Effects of ionic strength and temperature on the aggregation and deposition of multi-walled carbon nanotubes

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ABSTRACT

The aggregation and deposition of carbon nanotubes (CNTs) determines their transport and fate in natural waters. Therefore, the aggregation kinetics of humic-acid treated multi-walled carbon nanotubes (HA-MWCNTs) was investigated by time-resolved dynamic light scattering in NaCl and CaCl₂ electrolyte solutions. Increased ionic strength induced HA-MWCNT aggregation due to the less negative zeta potential and the reduced electrostatic repulsion. The critical coagulation concentration (CCC) values of HA-MWCNTs were 80 mmol/L in NaCl and 1.3 mmol/L in CaCl₂ electrolyte, showing that Ca²⁺ causes more serious aggregation than Na⁺. The aggregation behavior of HA-MWCNTs was consistent with Derjaguin–Landau–Verwey–Overbeek theory. The deposition kinetics of HA-MWCNTs was measured by the optical absorbance at 800 nm. The critical deposition concentrations for HA-MWCNT in NaCl and CaCl₂ solutions were close to the CCC values, therefore the rate of deposition cannot be increased by changing the ionic strength in the diffusion-limited aggregation regime. The deposition process was correlated to the aggregation since larger aggregates increased gravitational deposition and decreased random Brownian diffusion. HA-MWCNTs hydrodynamic diameters were evaluated at 5, 15 and 25°C. Higher temperature caused faster aggregation due to the reduced electrostatic repulsion and increased random Brownian motion and collision frequency. HA-MWCNTs aggregate faster at higher temperature in either NaCl or CaCl₂ electrolyte due to the decreased electrostatic repulsion and increased random Brownian motion. Our results suggest that CNT aggregation and deposition are two correlated processes governed by the electrolyte, and CNT transport is favored at low ionic strength and low temperature.

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Introduction

Carbon nanotubes (CNTs) have attracted significant attention due to their remarkable physiochemical properties. They have potential electronic, energy, medical, and environmental applications (Barinov et al., 2009; De Volder et al., 2013; Mu et al., 2009; Ali et al., 2015). However, wide application will cause the release of CNTs into the ecosystem, which may lead to environmental risk. CNTs have been reported to be toxic to microbes, plants, fish, and mammals (Pasquini et al., 2012; Ma et al., 2015; Cheng and Cheng, 2012; Zhang et al., 2012a). Therefore, the transport of CNTs in the ecosystem has become a hot research field, which is related to both CNT application and evaluation of its environmental hazard.
Aggregation and deposition processes determine the stability of CNTs in suspension, which is important to estimate their transport and fate in the aqueous environment. Natural organic matter (NOM) is a ubiquitous component of natural waters and plays a key role in the aggregation and deposition of particles and colloids in environmental systems. Adsorbed NOM prevents CNT aggregation through electrostatic repulsion and steric effects (Hyung et al., 2007; Chowdhury et al., 2012), therefore increases the colloidal stability. Cations and ionic strength also have significant influence on particle aggregation. Divalent cations can form cation bridges between negatively-charged particles, which accelerate particle aggregation (Chen and Elimelech, 2007). The larger aggregates usually are faster to deposit due to increased gravity and decrease random Brownian diffusion (Petosa et al., 2010). However, little experimental work to date has investigated the connection between particle aggregation and deposition.

The temperature changes in the natural aqueous system may also affect CNT aggregation and deposition. High temperature corresponds to energy input into a particle suspension, which may lead to disruption of interaction forces, increased random Brownian motion of nanoparticles and chances of particle–particle collision, and decreased zeta potential (Zhang et al., 2012b). Although temperature has been considered to be important for nanoparticle stability and transport (Grasso et al., 2002; Karimian and Babaluo, 2007; Li and Elimelech, 2004), the existing studies have not obtained consistent results due to the multiple factors related to temperature. Elevated temperature has been reported to decrease the aggregation kinetics of CeO$_2$ nanoparticles (NPs) (Zhang et al., 2012b). However, in a study on single wall carbon nanotubes, the colloidal stability decreased significantly from 20 to 40°C (Adelye and Keller, 2014). Therefore, the relationship between CNT colloidal stability and temperature needs to be further addressed, especially in the presence of NOM. Understanding the effects of temperature is helpful to estimate CNT transport in different seasons.

