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Natural Organic Matter (NOM) Adsorption to Multi-Walled Carbon Nanotubes: Effect of NOM Characteristics and Water Quality Parameters

HOON HYUNG AND JAE-HONG KIM*

School of Civil and Environmental Engineering, Georgia Institute of Technology, 200 Bobby Dodd Way, Atlanta, Georgia 30332

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The effect of natural organic matter (NOM) characteristics and water quality parameters on NOM adsorption to multiwalled carbon nanotubes (MWNT) was investigated. Isotherm experiment results were fitted well with a modified Freundlich isotherm model that took into account the heterogeneous nature of NOM. The preferential adsorption of the higher molecular weight fraction of NOM was observed by size exclusion chromatographic analysis. Experiments performed with various NOM samples suggested that the degree of NOM adsorption varied greatly depending on the type of NOM and was proportional to the aromatic carbon content of NOM. The NOM adsorption to MWNT was also dependent on water quality parameters: adsorption increased as pH decreased and ionic strength increased. As a result of NOM adsorption to MWNT, a fraction of MWNT formed a stable suspension in water and the concentration of MWNT suspension depended on the amount of NOM adsorbed per unit mass of MWNT. The amount of MWNT suspended in water was also affected by ionic strength and pH. The findings in this study suggested that the fate and transport of MWNT in natural systems would be largely influenced by NOM characteristics and water quality parameters.

Introduction

As the evidence for toxicological effects of carbon nanotubes (CNT) is rapidly accumulating (*1–3*), understanding the fate and transport characteristics of CNT in the natural environment during unintended discharge is becoming an important issue. In particular, an exposure route involving natural waterways, which has traditionally not been considered as these molecules are extremely hydrophobic, has been receiving a widespread interest. Our recent study (*4*) showed that pristine multiwalled carbon nanotubes (MWNT) could be stabilized (suspended) in the aqueous phase by natural organic matter (NOM) which might provide sterically and electrostatically stable surfaces to MWNT after adsorption to MWNT. This finding suggested that the dispersal of carbon based nanomaterials, CNT in particular, in the natural aquatic environment might occur to a higher extent than predicted based only on the hydrophobicity of these materials. In order to accurately predict the behaviors of MWNT in the environment, the mechanism of interaction between NOM and CNT and the effect of water quality on this interaction need to be elucidated.

NOM is a mixture of chemically complex polyelectrolytes with varying molecular weights, produced mainly from the decomposition of plant and animal residues (*5*). Due to the carboxylic and phenolic moieties distributed throughout the entire molecule, NOM generally carries a negative charge in the natural environment (*6*). These physical and chemical characteristics of NOM are likely to be closely related to the mechanism of NOM interaction with CNT. Compared to NOM adsorption onto CNT, the mechanism of NOM adsorption onto activated carbon is relatively well-known due to the rich history of application to water treatment. A few characteristics of NOM interaction with activated carbon are noteworthy and might be helpful for interpretation of CNT-NOM interaction.

First, the adsorption capacity and strength strongly depend on the type of NOM and the type of activated carbon. Factors affecting adsorption have been reported to include size and chemical characteristics of NOM as well as pore structure and surface chemistry of activated carbon (*5–8, 11*). Second, due to the polydisperse nature of NOM, different fractions of NOM tend to have a different degrees of adsorptive interactions with the adsorbent (*7*). This preferential adsorption is reflected by the occurrence of dose-dependent isotherm relationship. For example, the strongly adsorbable fraction of NOM exhibits a more favorable adsorption at lower activated carbon dose. Finally, NOM adsorption is affected by water quality parameters such as ionic strength and pH which influence the charge and configuration of NOM (*6*). Specifically, the adsorption of negatively charged NOM to the activated carbon surface generally increases as ionic strength increases and pH decreases (*5, 8–11*).

