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Heteroaggregation of Multiwall Carbon Nanotubes and Naturally Occurring Colloids in Aquatic Systems

by

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Abstract

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The heteroaggregation of engineered nanoparticles (ENPs) with naturally occurring colloids (NOCs) plays an important role in determining the ultimate fate and transport of nanomaterials in the environment. The objective of this research was to characterize the potential for heteroaggregation between functionalized multiwall carbon nanotubes (MWCNTs) with NOCs in the aquatic environment. Carboxylated MWCNTs (COOH-MWCNTs) and amine functionalized MWCNTs (NH2-MWCNTs) were studied. The natural clay kaolinite was chosen as a model NOC due to its widespread presence in the natural environment and unique charge heterogeneity. In this study, the aggregation between CNTs and kaolinite was analyzed for a range of CNT:NOC ratios and pH as well as in different source waters in a series of sedimentation and aggregation experiments. Sedimentation was monitored using ultraviolet-visible (UV-VIS) spectroscopy, while aggregation was characterized by dynamic light scattering. The heteroaggregation of the COOH-MWCNTs was found to be heavily dependent on pH and the CNT:NOC ratio. The sedimentation rate of the CNT-NOC mixture indicated by UV-VIS spectroscopy and average particle size measured by DLS both increased at low pH while the CNT
solution remained stable over time when tested at the same solution chemistry. As the CNT:NOC ratio decreased, the CNT-NOC mixture demonstrated enhanced sedimentation behavior at pH 3. The enhanced sedimentation coupled with increasing particle size of the mixture indicated the presence of CNT-NOC heteroaggregates. At higher pH, no enhanced sedimentation occurred for the range of ratios tested. The NH₂-MWCNTs were not dispersible at neutral pH were therefore only tested at pH 3. All solutions regardless of ratio indicated no significant evidence of enhanced sedimentation due to heteroaggregation for the NH₂-MWCNTs in this study. Filtered and unfiltered natural water samples from Lake Houston and the Trinity River were also analyzed and found to significantly enhance the sedimentation of the CNTs at neutral pH. The unfiltered samples exhibited enhanced sedimentation of the COOH-MWCNTs compared to the filtered samples. There was also evidence of enhanced removal of other particles present in the natural water sample due to the addition of CNTs. This indicates that the presence of CNTs could affect the transport of other contaminants in aquatic systems, altering the distribution of contaminants particularly at the sediment-water interface. These results suggest that NOCs enhance the sedimentation of CNTs in the natural environment and are highly dependent on pH and the ratio of carbon nanotube to natural colloid.
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1. Introduction and Research Objectives

Science and technology developed at the nanoscale has the potential to lead to great improvements across a wide range of disciplines. As engineered nanomaterials continue to enhance commercial and industrial goods, the production of these specialized materials will continue to grow. In order to fully realize the economic and technological advances connected with this new technology, a sustainable methodology that balances the economic gains with environmental concerns must be applied. Natural aquatic systems, including valuable freshwater sources such as rivers and streams play a key role in ensuring both human and environmental health. Accidental release, discharge from wastewater treatment plants and manufacturing facilities, as well as storm water runoff could all result in nanoparticles entering natural water systems. This could greatly increase the chance for human exposure as well as adverse environmental consequences. One example of this importance concerns the interactions taking place at the water-riverbed interface, known as the hyporheic zone.

The hyporheic zone functions as an important ecotone between stream water and the subsurface. This sensitive area influences the health of both environments, and is highly susceptible to contamination. When ENPs are released into river systems, the water containing these particles can intermix with the streambed sediment. This process is known as hyporheic exchange, and takes place at the sensitive interface between the water and riverbed (Figure 1). Previous
research has shown that the advective pumping due to hyporheic exchange as well as subsurface filtration result in significant deposition of ENPs and colloids in the streambed (Boncagni, Otaegui and Evelyn). When ENPs and ENP-associated natural colloids deposit in the sediment, they are removed from the water column and can function as an underwater source of contamination. ENP transport during hyporheic exchange will also influence the health of the benthic communities that live at this interface, and affect the overall aquatic food web. This could potentially upset the delicate ecosystem at this interface and serve as an important transport mechanism for ENPs in the aquatic environment.

