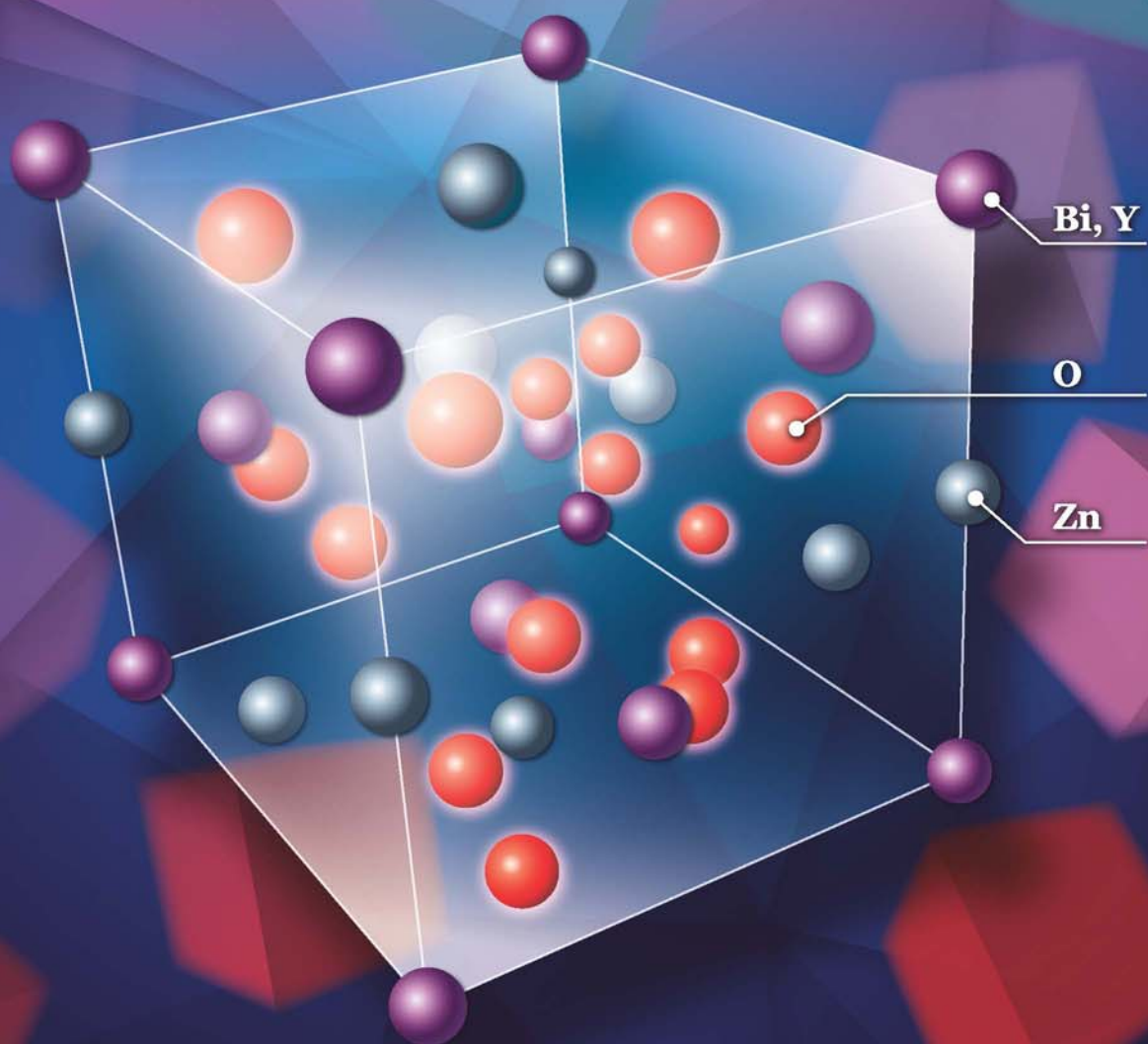


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A settling curve modeling method for quantitative description of the dispersion stability of carbon nanotubes in aquatic environments

Lixia Zhou, Dunxue Zhu, Shujuan Zhang*, Bingcai Pan

State Key Laboratory of Pollution Control and Resource Reuse, School of the Environment, Nanjing University, Nanjing 210023, China

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ABSTRACT

Understanding the aggregation and deposition behavior of carbon nanotubes (CNTs) is of great significance in terms of their fate and transport in the environment. Attachment efficiency is a widely used index for well-dispersed CNT solutions. However, in natural waters, CNTs are usually heterogeneous in particle size. The attachment efficiency method is not applicable to such systems. Describing the dispersion stability of CNTs in natural aquatic systems is still a challenge. In this work, a settling curve modeling (SCM) method was developed for the description of the aggregation and deposition behavior of CNTs in aqueous solutions. The effects of water chemistry (natural organic matter, pH, and ionic strength) on the aggregation and deposition behavior of pristine and surface-functionalized multi-walled carbon nanotubes (MWCNTs) were systematically studied to evaluate the reliability of the SCM method. The results showed that, as compared to particle size and optical density, the centrifugal sedimentation rate constant (k_s) from the settling curve profile is a practical, useful and reliable index for the description of heterogeneous CNT suspensions. The SCM method was successfully applied to MWCNT in three natural waters. The constituents in water, especially organic matter, determine the dispersion stability of MWCNTs in natural water bodies.

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Introduction

Carbon nanotubes (CNTs) are allotropes of carbon with a cylindrical nanostructure having extraordinarily high length-to-diameter ratios. As a new class of nanomaterials, the unique physicochemical properties of CNTs make them widely applicable in many fields, such as microelectronics (Rosen et al., 2000), energy storage materials (Che et al., 1998), composites (Ajayan et al., 1994), nanoproboscopes and sensors (Baughman et al., 1999). The ever-rising demand and decreasing cost make their release into the atmosphere, soil and natural waters inevitable.