Differences between activated carbon and CNT also need to be recognized for the proper interpretation of CNT-NOM adsorption phenomena. First, the activated carbon consists of micropores with different sizes which provide sites for NOM adsorption. CNT in contrast provide adsorption sites only along the surface of a cylindrical structure (*12*). Second, the chemical structure of the activated carbon, which contains carbons of varying degree of saturation and oxidation state as well as functional groups formed during activation process (*7*), is fundamentally different from that of CNT, which consist only of globally conjugated unsaturated carbons in three-dimensional arrays.

The objective of this study was to investigate the effect of NOM characteristics and water quality parameters on adsorptive interaction between MWNT and NOM in aqueous phase. The characteristics of NOM adsorption to MWNT was studied from batch isotherm experiments, which were performed with various NOM samples under different pH and ionic strength conditions. The experimental result was analyzed using Freundlich isotherm model and critically compared to the adsorption of activated carbon. Finally, the amount of stable MWNT suspension formed in water as a result of NOM adsorption under varying conditions was quantitatively analyzed.

Experimental Section

Materials. MWNT (10−20 nm diameter × 10−30 μm length) with over 95% purity was obtained from the Cheap Tubes Inc. (Brattleboro, VT). Suwannee River natural organic matter (SRNOM), Suwannee River humic acid standard II (SRHA), Suwannee River fulvic acid standard II (SRFA), Leonardite

* Corresponding Author phone: (404) 894-2216; fax: (404) 385-7087; e-mail: jaehong.kim@ce.gatech.edu.

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humic acid standard (LHA), Elliott soil humic acid standard (ESHA), Nordic lake humic acid reference (NLHA), Nordic lake fulvic acid reference (NLFA), Waskish peat humic acid standard (WPHA), and Waskish peat fulvic acid standard (WPFA) were purchased from the International Humic Substances Society (IHSS) (St. Paul, MN). Elemental and carbon compositions of the NOMs are provided in Table S1 (Supporting Information). NOM stock solution was prepared by mixing a known amount of NOM with ultrapure water for 24 h. Dissolution of NOM was facilitated by adding NaOH to increase the solution pH to 7. After measuring the total organic carbon (TOC) content of the stock solution by a TOC-Vw analyzer (Shimadzu, Columbia, MD), the solution was diluted to target NOM concentrations. Ultrapure water produced by a Milli-Q water filtration system (Millipore, Billerica, MA) was used for the preparation of all the solutions.

Isotherm Test. Isotherm relationship for NOM adsorption to MWNT was evaluated by a modified bottle-point technique (*5*), where each data point of the isotherm was determined by an individual batch experiment. Both constant adsorbent method and constant adsorbate method were adopted. For all the isotherm experiments, NOM solution was buffered with 1 mM phosphate (NaH_2PO_4) and ionic strength was adjusted with NaCl. The solution pH was adjusted using NaOH and HCl. The mixture of MWNT powder and NOM solution in a 40 mL vial was agitated using a magnetic stirrer for 6 days. Independent kinetic study suggested that the adsorption of NOM reached saturation within 2 days of mixing. Control experiments with blank samples confirmed that the loss of NOM in the solution resulted only from adsorption to MWNT. After 2 days of quiescent settling, samples were taken for further analyses. All the isotherm experiments were performed at 22 °C. Further details on adsorption experimental conditions are provided in Table S2.

Analysis. The concentration of NOM was measured by a TOC-Vw analyzer (Shimadzu, Columbia, MD). The equilibrium NOM concentration after adsorption (C_e) was analyzed after removing MWNT with a 0.2 μm Acrodisc nylon membrane syringe filter (Pall Corporation, Ann Arbor, MI). Once C_e was determined, the equilibrium concentration of NOM adsorbed on the unit mass of MWNT, q_e (mg C/g MWNT), was obtained by the following equation:

$$q_e = \frac{C_0 - C_e}{D} \tag{1}$$

where C_0 (mg C/L) = the initial concentration of NOM and D (g MWNT/L) = dosage of MWNT.