In natural river systems naturally occurring colloids (NOCs) complicate nanoparticle aggregation and deposition, and must be considered in order to fully predict the transport of ENPs in the environment. Figure 2 shows the structures of potential NOC-ENP aggregates. The difference in particle size between NOCs and ENPs accounts for the complexity and variety of possible heteroaggregates. Figure 2a demonstrates the variety of possible homo- and hetero- aggregates. The systems I, II, and III represent a proposed variety of heteroaggregates with various amounts of ENP coverage, dependent on the attachment efficiency ($\alpha$) of the NOC-ENP
collisions. It is also possible that the ENPs and NOCs can undergo homoaggregation before forming large NOC-ENP heteroaggregates (Figure 2a, IV). The addition of natural organic matter (NOM) complicates heteroaggregation further, as the speed of NOM adsorption will dictate the formation of the aggregates. When preexisting or fast NOM adsorption occurs, heteroaggregation between ENPs and NOCs is hindered (Figure 2b). However, when NOM adsorption slows, heteroaggregation may be enhanced (Figure 2c). This work consists of the first efforts made in investigating heteroaggregation of ENPs and naturally occurring colloids.

![Diagram showing the structure of NOC-ENP aggregates.](image)

The primary research objective of this project was to characterize the potential for heteroaggregation between functionalized MWCNTs with NOCs in the aquatic environment. In this study, the aggregation between CNTs and kaolinite was analyzed for a range of CNT:NOC ratios and pH as well as in different source waters in a series of sedimentation and aggregation experiments. Sedimentation was monitored using ultraviolet-visible (UV-VIS) spectroscopy, while aggregation was characterized by dynamic light scattering.
2. Research Literature Review

2.1 Fate and transport of engineered nanoparticles in the environment

The fate and transport of ENPs in the natural environment plays a key role in predicting potential hazards related to nanotechnology. In the last decade, several studies have made efforts in predicting the distribution of ENPs in natural systems and their expected concentrations. In Petersen et al. 2011, several potential pathways for CNT’s release into the natural environment are outlined, including release from consumer products such as plastics or electronics, accidental or purposeful incineration, and water treatment plants (Mueller and Nowack) (Petersen, Liwen and Nikolai). These pathways all eventually lead to CNTs entering natural water systems. There have been several efforts attempting to predict the environmental concentration of ENPs in the natural environment, with a wide range of possible concentrations, ranging from 0.003 ng/L (fullerenes) to 21 ng/L (TiO₂) (Mueller and Nowack) (Gottschalk, Sonderer and Scholz). The predicted CNT concentrations range from 0.005 ng/L to 0.008 ng/L in freshwater systems (Mueller and Nowack). The concentrations of colloidal matter will typically be much higher than the ENP concentration, typically in a range of 1 mg/L to 10 mg/L (Klaine, Alvarez and Batley) (Boxall, Chaudhry and Sinclair). However, as production and applications of these materials continue to grow, the concentrations in the environment are also expected to increase (Gottschalk, Sonderer and Scholz). In a study conducted by the Woodrow Wilson International Center for Scholars Project on Emerging Nanotechnologies, the amount of consumer goods containing
nanomaterials increased by 521% (212 products to 1317 products in the inventory) from 2006 to 2011 (Woodrow Wilson International Center for Scholars). This demonstrates the importance of continuing to research ENPs as the environmental concentrations can only be expected to increase in the future.

Although the modeled present concentrations appear quite low, there are two remaining concerns: 1) Some ENPs are still predicted to exceed the predicted no effect concentrations in some areas of the world (Mueller and Nowack) and 2) the partitioning of ENPs into the sediment may result in the accumulation of ENPs in specific environments, such as in streambed sediment. The efforts in understanding and predicting the interactions at the sediment-water interface remain insufficient, and require more study. The spatial distribution of ENPs within the specific media (water, air) is not well understood. For example, the concentration of ENPs could be higher at the source of release compared to the overall system evaluated.

In order to evaluate the risks MWCNTs pose to human and environmental systems, it is important to understand both the toxicity of MWCNTs as well as potential for exposure. This literature review focuses on the current state of knowledge concerning the transport of MWCNTs in the natural environment. First, the characteristics and properties of MWCNTs along with current toxicity information will be covered in section 2.1.1. Then, a summary of current knowledge concerning the transport of MWCNT in the environment will be covered in two sections focusing on the aggregation behavior of MWCNTs in sections 2.1.2 and 2.1.3.
2.1.1 MWCNTs

