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Elucidating Adsorptive Fractions of Natural Organic Matter on Carbon Nanotubes

Mohamed Ateia,*[,†] Onur G. Apul,[‡,§] Yuta Shimizu,[†] Astri Muflihah,[†] Chihiro Yoshimura,[†] and Tanju Karanfil[∥]

[†]Department of Civil and Environmental Engineering, Tokyo Institute of Technology, 2-12-1-M1-4 Ookayama, Tokyo 152-8552, Japan

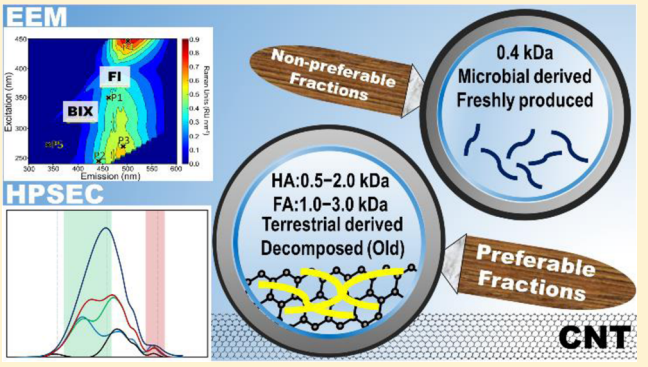
[‡]Department of Civil and Environmental Engineering, University of Massachusetts Lowell, Lowell, Massachusetts 01854, United States

[§]School of Sustainable Engineering and the Built Environment, Arizona State University, Tempe, Arizona 85259, United States

[∥]Department of Environmental Engineering and Earth Sciences, Clemson University, Anderson, South Carolina 29625, United States

Supporting Information

ABSTRACT: Natural organic matter (NOM) is a heterogeneous mixture of organic compounds that is omnipresent in natural waters. To date, the understanding of the adsorption of NOM components by carbon nanotubes (CNTs) is limited because of the limited number of comprehensive studies in the literature examining the adsorption of NOM by CNTs. In this study, 11 standard NOM samples from various sources were characterized, and their adsorption behaviors on four different CNTs were examined side-by-side using total organic carbon, fluorescence, UV−visible spectroscopy, and high-performance size-exclusion chromatography (HPSEC) analysis. Adsorption was influenced by the chemical properties of the NOM, including aromaticity, degree of oxidation, and carboxylic acidity. Fluorescence excitation−emission matrix (EEM) analysis showed preferential adsorption of decomposed and terrestrial-derived NOM compared to freshly produced and microbial-derived NOM. HPSEC analysis revealed preferential adsorption of fractions in the molecular weight range of 0.5−2 kDa for humic acids but in the molecular weight range of 1−3 kDa for all fulvic acids and reverse-osmosis isolates. However, the smallest characterized fraction (MW < 0.4 kDa) in all samples did not adsorb on the CNTs.



1. INTRODUCTION

Natural organic matter (NOM) is ubiquitous in fresh waters and is found in concentrations that range from 1−2 (mg of C)/L to 40 (mg of C)/L depending on the source and climate.[1,2] The presence of NOM, which is a mixture of complex polyelectrolytes, during water treatment processes presents a broad range of problems, such as an increase in chemical demands, the formation of disinfection byproducts, the occurrence of taste and odor problems, and the fouling of activated carbons and membranes.[3,4] Therefore, several processes have been employed to remove NOM from water, including coagulation, membrane filtration, ion exchange, advanced oxidation processes, and adsorption.[5]

Carbon nanotubes (CNTs), with their high surface areas, hydrophobicity, porosity, and rapid sorption kinetics, have been explored as one of the next-generation adsorbents.[6,7] Over the past decade, extensive studies have investigated applications of CNTs in the adsorption of several organic and inorganic water contaminants.[8,9] Furthermore, the interactions between CNTs and NOM have been examined in some studies.[1,10−17] Mechanisms for the adsorption of NOM components by CNTs include hydrophobic interactions, $\pi-\pi$ interactions, hydrogen-bonding interactions, and electrostatic interactions.[10,18] These interactions are influenced by (1) the characteristics of the CNTs (e.g., surface area, pore volume, and surface functionalities),[10,14,19] (2) the NOM molecular structure and composition (e.g., molecular weight and size),[13,19] and (3) the solution chemistry (e.g., pH, water temperature, and ionic strength).[1,10]

It was also reported that the conformation and composition of the NOM remaining in water will change as a result of adsorption processes due to NOM fractionation.[15,20] However, there are no comprehensive studies in the literature examining the adsorption of NOM by CNTs. The limited observations in previous studies are due to a number of factors: (1) different

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Table 1. Types, Codes, and Selected Physicochemical and Fluorescence Properties of Natural Organic Matter Samples Used in This Study

code	catalog no.	$SUVA_{254}$[b] [L/(mg m)]	M_w[c] (kDa)	M_n[c] (kDa)	ρ[d]	EEM[a] indexes	
						FI[e]	BIX[f]
			Humic Acids				
ESHA	4S102H	6.2	5.8	1.0	5.8	0.84	0.25
PPHA	1S103H	6.9	6.2	1.5	4.2	0.86	0.24
LHA	1S104H	7.0	4.8	1.0	4.8	0.94	0.28
SRHA	2S101H	4.9	3.9	1.4	2.7	1.00	0.25
			Fulvic Acids				
SRFA1	2S101F	3.5	1.8	1.0	1.8	1.19	0.27
SRFA2	1S101F	4.0	1.8	1.2	1.5	1.16	0.24
PPFA	2S103F	3.9	1.4	0.9	1.7	1.29	0.30
NLFA	1R105F	4.6	1.8	1.0	1.8	1.20	0.28
			RO Isolates				
NNOM	1R108N	3.6	1.3	0.6	1.9	1.33	0.31
MNOM	1S110N	2.6	1.3	0.7	1.7	1.49	0.39
SNOM	1R101N	3.3	1.5	0.8	1.8	1.34	0.30

[a]Excitation−emission matrix. [b]Specific UV absorption (SUVA) values were calculated by dividing the UV absorbance at 254 nm (m^{-1}) by the dissolved organic carbon (DOC) concentration (mg/L). [c]Weight-average molecular weight (M_w) and number-average molecular weight (M_n) measured using HPSEC. [d]Polydispersity (ρ) calculated as M_w/M_n. [e]Fluorescence index (FI) calculated as the ratio of the emission intensity at Em 450 nm relative to that at Em 500 nm at Ex 370 nm. [f]Freshness index (BIX) calculated by taking the intensity ratio of Em 380 nm relative to Em 430 nm at Ex 310 nm.

