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Influence of Surface Oxygen on the Interactions of Carbon Nanotubes with Natural Organic Matter

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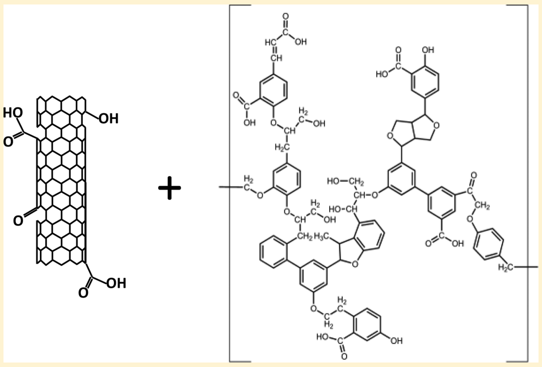
Supporting Information



ABSTRACT: The sorption properties of natural organic matter (NOM) with oxidized multiwalled carbon nanotubes (O-MWCNTs) in simple electrolytes has been studied, as well as the effect that NOM concentration, pH, and O-MWCNT surface chemistry have on CNT stability under environmentally relevant conditions. As O-MWCNT oxygen content increased, NOM sorption decreased in simple electrolytes for a common set of solution conditions. For each O-MWCNT, NOM sorption increased with increasing ionic strength and decreasing pH, although the sensitivity of NOM sorption to these water quality parameters increased as the O-MWCNT oxygen content increased. Collectively, these observations indicate that NOM sorption by O-MWCNTs is determined by favorable hydrophobic $\pi-\pi$ interactions that are moderated by repulsive electrostatic forces between negatively charged carboxylic acid functional groups on the O-MWCNTs and NOM. Stability studies conducted in artificial groundwater revealed that CNT stability is influenced by both the NOM concentration and pH, but stability was largely independent of the O-MWCNT oxygen concentration. These findings contrast with the marked effect that surface oxygen has on CNT stability in simple electrolytes. Electrophoretic mobility measurements revealed that the stabilizing effects of adsorbed NOM are due to the introduction of steric repulsion between NOM-coated CNTs, rather than from changes to surface charge.

INTRODUCTION

Natural organic matter (NOM) consists of negatively charged macromolecules and is a ubiquitous component of all natural aquatic environments.[1,2] NOM molecules contain hydrophobic segments in addition to hydrophilic carboxylic acid and phenolic functionalities and readily adsorb onto most particles and surfaces encountered in natural waters.[3] Consequently, NOM plays an important role in determining the colloidal stability of suspended particles. In part, this is a consequence of the fact that adsorbed NOM alters a particle's surface charge[4,5] and thereby influences electrostatic repulsive forces. The presence of adsorbed NOM also generates a macromolecular coating on the particle's surface. This introduces repulsive steric particle–particle interactions that pose significant barriers to aggregation and deposition.[6−8] Indeed, numerous studies on different inorganic and organic particles have confirmed that adsorbed NOM strongly influences, and in many cases, controls particle stability in water.[4,5,9−12]

Motivated by the need to understand the fate and transport of engineered nanomaterials in natural waters, several studies have examined the interactions of NOM with carbon nanotubes (CNTs). For example, Kim et al. have shown that pristine multiwalled carbon nanotubes (MWCNTs), which are extremely hydrophobic and do not form stable suspensions in polar solvents, are stabilized in water after NOM adsorption.[13] It has also been shown that NOM adsorption increases the colloidal stability of oxidized single-walled CNTs.[14] Other studies have focused on measuring the extent of NOM sorption onto CNTs, motivated by the possibility that CNTs could be used as fixed bed sorbents or active components in new membrane technologies designed to remove NOM from drinking water.[15,16] Indeed, comparative adsorption studies using different carbonaceous sorbents suggest that CNTs may be more efficient NOM sorbents than granular activated carbon.[15] CNT–NOM adsorption studies have also found that NOM adsorption is influenced by CNT properties (e.g., diameter) and water quality parameters (e.g., pH and ionic strength).[13] In other related studies designed to investigate how NOM composition influences the sorption properties of NOM with pristine CNTs, the extent of NOM adsorption and the mass of CNTs that could be stabilized in solution at a given concentration of NOM were both found to be proportional to the NOM's aromatic content.[13] These results were taken to suggest a sorption mechanism that is regulated by the strength of $\pi-\pi$ interactions.[13] In support of this basic sorption

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mechanism, studies conducted with CNTs and different aromatic hydrophobic organic chemicals (HOCs) such as phenanthrene and tetracene, have shown that the larger aromatic molecules with the more extensive π-systems adsorb more strongly to CNT surfaces.[17,18]

Understanding CNT behavior in natural conditions is imperative given the likelihood of future CNT contamination in the environment. For example, CNT particles could be released unintentionally when products that contain CNTs, such as polymer nanocomposites, are discarded and degrade in the environment.[19] Alternatively, CNTs could enter the environment from accidents or poor practice during production, transport, or use. Another related issue is that for an increasing number of technological and commercial applications, the size, shape, chemical composition, and interfacial properties of engineered nanomaterials (ENMs) are being tailored.[20,21] Consequently, it is important to determine the range of environmentally relevant aquatic conditions over which the surface chemistry of the "as-released" nanoparticles influences the particle's behavior; and conversely, the conditions under which adsorbed NOM may dominate particle behavior and suppress the role of the particle's nascent surface chemistry. Studies to address this question are starting to emerge. For example, Nason et al. used a suite of 5−12 nm gold nanoparticles with different anionic, neutral, and cationic capping agents, and discovered that in the presence of 5 mg DOC/L (ppm) of Suwannee River Humic Acid, the role of the adsorbed NOM is more important than the underlying capping agent in determining particle stability.[22] In another related study, Gondikas et al. identified the relationship between the surface density of sorbed cysteine and the effect that this NOM surrogate has on the colloidal stability of ZnS nanoparticles.[5]

