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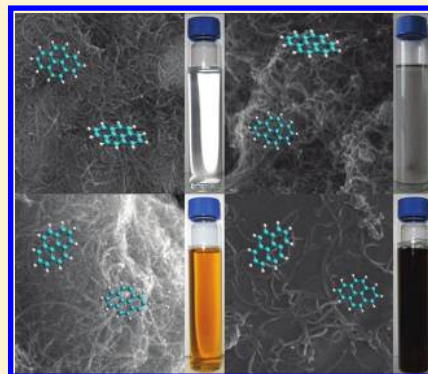
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S Supporting Information

ABSTRACT: Sonication and humic acids (HA) are known to disperse carbon nanotube (CNT) suspensions, but potential effects on sorption of chemicals to CNTs remain poorly understood. We applied a passive sampling method to investigate the influence of dispersion/aggregation on sorption of pyrene to CNTs. Sonication broke down CNT aggregates and increased pyrene sorption affinity by up to 1.39 orders of magnitude. Sorption surfaces newly exposed by sonication remained available to pyrene even after reaggregation occurred, suggesting an irreversible effect of sonication. The presence of HA decreased sorption of pyrene to CNTs, but at the highest HA concentration investigated (200 mg/L), sorption affinity was still 1.90 orders of magnitude larger than sorption of pyrene to HA alone. Specific interactions between pyrene and CNTs were thus still taking place, in spite of the presence of a HA coating on the CNTs' surface. A greater suppression of sorption by CNTs occurred when the HA addition was combined with a sonication pretreatment. Sorption isotherm fitting indicated that the maximum sorption capacity, sorption affinity, and heterogeneity of the CNT surface were all affected by sonication and the presence of HA at a concentration as low as 1 mg/L. The present results contribute to an improved understanding of the sorption behavior of CNTs in both natural and wastewater systems.



INTRODUCTION

Over the past decade, carbon nanotubes (CNTs) have gained increasing attention due to their unique properties. CNTs have a strong affinity toward organic compounds and have therefore been proposed as superior sorbents for water treatment or solid-phase extraction cartridges.¹ In addition, the production of CNTs increases rapidly and release of the particles into the environment is inevitable. There is concern that CNTs might facilitate the relocation of hydrophobic organic contaminants in the environment.² Both during CNT usage as sorbents and relocation of contaminants in the environment, sorption to CNTs might be influenced by their aggregation state. Depending on the production and release routes, CNTs may be discharged as large aggregates and/or in dispersed forms.³ After their release, interactions with substances present in the environment will further affect the dispersion status of CNTs. For instance, natural organic matter (NOM) has been shown to significantly increase the stability of CNT suspensions.^{4,5}

Potential effects of dispersion/aggregation events on sorption behavior toward organic contaminants remain poorly understood. Several researchers have reported a decrease in the sorption potential of pristine CNTs in the presence of NOM.^{6,7} However, in these studies, dispersed CNTs were preliminarily excluded from the analysis by centrifugation^{6,7} or settling.⁸ Existing results therefore only refer to large CNT aggregates and there is currently very limited data on the sorption potential of partially/fully dispersed CNT systems. Yet,

understanding the influence of dispersion/aggregation phenomena on sorption is essential for evaluating the potential environmental impact of CNTs and their application as sorbent.

The lack of data relating to dispersed CNTs can be mainly explained by limitations associated with the generally applied batch sorption test set ups that do not allow investigations on dispersed systems, consisting of inseparable nanoparticles. We previously validated a passive sampling method (polyoxymethylene solid phase extraction, POM-SPE) which allows studying sorption of polycyclic aromatic hydrocarbons (PAHs) onto both aggregated and dispersed CNTs.⁹ Even though long equilibrium times are needed for POM-SPE, in the present study we applied this method to investigate the influence of dispersion on sorption behavior of CNTs. The objectives were to investigate the effects of (i) CNT pretreatments (sonication, shaking) and (ii) natural dispersants (humic acids; HA) on the sorption characteristics of the CNT system. Sonication is an efficient method to disperse CNTs and is often applied in the presence of dispersants, such as polymers, surfactants, and HA.¹⁰ To our knowledge, the effect of an efficient dispersion (e.g., by sonication in the presence of dispersants) on the

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sorption potential of CNTs has however not been investigated yet. Single point sorption coefficients and sorption isotherms for pyrene were measured over a wide range of concentrations and in the presence of HA (1–200 mg/L). CNT suspensions were extensively characterized by microscopic, spectroscopic, and size distribution measurements in order to support mechanistic interpretations of the results.

MATERIALS AND METHODS

Sorbents and Chemicals. A polyoxymethylene sheet (POM; thickness 0.5 mm; density 1.41 g/cm³) was purchased from Vink Kunststoffen BV, Didam, The Netherlands. The POM sheet was cut into strips (1 × 1 cm; 1 × 10 cm) and cold-extracted with hexane (30 min) and methanol (3 times for 30 min) as described in Jonker and Koelmans.¹¹ Multiwalled CNTs were provided by Baytubes (Luverkusen, Germany; C150HP, synthesized by vapor deposition, >99% purity; properties listed in Table S1 of the Supporting Information, SI).