Due to their nanoscale, CNTs easily go through the skin and penetrate the cell membrane of biological tissues, incurring an inflammatory response (Klaine et al., 2008). Once entering a water

body, CNTs, with their strong hydrophobicity and large specific surface area, readily associate with organic matter in water, and eventually enter the human body by the food chain (Klaine et al., 2008). Toxicological studies have proved that the toxicity of nanoparticles depends largely on their size (Limbach et al., 2005; Zhu et al., 2008; Panessa-Warren et al., 2009; Keller et al., 2010; Manna and Rana, 2012). Because of van der Waals and electrostatic forces between the walls, CNTs are extremely prone to aggregate spontaneously in agglomerates or bundles. Natural organic matter (NOM), which is ubiquitous in natural waters, can cause surface modification of CNTs and change their aggregation behavior. The dispersion stability of CNTs can greatly influence their bioavailability and sedimentation in natural waters. Thus, understanding the aggregation and deposition behavior of CNTs

* Corresponding author. E-mail: sjzhang@nju.edu.cn (Shujuan Zhang).

is of great significance in terms of their fate and transport in aquatic environments.

The size distribution of CNT aggregates is an index of their dispersion stability. Currently, time-resolved dynamic light scattering (DLS) is the most widely used experimental technique to detect the size distribution profiles of CNT particles in aqueous solutions. Since small particles in solutions undergo Brownian motion, the distance between the particles in solution is constantly changing with time. Thus, a time-dependent fluctuation in the scattering intensity can be observed. The DLS technique is useful in well-dispersed systems. For DLS determination, a standard protocol is to sonicate CNT suspensions for a certain time interval, and then take the stable supernatant for further analysis (Bhabak and Mugesh, 2010; Krause et al., 2010; Saleh et al., 2010; Shi et al., 2010). In this way, a reliable time-dependent particle size profile can be obtained. Attachment efficiency (α) is used to reflect the dispersion stability of CNTs. A fast aggregation rate constant (k) can be determined from the slope of the initial change of the hydrodynamic diameter with time (Chen et al., 2006; Chen and Elimelech, 2007):

$$k_{\text{occ}} \frac{1}{N_0} \left(\frac{dD_h}{dt} \right)_{t \rightarrow 0} \quad (1)$$

where N_0 is the initial CNT particle concentration; D_h is the hydrodynamic diameter.

By normalizing k in a given solution, an empirical α can be obtained:

$$\alpha = \frac{\frac{1}{N_0} \left(\frac{dD_h}{dt} \right)_{t \rightarrow 0}}{\frac{1}{N_{0,\text{fav}}} \left(\frac{dD_h}{dt} \right)_{t \rightarrow 0,\text{fav}}} = \frac{k}{k_{\text{fav}}} \quad (2)$$

where, the subscript 'fav' refers to diffusion-limited (favorable) aggregation conditions.

Undoubtedly, study of the behavior of CNTs in well-dispersed solution is helpful for us to understand their transport in aquatic environments. However, in most cases, the CNTs released to water bodies are heterogeneous in particle size. The fate of CNTs in natural water largely depends on hetero-aggregation (Chen et al., 2010). For CNT suspensions of wide particle distribution and large particle size, it is difficult to get reliable data from DLS. Comparatively, the static light scattering (SLS) method has a much larger detection range than that of DLS. It can detect particles of size ranging from nanometers to microns. However, since SLS is a static method, it cannot track the aggregation behavior of particles. Describing the dispersion stability of CNTs in natural waters is still a technical challenge in the investigation of their fate and transport in aquatic environments.

Centrifugation is a useful process in preparative or analytical study of CNTs (Lu et al., 2006; Arnold et al., 2008; Azoubel and Magdassi, 2010; Bonaccorso et al., 2010; Rashmi et al., 2011; Harel et al., 2013). For example, density gradient ultracentrifugation can be used for the separation or density measurement of CNTs

(Bonaccorso et al., 2010). By recording the variation of light transmission of centrifugally homogenized CNT suspensions as a function of settling time or as a function of liquid depth, the temporal or spatial distribution of CNT particles can be obtained (Azoubel and Magdassi, 2010; Rashmi et al., 2011; Harel et al., 2013). Such an analysis can provide a full view of the aggregation and deposition behavior of CNTs. Both the diffusion and sedimentation parameters of CNTs can be obtained from the collected data. However, such an analysis is only suitable for a supernatant without insoluble aggregates. In addition to an expensive ultracentrifuge, high-end instruments are needed for real-time and *in situ* monitoring.

The objective of this work is to develop a facile settling curve modeling method for quantitative description of the aggregation and deposition behavior of CNTs in aquatic environments. Pristine and surface-functionalized multi-walled CNTs, labeled as MWCNT, MWCNT-OH, MWCNT-COOH, were employed as the target CNTs. Settling curves of these CNTs, i.e., absorbance of CNT suspension versus relative centrifugal force profiles, were collected. Compared with the results from laser particle size analysis, the obtained centrifugal sedimentation rate constants from the settling curves were used as indices for the dispersion stability of CNTs in aquatic systems. The effects of water chemistry, including NOM, solution pH, and ionic strength, on the stability of CNTs were systematically investigated. Moreover, the dispersion stability of the CNTs in three surface waters was studied to explore the aggregation and deposition of CNTs, if released into aquatic environments.

1. Materials and methods

1.1. Materials

Three commercially available CNTs, i.e., MWCNT, MWCNT-OH, MWCNT-COOH, were purchased from Chengdu Organic Chemicals Co., Ltd., Chinese Academy of Sciences and used as received without any pretreatment. These CNTs were synthesized by chemical vapor deposition (CVD) from a CH_4/H_2 mixture using Ni as a catalyst, and purified by mixed $\text{H}_2\text{SO}_4/\text{HNO}_3$ solutions to remove the catalyst and amorphous carbon. Functionalized MWCNTs were prepared by oxidizing the pristine MWCNT in a KMnO_4 solution. The specific surface areas of these MWCNTs were measured with a Micromeritics ASAP 2020 analyzer (Micromeritics, USA) by using the Brunauer-Emmett-Teller (BET) model. Contents of functional groups were determined with a potentiometric titrator (Mettler Toledo T50, Switzerland). Some physico-chemical properties of the studied CNTs are summarized in Table 1.