One of the most important variations in the nascent surface chemistry of CNTs is derived from the presence of dissociable, hydrophilic, oxygen-containing functional groups. These groups are either grafted deliberately into the CNT sidewalls during covalent functionalization strategies designed to improve particle dispersion properties, or grafted inadvertently as a result of incidental exposure to oxidizing conditions.[23−25] In prior studies, we have used both as-received pristine CNTs as well as a suite of oxidized CNTs (created using popular acid treatments) to probe the influence of such surface oxides on colloidal stability and sorption properties in simple solutions that do not contain NOM.[26−30] Results from these studies have shown that surface oxides exert a profound influence on environmentally relevant properties of CNTs in well-defined, simple solutions containing monovalent electrolytes.

The present investigation is focused on two topics related to NOM interactions with oxidized multiwalled carbon nanotubes (O-MWCNTs), specifically, the extent to which surface oxides influence (a) NOM sorption and (b) particle stability in the presence of NOM. To simplify interpretation of results, we controlled the chemical character of the NOM by using a single source of NOM throughout. The emphasis in the first part of the study was to use our ability to vary the CNT surface chemistry to probe the fundamental nature of the CNT−NOM sorption interaction. In the second part of the study, the focus was placed on evaluating the relative importance that NOM concentration, pH, and CNT surface chemistry play in determining particle stability under environmentally relevant conditions. In addition to the fundamental scientific value, the more detailed understanding of NOM−CNT interactions provided by this work also has relevance to the environmental health and safety (EHS) effects of CNTs, including toxicity,[31] and the development of membranes that incorporate CNTs for use in water treatment strategies.[32]

■ EXPERIMENTAL SECTION

Details of the starting materials (MWCNTs and NOM, the latter obtained from the Dismal Swamp), the oxidation of MWCNTs, and surface characterization of O-MWCNTs have been published elsewhere[28,29,33−37] and are summarized in the Supporting Information (SI, including Figure S1). Key aspects of prior work as it relates to the present study are that (i) different oxidative treatments can be used to create a suite of O-MWCNTs which exhibit similar physicochemical properties, except for the changes in surface chemistry,[28,29] and (ii) in simple electrolytes the extent of oxidation has a marked effect on the stability and sorption properties of CNTs.[27−30,38]

Sorption Experiments. NOM concentrations were determined by measuring the UV−vis absorbance at 300 nm (Varian Cary 50; 1 cm path length quartz cell). Calibration experiments showed that the UV−vis absorbance at 300 nm was directly proportional to the NOM concentration (R^2 = 0.9999). UV_{300} was used instead of the more commonly used UV_{210} or UV_{254} values, because analyzing at 300 nm minimized spectral interferences originating from trace organics that leached from the experimental setup. In preparing the O-MWCNTs for sorption experiments it was found that a rinse with 4 M NaOH was an important step because it removed loosely bound amorphous carbon, which could otherwise pass through the filter and increase the apparent NOM concentration.

In all sorption experiments, polypropylene screw-cap vials (5 mL nominal volume, Spectrum Chemical) were filled with MWCNTs (0.5−1.0 mg dry mass of pristine or oxidized MWCNT) and a 3 mL solution containing NOM (0−84.2 mg DOC/L). This solid−liquid ratio was chosen to give an NOM uptake of between 20 and 80%. Background ionic strengths (1−1000 mM) were set using NaCl; pH was set at 4.7 or 6.0 using an acetate buffer; pH 9.0 was attained using a carbonate buffer. In all cases, the concentration of the buffer in solution was ≈0.5 mM. After each vial had been prepared, it was briefly shaken and placed in a horizontal, temperature-controlled (25 °C) water-bath shaker (GCA Corp. Chicago, IL) operating at 100 strokes per minute, where it was allowed to equilibrate in the dark. Kinetic sorption experiments (Figure S2) revealed that 96 h was sufficient for NOM uptake to reach equilibrium. Each sorption experiment was performed in triplicate.

After NOM−MWCNT equilibration had been attained, solid−liquid separation was achieved by filtering the contents of each vial through a single use (0.2-μm PES) syringe filter. The NOM remaining in the filtrate ($C_{e,\mathrm{Measured}}$) was determined by measuring the absorbance at 300 nm. All sorption data were analyzed by fitting to the Freundlich isotherm:

$$q_e = K_f C_e^{\,n}$$

Here, K_f and n are empirical fitting parameters that provide a measure of sorption capacity and sorption site heterogeneity, respectively;[39,40] C_e (mg DOC/L) is the equilibrium concentration of NOM remaining in solution, and q_e is the mass of NOM adsorbed per gram of MWCNT at equilibrium. Best-fit isotherms were determined by linear regression of the log-transformed data using a least mean weighted squared error method, appropriate for constant relative error among data.[41]