Table 2. Characteristics of All Carbon Nanotubes Used in This Study

code	type	SA[a] (m^2/g)	PV_{total}[a] (cm^3/g) [%]	PV_{micro}[a] (cm^3/g) [%]	PV_{meso} (cm^3/g) [%][a]	PV_{macro} (cm^3/g) [%][a]	OD[b] (nm)	oxygen content[c] (wt %)	purity[b] (%)	supplier
C1	MWCNTs	136	0.45 [100]	0.02 [4]	0.34 [68]	0.14 [28]	3−20	0.30	>95	Wako Chemicals, Japan
C2	SWCNTs	380	0.9 [100]	0.05 [5]	0.81 [91]	0.04 [4]	1−2	1.32	>90	Alpha Nano, Chinese Academy of Science, China
C3	MWCNTs	114	0.47 [100]	0.02 [3]	0.36 [65]	0.18 [32]	5−10	0.21	>98	Alpha Nano, Chinese Academy of Science, China
C4	MWCNTs	96	0.4 [100]	0.01 [2]	0.34 [76]	0.10 [22]	10−20	0.25	>98	Alpha Nano, Chinese Academy of Science, China

[a]BET surface areas, pore volumes and pore size distributions were measured from nitrogen physisorption data at 77 K obtained with ASAP 2020 analyzer (Micromeritics Instrument Corp., Norcross, GA). SA is surface area, PV_{total} is the total pore volume, PV_{micro} is the volume of micropores (i.e., PV < 2 nm), PV_{meso} is the volume of mesopores (i.e., 2 nm < PV < 50 nm), and PV_{macro} is the volume of macropores (i.e., PV > 50 nm). [b]Information provided by the suppliers. [c]Oxygen contents analyzed using a Flash Elemental Analyzer 1112 series (Thermo Electron Corporation).

types of NOM used in these studies (i.e., different chemical and physical characteristics), (2) limitations in the number of NOM samples tested under different experimental conditions, and (3) limited and different techniques employed in NOM characterization [e.g., high-performance size-exclusion chromatography analysis (HPSEC)[10,12] vs E2/E3 (UV absorbance at 250 nm/365 nm) and E4/E6 (UV absorbance at 465 nm/665 nm)].[11,15]

In this study, our objective was to systematically investigate the adsorption behavior of 11 NOM samples from various sources by performing isotherm and kinetic experiments and using a suite of NOM characterization techniques (total organic carbon, fluorescence, UV−vis spectroscopy, and HPSEC). The results provide a more robust understanding of the adsorption behavior of NOM samples on CNTs in natural waters and the potential applications for water treatment.

2. MATERIALS AND METHODS

2.1. Materials. Four standard humic acids [Elliott Soil IV (ESHA), Pahokee Peat (PPHA), Leonardite (LHA), and Suwannee River II (SRHA)], four standard fulvic acids [Suwannee River II (SRFA1), Suwannee River I (SRFA2), Pahokee Peat II (PPFA), and Nordic Lake (NLFA)], and three reverse-osmosis (RO) isolates [Nordic Reservoir (NNOM), Upper Mississippi River (MNOM), and Suwannee River (SNOM)] were purchased from the International Humic Substances Society (IHSS). The chemical properties of the NOM samples, including elemental composition/ratio, carbon species, concentrations of acidic functional groups, fluorescence indexes, and average molecular weights, are listed in Tables 1 and S1.

Three different types of multiwalled carbon nanotubes (MWCNTs) and one type of single-walled carbon nanotubes (SWCNTs) were purchased from Wako Pure Chemicals, Osaka, Japan, and Alpha Nano Technology Co., Chinese Academy of Science, Chengdu, China. The characteristics of all carbon nanotubes used in this study are listed in Table 2. The Brunauer−Emmett−Teller (BET) surface areas, pore volumes, and pore size distributions were measured from nitrogen physisorption data obtained at 77 K with an ASAP 2020 analyzer (Micromeritics Instrument Corp., Norcross, GA). The oxygen contents of the adsorbents were analyzed using a Flash Elemental Analyzer 1112 series (Thermo Electron Corporation).

2.2. Preparation of NOM Solutions. NOM samples (25−50 mg) were dissolved in a 0.01 M NaOH solution to prepare a stock solution of 10 g/L. The pH of each NOM solution was

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adjusted to 7.0 ± 0.2 with 0.01 M HCl or 0.01 M NaOH. The volume of acid or alkali solution was recorded and was taken into account during the calculation of the final NOM concentration. All stock solutions were stored in the dark and refrigerated (4 °C), when not in use.

