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 8.0-17.9 mg/L as DOM were varied from 50-200 mg/L dissolved organic carbon (DOC). The critical coagulation concentration (CCC) values were estimated to be 41.4 mM NaCl and 5.3 mM CaCl₂ in the absence of DOM. The presence of SDOM and MDOM

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significantly retarded the aggregation rate of MWCNTs. The CCC values increased to 120 mM NaCl and 14.8 mM CaCl₂ 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.

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Key words: Carbon nanotubes; dissolved organic matter; agricultural waste; suspension; aggregation

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 P,

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 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 and Wastewater, 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

66 from agricultural wastes) will affect the behavior of CNTs in natural aquatic environments. DOM
67 from wheat straw represents a pristine DOM without experiencing any decomposition processes
68 while DOM from cow manure underwent decomposition and fermentation in the cow bodies. The
69 two DOMs will differ from those aquatic DOMs and soil humic substances in molecular weights,
70 aromaticity and polarity, thus likely their ability to suspend CNTs.

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

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

85 The specific objectives of this work, therefore, were to (1) investigate whether DOMs extracted
86 from wheat straw and cow manure can facilitate the dispersion and stabilization of CNTs; and (2)
87 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 CH₄/H₂ mixture at 700 °C with Ni particles as a catalyst, and purified by mixed HNO₃ and H₂SO₄ 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 (CaCl₂·2H₂O) 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 20-25µm pore size), and a 0.45 µm cellulosic 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 ¹³C 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 ¹³C frequency of 75.4 MHz. The ¹³C 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: $O(\%) = 100 - (C + H + N + S + \text{Ash})$ (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 the material was then sonicated with a probe sonicator (S-4000, Misonix Inc., New York, USA) for 30 min at an energy level of 50 W. The suspension was centrifuged at 3000 rpm for 30 min and the supernatant was then carefully decanted as the stock suspensions. The pH of the stock suspension was measured to be 5.4 ± 0.2 . The suspensions were filtered through a 0.2 µm PTFE filter (Whatman) to remove the MWCNTs, and the concentration of TX100 was measured by the UV-vis spectrometer at the wavelength of 275 nm. The final equilibrium concentration of TX100 in the supernatants was 891 mg/L. The

stabilized-MWCNT concentration in TX100 solution was determined to be 24.1 mg/L.

2.5. Quantification of MWCNTs

The concentration of MWCNTs in the supernatant was quantified using a UV-vis spectrometer (Agilent 8453, USA) at 800 nm (Bai et al., 2010). MWCNT-stock suspension (50 mg/L) was prepared in the presence of 0.1% TX100 using successive sonication protocol. After sonication, no agglomerates were visible in suspension, at the suspension-surface, at the walls or at the bottom of the vial (Schwyzer, 2011). The calibration curve is shown in Fig. S2.

2.6. Stability of TX100-dispersed MWCNT in water with surfactant or DOM

Although critical micellar concentration (CMC) values of surfactants will have great effects on the dispersion and stability of CNTs, environmentally relevant concentrations of less than 50 mg/L which are far below their CMC values were considered in this study. The stable MWCNT suspensions were mixed with the surfactant or DOM solutions (SDS, SDBS, CTAB, TA and GA at 50 mg/L, SDOM and MDOM at 50 mg/L DOC) at the suspension-solution ratios of 1:9, 3:7 and 5:5, respectively. Each sample was run in duplicate. The MWCNT suspension-solution mixture were shaken for 48 h (150 rpm, 25 °C), and then settled for 24 h. The resultant supernatants were measured at 800 nm for MWCNT concentration. SDOM and MDOM at concentrations below 200 mg/L DOC showed negligible absorbance at 800 nm. The hydrodynamic diameters (D_h) and zeta potentials of the resultant supernatants were also determined using a 90 Plus Particle Size and Zeta Potential Analyzer (Brookhaven Instruments Corporation, NY, USA).

The stabilities of MWCNT suspensions diluted by different solutions were quantified using the

absorbance of the supernatants at 800 nm normalized by that of the suspension diluted with water.

A stability value larger than 1 means the surfactant or DOM in the solution can facilitate the stabilization of MWCNT suspensions.