Two types of multiwall carbon nanotubes (MWCNTs) were chosen as the primary ENPs of study. Carboxylated MWCNTs (COOH-MWCNTs) and amine functionalized MWCNTs (NH2-MWCNTs) were chosen to study the effect differing surface charges have on the heteroaggregation potential with NOCs. While COOH-MWCNTs carry a net negative charge, NH2-MWCNTs are positively charged at neutral pH. This allows the effect differing surface charges have on the aggregation of ENPs in natural systems to be tested. MWCNTs are used in a variety of commercial goods and industrial materials as their unique structure results in impressive chemical and physical characteristics such as heightened elasticity and strength (Baughman, Zakhidov and de Heer). MWCNTs have many unique electrical properties as well; large surface area and high electrical conductivity have led to research concerning their application as super capacitors and actuators (Terrones). They are currently being researched and optimized for use in electronic devices, building materials, and biomedical applications among many more applications that span a wide range of disciplines (Baughman, Zakhidov and de Heer) (Sanchez and Sobolev) (Endo, Hayashi and Kim). However, the data related to their fate and transport in the environment is limited. More research is required to ensure responsible use and disposal of this promising material.

There have been several studies examining potential health and environmental impacts of CNTs including studies examining the toxicity of MWCNT to a variety of organisms. MWCNT have been found to be cytotoxic to some bacteria
(E. coli) and cause mitochondrial damage in protozoa (Zhu, Li and Cal) (Seoktae Kang). Additionally, toxicity to fish and human cells has been found, as MWCNTS were found to cause direct DNA damage to human epithelial lung cells and long-term and acute toxicity in Zebrafish (Fresegnnaa) (Cheng). However, interactions with other particles in the natural environment will dictate the human and environmental exposure to MWCNT. In order to fully assess the risks connected to MWCNT production and use, a better understanding of their transport and ultimate environmental fate is required.

Sedimentation functions as a key removal mechanism of ENPs from the bulk water. Therefore, it is important to study processes that affect the settleability of these particles—primarily aggregation—in order to better model the transport of ENPs in river systems. Petrosa et al. 2010 outlines the state of research concerning aggregation and deposition studies of ENPs (Petosa, Jaisi and Quevedo). Lin et al. 2009 found that the aggregation on MWCNTs did not correlate with the diameter of the MWCNT (Lin, Liu and Yang). Hyung et al. found that the presence of a surfactant and natural organic matter resulted in stabilization of MWCNT solutions, and Kennedy et al. determined that the presence of functional groups also increased the stability of the CNT, with the hydroxyl group as the least stable group and the carboxyl group resulting in the strongest stabilizing effect (Hyung, Fortner and Hughes) (Kennedy, Hull and Steevens). Most of the aggregation studies have focused on the homoaggregation of ENPs in the environment.
2.1.2 Homoaggregation

Aggregation between monodispersed colloidal particles of the same type is known as homoaggregation. The mechanisms governing the homoaggregation of nanoparticles have been thoroughly examined, and the classical colloid theory has been found to reasonably describe these interactions (Petosa, Jaisi and Quevedo). This theory, known as the DLVO theory (named for researchers Derjaguin, Landau, Vervey, and Overbeek), has been traditionally used to describe both particle-particle aggregation as well as deposition onto a collector surface (Verwey and Overheek) (Derjaguin and Landau). This theory of colloidal stability incorporates the effects of both attractive and repulsive forces to determine the overall stability of colloidal particles. The overall interaction energy is determined by calculating the sum of electric double-layer (attractive or repulsive) and van der Waals (attractive) interactions. The electric double layer describes the distribution of ions surrounding a charged colloid. As seen in Figure 3, the positive ions are concentrated at the particle surface due to attractive forces (Clark). However, electroneutrality is preserved as both the cations and anions approach the same value as the distance from the negatively charged surface increases. The thickness of the surface charge and the ions attracted to the surface is known as the double-layer thickness. This characteristic thickness plays an important role in determining how the particle interacts with other particles or deposits onto surfaces. When particles approach each other, the double layers of each particle will interact and could
impede or aid in aggregation depending on the particle surface charge and thickness of the double layer.

Many studies have shown that the homoaggregation of ENPs generally follows the DLVO theory. Saleh et al. demonstrated that the aggregation of MWCNTs could be induced by increasing the electrolyte concentration (Saleh, Pfefferle and Elimelech). This supports the classic colloid theory as elevating the salt concentration compresses the double layer, suppressing electrostatic repulsive forces. This is in agreement with the Schulze-Hardy rule, which states that cations with higher valence are more likely to coagulate (Sano, Okamura). Many other studies have shown similar results for a variety of nanoparticles including Liu et al 2009, which found that boron nanoparticles follow aggregation patterns of classical colloids and supported the DLVO theory (Liu, Wazne and Christodoulatos). However, the DLVO theory is designed for predicting the interactions between spherical particles, so the application to ENPs with large aspect ratios such as CNTs does not yield accurate results. This prevents the direct application of the classical colloid theory to the prediction of CNT transport.