Suwannee river HA were selected as model HA (Standard II, International Humic Substances Society). HA solutions of 1–200 mg/L were prepared in 25 mg/L NaN₃ background (as biocide). First, 300 mg HA were dissolved in 5 mL 0.1 M NaOH. The solution was then diluted with background solution to obtain a 1 g/L HA stock solution. The pH was adjusted from acidic to neutral (pH 7.06) using 0.1 M NaOH. The HA stock solution was then gradually diluted to concentrations of 1–200 mg/L (1, 5, 10, 20, 40, 100, 200 mg/L).

Pyrene (99.0%) and pyrene-d10 (99.5%) were purchased from Dr. Ehrenstorfer (Germany). All stock solutions were prepared in methanol. Hexane and methanol were of residue analysis grade (Lab Scan, Dublin, Ireland and Acros Organics, Geel, Belgium).

Sorption Experiments. All experiments were carried out at 20 ± 1 °C and using background solution prepared with 25 mg/L NaN₃ as biocide (pH 7.06). One milligram of CNTs (weighed on a Mettler Toledo MX5 micro balance) and 50.00 mL of HA solution (0–200 mg/L) were added to glass vials (diameter 2.3 cm, depth 13.8 cm). Samples (CNT concentration 20 mg/L) were then pretreated according to one of the following three protocols: (i) shaking by hand for 1 min (Bulk/CNTs), (ii) sonication for 2 h (So/CNTs) or (iii) sonication for 2 h followed by horizontal shaking (180 rpm) for 6 days (So-Sh/CNTs). When sonicating, 20 sample vials were immersed into the sonication bath (Bandelin sonorex super rk106 bath, 35 kHz, diameter 24.5 cm). The water level in the bath was the same as in the samples (depth 10.2 cm). A POM strip (approximately 0.1–1 g, depending on the intended concentration) was subsequently added to each sample and pyrene was spiked. The volume of methanol (spiking solvent) was kept at 0.16% for all samples to minimize solvent effects. For each of the three pretreatments, sorption coefficients (K_{CNT}) were measured for a single initial concentration of pyrene (150 µg/L). In addition, full sorption isotherms were measured for So-Sh/CNTs (pyrene equilibrium concentration ranged over 5 orders of magnitude from 0.0001 to 20 µg/L). All vials were horizontally shaken (180 rpm) for 28 days to ensure equilibration. POM strips were then taken out of the vials, rinsed with deionized water and wiped with a wet tissue. They were then extracted with methanol by accelerated solvent extraction (ASE 200, Dionex, USA; 1500 psi, 100 °C), with pyrene-d10 as internal standard. Extracts were concentrated

under N₂ prior to GC-MS analysis, as described in our previous study.⁹ Blanks without pyrene were prepared for each pretreatment as method blanks and used as characterization samples in the following section. Control samples with pyrene indicated that losses were <6% after 28 days of shaking. The sorption coefficient of pyrene by HA (K_{HA}) was measured at 100 and 200 mg/L HA (pyrene initial concentration of 50 µg/L) and included in the mass balance calculations to derive CNT sorption coefficients (SI Tables S2 and S3). Sorption of HA to POM was tested at three HA concentrations (5, 100, and 200 mg/L) and was shown to be negligible (SI Figure S1).

Characterization of CNTs. For each pretreatment, CNTs were imaged by scanning electron microscopy (SEM). Particular attention was paid to maintaining the structure of the CNT aggregates as they occurred in the sorption test (method details available in SI Figure S2). CNT settling behavior was characterized by UV–vis spectrometry at 800 nm absorbance (Varian Cary 50 UV–vis spectrophotometer).⁴ Note that 0.16% of methanol did not affect the characteristics of the CNT aggregates (see SI). Size distribution was determined using a particle size analyzer based on a time of transition principle (TOT, GALAI Production Ltd., Israel). The surface functional groups of CNT were detected with Fourier transform infrared spectroscopy (FTIR). The hydrodynamic diameter of CNT aggregates remaining in suspension after 2 days of settling was measured by dynamic light scattering (DLS, Malvern ZetaSizer Nano). Finally, CNT suspensions were freeze-dried and outgassed before measuring adsorption–desorption isotherms of nitrogen at 77 K (Quantachrome, NOVA 2000e) and deriving the surface area and pore volume of CNT aggregates. All methods were applied at the end of the 28 days shaking period. Further details are available in the SI.