2.7. Aggregation kinetics of TX100-dispersed MWCNT in the presence of DOM

Change of the MWCNT D_h as a function of electrolyte concentration, in the absence or presence of DOM was measured with a dynamic light scattering (DLS). The detector employed a laser beam at 90° with a 15 s time interval. 1.5 mL MWCNT stock suspension and a specific amount of each electrolyte (NaCl or CaCl₂) and DOM were pipetted into a DLS cuvette to initiate the aggregation. The initial concentration of MWCNT was 12.05 mg/L. The cuvette was immediately placed in the DLS instrument after vortexing for 1 s. The D_h measurements were conducted over periods ranging from 10 to 60 min to obtain an approximately 30% increase in the original hydrodynamic radius of MWCNTs (Saleh et al., 2008). The initial aggregation rate constants (k) of MWCNTs are proportional to the initial rate of increase of D_h with time and the inverse of MWCNT concentration N_0

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

As the MWCNT concentration in all aggregation experiments was identical, the attachment efficiency, α , can be calculated by normalizing the initial slope of the aggregation profile of a given solution chemistry by the initial slope obtained for favorable (fast) aggregation conditions:

$$\alpha = \frac{1}{W} = \frac{\frac{1}{N_0} \left(\frac{dD_h(t)}{dt} \right)_{t \rightarrow 0}}{\frac{1}{(N_0)_{fast}} \left(\frac{dD_h(t)}{dt} \right)_{t \rightarrow 0, fast}} = \frac{\left(\frac{dD_h(t)}{dt} \right)_{t \rightarrow 0}}{\left(\frac{dD_h(t)}{dt} \right)_{t \rightarrow 0, fast}}$$

where the subscript “fast” indicates the favorable (nonrepulsive) aggregation conditions (Chen and Elimelech, 2006; Dai, 2007; Ju et al., 2012; Mashayekhi et al., 2012).

2.8. Statistical analysis

Statistical tests were performed with the SPSS software (SPSS 19.0 for Windows, IBM Group Inc., 2010). Non-parametric Kruskal-Wallis tests were used to compare the difference among different treatments. Statistical significance was accepted at $P < 0.05$.

3. Results and discussion

3.1. Characterization of DOMs

The major properties of the two DOM samples are shown in Table 1. The C, H, O, N and S contents of MDOM were slightly higher than those of SDOM, while the ash content of MDOM was lower than that of SDOM. It is not surprising that the ash contents of the DOM samples are very high because the salts were not removed. These ash content values are lower than that of the DOM extracted from sludge (63.74%) while higher than that of the DOM extracted from straw (48.51%) (Song et al., 2008). Lower H/C and higher A_{254}/DOC values for MDOM indicate that MDOM has relatively higher aromaticity than SDOM. The E4/E6 ratios of SDOM and MDOM were 8.83 and 7.66, respectively, indicating that MDOM had a relatively higher molecular weight. The electrical conductivity values indicate that the SDOM solution has a higher ionic strength than the MDOM solution with the same DOC concentration. All these differences between SDOM and MDOM might affect their adsorption on MWCNTs, thus their ability to disperse and stabilize the MWCNTs. Table 2 presents the molecular weights and structural composition of the two DOMs

and those commonly used in other studies. It can be seen that MDOM has a higher molecular weight than SDOM, and the molecular weight of the two DOMs used in this study are between those of Suwannee River fulvic acid (FA) and Suwannee River humic acid (HA), while smaller than that of Aldrich HA. The aromaticity of the two DOMs used in this study are far below those of Suwannee River FA and HA, as well as Aldrich HA. The contents of aliphatic and polar carbon for SDOM are higher than those for MDOM, while the content of aromatic carbon for SDOM are lower than that for MDOM.

Analysis of FTIR spectra of the two DOMs showed a similar pattern of the major absorption bands (Fig. 1). The broad band around 3400 cm^{-1} is assigned to OH-stretching of phenol, hydroxyl, and carboxyl groups. The small peak at $2920\text{-}2977\text{ cm}^{-1}$ might be attributed to asymmetrical stretching of C-H in CH_3 or CH_2 . The band around $1590\text{-}1640\text{ cm}^{-1}$ represents contribution from aromatic C=C stretching and C=O stretching of conjugated carbonyl groups. Signals in the $1400\text{-}1428\text{ cm}^{-1}$ region is assigned to the aliphatic C-H deformation and symmetrical C-H bending vibrations from aliphatic CH_3 . Absorption near 1100 cm^{-1} might be attributed to the C-O stretching of polysaccharide or polysaccharide-like substances. A weak absorption at $596\text{-}628\text{ cm}^{-1}$ is assigned to unsaturated bond and benzene ring. The FTIR spectra of the two DOMs are very similar to that reported for DOMs extracted from sludge and straw (Song et al., 2008).