Table 1 – Properties of the studied MWCNTs.

CNT	OD ^a (nm)	Purity (wt.%)	Length (μm)	Bulk density (g/cm^3)	S_{BET}^b (m^2/g)	CFG ^c (mM/g)
MWCNT	10–20	>95	10–30	0.22	153.3	N.D. ^d
MWCNT-OH	10–20	>95	10–30	0.22	180.2	0.098
MWCNT-COOH	10–20	>95	10–30	0.22	206.6	0.014


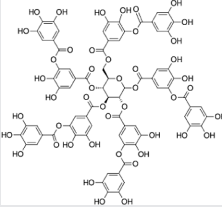
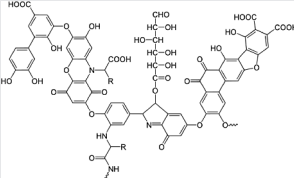
^a Outer diameter, measured by transmission electron microscopy, $n = 100$.

^b Specific surface area, calculated with the BET model.

^c Content of surface functional groups, determined by the potentiometric titration.

^d Not detectable.

Table 2 – Molecular information of gallic acid, tannic acid, and humic acid.

Name	Chemical formula	Molar weight (g/mol)	Molecular structure
Gallic acid	$C_7H_6O_5 \cdot H_2O$	188.13	
Tannic acid	$C_{76}H_{52}O_{46}$	1701.20	
Humic acid ^a	–	600–1000 ^b	

^a A model structure of humic acid, cited from Stevenson FJ (1994) Humus chemistry: genesis, composition, reactions. John Wiley & Sons, New York.

^b Provided by the supplier.

Three organic acids, gallic acid (GA), tannic acid (TA), and humic acid (HA), were used as model or real NOM. The GA monohydrate was purchased from Sinopharm Chemical Reagent Co., China. TA and HA were purchased from Sigma-Aldrich. Three water specimens from the Yangtze River, Jiuxiang River, and Xuanwu Lake were collected to evaluate the dispersion of CNTs in natural water bodies. The Yangtze River is the longest river in Asia. The Yangtze River specimen was collected from one of the tributaries near Nanjing. The Jiuxiang River is a tributary of the lower Yangtze River in the east suburb of Nanjing. The Jiuxiang River

specimen was sampled from the Xianlin campus of Nanjing University. Xuanwu Lake is a beautiful scenic spot protected by China. The Xuanwu Lake specimen was collected at Xuanwu Park in front of the Nanjing Railway Station. The collected water specimens were initially left standing for 24 hr, and then filtered by a 0.45 μm membrane. The filtrates were stored at 4°C in the dark. All experiments with these water samples were completed within one month. The molecular information of the three organic acids and the sampling sites of the three surface waters are illustrated in Table 2 and Fig. 1.



Fig. 1 – Sampling sites (red arrows) of Yangtze River, Jiuxiang River and Xuanwu Lake specimens.

Table 3 – Water quality parameters of the three natural waters.

	TN (mg/L)	SS (mg/L)	DOC (mg/L)	SUVA ₂₅₄ (L/(mg·m))
Yangtze River	2.70 ± 0.01	9.96	21.70 ± 0.20	0.25
Jiuxiang River	12.09 ± 0.12	3.68	40.58 ± 0.24	0.26
Xuanwu Lake	2.36 ± 0.01	3.84	21.48 ± 0.11	0.28

1.2. Sample preparation

NOM solutions were prepared by adding 10 mg organic acid to 1 L ultrapure water and sonicating for 3 min with an ultrasonic oscillator, KQ5200DE (200 W and 40 KHz, Kun Shan Ultrasonic Instruments Co., Ltd, China). For HA solutions, the pH was adjusted by adding a certain amount of NaOH to dissolve the HA powder. After settling overnight in the dark, all solutions were filtered by a 0.45 μm filter membrane. The final pH of the HA solution was 11.5 ± 0.3. The pH of GA and TA was 7.0 ± 0.3. Before experiments, all NOM solutions were stored in the dark at 4°C.

Glass tubes containing 3 mg of MWCNTs and 50 mL of NOM solutions were sonicated in a water bath for 4 hr. After

sonication, the suspensions were used directly for centrifugal sedimentation and particle size analysis. Each test, including the blank (no organic acid), was run at least in duplicate. Some of them were repeated more than 3 times. Effects of pH and ionic strength on the dispersion stability of MWCNT were evaluated with the same procedures. The solution pH was adjusted using NaOH and HCl. Ionic strength was adjusted using NaCl solutions of different concentrations.

1.3. Sample characterization

The dissolved organic carbon (DOC) concentration and the total nitrogen (TN) contents of water samples were detected through combustion catalytic oxidation at 680°C and 72°C, respectively (TOC-L Analyzer, Shimadzu, Japan). Specific ultraviolet absorbance (SUVA₂₅₄), a useful parameter for estimating the dissolved aromatic carbon content, was calculated using the UV absorbance at 254 nm divided by the DOC concentration. The residues on the 0.45 μm membrane were dried at 105°C in an oven to constant weight. The mass difference of the membrane before and after filtration was recorded as the content of suspended solids (SS). The characteristics of the three natural water samples are listed in Table 3. Water samples filtered through a 0.45 μm filter were analyzed by excitation–emission