Stability of MWNT in the NOM solution, the quantitative measurement of stable suspension of MWNT due to the NOM adsorption, was determined by visible light absorbance at 800 nm (VIS_{800}) (8453 UV−vis spectroscopy system, Agilent, Palo Alto, CA) after 6 days of mixing and 2 days of settling. VIS_{800} was measured after separating the stable MWNT suspension from the bulk using Whatman 541 filter (20−25 μm nominal pore size, Florham Park, NJ). Our previous study verified that VIS_{800} (i.e., transmittance decrease due to light scattering by suspended MWNT) was linearly correlated with the MWNT concentration measured by a Thermal Optical Transmittance (TOT) analyzer (*4*). The study also verified that the TOT analysis accurately measure the concentration of MWNT in a solution containing both MWNT and NOM (*4*). In this study, VIS_{800} calibrated with those obtained using a TOT analyzer (Sunset Laboratory, Tigard, OR).

The molecular weight distribution of NOM was analyzed by a Hewlett-Packard 1100 high performance liquid chromatography (HPLC) system (Wilmington, DE) equipped with a Waters Protein-Pak 125 SEC column (Milford, MA), a commonly used column for NOM fractionation (*13–15*) (mobile phase = 0.1 M NaCl solution buffered with 1 mM phosphate at pH 6.8, temperature 40 °C). UV absorbance at 254 nm (UV_{254}) of eluent was monitored by a diode-array detector (DAD). Electron microscopic images were analyzed by a Philips 120 transmission electron microscope (TEM) (New York, NY). A TEM specimen was prepared by placing a droplet of fullerene suspension on a copper carbon grid (Electron Microscopy Science, Hatfield, PA) and drying overnight at room temperature.

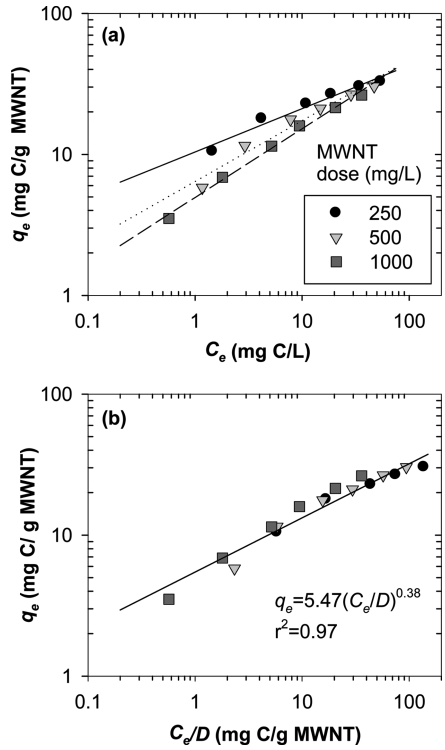

FIGURE 1. Adsorption of SRNOM to MWNT. (a) Isotherm experimental data and Freundlich adsorption isotherm model fit. (b) Normalized data and normalized Freundlich adsorption isotherms model fit. (both at 22 °C, pH 7.0, [NaCl] = 5 mM, [NaH_2PO_4] = 1 mM).

Results and Discussion

Adsorption Isotherm. Results from isotherm experiments performed under varying initial concentrations of SRNOM and MWNT are shown in Figure 1a. The isotherms were adsorbent-dose dependent, i.e., different adsorption isotherms, which were linear in a log scale, were obtained at different MWNT doses. Similar adsorbent-dose dependence phenomenon has been observed in previous studies on the adsorption of NOM onto activated carbon (*5, 10*). Each isotherm at the same MWNT dose fitted well with the following Freundlich isotherm model which has been commonly used to represent aqueous phase adsorption phenomena:

$$q_e = K_F C_e^{1/n} \tag{2}$$

where, K_F ((mg C/g MWNT)/(mg C/L)$^{1/n}$) and $1/n$ (dimensionless) represent Freundlich constant and Freundlich exponent, respectively. Generally, K_F increases as the adsorption capacity of the adsorbent increases and $1/n$ decreases as the adsorption strength increases. As the initial MWNT dose decreased, more SRNOM adsorbed per unit mass of MWNT and consequently q_e increased. This increase was less pronounced when equilibrium SRNOM concentration (C_e) increased, and the isotherms merged at the highest C_e. Deviation from a single solute isotherm, where a unique