In this study, the most commonly produced and applied pristine multi-walled carbon nanotubes (MWCNTs) are selected due to their high global production and their inevitable release into the environment. Production of MWCNTs will reach nearly 12,766 metric tons in 2016, mainly driven by use in polymers and composites for automotive components, structural aerospace parts, lithiumion batteries, and some other markets (Jeong et al., 2015). Humic acid (HA) is a major organic constituent of many streams, lakes, and ocean water (Stevenson, 1994). Therefore, the MWCNTs are treated with HA to simulate their interaction with NOM in natural waters. To explore the relationship between aggregation and deposition, and to investigate the effects of ionic strength and temperature, the MWCNT aggregation and deposition experiments are performed in varied electrolytes at different temperatures. MWCNT aggregation was measured by dynamic light scattering (DLS) and deposition was measured by optical absorbance at 800 nm. Our findings will be important to understand CNT transport in the natural waters and to estimate its environmental risk.

1. Experimental section

1.1. Materials

Pristine MWCNTs with length of 1–10 μm were purchased from Chengdu Organic Chemistry Co. Ltd., Chinese Academy of Sciences. The specific surface area (SSA) of MWCNTs was 127 m$^2$/g measured by the multi-point Brunauer–Emmet–Teller method.

HA extracted from leonardite was purchased from Aladdin Reagent Co. The commercial HA was characterized in our previous study (Hu et al., 2014). In summary, it contains 40.2% C, 3.76% H, 49.1% O, 0.99% N, 0.86% S, and a high content of aromatic groups and carboxylic groups. Its aromaticity is 47.92% reflected by solid state $^{13}$C nuclear magnetic resonance spectroscopy (Hu et al., 2014). HA powder was dissolved in deionized (DI) water to 1000 mg/L and was sonicated by a KQ3200E sonicator (Kunshan Ultrasonic Instruments, China) for 30 min. The HA solution was filtered via a 0.22 μm syringe filter to remove undissolved residues. The mass loss after filtration is less than 1.5%. The quantitative standard curve of HA solution was obtained by a ultraviolet-visible (UV–vis) Spectrometer (TU-1900, Beijing Purkinje General Instrument) at 210 nm.

DI water (18.25 MΩ/cm) was used in experiment. The NaCl (1 mol/L) and CaCl$_2$ (0.1 mol/L) electrolyte stock solutions were prepared and filtered through a 0.22 μm syringe filter before use.

1.2. Preparation of HA-treated MWCNT suspension

The HA-treated MWCNTs (HA-MWCNTs) were prepared by a modified method based on previous studies (Li and Huang, 2010; Saleh et al., 2010). To prepare HA-MWCNTs, 6 mg MWCNTs was mixed with HA solution (100 mg/L, 30 mL). The mixture was adjusted with 0.1 mol/L HCL/NaOH to pH 5–6, and was shaken (120 r/min, 25°C) for 48 hr to allow HA to adsorb on MWCNTs. The HA-MWCNTs were centrifuged (3160 × g, 30 min) to remove unadsorbed HA in supernatant, then washed twice with DI water. The amount of adsorbed HA on MWCNTs was 70.5 ± 7.5 mg/g, which was calculated from the HA equilibrium concentration in supernatant and the HA loss in the washing process. After washing, HA-MWCNTs were dispersed in DI water by mild sonication (40 kHz, 25°C) for 2 hr. Then the HA-MWCNT dispersion was centrifuged (3160 × g, 30 min) to obtain a stable suspension (20 mg/L). The suspension was adjusted to pH 7.2 with 0.1 mol/L HCl/NaOH and kept as a stock suspension. After removing MWCNTs with a 0.22 μm syringe filter, the free HA in stock suspension was measured to be less than 2 mg/L by a UV–vis spectrophotometry. Such HA treatment simulated the condition that MWCNTs were fully interacted with sufficient amount of HA.