3.2. Dispersability of MWCNTs by DOM

The main properties of SDOM- or MDOM-dispersed MWCNT are presented in Table 3. The MWCNT concentration in the supernatant was below the detection limit in the absence of DOMs. The introduction of SDOM or MDOM effectively facilitated the suspension of MWCNTs. TEM

images of MWCNT in DOM solutions (Fig. S3) indicate that most of the MWCNT were individually suspended. The dispersed MWCNT concentration showed a significant ($P < 0.05$) increase with increasing DOM concentration, ranging from 8.3 to 17.9 mg/L for SDOM treatments, and 8.0 to 17.2 mg/L for MDOM treatments, respectively. If molecular weights and aromaticity are the dominating factors for determining the propensity of DOM to suspend MWCNTs, MDOM would have suspended more MWCNTs than SDOM. However, SDOM got a slightly higher concentration of MWCNT suspension, mainly because more SDOM was adsorbed to MWCNT than MDOM (Table S2). This can be explained by the difference in ionic strength, which lead to a higher DOM adsorption at higher ionic strength (Hyung and Kim, 2008). Hyung et al. (2006) reported that 6.92 mg/L of MWCNT was stably suspended when the initial concentrations of MWCNTs (average diameter and length were 140 ± 30 nm and 7 ± 2 μ m, respectively) and Suwannee River natural organic matter were 500 mg/L and 100 mg/L DOC, respectively. The concentration of MWCNT suspension was much lower than that of this study (13.3 mg/L for SDOM and 12.1 mg/L for MDOM), likely because of the different properties of MWCNTs and DOM used in the studies, as well as the difference in the stabilization method. Due to the different properties of CNTs used in different researches, it is really difficult to compare our results with those of other studies. Therefore, we used SDS to disperse the same MWCNTs as those used for SDOM and MDOM treatments, suspended MWCNT concentration of 2.8 mg/L was obtained with SDS at 100 mg/L DOC. This means that SDOM and MDOM showed superior performance over SDS in suspending the MWCNTs. The zeta potentials differed significantly among different treatments while no significant difference was observed for D_h ($P < 0.05$). The zeta potentials decreased with increasing DOM concentrations, implying a more stable suspension at higher

DOM concentration. The zeta potential of MDOM dispersed MWCNTs was more negative than that of SDOM, which can be attributed to the higher salt ions in SDOM which neutralized more negative charges in the MWCNT suspensions, thus decreased the electrostatic repulsion.

3.3. Stability of pre-dispersed MWCNTs with DOM

In order to compare SDOM and MDOM with other frequently used surfactants and DOMs, SDS, SDBS, CTAB, TA and GA were used to dilute the TX100-dispersed MWCNT suspensions. The stabilities of TX100-dispersed MWCNT suspensions diluted by different surfactant and DOM solutions are shown in Fig. 2. Visible MWCNT deposition was observed in all the vials. MWCNT deposition increased with increasing dilution ratios. Except for TA and GA, the stability values of all the suspensions diluted by surfactants and DOMs are greater than 1, indicating that these substances in the water can effectively facilitate the stabilization of MWCNT. SDS, SDBS and CTAB have comparable capability to stabilize MWCNT suspension. Two possible reasons were the dilution of MWCNT suspension by water more or less precipitated the suspended MWCNT and/or the involvement of DOMs would increase the quantification of suspended MWCNT. The samples diluted with SDOM and MDOM at 50 mg/L DOC showed the highest stability of MWCNT. Similarly, SDOM had comparable or slightly higher ability than MDOM in stabilizing the pre-dispersed MWCNT as happened to the dry form of MWCNTs. While for TA and GA, comparable or less stable suspensions were observed, comparing with that diluted with water. However, Lin and Xing (2008) have demonstrated that TA can stabilize MWCNT suspensions. It can be speculated that the aggregation of MWCNT particles in this study was resulted from the interaction between TX100 and TA, which needs further study in the future. The decrease of zeta

potentials might also contribute to the deposition of MWCNTs by TA and GA, which will be described in more detail later in this paper.