TABLE 1. Freundlich Adsorption Model Parameters for Various NOMs[a]

	K_F[b]	$1/n$[c]
SRNOM	5.471 (4.644−6.445)[a]	0.384 (0.333−0.435)
SRHA	9.825 (7.736−12.477)	0.2 (0.122−0.277)
SRFA	5.449 (4.598−6.460)	0.348 (0.294−0.400)
ESHA	11.341 (9.419−13.654)	0.225 (0.163−0.287)
LHA	13.088 (10.899−15.718)	0.212 (0.151−0.274)
NLHA	11.633 (9.617−14.072)	0.222 (0.159−0.286)
NLFA	6.94 (5.890−8.176)	0.324 (0.271−0.376)
WPHA	12.422 (10.644−14.497)	0.225 (0.173−0.276)
WPFA	8.437 (6.620−10.751)	0.278 (0.198−0.357)

[a] Values in the parentheses for K_F and n are 95% confidence intervals. Number of observation. N is 15 for each NOM. [b] (mg C/g MWNT)$^{(1-1/n)}$. [c] dimensionless.

isotherm can be obtained regardless of the initial adsorbate concentration or adsorbent dose, is attributed to the heterogeneity of NOM and consequential occurrence of preferential adsorption (*16, 17*). NOM is a mixture of natural polymers with different adsorption capacity. Therefore, at small adsorbent dosage, highly adsorbable portions of NOM preferentially adsorb onto adsorbent and they would dominate the adsorption behavior of NOM. However, as adsorbent dosage increases, less adsorbable portions start to participate in adsorption and overall adsorption would be also influenced by less adsorbable portions. In such a case, it is known that a unique isotherm is obtained by normalizing the equilibrium adsorbate concentration (C_e) by adsorbent dose (D) as follows (*5, 19, 20*):

$$q_e = K_F\left(\frac{C_e}{D}\right)^{1/n} \quad (3)$$

A normalized Freundlich isotherm model fitted with experimental data (Figure 1b) could reasonably well incorporate dose dependency of NOM adsorption. The experimental results obtained with the other NOMs investigated in this study also matched reasonably well with the normalized Freundlich model (Figure S1). The fitted model parameters for all the NOMs are summarized in Table 1. Some deviations of experimental data at low/high ends of isotherms in the figures could have resulted from the adsorbate concentration dependency of Freundlich isotherm model (*7*). Experimental results were also analyzed using a Langmuir isotherm model (results not shown) after dose normalization, but fitting accuracy was comparable to the normalized Freundlich model at best.

Effect of NOM Type. Results summarized in Table 1 suggest that the adsorptive interaction between NOM and MWNT was strongly dependent on the type of NOM. For example, less soluble, higher molecular weight humic acids had generally higher adsorption capacity than fulvic acids. Various functionalities of the NOMs identified in the previous study (*21*) using ^{13}C NMR were compared with adsorption characteristics. Among various carbon functionalities present in NOM (e.g., carbonyl, carboxyl, aromatic, acetal, heteroaliphatic, and aliphatic carbons), aromatic carbon content showed the strongest linear relationship with K_F (Figure 2) regardless of source (i.e., lake, soil, or river) and type (i.e., bulk, fulvic or humic) of NOMs. Some deviation from the linearity, which might originate from the existence of different elemental composition and functional groups in NOMs, was also observed. Nevertheless, the finding that the adsorption capacity is closely related to the aromatic group content in NOM is consistent with past studies which reported that the attractive interaction between chemical compounds containing the aromatic moiety and CNT was largely driven by π–π interaction (*22, 23*). Specifically, a previous study (*22*) suggests that a benzene ring present in a surfactant that shielded the CNT surface would stack upon benzene ring present in the CNT. Gotovac et al. (*24*) reported that the adsorption of tetracene (4 benzene rings) was 6 times greater than that of phenanthrene (three benzene rings). The strong correlation between adsorption capacity and aromatic content of NOM implies that aromatic fractions of NOM, which can range from ca. 10−40% (C/C) depending on the source and age (*21*) could be a useful measure to evaluate the level of NOM adsorption onto MWNT and consequently the dispersion of MWNT in natural waters.