1.3. Quantification of HA-MWCNT suspension

The HA-MWCNT suspension was quantified according to previous methods (Yu et al., 2007; Yang et al., 2013). MWCNTs (1 mg) were mixed with 40 mL of 4 mg/mL sodium dodecyl sulfate (SDS) solution and were sonicated at 25°C for 2 hr to obtain a uniform stock suspension. The stock suspension was
1.4. Transmission electron microscopy imaging

The morphologies of untreated and HA-MWCNTs were imaged by a JEM-1011 (JEOL, Japan) transmission electron microscopy (TEM) at a 100 kV electron emission. After a 30-min sonication, a drop of freshly diluted MWCNT/HA-MWCNT suspension (5 mg/L) was put on a copper mesh grid. Then the grid was dried in air under an infrared lamp.

1.5. Measurements of hydrodynamic diameters

Hydrodynamic diameter \(D_h\) of HA-MWCNTs was measured by a Malvern Zetasizer (Nano ZS90, Malvern Instruments Ltd., UK) DLS instrument. The freshly-made HA-MWCNT stock suspension was diluted to 9 mg/L at pH 7.2 and injected into a new test cell. The test cell was static in the DLS sample chamber for 10 min to reach the set temperature. Either NaCl or CaCl\(_2\) electrolyte was added into the test cell to reach the desired ionic strength and mixed by pipette several times. Then DLS measurements were started immediately to observe the HA-MWCNT aggregation process. The scattered light intensity was measured at a 90° scattering angle, and each auto correlation function was assembled at a 15-sec interval. To evaluate the effects of ionic strength on \(D_h\) of HA-MWCNTs, NaCl was set from 10 to 200 mmol/L, and CaCl\(_2\) was set from 0.5 to 200 mmol/L. The \(D_h\) of HA-MWCNTs was monitored at 25°C for 1.5 hr. \(D_h\) of HA solution was also evaluated by DLS measurements at 25°C under the same experimental condition as HA-MWCNT. The measurement was conducted using 20 mg/L HA due to the detection limit at low HA concentration. NaCl concentration was set from 0.5 to 4 mol/L, and CaCl\(_2\) was set from 3 to 40 mmol/L.

To study the effects of temperature on \(D_h\) of HA-MWCNT aggregation, the system temperature was set to 5, 15 or 25°C. \(D_h\) of 9 mg/L HA-MWCNTs in 50 mmol/L NaCl and 1.0 mmol/L CaCl\(_2\) was monitored for 1.5 hr by DLS measurements.

1.6. Determination of HA-MWCNTs aggregation kinetics

The initial aggregation kinetics showed an initial increase in intensity-weighted \(D_h\) with respect to time \(t\), as measured by DLS. The aggregation kinetics can be expressed by the following second-order rate equation (Holthoff et al., 1996; Schudel et al., 1997):

\[
\frac{d(D_h(t))}{dt} \propto k N_0
\]

where, \(N_0\) is the initial concentration of basic particles and \(k\) is the aggregation rate constant. Previous research demonstrated the application of Eq. (1) in CNT agglomeration kinetics (Smith et al., 2009; Li and Huang, 2010; Yi and Chen, 2011). In our experiments, 9 mg/L HA-MWCNT suspensions were used for the aggregation kinetics studies. Generally, \(D_h\) is linearly correlated to time. The initial intensity-weighted hydrodynamic diameters \((D_{h0})\) increase at least 75%. However, at low NaCl/CaCl\(_2\) concentrations, the HA-MWCNTs aggregate much more slowly and \(D_h\) could not reach 1.75 \(D_{h0}\) so the regression analysis was conducted to 30 min instead of 1.75 \(D_{h0}\). The aggregation attachment efficiency \(\alpha\) is calculated using Eq. (2). The attachment efficiency \(\alpha\) was calculated from Eq. (2) by normalizing the initial slope of the aggregation visibility at different electrolyte concentrations (Holthoff et al., 1996; Schudel et al., 1997):

\[
\alpha = \left(\frac{k}{k_{fast}}\right) = \frac{1}{N_0} \left(\frac{dD_h(t)}{dt}\right)_{t=0} / \left(\frac{dD_{h0}}{dt}\right)_{t=0,fast}
\]

where, “fast” means favorable conditions of nonrepulsive aggregation. The value of \(\alpha\) (ranging from 0 to 1) is used to quantify the initial aggregation kinetics of MWCNTs under different solution conditions.