To convert $C_{e,\mathrm{Measured}}$ to C_e, two control experiments were conducted in parallel with each sorption experiment. One control was designed to quantify NOM losses due to sorption by the experimental apparatus ($\mathrm{NOM_{LOSS}}$), and another to determine the extent to which MWCNTs passed through the filter and thereby contributed to $\mathrm{UV_{300}}$ and thus $C_{e,\mathrm{Measured}}$; this value was referred to as $\mathrm{UV_{300\text{-}CNT}}$. With respect to $\mathrm{NOM_{LOSS}}$, no NOM was lost to the poly propylene vials, but some NOM was retained by the PES filter. To quantify these losses, control studies were performed (in triplicate) in the absence of MWCNTs to measure the amount of NOM retained by the filter for each NOM concentration and solution condition (pH, ionic strength). Results from these studies showed that although NOM sorption by the filter varied with the solution conditions, for each solution condition examined $\mathrm{NOM_{LOSS}}$ was reproducible (±0.19 mg DOC/L) among the replicates. To determine $\mathrm{UV_{300\text{-}CNT}}$, controls (performed in triplicate) composed of only CNTs and water were passed through the filter under the same conditions (including CNT type and loading, solution pH, and ionic strength) used to measure NOM sorption. By measuring $\mathrm{UV_{300}}$ values obtained in these control studies, the amount of MWCNTs that passed through the PES filter and thereby contributed to $C_{e,\mathrm{Measured}}$ was determined ($\mathrm{UV_{300\text{-}CNT}}$). For each solution condition examined $\mathrm{UV_{300\text{-}CNT}}$ values were reproducible to ±0.009 mg DOC/L for pristine MWCNTs and ±0.03 mg DOC/L for the most highly oxidized MWCNTs. For $C_{e,\mathrm{Measured}}$ values greater than ≈4 mg DOC/L, the $\mathrm{UV_{300\text{-}CNT}}$ values corresponded to between 1 and 7% of $C_{e,\mathrm{Measured}}$ values. However, for comparatively low $C_{e,\mathrm{Measured}}$ values (<2 mg DOC/L), where the absolute magnitude of NOM sorption was relatively low, $\mathrm{UV_{300\text{-}CNT}}$ values could correspond to as much as 35% of $C_{e,\mathrm{Measured}}$. Since the MWCNT mass that passed through the PES filters (<0.03 mg) was always much smaller than the MWCNT mass initially added (>0.5 mg) the MWCNT mass and NOM trapped within the PES filters can also be reasonably assumed to be negligible.

Once $\mathrm{UV_{300\text{-}CNT}}$ and $\mathrm{NOM_{LOSS}}$ values had been determined for each sorption experiment, C_e was determined using the following expression:

$$C_e = C_{e,\mathrm{Measured}} - \mathrm{UV_{300-CNT}} + \mathrm{NOM_{LOSS}}$$

Particle Stability Measurements. The stability of O-MWCNTs in the presence of NOM was measured in both simple electrolytes (NaCl) and artificial groundwater (AGW;[42] composition given in Table S1). Primary stock dispersions of O-MWCNTs were prepared by sonicating 2 mg of O-MWCNT powder in 100 mL of DI water for 20 h using a low-power (70 W) bath sonicator (Branson), followed by 5 min of centrifugation at 1000 rpm. Centrifugation was used to eliminate any MWCNT bundles that had not suspended, as well as any glass etched from the flask by the sonication. A secondary stock was prepared by first diluting the NOM with DI water and then adding O-MWCNTs from the primary stock. The O-MWCNT concentration in these secondary O-MWCNT/NOM stock solutions was kept constant at 2.9 mg DOC/L, while the NOM concentration ranged from 0 to 10 mg DOC/L. Primary stock solutions of AGW or NaCl were also prepared at a concentration twice that of the value desired in the experiment. To obtain a pH of 6.0 or lower, solutions containing MWCNT/NOM, AGW, or NaCl were buffered using 1.0 mM sodium acetate, while for pH values greater than 7.0 at least 1.0 mM sodium bicarbonate was added to the solution.

To initiate aggregation, the MWCNT/NOM and AGW (or NaCl) stock solutions were mixed in a 1:1 volume ratio followed by 1 min of vigorous shaking. (Thus, NOM concentrations in aggregation experiments ranged from 0 to 5 mg DOC/L.) Solutions were then allowed to sit for a prescribed time period during which particle aggregation and settling was allowed to occur under perikinetic flocculation conditions. At the end of this settling time, the pH was measured to ensure that it had remained stable (±0.3) before the solution was centrifuged at 4000 rpm for 1 h to remove aggregated MWCNTs from the supernatant. After centrifugation, the average absorbance of the solution between 800 and 900 nm was measured by UV−vis and used to determine the concentration of MWCNTs that remained suspended (N). This wavelength range was chosen because NOM does not absorb significantly above 800 nm (see Figure S3). In these experiments we used a 5-cm path length UV−vis cell which allowed us to determine O-MWCNT concentrations in the "mg/L" concentration range even at wavelengths 800−900 nm, where the detection sensitivity of MWCNTs is lower than at shorter wavelengths.