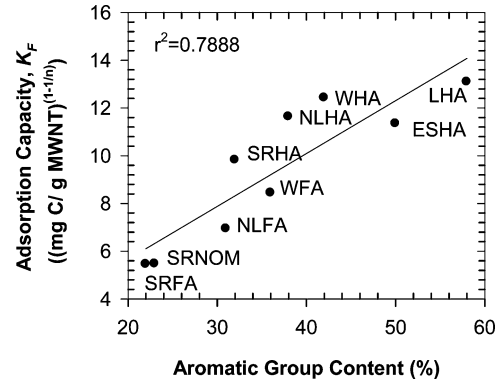

FIGURE 2. Relationship between the aromatic group content of NOM and NOM-MWNT adsorption capacity (K_F).

From the isotherm parameters calculated for each NOM (Table 1), it is also notable that K_F is inversely proportional to $1/n$ for all the NOMs tested in this study (Figure S2). This suggests that the capacity and the strength of NOM adsorption are proportional to each other, which is not always the case for NOM adsorption to activated carbons. In case of activated carbon, the adsorption capacity is mainly determined by surface area of carbon's porous structure available for adsorption, and many of the smaller pores are not accessible to the larger, more strongly adsorbing NOM molecules. Even for the same activated carbon, the area available for adsorption varies with molecular size distribution and characteristics of NOM. Such variation is not necessarily related to chemical composition of NOM that governs adsorption strength between the NOM and the surface. In contrast, MWNT do not have pores available for adsorption and, therefore, NOM adsorption is less influenced by the physical structure of the adsorbent. Consequently, NOMs with greater adsorption strength are likely to have greater adsorption capacity to MWNT as experimental results suggested.

Preferential Adsorption. Preferential adsorption of the higher molecular weight faction of SRNOM to MWNT was evident when size exclusion chromatograms of the nonadsorbed portion of NOM at different MWNT doses were examined (Figure 3). As MWNT dose was increased, higher molecular weight faction (i.e., fractions appearing at lower retention time) was removed to a greater extent. Similar phenomena were observed from the SEC analyses performed with other types of NOM such as SRHA and SRFA (Figure S3). This observation is in accordance with previous studies performed with the polydispersed polymers and nonporous adsorbents where preferential adsorption of high molecular

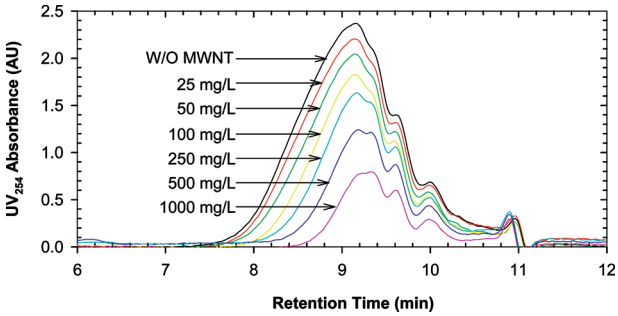

FIGURE 3. Size exclusion chromatograms of SRNOM. Lines in the graph show the fractions of SRNOM that were not absorbed after adding various doses of MWNT.