1.7. Measurements of zeta potentials of HA-MWCNTs

The effect of electrolyte on the zeta potential (\(\zeta\)) of HA-MWCNTs was monitored by the Malvern ZS90 ZetaSizer, and was measured at a series of concentrations (NaCl: 10 to 200 mmol/L, CaCl\(_2\): 0.5 to 20 mmol/L) at pH 7.20 ± 0.05 and 25°C. In addition, the \(\zeta\) of HA-MWCNTs in 50 mmol/L NaCl and 1.0 mmol/L CaCl\(_2\) was measured at 5, 15 and 25°C. To reach the desired temperature, HA-MWCNT samples were placed in the instrument sample chamber for 10 min before measurements, and each sample was measured five times.

1.8. Sedimentation of HA-MWCNTs

The sedimentation rate of HA-MWCNT suspensions was evaluated by measuring the optical absorbance at 800 nm using a UV-vis spectrophotometer. The freshly-made HA-MWCNT suspension (9 mg/L, 3 mL) was scanned continuously for 3 hr at pH 7.2 and 25°C. To study the effects of electrolyte, the scan started (time 0) immediately after the quick pipette mixing with NaCl or CaCl\(_2\) electrolyte. All measurements were conducted in the square cuvettes with a 1-cm light path. The suspension was measured at 1.5 cm above the bottom of the cuvettes, which was coincident with the center of the light beam.

2. Results and discussion

2.1. Morphology of MWCNTs after HA treatment

The morphologies of untreated and HA-MWCNTs are presented in Fig. 1. MWCNTs attach to each other due to the drying process on TEM grids. Untreated MWCNTs aggregate seriously and few single MWCNTs are visible (Fig. 1c). HA
treatment significantly improves the dispersion of MWCNTs, which can be reflected from the loose distribution observed in the TEM image in Fig. 1a. HA adsorbs on CNTs through van der Waals forces and π–π stacking (Lin et al., 2012), or through polar interaction with functional groups (mainly oxygen-containing groups) and electrostatic interaction (Chen et al., 2008). HA adsorption has been reported to successfully disperse MWCNTs through electrostatic repulsion and steric effects (Saleh et al., 2010). In our study, adsorption of 70.5 ± 7.5 mg/g HA disperses MWCNT aggregates to thin bundles or individual tubes (Fig. 1a and c). However, the adsorbed HA did not change the morphology of MWCNTs in DI water. When HA-MWCNT samples are dried in CaCl₂ solution, the TEM image shows some opaque irregular patches attached on the MWCNTs (white arrows in Fig. 1b), which is the HA coated onto MWCNT surface. Therefore, the nearby MWCNTs then attach to each other through the HA chains and Ca²⁺, which connects the carbon tubes and also makes the HA visible at the connection points (Fig. 1b).

### 2.2. Effects of ionic strength on HA-MWCNT aggregation

Aggregation kinetics studies of HA-MWCNTs in 10–120 mmol/L NaCl and 0.1 mmol/L CaCl₂ electrolyte (b). Untreated MWCNTs are imaged (c) to compare with HA-MWCNTs. The white arrows indicate some opaque irregular patches attached on the MWCNTs, which is the HA coated onto MWCNT surface.

Fig. 1 – Transmission electron microscopy images of humic acid treated multi-walled carbon nanotube (HA-MWCNT) samples dried in deionized water (a) and in 0.1 mmol/L CaCl₂ electrolyte (b). Untreated MWCNTs are imaged (c) to compare with HA-MWCNTs. The white arrows indicate some opaque irregular patches attached on the MWCNTs, which is the HA coated onto MWCNT surface.