Sorption Models and Statistics. Six sorption models previously applied to describe sorption by carbonaceous materials^{12–15} were fit to the isotherms: Freundlich (FM), Langmuir (LM), dual Langmuir (DLM), Toth (TM), dual-mode (DMM), and Dubinin–Ashtakhov model (DAM). Description of the models and their parameters are available in SI Table S4. The goodness of fit was evaluated and compared based on the r^2 values, mean weighted square errors (MWSE), and Akaike's Information Criterion (AIC), as described previously⁹ (calculation details are available in the SI). All statistical tests and parameter optimizations were performed with SigmaPlot 11.0 for Windows.

RESULTS AND DISCUSSION

Effect of Sonication in the Absence of HA. Sorption of pyrene was significantly enhanced by sonication. Log K_{CNT} values were 8.61, 8.64, and 7.24, for So/CNTs, So-Sh/CNTs, and Bulk/CNTs, respectively (SI Table S5). For the first sonication treatment (So/CNTs, for which suspensions were spiked with pyrene directly after sonication), sonication broke down CNT aggregates and reduced their size from 40–500 µm down to 0.6–60 µm (based on SEM, TOT, and DLS; see SI Figures S2–S4). The increase in sorption affinity may thus be explained by an increase in the outer surface available for sorption, which would imply that inner surfaces of Bulk/CNTs aggregates were, at least partially, not available for pyrene sorption. This hypothesis was tested by measuring the surface area of particles in both the original and the sonicated suspensions. Unexpectedly, the BET measurements indicated a decrease in surface area of CNTs upon sonication (SI Figure S6). As suggested by Arai et al.,¹⁶ sonication may however

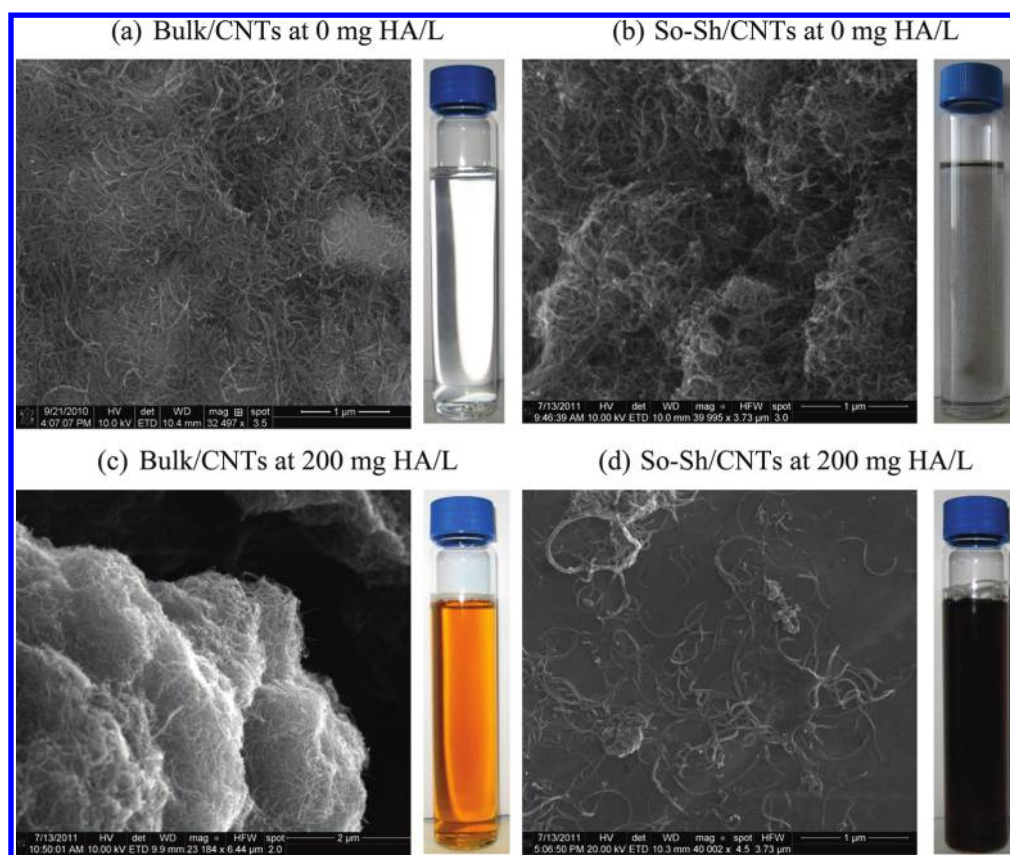


Figure 1. Scanning electron microscopy images and digital photos of Bulk/CNTs and CNTs pretreated by sonication followed by 6 days shaking (So-Sh/CNTs), in the presence of 0 (a,b) and 200 mg HA/L (c,d).

result in the formation of amorphous carbon that can block some of the pores during the drying procedure preceding the BET measurement, leading to erroneous measurements.