The MWCNT D_h of different mixtures is shown in Fig. 3. All the ionic surfactants, SDOM and MDOM resulted in significant increase of MWCNT D_h ($P < 0.05$), which mainly comes from the action of Na^+ (in SDS, SDBS, SDOM and MDOM), K^+ (in SDOM and MDOM), NH_4^+ (in CTAB), or some divalent ions (Ca^{2+} and Mg^{2+}) in the SDOM and MDOM. SDOM resulted in the largest particle size, which is consistent with its high ash content (Table 1). The MWCNT D_h in suspensions diluted with TA and GA showed no significant difference from that diluted with water. Fig. 4 shows the zeta potentials of different mixtures. TX100-dispersed MWCNTs were negatively charged, which might come from the hydroxyl and carboxyl groups of MWCNTs that are created during strong acid treatment for end-cap opening and purification (Clark et al., 2011; Lin and Xing, 2008). Surfactants may adsorb to the MWCNT surface through hydrophobic interaction, with their hydrophobic tails binding to the MWCNT surface and hydrophilic head groups extending towards the solution (Bai et al., 2010). Since the adsorption of surfactants could transfer charges to the MWCNT surface, anionic surfactants SDS and SDBS made zeta potentials more negative, while cationic surfactant CTAB reversed the charges to positive. SDOM and MDOM led to less negative MWCNT surface due to the neutralization by cations. All the ionic surfactants (SDS, SDBS and CTAB) led to significant increase ($P < 0.05$) of absolute zeta potentials, indicating that electrostatic stabilization plays important role in the increasing stabilization of MWCNT by ionic surfactants. Since the absolute zeta potentials are similar, these ionic surfactants obtained comparable stabilization of MWCNT suspensions (Fig. 2).

It is interesting to note that although the samples diluted by SDOM and MDOM solution exhibited

the lower zeta potential values, they had higher stabilities of MWCNT suspension. This indicates that electrostatic repulsion may not be the primary mechanism for the increased stabilization of MWCNT by DOMs. The steric repulsion would be the main cause.

For TA and GA, they also make the zeta potentials less negative, which might result from the change of pH (Table S3). The addition of TA and GA made the solution more acid, weakening the dissociation of hydroxyl and carboxyl groups. The decrease of zeta potentials accounted for part of the destabilization of MWCNT suspensions by TA and GA.

3.4. Aggregation of pre-dispersed MWCNTs in the presence of DOM

The attachment efficiencies of MWCNTs as functions of NaCl and CaCl₂ concentrations in the absence and presence of DOM are plotted in Fig. 5. Distinct unfavorable (slow) and favorable (fast) aggregation regimes were observed for MWCNTs in the presence of both NaCl and CaCl₂, indicating the aggregation of MWCNTs is in agreement with the DLVO theory (Chen and Elimelech, 2006). At low ionic strength, an increase in salt concentration leads to a corresponding increase in attachment efficiency. While at higher ionic strength, the increase in electrolyte concentration has no effect on the attachment efficiency. This is consistent with the results of other researches (Bouchard et al., 2012; Ju et al., 2012; Saleh et al., 2008). The CCC can be determined from the intersections between the extrapolations through the unfavorable and favorable regimes (Chen and Elimelech, 2006). The CCC values in the absence of DOM are estimated to be 41.4 mM for NaCl and 5.3 mM for CaCl₂, which would be even higher if the DOM would be deashed. These values are higher than 25 mM NaCl and 2.6 mM CaCl₂ reported for MWCNTs by Saleh et al. (2008), while lower than the 120 mM NaCl reported by Ju et al. (2012). These differences in

CCC values likely resulted from the difference in MWCNTs and dispersants that used in different studies.

The addition of DOM had a significant influence on the aggregation behavior of MWCNTs. A dramatic decrease in the attachment efficiency and an apparent increase in CCC values were observed. This observation is consistent with the effect of humic acid on the aggregation behavior of nanoparticles (Dai, 2007; Ju et al., 2012). The presence of SDOM at 5, 10 and 20 mg/L DOC yielded the CCC values of 86.9, 114 and 120 mM for NaCl treatments and 9.4, 12.2, 14.8 mM for CaCl₂ treatments, respectively. In the case of MDOM, the CCC values are calculated to be 112, 150, 201 for NaCl treatments and 12.3, 13.7, 15.8 mM for CaCl₂ treatments, respectively. It is apparent that MDOM has better ability to stabilize the MWCNTs. This can be ascribed to the lower ionic strength, higher aromaticity and molecular weight of MDOM (Table 1 and Table 2). Over the range of NaCl and CaCl₂ concentrations studied, SDOM and MDOM could effectively decrease the aggregation and increase the stabilization of MWCNT suspensions.