weight fractions was observed (*16, 17*). However, the opposite molecular weight dependence was reported when adsorbent was porous (e.g., activated carbon). From the SEC study on the Laurentian humic acid adsorption to activated carbon, Kilduff et al. (*10*) suggested that lower molecular weight fraction of the humic acid more favorably adsorbed to activated carbon than the higher molecular weight fraction. Summers and Roberts (*6*) examined activated carbon adsorption of Aldrich humic acid fractionated by molecular weight and observed greater adsorption of the low molecular weight fraction. The apparent preferential adsorption of the low molecular weight fraction in the case of activated carbon adsorbtion would result from the size exclusion effect of pores within the activated carbon structure (i.e., small adsorbates can access both small and large pores, but large adsorbates can not access small pores) (*6*). However, when the adsorption was evaluated on the basis of the accessible surface area, the larger molecules were found to have greater adsorption capacity to activated carbon (*5*), which is consistent with findings from this study.

Effect of Water Quality Parameters. NOM adsorption to MWNT was greatly influenced by water quality parameters such as ionic strength and pH. At the same equilibrium SRNOM concentration in the liquid phase (C_e), the solid phase SRNOM concentration (q_e) was the highest in the solution containing 0.1 M NaCl and the lowest without NaCl (Figure 4a). The experimental data fitted well with the Freundlich isotherm model at each ionic strength. Adsorption capacity, expressed in terms of K_F, increased as ionic strength increased ($K_F = 6.72$ (mg C/g MWNT)$^{(1-1/n)}$ at NaCl = 0 M, 7.05 at NaCl = 0.01 M and 7.55 at NaCl = 0.1 M) presumably due to change in molecular configuration of NOM. Ghosh and Schnitzer (*25*) suggested that humic substances would become increasingly coiled and form more compact structures as ionic strength increased. Adsorption capacity would consequently increase as more molecules could occupy the same surface area (*10*). As the NOM molecule becomes more compact, the area for NOM-MWNT interaction would be reduced and the attractive force per individual NOM molecule to MWNT surface would decrease. Consequently, $1/n$ increased (i.e. adsorption strength decreased) as ionic strength increased ($1/n = 0.39$ at NaCl = 0 M, 0.48 at NaCl = 0.01 M and 0.60 at NaCl = 0.1 M). This is also consistent with the observation made in Figure 3 that NOM with larger molecular size adsorbed to MWNT more effectively due to greater level of adsorptive interaction possible per NOM molecule with MWNT surface. At higher ionic strength, enhanced double layer compression in SRNOM-MWNT agglomerates would also enhance SRNOM adsorption onto MWNT.

Figure 4b shows the effect of pH on SRNOM adsorption to MWNT. The adsorption capacity decreased as pH increased (i.e., $K_F = 8.31$ (mg C/g MWNT)$^{(1-1/n)}$ at pH 5.0, 5.10 at pH 7.0 and 2.96 at pH 9.0), consistent with previous observations made with NOM adsorption to various other adsorbents (*18, 26, 27*). As pH increases, the NOM molecules will become

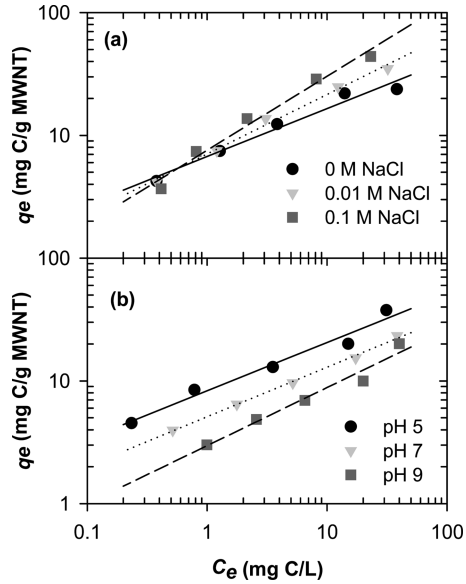

FIGURE 4. Effect of (a) ionic strength (at 22 °C, pH 7.0, [NaH_2PO_4] = 1 mM) and (b) pH (at 22 °C, [NaCl] = 5 mM, [NaH_2PO_4] = 1 mM) on SRNOM adsorption to MWNT. Lines denote Freundlich adsorption isotherm model fit.