For the second sonication treatment (So-Sh/CNTs), sonication was followed by an additional 6 days shaking period, during which reaggregation occurred, as evidenced by a wider particle size distribution and faster settling of So-Sh/CNTs as compared to So/CNTs (SI Figure S3 and S6). At the time of pyrene spiking, the outer surface area of So-Sh/CNTs was thus less than that of So/CNTs. However, the sorption affinity of So-Sh/CNTs was similar to that of So/CNTs ($p = 0.959$, SI Table S5). This indicates that the extra surface exposed by sonication remained available to pyrene after reaggregation occurred and suggests that sonication irreversibly increased the sorption potential of CNTs in aqueous suspension. Further characterization by SEM showed that sonicated CNT aggregates exhibited much looser structures than Bulk/CNTs (Figure 1a,b). This may be explained by a partial oxidation of the CNT surface during sonication (as suggested by FTIR measurements; see SI Figure S5), which will reduce the van der Waals attractive forces responsible for the tightly bound structure of Bulk/CNT aggregates.¹⁷ Looser structures imply that more pores located within So-Sh/CNT aggregates will be available to pyrene, relative to Bulk/CNTs. Note that “pores” here refer to the space between the aggregates or between individual CNTs (hereafter referred to as interaggregate and inter-CNT pores, respectively). Even though oxidation is known to decrease PAHs sorption to CNTs,²⁷ the present observations confirm that the effect of structure is overwhelming the effect of surface chemistry.

Because fitting isotherms with model equations can aid in obtaining information on sorption mechanisms, the isotherm of pyrene sorption to So-Sh/CNTs was compared with that of Bulk/CNTs⁹ (Figure 2). Of the six sorption models tested, the Dubinin–Ashtakhov (DAM) and Toth model (TM) gave the best isotherm fit, based on our multicriteria evaluation ($r^2 > 0.95$). Both DAM and TM were originally used to describe gas

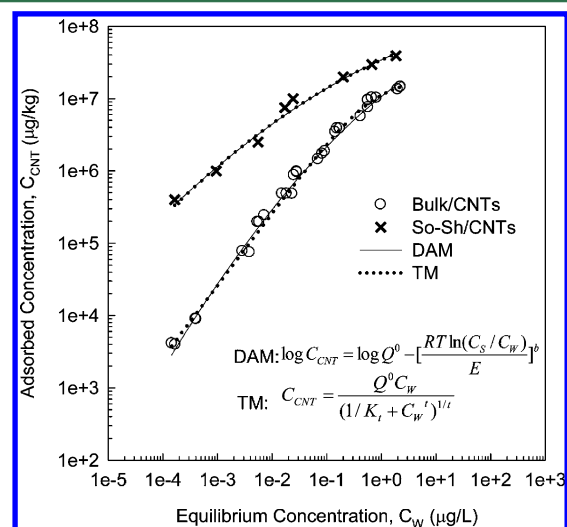


Figure 2. Sorption isotherms of pyrene to Bulk/CNTs (O) and CNTs pretreated by sonication followed by 6 days shaking (So-Sh/CNTs; X), in the absence of humic acids. The lines represent the fits by the Dubinin–Ashtakhov (DAM; —) and Toth (TM;) model.

sorption, but were later also applied to adsorption from aqueous phases. The DAM is based on the Polanyi theory, which assumes that for a molecule located within the attractive force field of a sorbent, an adsorption potential exists between the molecule and the sorbent surface. Polanyi theory based models have often been used to describe sorption of organic compounds by CNTs.¹⁸ The TM is derived from the potential theory, which is an empirical equation developed to improve Langmuir isotherm fittings. TM has proven to be useful for describing sorption of organic compounds onto carbonaceous materials,^{19–21} but the model so far has only been used in one study to describe sorption of acetone, *n*-hexane, and trichloroethylene to CNTs.²² Sorption parameters derived from DAM and TM were compared for So-Sh/CNTs and Bulk/CNTs. Sonication increased the maximum sorption capacity of CNTs by 0.17 and 1.28 orders of magnitude as derived from the DAM and TM fit, respectively. Probably, this will be related to the greater surface available for sorption, as discussed above. Similar effects have also been reported for natural talc and activated sludge, for which pretreatments by sonication increased the maximum sorption capacity of naphthalene²³ and heavy metals,²⁴ respectively.

The Toth exponent, t , is an indicator of surface heterogeneity. When $t = 1$, TM reduces to LM and represents an homogeneous population of sorption sites.²⁵ The further t deviates from unity, the more heterogeneous the sorbent surface is. For Bulk/CNTs, t was close to unity ($t = 1.03$, SI Table S6), indicating that sorption is likely to be equivalent to a monolayer sorption, as argued previously.⁹ For So-Sh/CNTs, $t = 0.18$ (SI Table S7), indicating that sonication significantly increased the heterogeneity of the CNT surface. By breaking down CNT aggregates, sonication probably produced defects such as bending, buckling, and breaking.²⁶ Sites of varying energy may be created at the disrupted surfaces, resulting in higher heterogeneity. The oxidation induced by sonication (based on FTIR, SI Figure S5) may also contribute to the increase in heterogeneity.