2.3. Adsorption Isotherms. Batch reactors were used to perform adsorption experiments. Each NOM stock solution was diluted with 1 mM phosphate buffer solution and then adjusted to pH 7.0 ± 0.2. Based on preliminary kinetic experiments, the equilibrium time was set at 24 h [section S1 in the Supporting Information (SI)]. Adsorption isotherm experiments were carried out under different conditions: (1) constant CNT dose and variable NOM concentration (2.5−60 mg/L) and (2) variable CNT dose [125−500 (mg of CNTs)/L] and constant NOM concentration. At the end of the equilibrium time, samples were collected, filtered [with a prewashed 0.45-μm polyethersulfone (PES) filter, Membrane Solutions, Tokyo, Japan], and kept refrigerated until further measurements. The adsorbed NOM amounts [measured as dissolved organic carbon (DOC)] were determined by subtracting the concentration of dissolved NOM remaining in the solution from the initial concentration. Each isotherm point was measured in triplicate, and variations are reported as standard errors. Blank experiments (with no adsorbents) were conducted in parallel, and the changes in NOM concentration in the blanks were found to be negligible.

2.4. Analysis. DOC concentrations were quantified using a total organic carbon (TOC) analyzer (Shimadzu V-series, TOC-CHP, Kyoto, Japan). The UV absorbance at 254 nm was obtained with a UV−visible spectrophotometer (Shimadzu UV-1800, Kyoto, Japan). The specific UV absorption ($SUVA_{254}$) values were calculated by dividing the UV absorbance at 254 nm (m^{-1}) by the DOC concentration (mg/L). The average molecular weights of all samples were determined using a high-performance size-exclusion chromatography (HPSEC) unit (Shimadzu Prominence, Kyoto, Japan), an SEC column [Shodex column (SB-803 HQ)], and a mobile phase of 75% phosphate buffer +25% acetonitrile (Wako Pure Chemicals Ltd., Osaka, Japan) adjusted to pH 7. Detection of NOM was achieved with a UV detector set at 254 nm. Poly(styrene sulfonate) (PSS) standards (1.0, 4.6, 18, and 67 kDa) were purchased from Polyscience Inc. and were used as standard molecular weights. Molecular weights and polydispersities were determined according to the method of Chin et al.[21] It should be noted that the calculated average molecular weight values obtained by HPSEC with UV−vis detectors are skewed by the SUVA of the DOC. Variations in molecular-weight values obtained by HPSEC in different studies are due to changes in the mobile phases, electrostatic repulsion, and column type; nevertheless, SEC is a useful technique for comparing changes in molecular weights among different samples.[22]

Excitation−emission matrix (EEM) fluorescence was measured as described by Murphy et al.[23] using an RF-5300 fluorescence spectrometer (Shimadzu Corp., Kyoto, Japan) and a quartz cuvette (1-cm path length). Raw EEM data were collected from 240 to 450 nm for excitation (Ex, at 5-nm intervals) and from 300 to 600 nm for emission (Em, at 2-nm intervals). EEM spectra were processed by spectral correction, inner-filter correction, Raman correction, and quinine sulfate calibration and then analyzed using the FDOMcorr toolbox.[23] The excitation−emission pairs (peak picking)[24] used in this study are described in Table S2. Fluorescence intensities are reported in Raman units (RU). The fluorescence index (FI) was calculated as the ratio of the emission intensity at Em 450 nm relative to that at Em 500 nm at Ex 370 nm. The freshness index (BIX) was calculated by taking the intensity ratio of Em 380 nm relative to that of Em 430 nm at Ex 310 nm.[25]

3. RESULTS AND DISCUSSION

3.1. Characterization of NOM. Variations in the molecular composition (i.e., percentages of C, O, and H) of the NOM used in this study are reported in Table S1. Generally, the carbon content was higher in the humic acids than in the fulvic acids and RO isolates, and the oxygen content was high for the NOM from aquatic sources. The heterogeneity of natural organic matter depends on its source (e.g., aquatic, soil-based), which also influences its adsorption behavior.[26] The sources of the NOM used in this study included soil (one humic acid), leonardite (one humic acid), peat (one humic acid and one

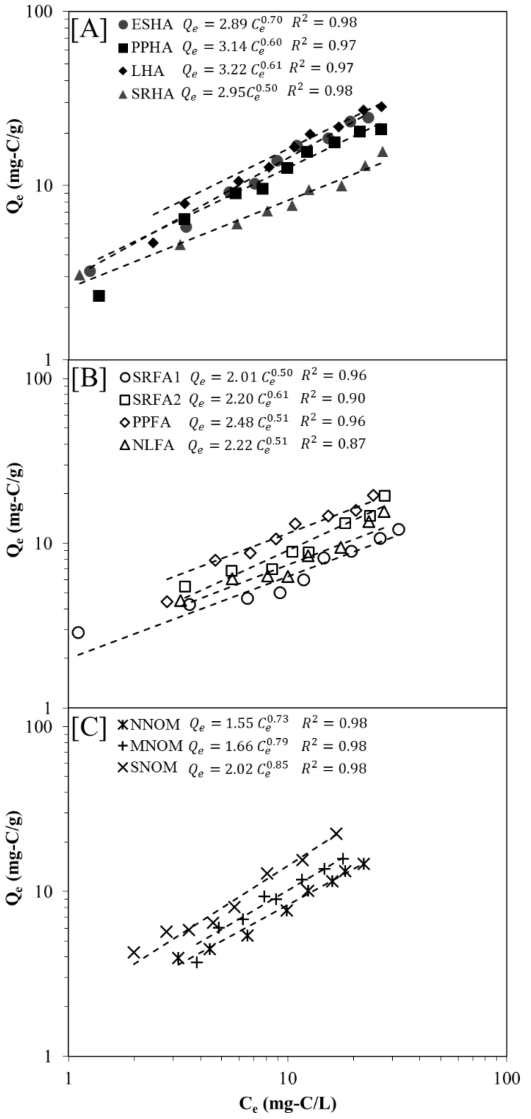

Figure 1. Isotherm results for (A) humic acids, (B) fulvic acids, and (C) RO isolates used in this study. The initial NOM concentration was increased at fixed CNT dose (C1/SSA = 134 m^2/g) at 250 (mg of CNT)/L and at the same equilibrium time of 24 h. Experimental data were fitted to the Freundlich model (dashed line).