In each particle stability study, separate control experiments were performed where each MWCNT/NOM stock solution was mixed in a 1:1 volume ratio with pH-buffered DI water rather than AGW/NaCl stock solutions. By measuring any change in the concentration of O-MWCNTs, these experiments controlled for any particle losses due to centrifugation or particle aggregation during the settling time that occurred in the absence of added electrolytes. After centrifugation, the concentration of O-MWCNTs in the supernatant (N_0) was determined by measuring the UV−vis as described in the previous paragraph. Compared to absorbance values before centrifugation, the O-MWCNT concentrations in these control studies after centrifugation decreased consistently by ≈5%. Since these decreases were constant for different samples and significantly less than the decrease in O-MWCNT concentration typically observed as a result of aggregation and settling, they did not affect the validity of the particle stability measurements. Consequently, the concentration ratio N/N_0 was used to measure the extent of MWCNT aggregation during each experiment.

Electrophoretic Mobility (EM) Measurements. EM data for two O-MWCNTs with different levels of surface oxygen were acquired as a function of added NOM concentration at pH 6 and 0.010 M NaCl using a capillary cell method (Zetasizer-3000HSa, Malvern Instruments). To verify instrument accuracy, reference experiments were conducted on polystyrene latex standard particles (part DTS1050) provided by Malvern Instruments Ltd.

■ RESULTS AND DISCUSSION

NOM Sorption onto MWCNTs Powders in the Presence of Simple Electrolytes. *A. Effect of MWCNT Surface Oxides on NOM Adsorption.* Isotherms for NOM adsorption onto various MWCNTs exhibiting five different surface oxygen concentrations are shown in Figure 1. Each experiment was conducted in triplicate under the same solution conditions (pH 6 and 0.001 NaCl ionic strength). Results show that in simple electrolytes, MWCNT surface chemistry influences NOM sorption affinity, and that sorption closely follows the Freunclich model (R^2 values >0.93; regression data are presented in Table 1). Analysis of Figure 1 also reveals that for any equilibrium NOM concentration (C_e), NOM sorption

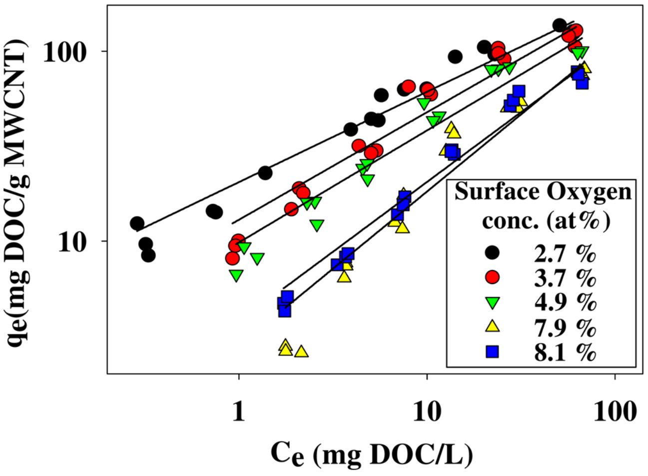

Figure 1. Sorption isotherms for NOM adsorption onto MWCNTs of varying surface oxygen concentrations measured at pH 6 and 0.001 ionic strength (NaCl electrolyte). Solid lines represent best fits to the Freundlich isotherm.

decreases as the MWCNT surface oxygen concentration increases. However, the degree of separation between the isotherms is sensitive to C_e, with the largest relative separation at the lowest C_e values. Additional insights into the effect that MWCNT surface chemistry exerts on NOM sorption can be obtained by examining the variation in the Freundlich K_f parameters, which provide a measure of sorption capacity.[29,39,40] As a function of surface oxygen concentration, K_f decreased from 20 for pristine MWCNTs to <4 for the most heavily oxidized MWCNTs (see Table 1 and Figure S4).

Some of the reasons surface oxygen impacts the sorption of NOM onto CNTs can be understood and rationalized by comparing the results in the present study with those of a previous study where the effects of surface oxides on the sorption of naphthalene, a prototypical HOC, were investigated.[29] In both studies, the CNT sorption capacity, as measured by the K_f values decreased systematically as the MWCNT surface oxygen concentration increased. This suggests that NOM sorption onto CNTs follows a similar mechanism to that of naphthalene, where sorption is determined by $\pi-\pi$ interactions between the aromatic portions of the sorbate and sorbent. In the present investigation, the decrease in NOM sorption as the MWCNT surface oxygen concentration increases can be rationalized by the fact that the aromatic content of the CNT surfaces will decrease as higher concentrations of hydrophilic oxygen-containing functional groups are incorporated into the graphenic sidewalls. In addition to the decrease in aromatic content, a second important factor that must be considered is the effect of electrostatic interactions on NOM sorption onto oxidized MWCNTs. At pH 6 both NOM and the oxidized MWCNTs will be negatively charged, principally as a result of deprotonated carboxylic acid groups. Since the negative surface charge on MWCNTs increases systematically with surface oxygen content,[28] greater electrostatic repulsions will exist between sorbate (NOM) and sorbent (MWCNT) as the nascent MWCNT surface oxygen concentration increases, further reducing the ability of NOM to adsorb onto the more oxidized MWCNTs. In contrast, there are no dissociable functional groups on HOCs (e.g., naphthalene) and so repulsive electrostatic forces will not influence the strength of sorption interactions between HOCs and CNTs. We believe that these differences are responsible for the more pronounced influence that CNT surface oxygen content has on the K_f values for NOM compared to naphthalene.[29] Analysis of Table 1 also reveals that the Fruendlich *n* parameter increases as the degree of surface oxidation increases. This observation can be rationalized by the effect that surface oxidation will have in creating lower energy NOM adsorption sites.