At higher electrolyte concentrations, the surface charges would be entirely screened, making it impossible for the electrostatic repulsion to be the stabilizing factor (Ju et al., 2012). It is indicated that steric repulsion due to the adsorption of DOM would be the mechanism for increased stabilization of MWCNTs. This was further confirmed by the decrease of zeta potentials in the presence of SDOM and MDOM (Fig. 4), indicating that electrostatic repulsion would not be the reason for increased stabilization of MWCNT suspension.

4. Conclusions

Comparing with some commonly used dispersants, DOM originated from wheat straw and cow

manure have comparable or even superior ability to disperse the dry MWCNT particles and stabilize the pre-dispersed MWCNTs, thus influencing the fate of MWCNTs and many other contaminants that can be adsorbed by MWCNTs. Our findings suggest that DOM from agricultural wastes need to be properly addressed in evaluating of environmental and health risks from MWCNT release.

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Fig. 1 FTIR spectra of DOM samples extracted from wheat straw (SDOM) and cow manure (MDOM)

Fig. 2 Stability of MWCNT suspensions diluted by different surfactant and DOM solutions

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2 Fig. 3 Hydrodynamic diameters of MWCNT in suspensions diluted by different surfactant and
3 DOM solutions

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6 Fig. 4 Zeta potential of MWCNT suspensions diluted by different surfactant and DOM solutions

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3 Fig. 5 Attachment efficiencies of MWCNTs as functions of a) NaCl and b) CaCl_2 in the absence
4 and presence of DOM

1 Table 1 Properties of dissolved organic matters extracted from wheat straw (SDOM) and cow manure (MDOM)

Sample	Elemental composition (%)					Aromaticity		Cation concentration (mg/L) [*]				Electrical		
	C	H	N	S	O	H/C	A ₂₅₄ /DOC [*]	K ⁺	Na ⁺	Ca ²⁺	Mg ²⁺	E4/E6 [*]	Ash (%)	conductivity
							(L·mg ⁻¹ ·cm ⁻¹)							(μS/cm) [*]
SDOM	19	2.74	1.72	2.67	18.7	1.73	1.6	12.4	1.68	1.19	0.79	7.66	55.2	253.5
MDOM	22.2	3.00	2.05	2.71	19.9	1.62	1.8	9.49	2.94	0.36	0.57	8.83	50.2	192.0

2 * Data measured at DOM concentration of 50 mg/L DOC.

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1 Table 2 Molecular weight, polydispersity, aliphatic carbon, aromatic carbon and polar carbon of DOM samples

Sample	Weight-averaged	Number-averaged	Polydispersity (ρ)	Aliphatic C (%)	Aromatic C (%)	Polar C (%)
	molecular weight	molecular weight				
	(Mw)	(Mn)				
SDOM	2632	1255	2.1	75.6	3.2	77.0
MDOM	3542	1964	1.8	71.1	3.8	69.1
Suwannee River FA	2310 ^a	1360 ^a	1.7 ^a	nd	24.8 ^a	nd
Suwannee River HA	3820 ^b	1810 ^b	2.1 ^b	nd	42 ^c	nd
Aldrich HA	4100 ^a	1630 ^a	2.5 ^a	nd	41 ^d	nd

2 ^aChin et al., 1994; ^b Chin et al., 1997; ^c Averett et al. 1987; ^d Ashley, 1996. nd means that a parameter was not determined.

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1 Table 3 Main properties of MWCNT suspensions dispersed by SDOM and MDOM

	DOM conc. (mg/L DOC)	pH	Suspended CNT conc. (mg/L)	D_h (nm)	ζ -potential (mV)
SDOM	50	8.49	8.3 ± 0.7	536 ± 11	-24.8 ± 1.2
	100	8.75	13.3 ± 0.1	501 ± 18	-26.5 ± 1.6
	200	8.81	17.9 ± 1.2	490 ± 12	-27.1 ± 3.5
MDOM	50	8.33	8.0 ± 0.8	497 ± 25	-29.6 ± 3.8
	100	8.61	12.1 ± 1.0	478 ± 6	-30.2 ± 2.0
	200	8.77	17.2 ± 0.6	472 ± 7	-33.1 ± 0.6

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