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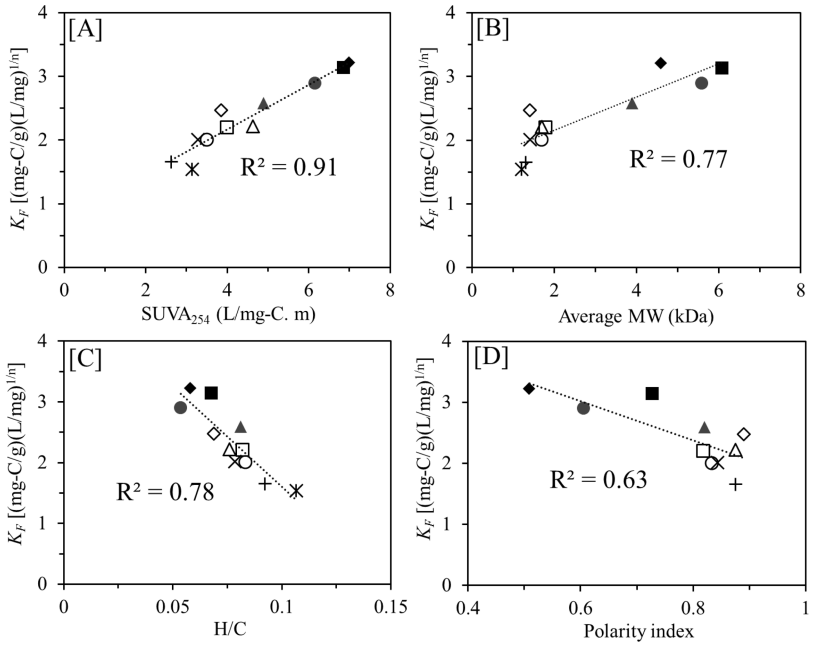

Figure 2. Relationships of the Freundlich constant K_F with (A) $SUVA_{254}$, (B) average molecular weight, (C) H/C atomic ratio, and (D) polarity index [i.e., (O + N)/C atomic ratio] for all NOM used in this study. (Gray solid circles, ESHA; solid squares, PPHA; solid diamonds, LHA; gray solid triangles, SRHA; open circles, SRFA1; open squares, SRFA2; open diamonds, PPFA; open triangles, NLFA; stars, NNOM; +, MNOM; ×, SNOM.)

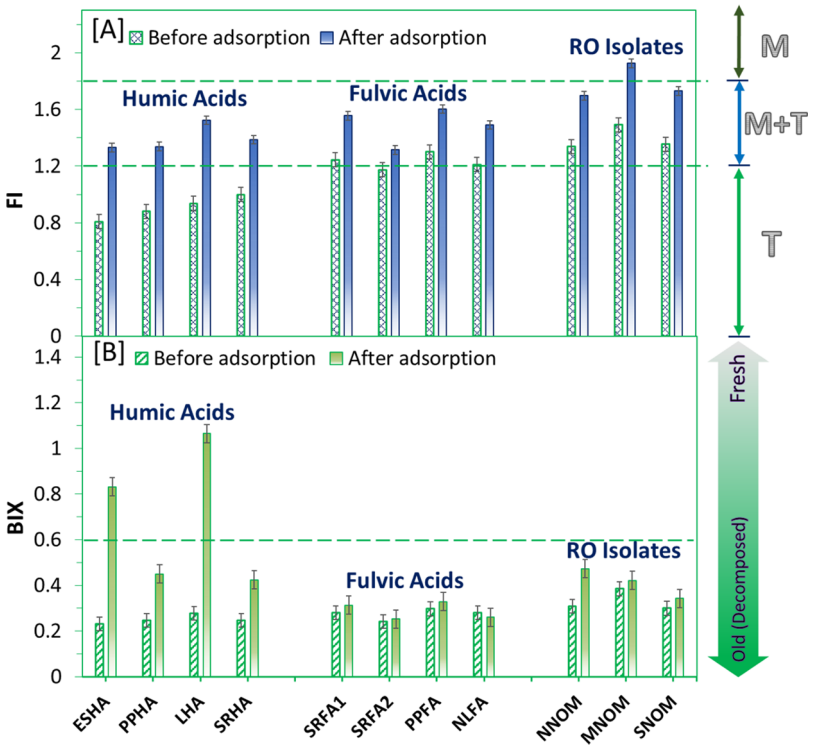

Figure 3. Changes in (A) florescence index (FI) and (B) freshness index (BIX) for all NOM samples in this study. C_e was 2−3 (mg of C)/L, the equilibrium time was 24 h, and the sample pH was 7 ± 0.2. T, terrestrial-derived DOM; M, microbial-derived DOM.

fulvic acid), and aquatic sources from rivers and lakes (one humic acid, three fulvic acids, and three RO isolates).