Results from the present study can also be compared and contrasted with those of Hyung et al., who studied the sorption of different sources of NOM with a common CNT; in some sense the inverse of the present investigation.[13] The present study maintains the aromatic content of the NOM (aromatic character of ~34%; see SI Table 1), but varies the hydrophilic/hydrophobic content of the CNT by controlling the degree of surface oxidation. A key finding of the Hyung et al. study was that K_f values increased in an approximately linear fashion with the sorbate's (NOM) aromatic content,[13] indicative of a sorption mechanism dominated by $\pi-\pi$ interactions. This is consistent with our finding that for a common source of NOM the K_f values decrease linearly with increasing levels of MWCNT surface oxidation (R^2 = 0.95; Figure S4) as the aromatic content of the CNT sidewalls decreases.

B. Influence of Solution Chemistry (pH and Ionic Strength) on NOM Sorption. Using a pristine (2.2 atomic % oxygen) and a highly oxidized (8.1 atomic % oxygen) MWCNT sample, we also examined the role that pH (4.7, 6.0, and 9.0) and ionic strength (0.001−1.000 M NaCl) played in regulating NOM sorption for MWCNTs with different surface chemistries. Results of these experiments, shown in Figure 2, indicate that, except for a slight decrease in NOM sorption at pH 9, NOM adsorption onto pristine MWCNTs is largely unaffected by changes in ionic strength or pH. This can be rationalized by recognizing that the pristine MWCNT surfaces are dominated by extended graphene sheets with very few surface oxides and exhibit almost no surface charge over a wide range of pH values.[28] Consequently, the sorption of NOM onto this type of unfunctionalized MWCNT is regulated exclusively by $\pi-\pi$ interactions, in the absence of any electrostatic repulsion, analogous to the sorption of HOCs onto CNTs and other carbonaceous materials. Consistent with this type of exclusively hydrophobic sorption mechanism, the sorbate−sorbent inter-

Table 1. Parameters for Freundlich Isotherms Based on Fitting the NOM Sorption Data Shown in Figure 1[a]

sorbent	surface oxides (at. %)	N^b	K_f (mg/g)/(mg/L)^n	n	R^2
pristine MWCNT	2.7	18	20 ± 1	0.48 ± 0.11	0.96
O-MWCNT(HNO_3)	3.7	18	13 ± 1	0.57 ± 0.12	0.93
	4.9	17	13 ± 1	0.59 ± 0.11	0.93
	7.9	18	2.8 ± 0.5	0.81 ± 0.08	0.94
O-MWCNT($KMnO_4$)	8.1	18	3.7 ± 0.6	0.74 ± 0.06	0.95

[a] Uncertainties in the K_f and n values represent the standard deviations about the mean for each value. [b] N = the number of observations.

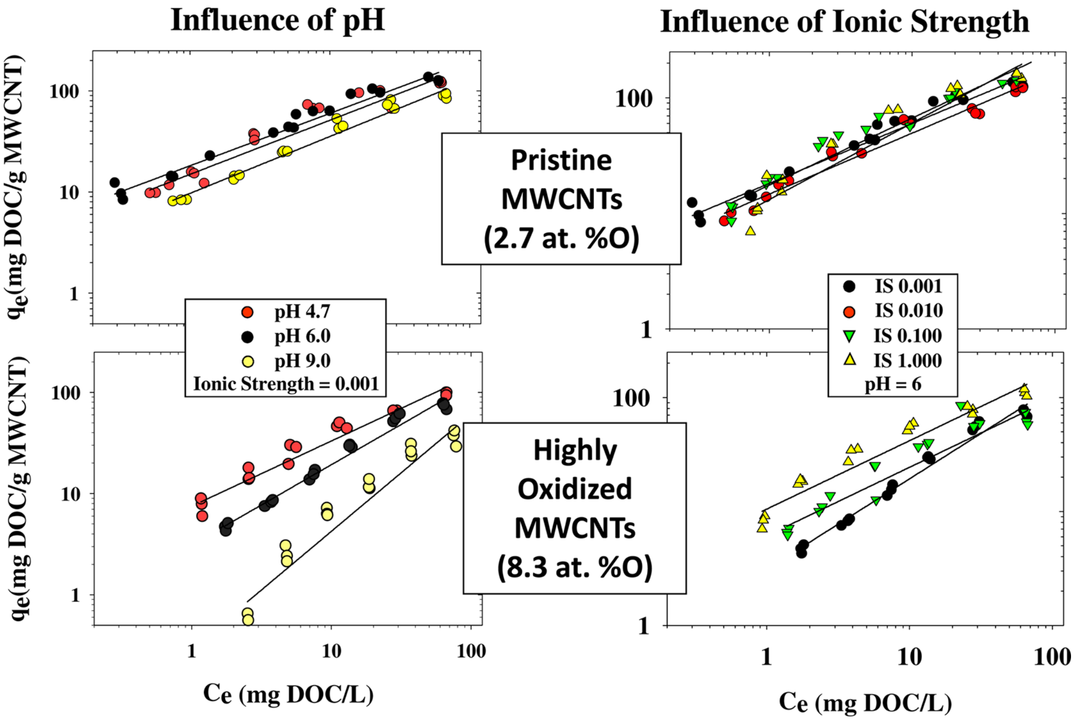

Figure 2. Influence of water quality parameters (pH, ionic strength) on NOM sorption onto pristine (upper two spectra) and highly oxidized (8.3% atomic oxygen) MWCNTs (lower two spectra). Solid lines represent best fits to the Freundlich isotherms.

action is essentially independent of changes to the charge of the sorbate (pH) or the characteristics of the double layer (ionic strength).