To date, only one study considered the potential effect of sonication on the adsorption behavior of CNTs. Cho et al.²⁷ observed no effect of sonication (and ball-milling) on the sorption isotherms of naphthalene by CNTs. The authors concluded that naphthalene sorption was independent of the CNT aggregate size, due to the full availability of sorption sites in the internal spaces of the aggregates. The discrepancy with the present study in which we found a strong effect of sonication for pyrene may perhaps be explained in terms of steric hindrance: narrow pores inside the Bulk/CNTs aggregates may be accessible to small molecules such as naphthalene, but not to larger molecules such as pyrene. However, it is also possible that the lack of sonication effect observed in ref 27 was (partially) due to insufficient debundling of CNTs under their conditions. The solid:liquid ratio of Cho et al.²⁷ (2 mg: 7 mL) was about 15 times higher than that in the present study (1 mg: 50 mL). Perhaps, a substantial fraction of tightly bundled tubes may remain under high solid:liquid conditions, whereas a low ratio as applied in the present study may allow sufficient debundling of the CNTs and consequently lead to a significant increase in sorption.

Overall, the present results highlight the importance of considering both the size and structure of sorbents in addition to performing sorption experiments, in order to gain information on the availability of both outer and inner surfaces. They furthermore indicate an irreversible increase in the

sorption of organic contaminants with a molecular size as large as that of pyrene after sonication of CNTs, most probably due to a combined increase in sorption capacity, affinity, and heterogeneity, as suggested by the isotherm fitting. As argued by Laurent et al.,²⁴ the effect of sonication on sorption may however depend on sonication power and duration. Further research is therefore required to fully quantify the impact of these parameters on the sorption behavior of CNTs.

Influence of HA on Single Point Sorption. For all pretreatments, $\log K_{\text{CNT}}$ values decreased exponentially with increasing HA concentration (Figure 3). The exponential

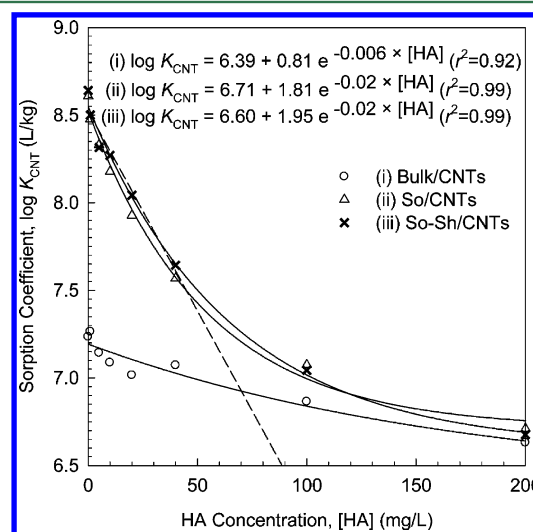


Figure 3. Logarithmic CNT-water distribution coefficients ($\log K_{\text{CNT}}$) for pyrene as a function of humic acid concentration, following three pretreatments: Bulk/CNTs (○); CNTs pretreated by sonication (So/CNTs; △), and CNTs pretreated by sonication and subsequent 6 days shaking (So-Sh/CNTs; ×). Solid lines are exponential fits of the relationships in the range 0–200 mg HA/L, whereas the dashed line is a linear fit for So-Sh/CNTs in the 0–40 mg HA/L range.

equation was selected to derive numbers that allow an easy comparison of the three treatments, the quantification of discrepancies, and the application of statistical tests. Competition and pore blockage mechanisms have previously been proposed to explain the suppression effect of NOM on the sorption of organic compounds by carbonaceous materials,^{6–8} and could also apply in the present case. Note that for all sorption experiments in this study, pyrene was spiked after pretreating CNTs together with HA. The effect of HA on pyrene sorption was much more pronounced for sonicated CNTs than for Bulk/CNTs (the exponential decrease rate was three times larger for sonicated CNTs, Figure 3). Therefore, HA molecules may have different accessibility to CNTs undergoing different pretreatments. Similarly to observations made for pyrene, interaggregate and –CNT pores of sonicated CNTs were probably accessible to large HA molecules, whereas this was only partly the case for Bulk/CNTs. HA molecules will thus have occupied more sorption sites on sonicated CNTs than on Bulk/CNTs, causing a more pronounced suppression effect for sorption of pyrene. Interestingly, at the highest HA concentration investigated (200 mg HA/L), sorption was similar for all three pretreatments (Figure 3 and SI Table S5). This indicates that sonication has two opposite effects on pyrene sorption in CNT suspensions. On the one hand, it increases the outer surface and widens interaggregate and

–CNT pores, hence providing more sorption sites for pyrene. On the other hand, the same applies to HA, rendering competition and pore blockage more efficient when combined with sonication. At 200 mg HA/L, both contrasting effects apparently resulted in the same sorption as to Bulk/CNTs.