Other major differences among the NOM samples were the $SUVA_{254}$ values and the average molecular weights (Figures S1 and S2). Aromaticity, as indicated by $SUVA_{254}$, was higher for the humic acids [4.9−7.0 L/(mg m)] (LHA > PPHA > ESHA > SRHA) than for the fulvic acids [3.4−4.6 L/(mg m)] (NLFA > SRFA2 > PPFA > SRFA1) and RO isolates [2.6−3.6 L/(mg m)] (SRNOM > NNOM > MNOM) (Table 1). This trend is in agreement with those reported in previous studies by Hyung and Kim[10] and Rodríguez and Núñez.[27] To the best of our knowledge, among the total of 11 NOM samples used in this study, the average molecular weights of only five (i.e., ESHA, LHA, SRHA, SRFA1, and SRFA2) were previously reported,

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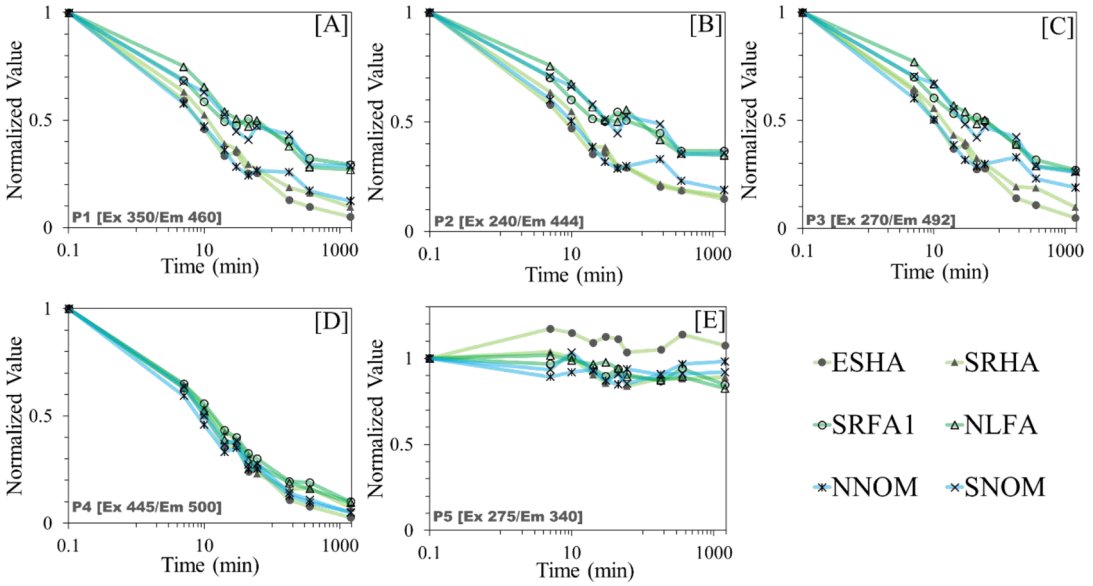

Figure 4. Kinetics of EEM peaks (P1−P5) for NNOM, SNOM, SRFA1, NLFA, ESHA, and SRHA. The initial NOM concentration was 5 mg/L, the CNT concentration was 250 mg/L, and the sample pH was 7 ± 0.2.

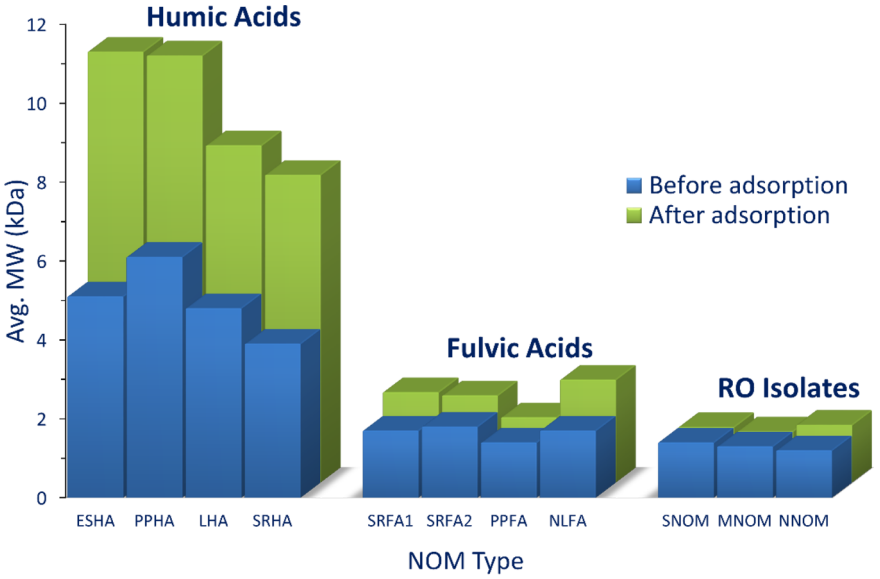

Figure 5. Changes in the average molecular weight for the samples of natural organic matter used in this study. C_e was 2−3 (mg of C)/L, the equilibrium time was 24 h, and the sample pH was 7 ± 0.2.

and the previously reported values showed, in general, good agreement with our measurements.[2,28−31] We also note that some previous studies reported incomparable average molecular weight values for some of the IHSS standard NOM samples; thus, these values were excluded from the comparison. For example, we found that average molecular weights reported for NLFA by Persson et al.,[32] for ESHA by Heo et al.,[33] and for SNOM by Wagoner et al.[34] were approximately 300%, 400%, and 1200% higher, respectively, than our average values. However, specific reasons for the overestimation of the values in those studies were not obvious because (1) some studies did not report some details of sample preparation (indicated by "N.A." in Table S3) and (2) the number of samples in each study was limited. A detailed comparison of the results and experimental conditions between this and previous studies is summarized in Table S3.