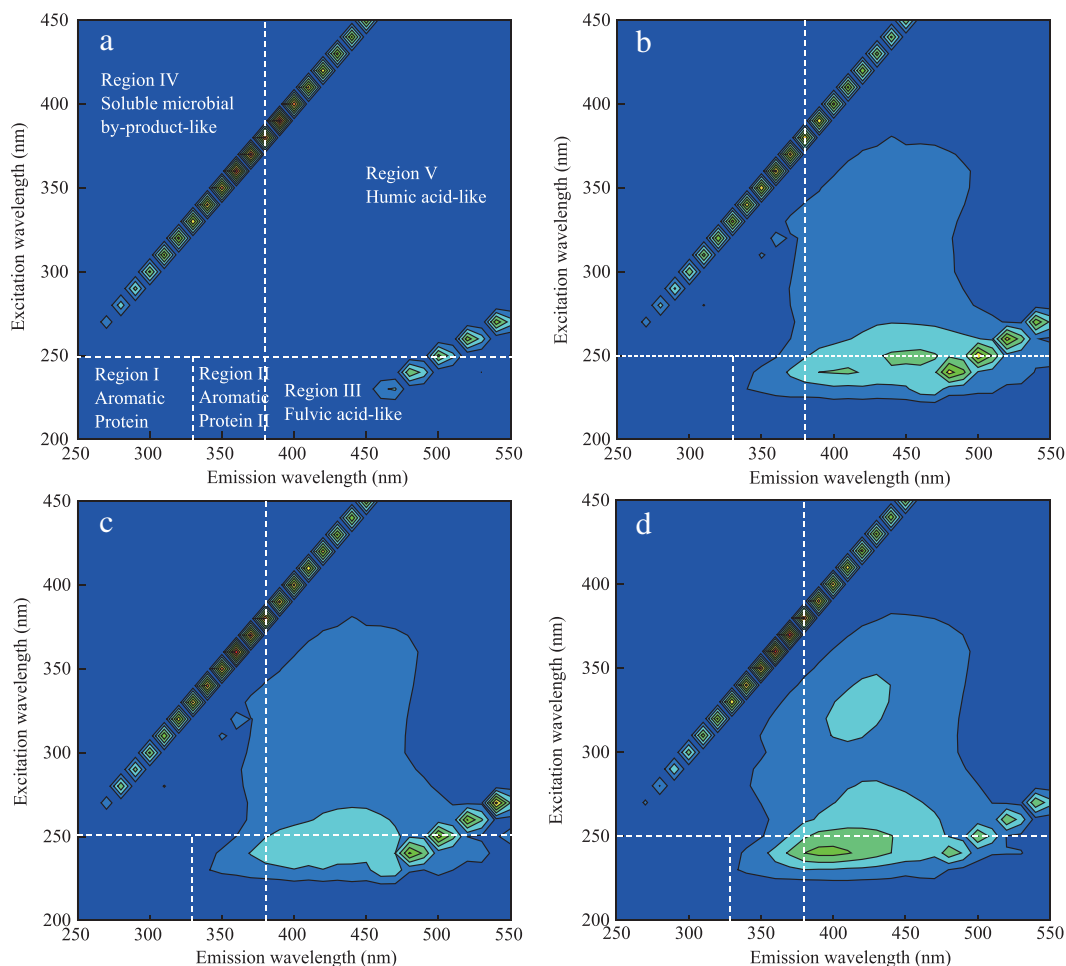


Fig. 2 – EEMs of ultrapure water (a), Yangtze River (b), Jiuxiang River (c), and Xuanwu Lake (d) water specimens.

matrix (EEM) fluorescence spectroscopy to characterize the dissolved organic matter (DOM) in the waters. The EEM results for the three surface waters are shown in Fig. 2.

1.4. Settling curve analysis

The sonicated CNT suspensions were centrifuged at relative centrifugal force (RCF) of 0.74, 1.32, 2.98, 8.3, and 16.21 kg^{-1} for 5 min at 25°C, respectively. The supernatants were collected and analyzed with a UV–visible spectrophotometer (Beijing Purkinje General Instrument Co., Ltd., China) at 500 nm. The TA and GA solutions had no absorption at 500 nm. The absorbance contribution of the HA remaining in the MWCNT supernatants was corrected using the absorbance differences at 500 nm before and after filtration of the supernatant. A control

experiment was performed by adding 3 mg of CNTs into 50 mL of ultrapure water, with otherwise identical procedures to the other experiments.

1.5. Particle size analysis

The size distribution profiles of CNT aggregates in the NOM solutions were measured immediately after sonication by a laser particle size analyzer (Winner 2008, Jinan Winner Particle Instruments Stock Co., Ltd., China). The intensity and spatial distribution of the scattering spectrum was related to the size distribution of the measured CNTs. The signals were recorded with a series of photoelectric detectors. The average value of 12 test data was calculated for the final result.