Over the whole HA concentration range, Bulk/CNT aggregates remained large and tightly bound (40–500 μm , Figure 1, and SI Figures S2 and S8). They settled down within 5 s, whereas the settling of sonicated CNTs took several hours, with the duration increasing with increasing HA concentration (SI Figure S7). In the presence of 5–200 mg HA/L, a significant fraction of sonicated CNTs formed small aggregates that remained in suspension even after 2 days (200–300 nm by DLS, SI Figure S4). At 0 and 1 mg HA/L, the supernatant of CNT suspensions contained larger aggregates relative to higher HA concentrations, with relatively loose structures resulting from the sonication effect (see above).

Overall, the characterization data indicated that HA could interact to a larger extent with CNTs pretreated with sonication than with CNTs pretreated with shaking only. During sonication, HA molecules may adsorb to debundled CNTs, with HA preventing reaggregation of CNTs to more tightly bundled aggregates. HA presumably cannot adsorb into the CNTs aggregates when only shaking was applied (see suspension photographs for the three pretreatments, SI Figure S8). These observations are consistent with those of Schwyzer et al.,¹⁰ who reported that in the presence of dispersants (20 mg/L natural organic matter or 2.5–5000 mg/L anionic, nonionic, and cationic surfactants), mild shaking for 20 days was not sufficient to separate and suspend CNTs effectively (only 1% suspended), whereas sonication resulted in 65% of suspended CNTs. As such, sonication most probably enhances the suppression effect of HA on sorption of chemicals by allowing more efficient competition and pore blockage to occur. Chen et al.⁶ reported that 50 mg HA/L suppressed the sorption of various nonionic aromatic compounds by about 0.2 orders of magnitude for pristine CNTs, which agrees with our observation for Bulk/CNTs. For graphite a much larger suppression of sorption was observed by Chen et al.⁶ This difference may be explained by the full accessibility of macro pores in graphite for HA molecules of any size, in contrast to the narrow pores in pristine CNT aggregates. The decrease in sorption reported for graphite however matches our results for So/CNTs and So-Sh/CNTs. Hence, sonicated CNTs behave similarly to macro-porous sorbents, in contrast to pristine CNTs.

For all pretreatments, the suppression effect of HA on pyrene sorption was particularly pronounced in the low HA concentration range (about 0–40 mg/L). This agrees with the more pronounced decrease in CNT surface area and pore volume in this range (SI Figure S6a,b). Wang et al.⁷ reported sorption isotherms of HA (extracted from a peat soil) on CNTs to follow a Langmuir-like shape, indicating that sorption of HA by CNTs will increase with increasing HA concentration until saturation occurs (maximum sorption capacity was 53–82 mg/g for the CNTs studied, depending on the CNT outer diameter).⁷ Such behavior can well explain the effects observed in this study: the sharp decrease in sorption observed for the HA concentration range 0–100 mg/L could be fit by a linear equation (slope = -0.02 ; $r^2 = 0.96$, Figure 3), probably reflecting the increase in surface area occupied by HA (initial portion of a Langmuir isotherm). Between 100 and 150 mg HA/L, surface saturation by HA presumably occurred, since

further addition of HA only resulted in a slight or no impact on pyrene sorption. If his hypothesis is true, at 200 mg HA/L the sorption capacity of CNTs for HA was most certainly exceeded, with the surface of CNTs then fully being covered with a HA layer. In such a situation, one would expect the HA concentration to be so high that pyrene molecules cannot directly interact with the CNTs surface, and K_{CNT} to be similar to K_{HA} . However, at 200 mg HA/L, $\log K_{\text{CNT}}$ was still 1.90 orders of magnitude larger than $\log K_{\text{HA}}$ (6.70 vs 4.80, respectively, SI Table S5). Exponential fits further suggested that $\log K_{\text{CNT}}$ does not reduce to $\log K_{\text{HA}}$ with increasing HA concentration ($\log K_{\text{CNT}}$ is always > 6.30 , Figure 3). The specific interactions between CNTs and pyrene may be either explained in terms of availability, where some sites are available to pyrene and not to HA and/or in terms of sorption mechanisms (e.g., π – π interactions) still occurring in spite of a HA layer on the CNTs surface.