In contrast, Figure 2c and d reveal that oxidized MWCNTs exhibit enhanced NOM sorption as the pH decreases and the NaCl concentration increases. This difference in behavior of the O-MWCNTs compared to the pristine MWCNTs is the result of introducing electrostatic repulsive forces between the negatively charged carboxylic acid groups present on both the NOM and the oxidized CNTs. The addition of these repulsive forces causes a reduction in NOM sorption, as was shown in Figure 1. However, the magnitude of these repulsive electrostatic forces will decrease when either (i) the negative charges on the NOM polyelectrolyte and the oxidized MWCNTs decrease at lower pH due to carboxylic acid group protonation, or (ii) the charges are more effectively screened from each other in solutions with higher concentrations of electrolytes. In summary, our experimental data illustrate that, although the extent of NOM adsorption onto pristine CNTs will always be greater than on oxidized CNTs in simple electrolytes, the sorption of NOM onto CNTs will be more sensitive to the water quality parameters when CNTs become oxidized.

Effect of NOM on the Stability of O-MWCNT Particles. Preliminary studies (for example, Figure S5) revealed that even in the presence of reasonably high NaCl concentrations (60 mM), measurable CNT aggregation in the presence of NOM only occurred sufficiently quickly (i.e., on a time scale compatible with time-resolved dynamic light scattering (TR-DLS)[43−46] or centrifugation[47−51]) over a relatively small range of NOM concentrations (<0.5 mg DOC/L). Efforts to conduct TR-DLS experiments at higher salt concentrations (>100 mM NaCl) were often hampered by a significant increase in particle size right after salt had been added to initiate aggregation (see Figure S6 for an example). We interpreted this effect as being due to an increase in NOM sorption prompted by the significant increase in ionic strength upon NaCl addition (see Figure 2). For these reasons, we decided to focus on evaluating the relative importance that NOM concentration, pH, and nascent MWCNT surface chemistry play in determining the nanoparticle's stability in a synthetic water that contains a more complex mixture of electrolytes, including multivalent cations. For these studies, we used centrifugation to remove particles that had grown above a certain size after a prescribed period of aggregation to measure particle stabilities, as described in the Experimental section. To verify the appropriateness of this technique, control studies were performed using three O-MWCNTs with different levels of surface oxygen in a simple electrolyte solution (30 mM NaCl). Results from these control studies, conducted after 12 h of aggregation time, are shown in Figure S7. These data reveal that for O-MWCNTs with 5.1, 7.1, and 9.0% oxygen, the fractions of O-MWCNTs remaining in solution (N/N_0) were 0.02, 0.34, and 0.71, respectively. This systematic linear increase in their stability toward aggregation by NaCl agrees with previous results we have obtained with this system, as measured by TR-DLS.[28] These control studies therefore validate the use of aggregation followed by centrifugation as a means to compare relative particle stabilities.

Figure 3a shows the results of particle stability studies conducted in the presence of artificial groundwater for O-MWCNTs with 5.1%, 7.1%, and 9.0% surface oxygen, plotted as a function of the added NOM concentration (0−5 mg DOC/L). This range of NOM concentrations was selected because it spans typical values encountered in natural waters.[52] A settling time of 30 min was sufficient to discriminate between the stability of O-MWCNT particles in different aqueous conditions. To explicitly probe the effect of aggregation time, however, an additional experiment was conducted in which the mixture was allowed to settle for 6 h instead of 30 min (Figure S8). As expected, the N/N_0 values decreased after a longer settling time, although the qualitative (linear) dependence of

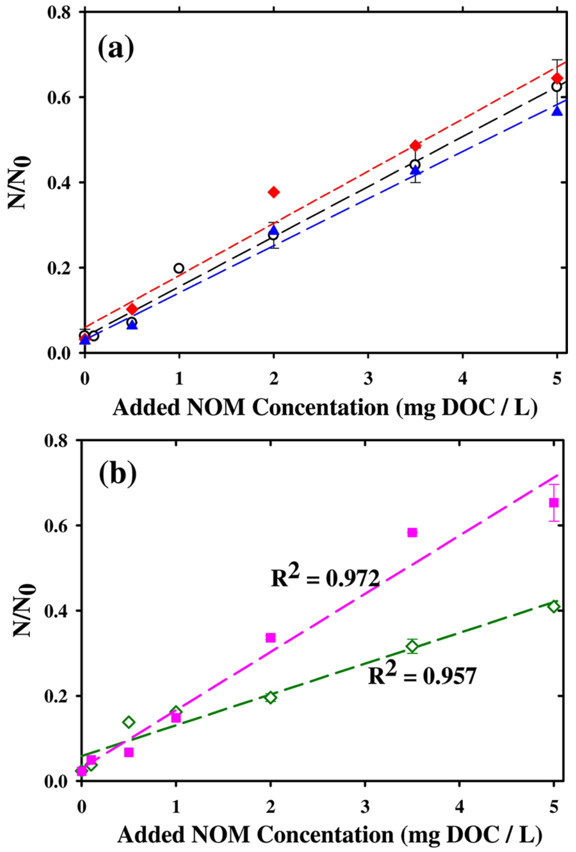

Figure 3. Fraction of O-MWCNTs remaining in suspension (N/N_0) after centrifugation following 0.5 h in artificial groundwater, plotted as a function of the added NOM concentration. In (a) N/N_0 values are shown for three O-MWCNTs with surface oxygen concentrations of 5.1% (diamonds), 7.1% (open circles), and 9.0% (triangles) studied at pH 6; (b) N/N_0 values are shown for an O-MWCNT with 7.1% oxygen measured at pH 5.0 ± 0.2 (open diamonds) and 8.0 ± 0.2 (squares). For each data set in (a) and (b) a best fit linear regression through the data points is shown as a dashed line. In (a) R^2 values for the three O-MWCNTs are 0.973 (5.1% oxygen), 0.991 (7.1% oxygen), and 0.990 (9.0% oxygen). In both (a) and (b) error bars show the standard deviation of replicates.