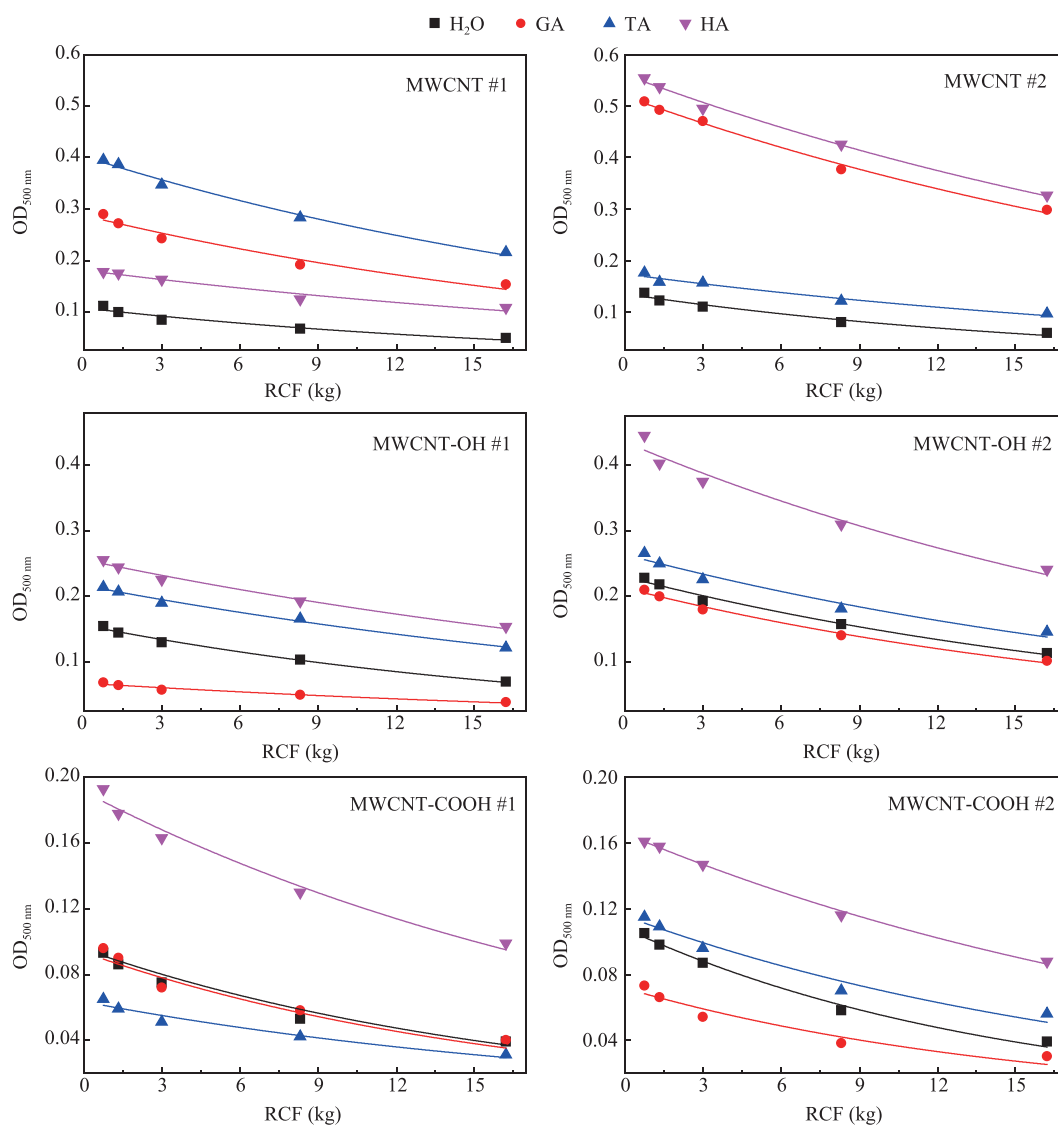


Fig. 3 – Settling profiles of MWCNTs (3 mg) in 50 mL of ultrapure water, gallic acid (GA), tannic acid (TA), and humic acid (HA) solutions at NOM concentration of 20 mg/L. Left panel: parallel sample #1, right panel: parallel sample #2. Scatter: experimental data, Curve: setting curve modeling (SCM) simulation. RCF: relative centrifugal force; NOM: nature organic matter.

2. Results and discussion

2.1. Settling curve modeling (SCM)

The optical densities of the MWCNT supernatants in four solutions at 500 nm ($OD_{500\text{ nm}}$) were collected as a function of RCF (Fig. 3). The data could be well fitted with the exponential decay model (Eq. (3)). The goodness of fit of Eq. (3) for the settling curves in Fig. 3 was relatively good (all r^2 were around 0.966 ± 0.023)

$$y = A_0 \times e^{-k_s x} \quad (3)$$

where, y is $OD_{500\text{ nm}}$, A_0 is the initial absorbance of CNT suspensions without centrifugal treatment, x is the RCF (kg), and k_s is the rate constant of centrifugal settling (kg^{-1}).

Eq. (3) can be written in a linear form by taking the natural logarithm of both sides of the equation. $OD_{500\text{ nm}}$ is a reflection of CNT concentration in aqueous solution. A large k_s indicates poor dispersion stability. Particles with larger k_s are more prone to aggregation and deposition. Therefore, k_s can be used to quantify the dispersion stability of CNT suspensions.

As illustrated in Fig. 4, a seemingly contradictory but actually interesting phenomenon existed in this case. There was a big discrepancy of $OD_{500\text{ nm}}$ for the same CNT in the three parallel runs (Fig. 4b). The discrepancy among the parallel samples might be caused by inhomogeneous dispersion of the CNTs. The sonication power used in this work was not sufficient to homogenize the CNTs. After a 4-hr sonication, the CNT suspensions were still heterogeneous. Some particles were exfoliated, while some others were still aggregated in bundles. For the MWCNT in ultrapure water, the sonication force determined the dispersion stability. However, for the MWCNT in HA solutions, apart from ultrasonic force, the interactions between MWCNT and HA also played a part. The steric repulsion caused by the adsorbed HA could separate MWCNT particles from each other. As a result, some bundles were broken, which increased

the diversity in particle size and worsened the heterogeneity of the MWCNT suspension. The real-time optical density ($OD_{500\text{ nm}}$) was sensitive to such a change. As a result, big differences were observed among the A_0 values in the three runs (Fig. 4b).

The greater discrepancy of A_0 for the MWCNT in HA suggests that, compared with the MWCNT in H_2O , the MWCNT particles in HA solution were more heterogeneous. This hypothesis was supported by the size distribution profiles of these suspensions. As shown in Fig. 5, there was only one convex peak for the MWCNT- H_2O sample (Fig. 5a), while there were 2–3 convex peaks for the MWCNT-NOM samples (Fig. 5b–d). For particle size analysis, the median diameter (D_{50} , the value of the particle diameter at 50% in the cumulative distribution) is usually used to represent the particle size. Nevertheless, D_{50} cannot reflect the particle size distribution of the sample, especially for poly-dispersed systems. As a supplement, $(D_{90} - D_{10}) / D_{50}$ (where D_{10} and D_{90} are the size values corresponding to the cumulative size distribution at 10% and 90%, respectively), is used to reflect the discrete degree of the particle size. A suspension with a larger discrete degree was more labile. The discrete degree of the MWCNT was 1.65 ± 0.15 in ultrapure water solution, while 2.81 ± 0.33 in HA solution, indicating that the size of the MWCNT aggregates was more convergent in ultrapure water than that in HA solution. This is consistent with the results shown in Fig. 4b.