Influence of HA on Sorption Isotherms. Figure 4 shows the sorption isotherms of pyrene measured in partially

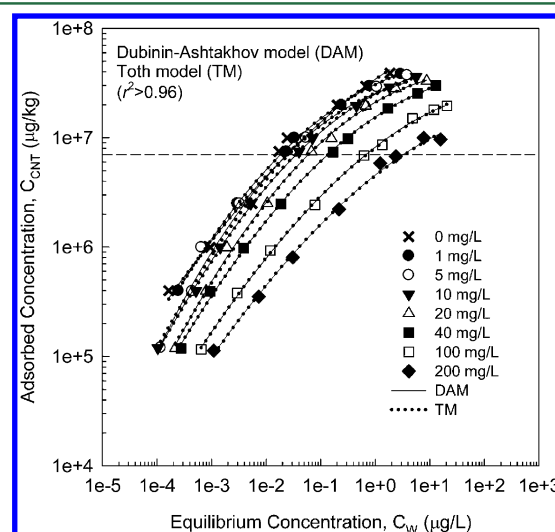


Figure 4. “Intrinsic” sorption isotherms of pyrene by CNTs pretreated by sonication followed by 6 days of shaking (So-Sh/CNTs), in the presence of 0–200 mg HA/L. The isotherms are fit by the Dubinin–Ashtakhov (DAM; —) and Toth (TM;) model. The horizontal dashed line represents the concentration at which single sorption coefficients were measured.

dispersed suspensions of So-Sh/CNTs in the presence of 1–200 mg HA/L, corresponding to HA/CNT mass ratios ranging from 0.05 up to 10 g of HA/g of CNTs. Two ways of interpreting the sorption of pyrene in the CNT–HA systems are considered below. First, “intrinsic” sorption by CNTs can be calculated by subtracting the amount of pyrene sorbed to HA (based on K_{HA} values presented in SI Table S3) from the total amount sorbed to the combined CNT–HA phase. Although sorption of HA on CNTs may experience fractionation, we assume adsorbed HA to behave the same as dissolved HA, an assumption also previously made when measuring sorption of HA to CNTs.⁷ In the second approach, HA and CNTs are considered as a whole sorbent, to which sorption is denoted as “extrinsic”. In this case, sorption is calculated from the total amount of pyrene sorbed to the overall CNT–HA matrix, divided by the total mass of HA and CNTs. Expectedly, “extrinsic” isotherms showed much weaker sorption than “intrinsic” isotherms, especially at high HA/CNT mass ratios

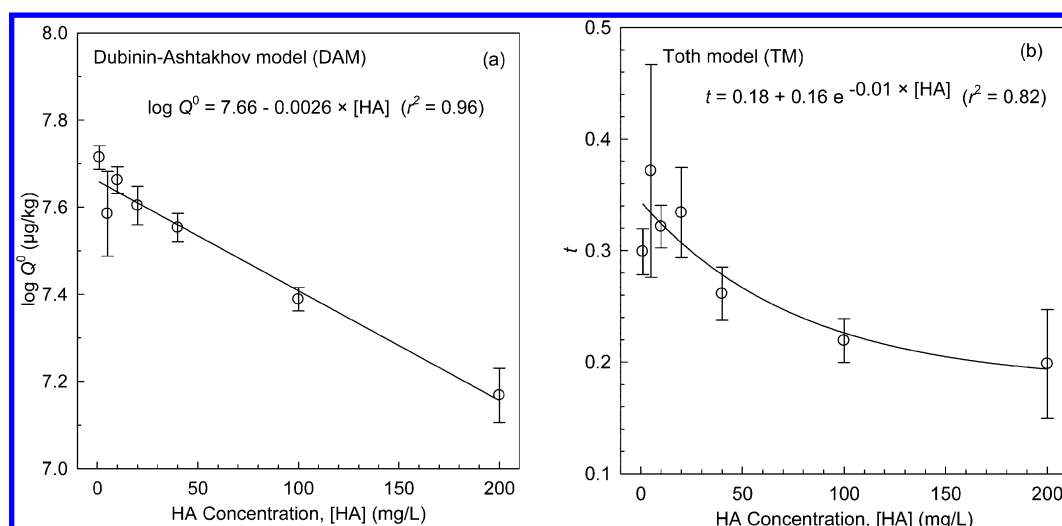


Figure 5. Decrease in (a) maximum sorption capacity (Q^0 , derived from DAM) and (b) Toth exponent (t , derived from TM) with increasing HA concentration. Note that parameters derived from the isotherm measured without HA are not included in the relationships.

(i.e., > 1 g of HA/g of CNTs, SI Figure S9). Differences between “intrinsic” and “extrinsic” isotherms are important to keep in mind when studying large ranges of HA. Neglecting sorption to HA is common practice,^{6,8} but should not be applied in the high HA range, as it may overestimate the effects of HA in decreasing sorption affinity to CNTs and artificially increase isotherm linearity.

The present paper therefore focuses on “intrinsic” sorption. Consistently with the single concentration sorption coefficients discussed above, “intrinsic” sorption isotherms indicated a significant decrease in sorption with increasing HA concentration (Figure 4). Based on the multicriteria evaluation, DAM and TM again gave the best isotherm fit ($r^2 > 0.96$, SI Table S8 and Figure S10). Although the Freundlich model (FM) was previously applied to describe sorption isotherms of organic compounds to CNTs in the presence of HA,⁸ Figure 4 clearly shows that isotherms measured over a wide concentration range are curved on a log–log scale and thus require fitting by more complex models. Below, relationships between DAM and TM parameters and HA concentrations are analyzed to gain further insight into the influence of HA on sorption by So-Sh/CNTs.