N/N_0 on NOM concentration observed in Figure 3 remained unchanged.

Figure 3 reveals that irrespective of the O-MWCNTs surface chemistry or pH, particle stabilities increased in direct proportion to the NOM concentration. This linear increase in N/N_0 as a function of NOM concentration indicates that the stability of O-MWCNTs under environmentally relevant conditions (i.e., solutions containing Na^+, Ca^{2+}, and Mg^{2+}) depends on the extent of NOM sorption. Based on an analysis of any of the sorption isotherms shown in Figure 1 or 2, the extent of NOM sorption should increase approximately linearly over an aqueous NOM concentration range of 0−5 mg DOC/L. This suggests that CNT stability itself also scales in direct proportion to the amount of NOM sorbed. We anticipate that the same qualitative relationship (i.e., linear) will exist for other types of NOM, although the quantitative nature (i.e., gradient) is likely to depend on the NOM's characteristics (e.g., hydrophobic, hydrophilic, aromatic content).[4,13,53] In the context of previous studies, the increased CNT stability toward aggregation in the presence of multivalent cations and NOM is consistent with the results of Saleh et al.[54] and Li et al.[14] (also obtained on CNTs), but in contrast to data obtained by Nason et al. who studied capped Au NPs and observed mostly a decrease in particle stability in the presence of NOM.[22]

Analysis of Figure 3a also reveals that for any NOM concentration particle stability is largely independent of the O-MWCNTs oxygen concentration, with each one of the O-MWCNTs exhibiting a similar linear dependence on NOM concentration. For example, at an added NOM concentration of 3.5 mg DOC/L the N/N_0 values for the O-MWCNTs with 7.1% and 9.0% oxygen are 0.44 and 0.43, respectively. Similarly, at an added NOM concentration of 5.0 mg DOC/L the N/N_0 values for the O-MWCNTs with 5.1% and 7.1% oxygen are 0.65 and 0.62, respectively. This relative insensitivity to the particle's nascent surface chemistry is in sharp contrast to the determinant role that oxygen concentration plays in regulating CNT stability in the presence of simple electrolytes and absence of NOM (e.g., Figure S7).[28]

The observation that the stability of each O-MWCNT is similar over a range of NOM concentrations under environmentally relevant conditions (artificial groundwater) suggests that the extent of NOM sorption is comparable on each of the three O-MWCNTs at the same NOM concentration and pH. This effect can be rationalized, at least in part, by the sorption results presented in the previous section (Figure 2) which reveal that differences in the amount of NOM sorbed on the two different MWCNTs diminishes as the ionic strength increases, due to more effective charge screening between the negatively charged O-MWCNTs and NOM. This is shown more explicitly in Figure S9, where the sorption of NOM onto pristine and highly oxidized MWCNTs are compared for ionic strengths ranging from 1 mM to 1 M NaCl. However, since the ionic strength of the artificial groundwater is ≈10 mM, analysis of Figure S9 indicates that ionic strength effects alone cannot rationalize the similar sorption behavior. One very likely reason for the similar sorption properties is the presence of multivalent cations (e.g., Ca^{2+}) in artificial groundwater which could act as bridges between the negatively charged carboxylate groups on the O-MWCNTs and the NOM, thus facilitating sorption. Specific ion effects involving Ca^{2+} ions have been reported to diminish the importance of the carboxylic acid group concentration in determining the stability of O-MWCNTs in the absence of NOM.[55] Thus, although the multivalent Ca^{2+} ion concentration will certainly influence the absolute stability of O-MWCNTs in the presence of NOM, experimental evidence from this and previous studies[55] suggests that the relative stability of O-MWCNTs with different levels of nascent surface oxygen concentration will be similar. This general lack of sensitivity to nascent surface chemistry would also seem likely to extend to other studies that have shown evidence of "enhanced NP aggregation" in the presence of NOM isolates at higher Ca^{2+} concentrations than the ones used in the present study.[12,22] Despite the overall insensitivity to O-MWCNT surface chemistry, however, it is noteworthy that there is a slight trend for particle stability to increase with decreasing MWCNT surface oxygen concentration, reflected in the different regression lines shown in Figure 3a. This suggests that the nascent surface chemistry may still be exerting a small influence on NOM sorption in synthetic water, although any such effect is significantly less important than the role of NOM concentration.