Contrary to the large differences among the A_0 values, the k_s values for the corresponding samples were almost the same in the three runs (Fig. 4c), demonstrating that the k_s value was a reliable and appropriate index for the description of the dispersion stability of CNT suspensions. Meanwhile, the sensitive A_0 was a good indicator for the degree of dispersion. In this SCM analysis, only two instruments are needed, an ordinary centrifuge and a spectrophotometer. Both are basic laboratory equipment. To further evaluate the applicability of this model, effects of water chemistry on the dispersion stability of the MWCNTs were studied with the SCM analysis.

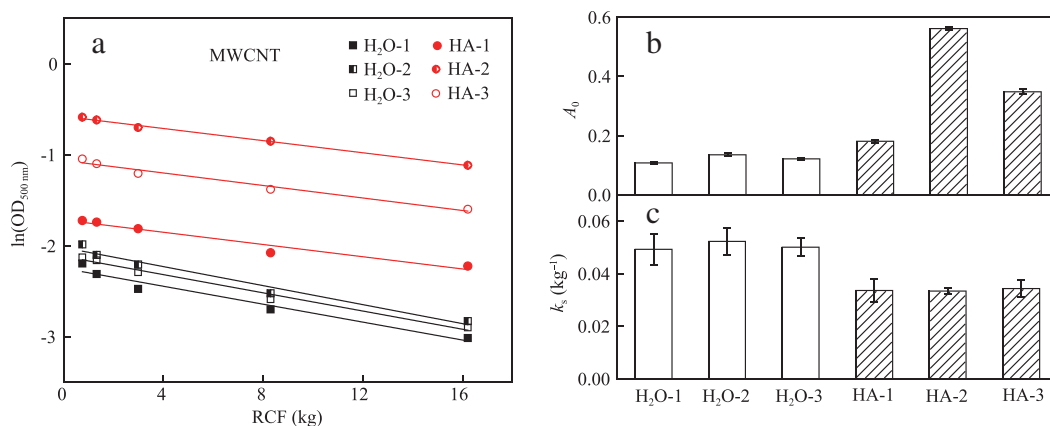


Fig. 4 – Stability profiles of the MWCNT in three parallel runs (#1, #2 and #3). (a) Settling curves in a linear form. Scatter: experimental data, Curve: SCM simulation. (b) The initial absorbance of the MWCNT suspensions. (c) k_s values. MWCNT: 3 mg in 50 mL of ultrapure water or HA solutions (10 mg/L).

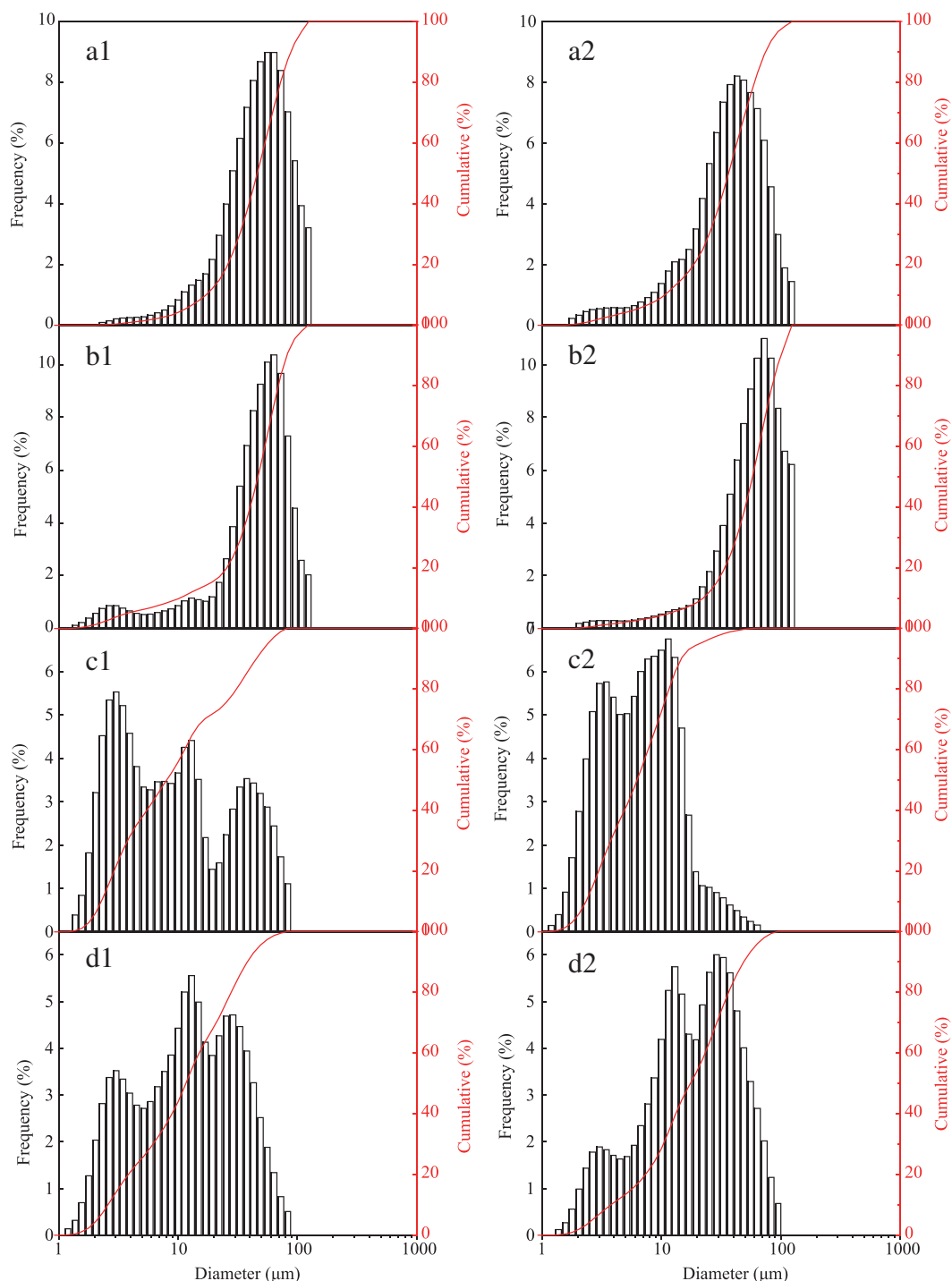


Fig. 5 – Particle size distribution profiles of MWCNT (3 mg) in 50 mL of ultrapure water (a), GA (b), TA (c), and HA (d). NOM concentration 10 mg/L. Left panel: parallel sample #1, right panel: parallel sample #2.

