in Table S1.

2.2. Dissolved organic matter extraction and characterization

Wheat straw and cow manure were extracted by deionized water using a solid/water ratio of 1:10 and 1:5 (w/v, dry weight basis), respectively, in a reciprocal shaker at 200 rpm and 25 °C for 24 h. The suspensions were centrifuged at 5000 rpm for 30 min, then, vacuum filtered through a filter paper (Whatman 20–25 μm pore size), and a 0.45 μm cellulous acetate filter (Whatman, Maidstone, UK) successively. The filtrates were freeze dried as powders and stored in a desiccator for later use. The two DOMs are referred to as SDOM and MDOM, respectively. The concentrations of SDOM and MDOM were measured at mg/L dissolved organic carbon (DOC) using a total organic carbon (TOC) analyzer (Shimadzu TOC-L CPH/CPN, Japan). The electrical conductivity of the DOM solution was measured at 25 °C by a YSI 3100 conductivity instrument (YSI, US). The salt ions in the DOM solution were determined using an inductive coupled plasma atomic emission spectroscopy (ICP-AES) (PerkinElmer, Optima 7000 DV). The ^{13}C CP/MAS NMR spectra were obtained using a Varian Infinity Plus-300 spectrometer equipped with a 4 mm double-resonance magic angle spinning probe head, operating at ^{13}C frequency of 75.4 MHz. The ^{13}C NMR spectra are presented in Fig. S1. The aliphatic carbon and aromatic carbon were determined by quantifying the peak area in the 0–109 ppm (Wang et al., 2011) and 110–160 ppm (Chin et al., 1997) chemical shift bands, respectively. The polar carbon of the DOMs was determined by quantifying the peak area in the 50–109 ppm and 145–220 ppm chemical shift band (Wang et al., 2011). The elemental compositions of these two DOMs were analyzed on an elemental analyzer (Vario EI III, Elementar, Germany), and oxygen content was determined by difference as follows: O(%) = 100–(C + H + N + S + Ash) (Calvelo Pereira et al., 2011). Ash contents were determined by dry combustion at 750 °C for 4 h (Song et al., 2010). The molecular weights were measured using the high-pressure size exclusion chromatography method as described by Yue et al. (2004). FTIR spectra were obtained using a Nicolet 380 FTIR spectrometer (Thermo Electron, USA) with a resolution of 2 cm^{-1} between wavenumbers of 400 and 4000 cm^{-1}. Specific UV absorbance at 254 nm was used to evaluate the aromaticity of DOM samples (Tusseau-Vuillemin et al., 2007; Yu et al., 2011). Absorbance of DOM solution at 465 and 665 nm was also measured to calculate the E4/E6 ratio, which is negatively correlated with molecular size (Yang et al., 2007; Yu et al., 2011).

2.3. Dispersion of MWCNTs with DOMs

Dispersion experiments were conducted using a batch equilibration technique. 40 mL DOM solutions with concentrations of 0, 50, 100 or 200 mg/L were added into 40-mL vials with 20 mg of MWCNTs. Each concentration point was run in duplicate. The vials were sealed with Teflon screw caps and were shaken at 150 rpm and 25 °C for 7 days. After equilibration, the vials were centrifuged at 3000 rpm for 30 min and the supernatants were measured with a UV–vis spectrometer at 800 nm to quantify the MWCNTs in aqueous phase. An aliquot of the supernatant was filtered through a 0.2 μm PTFE filter (Whatman) and the remaining DOM was measured using a TOC analyzer. Electron microscopic images were analyzed by a transmission electron microscope (TEM) (JEOL JEM-2010, Japan). A TEM specimen was prepared by placing a droplet of MWCNT suspension on a copper carbon grid and drying overnight at room temperature.

2.4. Preparation of pre-dispersed MWCNTs

A total of 80 mg of MWCNTs was introduced into 800 mL of 0.1% TX100 solution to yield an initial concentration of 100 mg/L, and