Figure 3b demonstrates that particle stabilities increase as the pH increases. For clarity, data are only shown for pH 5 and 8; data for all four of the pH values studied (5, 6, 7.3, and 8) are presented in Figure S10. The increase in O-MWCNT stability as a function of increasing pH is most likely a result of the increase in charge of the adsorbed NOM and the effect that these changes have on the conformation and effective thickness of the adsorbed layer. Thus, if the results on the effects of NOM concentration and O-MWCNT surface chemistry are considered collectively, it appears that under environmentally relevant conditions particle stability will be governed by sorbate (i.e., NOM) rather than sorbent (i.e., CNT) characteristics, specifically the amount and most likely the physicochemical characteristics of the adsorbed NOM. In a broader sense, these results highlight the differences between simple electrolytes, where CNT surface chemistry plays a determinant role in regulating particle stability and sorption properties,[28−30] and more environmentally relevant conditions where multivalent cations are present and the role of CNT surface chemistry is greatly diminished.[55]

The relative insensitivity of CNT stability to the particle's native surface chemistry in the presence of NOM is a consistent finding with the observations of Nason et al.[22] These authors found that for gold nanoparticles in the presence of 5 mg DOC/L Suwannee River Humic Acid, the controlling factor was the adsorbed NOM, rather than the capping agent. Based on this common finding from these two studies, which were conducted on very different types of nanoparticles, one question that arises is the extent to which other intrinsic nanoparticle characteristics (e.g., size and shape) influence NP stabilities under environmentally relevant conditions (i.e., in the presence of NOM and Ca^{2+}). Given the diverse range of NPs (e.g., spheres and rods) that either already exist or are being developed, the extent to which the intrinsic physicochemical properties of NPs can be "ignored" in determining particle stabilities in aquatic environments has significant ramifications in terms of the ease with which accurate and reliable environmental models could be developed to predict NP fate and transport.

For O-MWCNTs, the underlying rationale for the stabilizing effects of adsorbed NOM is revealed by the electrophoretic mobility (EM) measurements shown in Figure 4, plotted as a function of added NOM concentration. In the absence of NOM, the EM values of O-MWCNTs with 3.7 and 7.9% oxygen were −2.69 ± 0.05 ($\times 10^{-8}$ $m^2 V^{-1} s^{-1}$) and −3.00 ± 0.15 ($\times 10^{-8}$ $m^2 V^{-1} s^{-1}$), respectively. These values are consistent with the idea that increasing the level of CNT oxidation increases the number of negatively charged surface functional groups. In the presence of NOM, however, it is apparent that the EM and thus the effective surface charge on both O-MWCNTs decrease as the NOM concentration increases. This is presumably a result of a lower density of negatively charged carboxylic acid groups on the NOM-coated O-MWCNTs as compared to the bare O-MWCNTs. On the other hand, the stability of the O-MWCNTs was found to increase significantly in NaCl (Figure S5) and Ca^{2+} (Figure 3) as the NOM concentration increases. Thus, it must be the introduction of a steric barrier caused by adsorbed NOM macromolecules, rather than any changes in surface charge, which is responsible for the stabilizing effects of adsorbed NOM. Furthermore, Figure 4 shows that in the presence of NOM the EM values of the two O-MWCNTs quickly become statistically equivalent, consistent with the idea that the nascent O-MWCNT surface chemistry has become largely irrelevant in determining particle stability. It should be noted, however, that the stabilizing mechanism of NOM will depend on the particle under investigation and the detailed nature of the NOM. For example, in previous studies on metal oxide nanoparticles[4,5,8,11] the adsorption of NOM does increase the magnitude of the (negative) surface charge. In these instances the stabilizing effects of NOM will be due to both increased electrostatic repulsion and the introduction of steric repulsion.

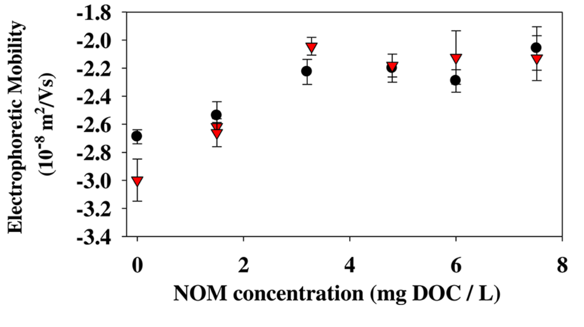

Figure 4. Effect of added NOM on the electrophoretic mobility of oxidized MWCNTs with 3.7% (solid circles) and 7.9% (inverted triangles) oxygen concentration, measured at pH 6 and 0.010 ionic strength (NaCl).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details describing the starting materials and the preparation and surface characterization of O-MWCNTs; chemical composition of the NOM (Table S1); Composition of the artificial groundwater used in particle stability experiments (Table S2); Size exclusion chromatography data for NOM (Figure S1); Kinetics of NOM uptake by MWCNTs (Figure S2); UV−vis spectra of NOM and O-MWCNTs (Figure S3); Variation in K_f as a function of O-MWCNT oxygen content (Figure S4); TR-DLS and aggregation/centrifugation studies showing the influence of NOM concentration on the stability of O-MWCNTs in the presence of NaCl (Figure S5); Aggregation profile of O-MWCNTs in the presence of NOM upon addition of relatively high concentrations (100 mM) NaCl (Figure S6); Influence of oxygen on the stability of O-MWCNTs in simple electrolytes as measured by aggregation/centrifugation studies (Figure S7); Effect of settling time on the fraction of O-MWCNTs remaining in suspension (Figure S8); Influence of NaCl concentration on the adsorption isotherms of NOM with O-MWCNTs (Figure S9); Influence of pH on the stability of O-MWCNTs in the presence of NOM as measured by aggregation/centrifugation (Figure S10). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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