less coiled and less compact due to greater charge repulsion, and the adsorption capacity might consequently decrease as discussed above. In addition, as pH increases, weakly acidic SRNOM with carboxylic and phenolic moieties becomes more negatively charged (*28*). Thus, in higher pH, repulsion between SRNOM and MWNT surface coated with SRNOM would increase, hindering further adsorption of SRNOM. However, the strength of adsorption did not show appreciable change (i.e., $1/n = 0.39$ at pH 5.0, 0.40 at pH 7.0 and 0.47 at pH 9.0).

Stability of MWNT in the Aqueous Phase. As a result of NOM adsorption to MWNT, a fraction of MWNT forms a stable suspension. TEM images of MWNT in SRNOM solutions (representative images shown in Figure 5) indicate that most of the MWNT were individually suspended. The amount of stable MWNT suspension in aqueous phase (C_{MWNT}) generally increased as the more SRNOM was adsorbed per MWNT (q_e) (Figure 6). Dispersion of MWNT is facilitated by the shielding of extremely hydrophobic MWNT surface with NOM which provides thermodynamically more favorable surface. Adsorbed NOM is also expected to contribute to steric and electrostatic stabilization. Therefore, for the same type of NOM, the amount of NOM adsorbed onto MWNT would determine the extent of MWNT stability in water, i.e., C_{MWNT} increased as q_e increased. C_{MWNT} seemed to be also influenced by the type of NOM. For example, at the same q_e, C_{MWNT} with SRHA was higher than that with SRNOM, implying that SRHA might have greater MWNT stabilization capacity than SRNOM (Figure 6). However, no obvious relationship was found between C_{MWNT} and NOM properties such as carbon functional groups, elemental composition, and distribution of acidic functional group. This is probably because other NOM properties such as electrostatic and configurational characteristics could collectively contribute to MWNT stability. For the same q_e, more MWNT were suspended when more MWNT were initially added to the solution (i.e., higher D).

The amount of MWNT suspended in water also strongly depended on solution ionic strength. The amount of MWNT suspended in water (C_{MWNT}) was plotted versus q_e at different ionic strengths in Figure S4. Experimental results scattered at lower C_{MWNT} due to analytical limitations. At higher ionic strength, much less MWNT was suspended despite the similar amount of SRNOM was adsorbed. For instance, even at high

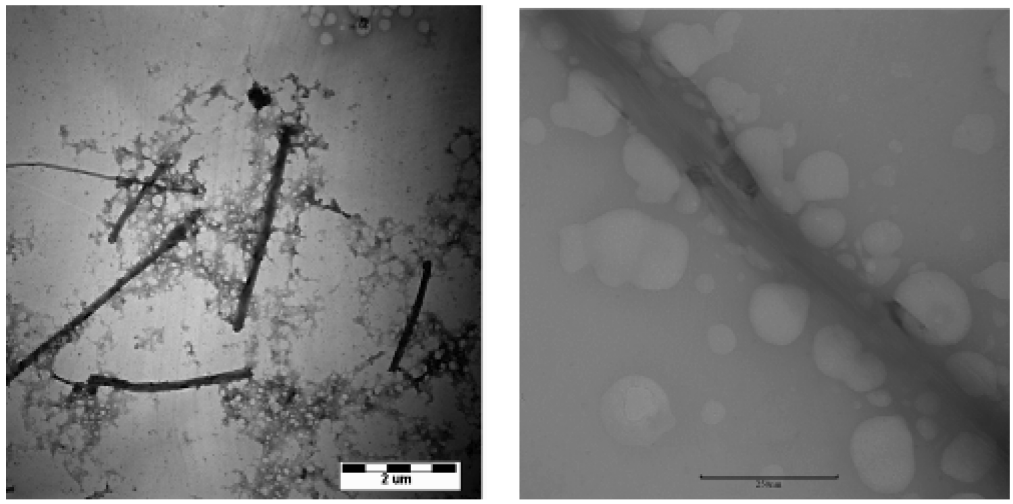

FIGURE 5. TEM images of MWNT stabilized in SR NOM shown at different magnifications. The bars represent 2 μm and 25 nm for (a) and (b), respectively. Evolution of bubble-like structures adjacent to MWNT surfaces, which formed as organic matter sublimed by high energy electron beam irradiation, was visible during the first a few seconds of TEM analysis (Figure 5b).