2.2. Effects of water chemistry

2.2.1. Natural organic matter

As aforementioned, NOM is ubiquitous in natural waters. How the dispersion and settling behavior of CNTs was affected by the NOM was investigated here with three organic acids as model or real NOM. Taking the k_s of CNTs in ultrapure water as the reference, the normalized centrifugal sedimentation

rate constant (Rk_s), i.e., the ratio of k_s (in solution) to k_s (in H_2O), was introduced here to directly reflect the influences. As illustrated in Fig. 6, the Rk_s values of the MWCNTs in the three NOM solutions were all less than 1, indicating that the organic acids could enhance the stability of both pristine and functionalized MWCNTs. Previous studies on relatively stable systems shared the same conclusion that TA (Lin and Xing, 2008; Lin et al., 2009) and HA (Saleh et al., 2008; Wang et al.,

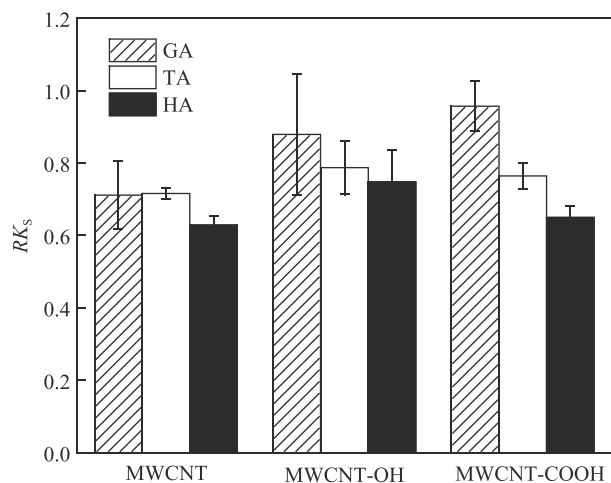


Fig. 6 – Normalized centrifugal sedimentation rate constant (Rk_s) of the MWCNTs (3 mg) in 50 mL of GA, TA and HA solutions. NOM concentration 10 mg/L.

2009) could stabilize MWCNTs in the aqueous phase. The adsorbed NOM molecules on MWCNTs caused steric repulsion between the outside walls of MWCNTs. As a result, the aggregation extent of MWCNTs was reduced. The adsorption of NOM on the surface of MWCNTs was mainly controlled by hydrophobic and π - π attractions (Islam et al., 2003; Tan and Resasco, 2005). Thus, the aromatic contents and the molecular size of NOM could greatly affect their interaction with MWCNTs (Hyung et al., 2007). The $SUVA_{254}$ of HA and TA (10 mg/L) was 3.75 and 4.99 L/(mg·m). GA, as a structural unit of TA (Table 2), has nearly the same aromaticity as that of TA. Although there was no significant difference in aromaticity, the molecular size of GA was only 1/10 of that of TA. The data shown in Fig. 6 demonstrated that under the given conditions, the stabilizing effect of NOM on the dispersion of the MWCNTs was positively related with the molecular size of the NOM. Besides the nature of NOM, the solution pH for the experiments conducted in the NOM solutions was different. For the sake of dissolution, the HA solution was alkaline whereas the TA and GA solutions were near neutral. Since there were functional groups on the surface

of the MWCNTs, the difference in solution pH might also contribute to the observed difference in stabilization, which will be further discussed in the next section.

2.2.2. Solution pH

The effect of solution pH on the dispersion stability of the MWCNT and the MWCNT-COOH is shown in Fig. 7a. Clearly, increasing the solution pH from acidic to neutral enhanced the stability of the MWCNT, whereas a further increase in solution pH led to no significant change in the stability of the MWCNT. Although the pristine MWCNT was not surface modified, according to the results from titration experiments, there were still some negatively charged functional groups on its surface. In acidic solutions, the negatively charged surface sites were neutralized, leading to a weakened repulsion between the nanotubes. When the solution pH was increased to a greater value than the point of zero charge, the surface of the MWCNT was negatively charged. The repulsion between the like charges stabilized the particles. As a result, the k_s was reduced with the increase of pH.

MWCNT-COOH, due to the relatively larger amount of surface functional groups, should be more sensitive to the solution pH than its pristine counterpart. As the solution pH was increased from 7 to 11, the k_s values were almost constant (Fig. 7a), demonstrating that the difference observed in Fig. 6 was not caused by the difference in solution pH (7 for GA and TA vs. 11 for HA).

2.2.3. Ionic strength

The adjustment of solution pH introduced ions into the solution. In natural waters, there are always varying kinds of salts. Therefore, ionic strength is an essential water chemistry parameter. With the ionic strength increased from 0 to 0.100 mol/L, the Rk_s of the MWCNT changed from 5.070 ± 0.130 to 10.434 ± 0.064 (Fig. 7b). In other words, a larger ionic strength led to worsened stability for the MWCNT. Since the CNTs were negatively charged, the increased Na^+ in solution caused increased charge screening, which would reduce the electrostatic repulsion between the MWCNT particles, and eventually resulted in increased aggregation and sedimentation. However, when the ionic strength was further increased to a certain point, the shielding effect decreased until a plateau was reached.