The ratio of CCC in NaCl and CaCl₂ is 62:1, which is very close to the Schulze–Hardy rule for cations of different charge (4⁺ : 2⁺ = 64:1) (Hsu and Kuo, 1995). Considering that the free HA may aggregate at high ionic strength and may disturb the HA-MWCNT Dₜ measurement, the aggregation kinetics of HA was monitored. The free HA in 20 mg/L HA-MWCNT stock suspension is less than 2 mg/L, but 2 mg/L HA and its aggregates are not detectable in our DSL measurement. Therefore, the HA concentration was increased to 20 mg/L, and the CCC was 2 mol/L in NaCl and 7 mmol/L in CaCl₂ (Fig. 2d), which are much larger than the CCC of HA-MWCNTs. This result indicates that free HA molecules are more difficult to aggregate compared with HA-MWCNTs, and their impact on the Dₜ measurement of HA-MWCNTs is negligible.

The zeta potential ζ of HA-MWCNTs in DI water or NaCl/ CaCl₂ electrolyte are negative at pH 7.2 (Fig. 3), which indicates that HA-MWCNTs are negatively-charged. In the regime of reaction-limited aggregation (α < 1), the negative charge of HA-MWCNTs exhibits strong electrostatic repulsion that obstructs aggregation. Increases in electrolyte concentration can effectively screen surface charge and compress the electric double layer surrounding the MWCNTs. Therefore, ζ values of HA-MWCNTs become less negative when increasing NaCl/ CaCl₂ concentration (Fig. 3). The electrostatic repulsion between HA-MWCNTs is reduced, leading to an increase of attachment efficiency (Saleh et al., 2010; Smith et al., 2009).

The zeta potential increases much faster in CaCl₂ than in NaCl (Fig. 3), which may be attributed to both the specific adsorption between Ca²⁺ and the oxygen-containing groups on the HA-MWCNT surface (Yi and Chen, 2011), and the neutralization effect of Ca²⁺ on negatively-charged HA in the inner Helmholtz plane (Akaighe et al., 2012). Ca²⁺ can form a cation bridge between negatively charged HA chains (Chen and Elimelech, 2007). Therefore, the nearby MWCNTs then attach to each other through the HA chains and Ca²⁺, which connects the carbon tubes and also makes the HA visible at the connection points (Fig. 1b).

When electrolyte concentration increased above 80 mmol/L in NaCl and 1.3 mmol/L in CaCl₂ electrolyte, the electrostatic repulsion between HA-MWCNTs is completely suppressed and the attachment efficiency stops increasing. The restraint of electrostatic repulsion leads to a diffusion-limited aggregation regime (α = 1) as shown in Fig. 2c. In the diffusion-limited regime, HA-MWCNT aggregation is not governed by electrostatic repulsion but by random Brownian motion.
2.2 hr, which indicates obvious HA-MWCNT deposition. When NaCl concentration increases to 80 or 120 mmol/L, significant deposition starts at 30 min. The deposition curves in 80 and 120 mmol/L NaCl electrolyte are almost coincident and with similar slopes, which indicates that the deposition has reached the critical state and the rate cannot be faster by further increases in NaCl concentration. The electrolyte concentration at the critical state is the critical deposition concentration (CDC), which is close to 80 mmol/L in NaCl for HA-MWCNT deposition. In CaCl2 electrolyte, no obvious deposition was observed at the concentration of 1 mmol/L. In 2 mmol/L CaCl2 electrolyte, the deposition curves of HA-MWCNTs drop sharply at 30 min, indicating it was already reaching the critical state. Therefore, the CDC of HA-MWCNT deposition in CaCl2 is between 1 and 2 mmol/L.

Fig. 2 – Hydrodynamic diameters of HA-MWCNTs increase in NaCl (a) and CaCl2 (b) electrolyte at pH 7.2. Attachment efficiency (c) of 9 mg/L HA-MWCNTs (c) and 20 mg/L HA (d) is as a function of NaCl or CaCl2 concentration. The CCC values for HA-MWCNTs are 80 mmol/L NaCl and 1.3 mmol/L CaCl2, respectively. The CCC values of free HA are 2 mol/L NaCl and 7 mmol/L CaCl2, respectively. CCC: critical coagulation concentration.