The EEM method is frequently being used for NOM characterization in water because of its high sensitivity, good selectivity, and preservation of samples.[35] Therefore, two EEM indexes, FI and BIX, were used to categorize the source and age of the NOM samples in this work. FI tracks the source of NOM as microbial-derived (e.g., organic matter from aquatic microorganisms) or terrestrially derived.[36] NOM samples with FI values greater than 1.8 and less than 1.2 are classified as microbial-derived NOM and terrestrial-derived NOM, respectively.[25] FI values between 1.2 and 1.8 indicate that the NOM is a mixture of microbial and terrestrial aquatic substances. In the present study, the FI values were higher for the fulvic acids (FAs) (1.16−1.29) and RO isolates (1.33−1.49) than for the humic acids (HAs) (0.84−1.0) (Table 1). Higher FI values for FAs than for HAs were previously reported by Rodríguez et al.,[37] and to the best of our knowledge, FI

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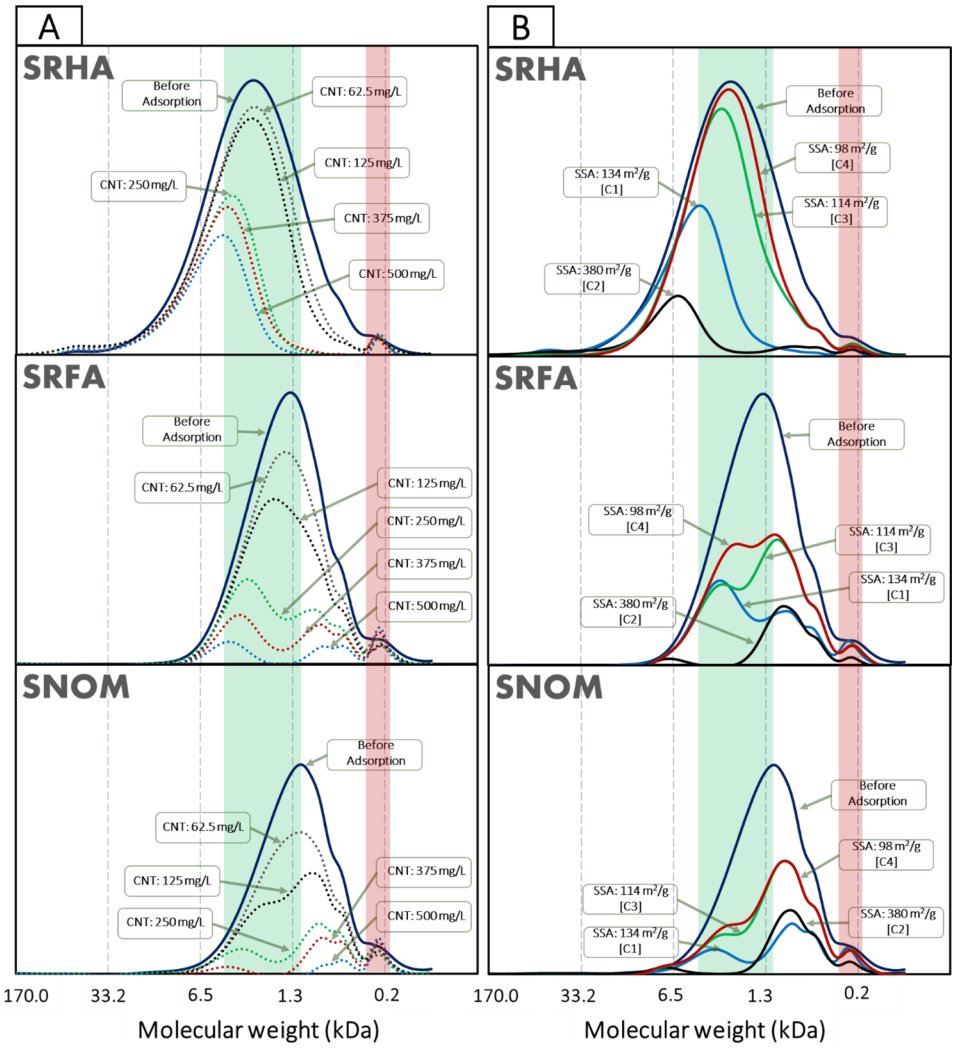

Figure 6. Molecular weight distributions for adsorption experiments with Suwanee River humic acid, fulvic acid, and RO isolates for (A) experiments at the same initial NOM concentration (10 mg/L) with five different CNT doses of one type of CNT (C1, 134 m^2/g) and (B) experiments with four different types of CNTs (C2, SWCNTs; C1, C3, and C4, MWCNTs) at the same initial NOM concentration (10 mg/L) with the same CNT dose [250 (mg of CNT)/L]. Green color highlights the molecular weight range for the preferentially adsorbed fraction. Red color highlights the molecular weight range for the nonprefered fraction.

values for standard IHSS RO isolates have not previously been reported in the literature. BIX is called the index of recent autochthonous contribution and can be determined as the ratio between the recently derived NOM and the decomposed (i.e., older) NOM.[38] According to the BIX classification, all of the NOM samples used in the present study appeared to be decomposed, with BIX values of less than 0.6, and none was freshly produced (BIX > 1) (Table 1). The BIX values for IHSS samples were reported to fall in the same range, between 0.2 and 0.4, in previous studies.[39] The NOM samples were further characterized based on EEM peaks (Table S2) and showed variations in component compositions (P1−P5), as illustrated in Figure S3. Detailed characterizations of the EEM peaks in this study are provided in section S2 of the SI.

3.2. Effect of NOM Molecular Properties on the Adsorption Affinity. The results of adsorption isotherm measurements and application of the Freundlich model for 11 NOM samples on four CNTs are presented in Table S4. The Freundlich model is described by the equation

$$Q_e = K_F C_e^{1/n} \quad (1)$$

where Q_e [(mg of C)/g] is the adsorption affinity, C_e [(mg of C)/L] is the equilibrium concentration, K_F {[(mg of C)/g]/[(mg of C)/L]$^{1/n}$} is the Freundlich constant, and $1/n$ is the Freundlich exponent.