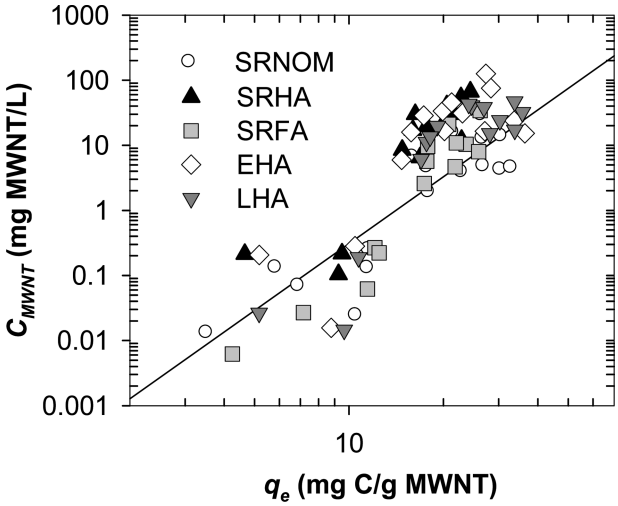

FIGURE 6. Dependency of the amount of MWNT suspended in water (C_{MWNT}) on the amount of various NOMs adsorbed onto MWNT (q_e).

q_e (>10 mg C/g MWNT), MWNTs were only slightly suspended (i.e., less than 1 mg/L) in the SRNOM solution with 0.1 M NaCl. This might be due to greater double layer compression in the high ionic strength solution. However, as MWNT used in this study has a very high aspect ratio (diameter ranges from ca. 10 to 20 nm and length ranges from ca. 10 to 30 μm) it is difficult to quantitatively analyze the zeta potential of MWNT. The effect of pH was less obvious than that of ionic strength, although electrostatic stabilization of NOM-MWNT agglomerates would be more efficient due to the deprotonation of NOM at higher pH and experimental data showed slight increase in C_{MWNT} at higher pH for the same q_e.

Environmental Significance. The results of this study suggested that the environmental fate of MWNT would be largely influenced by the amount and the type of NOM as well as solution chemistry such as ionic strength and pH. Other water quality parameters such as divalent ion contents and inorganic composition, which were not examined in this study, might play a critical role in determining the degree of NOM-MWNT interaction. For natural waters from different sources with different characteristics, the aromatic content and molecular weight distribution of NOM might be useful parameters to predict the extent of NOM adsorption and level of MWNT dispersion. Even though a wide range of NOM concentrations (2.5−50 mg C/L) was investigated, it is noted that NOM concentrations in some natural surface and ground waters are lower than concentration levels used in this study. Therefore, further study with actual surface and ground waters with relatively low NOM contents might be necessary for comprehensive understanding of interaction between NOM and MWNT.

In some aspects, NOM adsorption to MWNT was similar to that to activated carbon, i.e., occurrence of preferential adsorption and fitting to the Freundlich adsorption isotherm model. However, difference in physical structure of MWNT and activated carbon led to a few key differences in adsorption behavior such as preferential adsorption of higher molecular weight NOM onto MWNT. Understanding both similarities and differences between well-characterized activated carbon adsorption and MWNT adsorption should be helpful to understand not only the fate of MWNT in natural waters but also that of other carbon based nanomaterials such as single-walled carbon nanotubes and C_{60}.

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Supporting Information Available

Additional four figures and two tables are available. This material is available free of charge via the Internet at http://pubs.acs.org.

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