Fig. 3 – Zeta potentials of HA-MWCNTs in NaCl and CaCl2 at pH 7.20 ± 0.05, as a function of electrolyte concentration.
the rate of HA-MWCNT aggregation cannot be faster, therefore its deposition rate also stops increasing with ionic strength. Particle deposition is a complicated process, which is influenced by the collector surface properties, the density of aggregates, the medium chemistry and viscosity (Elimelech et al., 1998; Whitmer and Luijten, 2011). However, the correlation between HA-MWCNT aggregation and deposition is confirmed by the coincidence of CCC and CDC.

2.4. Effects of temperature on HA-MWCNTs aggregation

The change in $D_h$ of HA-MWCNTs with time was measured at 5, 15 and 25°C in 50 mmol/L NaCl and in 1.0 mmol/L CaCl$_2$ electrolyte (Fig. 5a and b). The electrolyte concentrations were below the CCC (1.3 mmol/L CaCl$_2$ and 80 mmol/L NaCl) for HA-MWCNT suspension, therefore the temperature-related aggregation kinetics were studied in the reaction-limited regime. HA-MWNTs aggregate faster at higher temperature in either NaCl or CaCl$_2$ electrolyte, therefore their attachment efficiency $\alpha$ increases with temperature: $\alpha_{5^\circ C} < \alpha_{15^\circ C} < \alpha_{25^\circ C}$ (Fig. 5c). In either NaCl or CaCl$_2$ electrolyte, the zeta potential of HA-MWCNTs increases with temperature: $\zeta_{5^\circ C} < \zeta_{15^\circ C} < \zeta_{25^\circ C}$ (Fig. 6). The $\zeta$ increase at high temperature has been reported for single wall carbon nanotubes, which results in faster sedimentation (Adeleye and Keller, 2014). Therefore, the increased temperature causes less negatively charged surfaces, and reduces the electrostatic repulsion among HA-MWCNTs. Moreover, high temperature also accelerates aggregation through increasing the random Brownian motion and collision frequency of particles (Crittenden, 2005; Zhang et al., 2012b). All of the above-mentioned mechanisms favor the CNT aggregation and sedimentation. Our results indicate that in natural waters, CNTs may have decreased mobility in summer (25°C) compared to winter (5°C).
However, a decline in attachment efficiency with increasing temperature has been observed for CeO2 NPs (Zhang et al., 2012b). This phenomenon is explained by the increased Brownian motion of water molecules increasing the hydrodynamic shear on the particle surface and possibly destabilizing the aggregated clusters of NPs (Ryan and Elimelech, 1996). These results indicate that the effect of temperature depends on the strength of the interactive force between particles and the firmness of the particle aggregates.

**3. Conclusion**

In this study, both ionic strength and temperature affect the aggregation and deposition kinetics of HA-MWCNTs. The fast aggregation in high ionic strength solution is attributed to the increased zeta potential and reduced electrostatic repulsion between HA-MWCNTs. Ca2+ causes more serious HA-MWCNT aggregation than Na+, because Ca2+ neutralizes negatively-charged HA in the inner Helmholtz plane and forms cation bridges between the HA chains. The deposition rate of HA-MWCNTs increases with ionic strength, but stops increasing after reaching the CDC. The HA-MWCNT deposition is related to its aggregation because the aggregates have large mass and reduced random Brownian motion compared with individual particles. Higher temperature accelerates HA-MWCNTs aggregation in both NaCl and CaCl2 due to the reduced electrostatic repulsion and increased random Brownian motion.

However, CNT aggregation and deposition in the natural waters are complicated processes, and are influenced by multiple factors. The aquatic organisms, such as microalgae and plants, may also play a role in CNT transport. Moreover, the interaction of CNTs with environmental surfaces, especially in porous media, should be considered to estimate the CNT transport. Although this research provides useful information on the effects of ionic strength and temperature, future studies are still needed to uncover other affecting factors and to better understand the transport and fate of CNTs in natural waters.

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