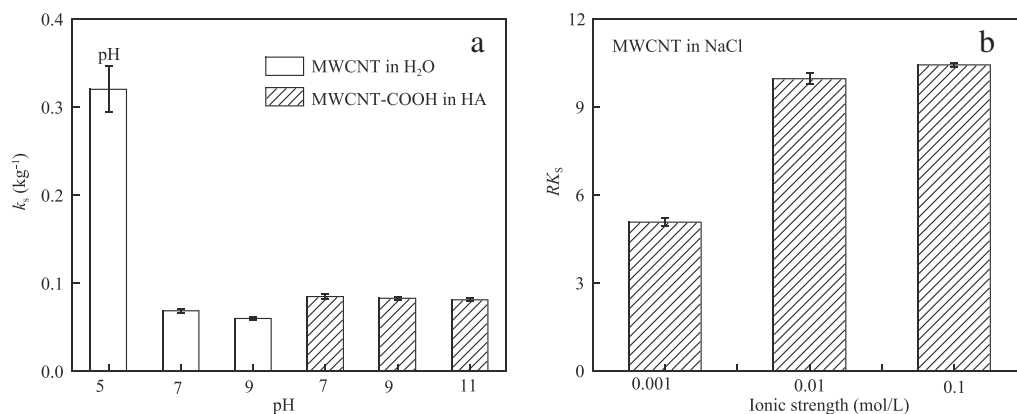


Fig. 7 – Effects of solution pH (a) and ionic strength (b) on the stability of MWCNTs (3 mg) in solution (50 mL).

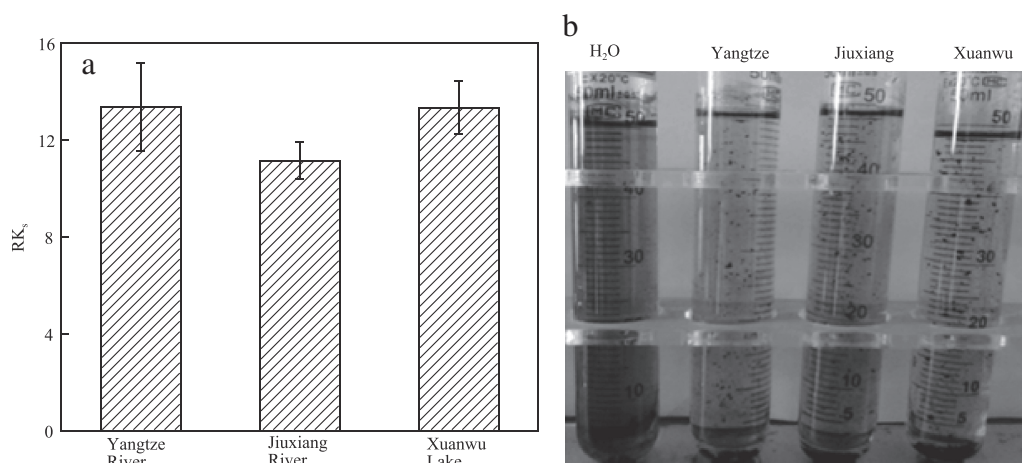


Fig. 8 – The Rk_s (a) and picture (b) of the MWCNT (3 mg) in Yangtze River, Jiuxiang River, and Xuanwu Lake water specimens (50 mL).

2.3. Dispersion stability of MWCNT in natural waters

The effects of NOM, solution pH and ionic strength on the dispersion stability of the MWCNTs derived from the SCM analysis were consistent with previous reports (Hyung and Kim, 2008; Saleh et al., 2008; Smith et al., 2009). Moreover, the system we studied better approximated complex natural environments. Therefore, we could claim that the SCM method was a reliable and feasible approach in the dispersion study of MWCNTs in aquatic environments.

Compared with other analytical centrifuge methods, the outstanding advantage of the SCM analysis developed in this work is its applicability to heterogeneous systems. Homogenization of the specimen is not required. Therefore, it is particularly suitable for the study of CNT particles in natural waters. The Rk_s of the MWCNT in the three water specimens had no great difference from each other (Fig. 8a). However, the k_s of the MWCNT in the three natural waters were almost an order of magnitude higher than that in the ultrapure water. The stability of the MWCNT in the three surface waters was markedly reduced. As shown in Fig. 8b, after sonication the MWCNT dispersed well in the ultrapure water, while bundles or clusters were formed in the natural waters. Besides the common NOM, extracellular polymeric substances (EPS) secreted by microorganisms (Staudt et al., 2004) might exist in the water samples. Due to their highly hydrophilic components (polysaccharides and proteins) and structure as a network of polymeric chains (Dogsa et al., 2005), adsorbed EPS could induce bridging between the MWCNT particles. According to previous studies (Chen et al., 2003; Mounier et al., 1999), five excitation–emission regions could be delineated from the EEM graphs. As shown in Fig. 2, the main DOM compositions in the three water samples were simple aromatic proteins such as tyrosine (Region II), fulvic acids (Region III) and humic acids (Region V), which were the typical organic matters in surface waters. However, there were still some soluble microbial by-products in the studied waters, which indicate the existence of EPS in the water samples. Due to the geographical differences, the

characteristics of the three water specimens were different. The Yangtze River water was taken from the inlet into Nanjing city. Due to the fast flow velocity, the SS was higher than those of the other two. Xuanwu Lake is landscape water, while the Jiuxiang River contains domestic sewage. The emissions of detergent and household garbage to the Jiuxiang River lead to a high nitrogen content. Water quality analysis of the three natural waters (Table 3) demonstrates that, except for SS, the Yangtze River water and the Xuanwu Lake water had similar parameters. The Jiuxiang River water had higher DOC and TN values. However, the $SUVA_{254}$ of the three surface waters showed no obvious difference. In view of the phenomenon observed in the NOM solutions, the worsened dispersion stability of the MWCNT in the natural waters might be contributed by the bridging effect of DOM.

3. Conclusions

In natural waters, CNT aggregates are heterogeneous in particle size. Their fate and transport are likely to be controlled by hetero-aggregation. With the SCM method developed in this work, we could not only intuitively reflect the dispersion of CNT suspensions through A_0 , but also could accurately quantify their stability through the k_s . The k_s values demonstrate that water chemistry had significant effects on the dispersion of CNTs. As a simple and facile approach, the SCM method provides a useful tool for the study of nanoparticles in heterogeneous systems.

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