Figure 1 shows the results of adsorption isotherm experiments for MWCNT C1 (Table 2). The Freundlich model showed a good fit with the isotherm data, as indicated by the coefficients of determination (R^2) ranging between 0.87 and 0.98 (Table S4), which agrees with previous reports of NOM adsorption on activated carbon,[2] carbon nanotubes,[10] and graphene nanomaterials.[3]

Based on the NOM sources, the adsorption capacities followed the order leonardite > peat > soil > aquatic. According to NOM type, the adsorption affinity of the humic acids was generally higher than that of the fulvic acids (Figure 1 and Table S4). This difference can be attributed to the higher aromaticity of the humic acids, as indicated by their $SUVA_{254}$ values (Table 1). Similar trends were previously reported for the adsorption of NOM by graphene and MWCNTs.[3,10] Among the NOM characteristics, $SUVA_{254}$, an indicator of aromaticity, showed a strong linear relationship with K_F

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regardless of the source and type of NOM (Figures 2A and S4).[10] The adsorption affinity was found to be inversely proportional to the H/C atomic ratio and the polarity index [i.e., the (O + N)/C atomic ratio] (see Figures 2C,D and S5). These findings show that hydrophobic repulsion from water and $\pi-\pi$ attractions are the main driving forces for adsorption between NOM and CNTs. In addition, the carboxylic acidity of the NOM showed a negative correlation with the adsorption affinity (Figure S6). A similar trend was previously reported for the adsorption of NOM samples with different carboxylic acidities on granular activated carbon.[2] Finally, NOM samples with higher average molecular weights exhibited higher adsorption affinities (Figure 2B); however, a detailed analysis of the effect of molecular weight will not be discussed further until section 3.4.

All adsorption results were also processed for the adsorption affinity (Q_e) at three different equilibrium concentrations [C_e = 5 ± 1, 11 ± 1, and 22 ± 1 (mg of C)/L]. According to our analysis, the examined adsorption capacities showed trends similar to those of K_F for the tested parameters. (See Figures S4−S6.)

Because of the oxygen-containing groups on their surface, CNTs have more hydrophilic character, which can result in the reduction of their adsorption capacities for organic compounds.[40] However, the surface oxygen contents of the CNTs used in this study fell in a narrow range (i.e., 0.21−0.30 wt % for the MWCNTs and 1.3 wt % for the SWCNTs) (Table 2). Thus, the dependence of the adsorption on the physical characteristics of the CNTs (i.e., surface area and pore size) was examined and is discussed in section S3 of the SI. The BET results showed that the CNTs had different surface areas (98−380 m^2/g) and pore volumes (0.4−0.9 cm^3/g) (Table 2). Because micropores (<2 nm) are not likely to be accessible to all NOM molecules,[12] only mesopores (2 nm > PV > 50 nm) and macropores (PV > 50 nm) were taken into account. Basically, the sorption coefficient ($K_d = Q/C_e$) was normalized to the surface areas and pore volumes of four different CNT samples (i.e., one SWCNT sample and three MWCNT samples) to adsorb SRHA, SRFA1, and SNOM. Wang et al.[12] reported that, in addition to the effect of pore size, that normalized adsorption affinity increased when they used CNTs with large outer diameters (ODs). This can be linked to the enhanced dispersion of CNTs with large ODs compared to those with small ODs[41] and/or the lower curvature of the surface of large-OD CNTs, allowing for better alignment of the adsorbate molecules.[42]

3.3. Preferential Adsorption Related to the Source and Age of NOM. Lavonen et al.[43] reported FI to be a good indicator for investigating the changes in NOM occurring during several different treatment processes in water treatment plants (e.g., coagulation, filtration, disinfection). Similarly, Rodríguez et al.[37] employed FI to monitor the compositional changes in humic substances after ozonation treatments. In another study, Kothawala et al.[44] used FI to evaluate the characteristics of NOM after sorption onto soil particles. In the present study, as reported in Table 1, the FI values for the bulk samples of NOM (i.e., before adsorption) indicated that all of the HAs were more likely to be terrestrial-derived NOM (FI < 1.2). However, the FAs and RO isolates shared the characteristics of mixtures of both terrestrial and microbial aquatic NOM (1.2 < FI < 1.8).[25,45] Figure 3A shows that the FI values for all NOM types increased after adsorption (FI > 1.2). This is an indication of the preferential adsorption of terrestrial-derived compounds. Such a finding is consistent with the notion that NOM samples with low FI values are rich in aromatic moieties (Figure S7A), as previously reported by Ateia et al.[46] and Shimabuku et al.[20] A high negative correlation (R^2 = 0.89) was also found between the FI values and the average molecular weights of all NOM samples (Figure S7B). This confirms the adsorption results reported in the previous section, where the adsorption affinity of the NOM types with high average molecular weights (i.e., HAs) was higher than that of the NOM types with lower average molecular weights (i.e., FAs and RO isolates).

In contrast to the results for FI, an increasing trend in BIX was observed only for HAs, whereas the BIX values changed only slightly for FAs and RO isolates after adsorption onto the CNTs. The BIX increments were more pronounced for ESHA and LHA, followed by PPHA and SRHA (Figure 3B); however, the overall trend illustrates the preferential adsorption for decomposed NOM fractions over freshly produced NOM. According to Hunt and Ohno[47] and Wang et al.,[48] one possible reason for this is that decomposed fractions (i.e., those with low BIX values) have higher C/N ratios and higher aromaticity than freshly produced NOM. Further, Figure S8 illustrates the gradual changes in FI and BIX with time in kinetic adsorption experiments using six NOM samples (i.e., ESHA, SRHA, SRFA, NLFA, NNOM, and SNOM). From these results, one can see that FI is more sensitive and would be more suitable for describing and tracking the changes in NOM composition.

NOM is a heterogeneous mixture of complex organic compounds. Therefore, preferentially adsorbed portions of NOM dominate the adsorption behavior at low concentrations, and the adsorption process would be limited by the available adsorption sites (i.e., surface area) at elevated NOM concentrations.[10] In this regard, further analysis showed that the variations in FI and BIX were also concentration-dependent. As shown in Figures S9 and S10, the changes in FI and BIX were pronounced at equilibrium concentrations (C_e) of up to 5 (mg of C)/L; however, at high concentrations, the FI and BIX values were similar to the original values before adsorption. Thus, the fluorescence index can serve as an easy and practical metric for tracking NOM fractionation during the adsorption process on CNTs.