In contrast to the sonication effect, the addition of HA significantly decreased the maximum sorption capacity and surface heterogeneity. Figure 5a shows that the maximum logarithmic sorption capacity ($\log Q^0$, $\mu\text{g}/\text{kg}$) derived from the DAM fit decreased linearly by 0.54 orders of magnitude going from 1 to 200 mg HA/L. This can be related to the decrease in surface area (SI Figure S6c) and/or pore volume (SI Figure S6d). The measured surface area corresponds to the combined CNT-HA system because of difficulties in separating HA and CNTs after freeze-drying. However, HA have a small surface area relative to CNTs (4.94 m^2/g , soil HA²⁸), and the correlation reported was therefore not influenced by the presence of HA. Wang et al.²⁹ previously reported that the addition of HA had a negligible influence on the sorption capacity of CNTs for phenanthrene, naphthalene, and 1-naphthol (<0.06 orders of magnitude). However, they (i) considered large CNT aggregates only (dispersed CNTs were discarded by centrifugation prior to the sorption test) and (ii) applied a presumed lower HA concentration (a coating of 85.5 mg of HA/g of CNTs was reported, but this cannot be directly

compared to the present experimental conditions, because of possible mass losses during the washing procedure applied in ref 29). Including both aggregated and dispersed CNTs, the present results support a significant suppression of the sorption capacity by HA, even at very low concentration (e.g., Q^0 decreased by 0.24 orders of magnitude after adding 1 mg HA/L).

The relationship between HA concentration and Q^0 derived from TM fits was less obvious than for DAM. This may be due to larger standard errors associated with the parameter (SI Table S7). Although the maximum sorption capacity may not easily be reached in the natural environment, a large decrease in the sorption capacity of CNTs can be expected in situations where both the concentrations of DOC and organic contaminants are high (e.g., in wastewater).

The sorption affinity (E for DAM and K_t for TM) decreased exponentially with increasing HA concentration (SI Figure S11a,b), consistently with the conclusions derived from the single point sorption experiments (Figure 3). The extent to which natural dispersants affect the sorption affinity of CNTs toward organic contaminants certainly depends on the concentration and type of contaminants, DOC, and CNTs considered. The present data suggest a difference in sorption affinity of at least 1 order of magnitude for pyrene when comparing natural water (i.e., low pyrene and HA concentrations) to, for example, wastewater systems (i.e., high pyrene and HA [DOC > 40 mg/L] concentrations). Even though sonication will not occur under the natural conditions, it may be part of the production process preceding the environmental release.

Regarding surface heterogeneity, both the Toth exponent t (Figure 5b) and the DAM parameter b decreased exponentially with increasing HA concentration (SI Figure S11c; the only purpose of the fit was to describe trends numerically and allow easy comparisons). Although b is often considered to be only a fitting parameter, it has previously been suggested to be inversely related to sorbent heterogeneity,^{30,31} which is also observed in the present results. Both models thus suggest that the CNT surface became more heterogeneous with increasing HA loading, which may be explained by the variety of functional groups introduced by HA molecules, such as carbonyl, carboxyl, aromatic, acetal, heteroaliphatic, and

aliphatic groups (SI Table S1). With increasing HA concentration, the quantity of functional groups will thus have increased, probably leading to the observed increase in CNT surface heterogeneity. Our observations are consistent with those of Koelmans et al.,³² who observed increasing nonlinearity of the “intrinsic” isotherms of polychlorinated biphenyl sorption to charcoal with increasing HA loading. It is important to note that despite the observed increase in heterogeneity with increasing HA, the highest surface heterogeneity was observed for CNTs without HA, as indicated by smaller t and b values at 0 mg HA/L (0.18 and 1.71, respectively) than at 1–200 mg HA/L (0.30–0.20 and 2.24–1.64, respectively, SI Table S7). Similarly, the results of Zhang et al.⁸ suggested that surface heterogeneity of CNTs was reduced after adding 4 mg DOC/L (based on the increase in Freundlich isotherm linearity). The authors hypothesized that (i) DOC preferably adsorbed to high energy adsorption sites on the CNT surface and/or (ii) the aggregation structure of CNTs was changed. The present results support the former hypothesis, with sites of high energy (here mainly generated by sonication) being the main source of surface heterogeneity.

During their life cycle, CNTs can undergo various dispersion/aggregation events that will significantly impact their sorption behavior. The present results demonstrate that both the nature (e.g., sonication or presence of dispersants) and the chronological sequence of the dispersion events are essential in determining the extent and irreversibility of the effects on sorption behavior of organic chemicals.

■ ASSOCIATED CONTENT

■ Supporting Information

Details of calculations using POM-SPE, CNT characterization (microscope images, size distribution, FTIR measurements, settling behavior in suspension, and size in the supernatant), isotherm fits and parameters for the six models evaluated. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

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