Although EEM fluorescence has been applied successfully to track the changes in NOM compositions after biological[43] and physical[37] treatment processes, very few studies have utilized this technique as a tracking tool for NOM preferential adsorption on graphene nanomaterials (e.g., see the articles by Peng et al.[17] and Lee et al.[26]). In the current study, five EEM peaks with different pairs reflected several fractions with variations in NOM source and size (Figure S3 and Table S2).[36,49] Figure 4 shows the normalized removal of each fraction for six NOM samples as a function of time. The terrestrial and hydrophobic components showed the highest preferential adsorption. The same observation was reported for the adsorption of landfill leachate on activated carbon[50] and soil-derived HAs on graphene oxide.[26] It also supports the conclusion based on the FI values that terrestrial fractions are preferentially adsorbed compared to microbial NOM. Interestingly, the intensity of P5 (Ex 270/Em 492) (Figure 4E) did not decrease after the adsorption of all of the NOM tested in this study on CNTs. This peak represents aromatic amino acids (protein-like or tryptophan-like components).[25,26] This observation was further examined by checking the molecular

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weights of the residual fractions, as discussed in detail in the next section.

3.4. Preferential Adsorption Based on the Average Molecular Weight of NOM. NOM contains mixtures of compounds that vary in aromatic content and adsorption capacity. Among the NOM types used in this study, all humic acids, with a wider molecular weight range (0.2−90 kDa) and higher polydispersities (ρ = 2.7−5.8), showed similar preferential adsorption in the molecular weight range between 0.5 and 2 kDa. Meanwhile, the adsorption in the range of molecular weights greater than 1 kDa was more preferable for all fulvic acids and RO isolates, which had a narrower molecular weight (0.2−10 kDa) and lower polydispersities (ρ = 1.5−1.9) (Figure S11). Thus, the molecular weight distribution was changed after adsorption, which was clearly reflected in the average molecular weights of the residual fractions (Figure 5). According to Gotovac et al.,[51] a higher number of benzene rings in the aromatic structure of a specific fraction increases its adsorption affinity on CNTs. This selectivity was examined and tracked as a function of time, as visualized in Figure S12. Further, the selective behavior was confirmed in two ways: (1) by increasing the CNT dose (increasing the SSA) (Figure 6A) and (2) by performing adsorption on different types of CNTs (Figure 6B). Previous studies on NOM adsorptive fractions on CNTs or graphene oxides reported only that the high-molecular-weight fractions are more preferable for adsorption. However, those studies drew their conclusions based solely on aquatic NOM[3,10] or soil FAs,[11] and details about the changes in NOM molecular composition (e.g., average molecular weight, molecular weight distribution, and polydispersity) were not reported.

Another observation in this study was the "selective" adsorption on CNTs of the fraction with molecular weights of 1−3 kDa from the bulk samples of FAs and RO isolates (Figures 6, S11, and S12). According to Lv et al.,[52] this fraction is likely to comprise aromatic molecular groups, based on a comparison of the results of HPSEC and Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR-MS). In another study, Li et al.[19] tested the adsorption by CNTs of styrene sulfonate (SS) and poly(styrene sulfonate) (PSS) samples with different molecular weight values (0.2, 4.3, 6.8, 10.0, 17.0, and 70.0 kDa) and found the highest adsorption capacity for PSSs with an average molecular weight of 4.7 kDa. It is important to highlight that, based on HPSEC, the small fraction (MW < 0.4 kDa) did not adsorb on the CNTs (Figures 6, S11, and S12). This finding supports the EEM results and can be linked to protein-like compounds (Figure 4E), which were also not removed by the CNTs. Cai et al.[3] reported the same lack of uptake of the small fraction for the adsorption of NOM on graphene oxides. Therefore, we conclude that NOM fractions with molecular weights of <0.4 kDa are more likely to be hydrophilic compounds that cannot adsorb on CNTs.[22]

In this study, the comprehensive characterization of NOM before and after adsorption along with the characterization of CNTs provided important insights into the adsorption of NOM on CNTs. The results indicate that FI can serve as an easy and practical metric for describing and tracking the fractionation of NOM during the adsorption process. Selective adsorption in the molecular weight range of 0.5−2 kDa for humic acids and in the molecular weight range of 1−3 kDa for all fulvic acids and RO isolates was also revealed. Given the wide variety of NOM samples in aquatic and soil environments, the findings of this study further help to clarify and predict the adsorption behavior of NOM samples on CNTs in natural waters and/or the potential application of CNTs for water treatment. However, further studies to examine and identify the adsorption fractions of NOM by CNTs using sensitive techniques (e.g., mass spectroscopy) are still needed to elucidate the factors controlling the adsorption behavior of this complex type of material.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.7b01279.

Adsorption kinetics (section S1, Table S5, Figure S13). EEM peaks description (section S2, Table S2, Figure S3). Effects of CNT surface area and pore volume on adsorption (section S3, Figures S14 and S15). NOM characteristics (Table S1). HPSEC results (Table S3, Figures S1, S11, and S12). Freundlich isotherm results (Table S4). $SUVA_{254}$ vs average molecular weight (Figure S2). K_F vs NOM molecular properties (Figures S4−S6). FI vs $SUVA_{254}$ and average molecular weight (Figure S7). FI and BIX values at different times (Figure S8) and with increasing concentrations (Figures S9 and S10) (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*Phone: 0081-80-3430-9753; e-mail: mohamedateia1@gmail.com.

ORCID

Mohamed Ateia: 0000-0002-3524-5513

Notes

The authors declare no competing financial interest.

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