The classical colloid theory has also failed to fully explain the interactions between ENPs and differing particles in polydisperse systems or solutions of
multiple monodisperse particles. Natural organic matter (NOM) has been shown to stabilize ENPs in a variety of studies (Petosa, Jaisi and Quevedo) (Hyung, Fortner and Hughes). Since NOM is found in large quantities in natural water sources, it will play a key role in the transport of ENPs. This stabilization by NOM has been explained by steric hindrance. Steric repulsion results in the stabilization of ENPs in the environment as the presence of NOM prevents aggregation (Franchi and O’Melia) (Pelley and Tufenkji). As discussed above, surface coatings of ENPs (CNTs in particular) have also been shown to promote stability in this same manner (Kennedy, Hull and Steevens).

Recently, the focus has shifted from homoaggregation studies to those that consider ENP’s interactions with colloidal particles that are commonly found in the environment.

2.1.3 Heteroaggregation

Heteroaggregation occurs between dissimilar colloidal particles. The heteroaggregation of ENPs in the natural environment is not well understood. Galindo-Gonzalez et al. found that the sedimentation of clay particles was strongly influenced by internal colloidal interactions between magnetite nanoparticles and clay minerals (Galindo-Gonzalez, de Vicente and Ramos-Tejada). Han et al. analyzed the affect clay minerals had on the stability of surfactant-facilitated CNTs, and found that the bridging between clay mineral and CNTs by surfactant played an important role in CNT stability (Han, Zhang and Lin). A recent review concerning the fate and risks of nanomaterials in the aquatic environment warned that the
heteroaggregation of ENPs and organic colloids could drastically change their fate and potential toxicity in the environment (Batley, Kirby and McLaughlin). These results demonstrate that further analysis of the heteroaggregation of ENPs and NOCs is needed, especially concerning their role in natural aquatic systems. The information gained through this research project will aid in the creation of improved transport models that are representative of the more complex natural aquatic environment.

There have been a limited amount of studies that examine heteroaggregation of ENPs in the natural environment. In Kim et al.’s study of the effects kaolinite had on the transport of polymer-modified zero valent iron ENPs (nZVI) in porous media, it was found that heteroaggregation between kaolinite and the nZVI particles in the pH range of 6-8 was due to the charge heterogeneity on the kaolinite surface (Kim, Phenrat and Tilton).

In a recent study by Huynh et al., the heteroaggregation of MWCNTs and positively charged hematite nanoparticles was found to have an optimum ratio for aggregation. In order to distinguish homoaggregation of MWCNTs during DLS analysis, low concentrations of MWCNT (~20 µg/L) were used in order to minimize their contribution to the light scattering. A ratio of 0.0316 MWCNT-hematite was found to result in an aggregation rate more than triple the rate of the hematite ENPs homoaggregation rate in the diffusion-limited system (Huynh, McCaffery and Chen). At all concentrations, MWCNTs and the hematite nanoparticles are resistant to homoaggregation due to electrostatic repulsion due to the low ionic strength of the solutions (0.1 mM NaCl). This allows for the elucidation of several mechanisms that
result in heteroaggregation though cryoTEM analysis and DLS: (1) Electrostatic and van der Waals attractive forces cause the formation of CNT-hematite nanoparticles, but the extent of aggregation is dependent on the ratio of CNT to hematite; (2) At very low CNT-hematite ratios, the number of hematite particles will far outweigh the presence of MWCNT. Thus every collision will likely result in a heteroaggregate until the MWCNT is coated with hematite nanoparticles and stabilizes. (3) As the CNT-hematite ratio increases, a bridging effect due to the large aspect ratios of CNT. This results in the formation of a network of CNT-hematite aggregates until an optimum ratio is reached. (4) After the CNT-hematite ratio exceeds its optimum, every hematite nanoparticle will attach to a CNT, causing the formation of a CNT-hematite nanocomposite with a negatively charged arm. This results in a blocking mechanism due to the repulsion between arms, limiting any further aggregation.

In a study conducted by Afroz et al., the heteroaggregation between gold nanospheres (AuNS) and single-walled CNTs coated with pluronic acid (PA-SWNTS) was studied for a variety of electrolyte concentrations (Afroz, Khan and Hussain). This study also utilized DLS quantified aggregation rates to quantify the extent of heteroaggregation. It was determined that enhanced heteroaggregation occurred in the diffusion limited aggregation regime. It also showed enhanced aggregation due to the addition of Suwannee River humic acid in the presence of Ca$^{2+}$ ions. Three mechanisms of heteroaggregation were proposed: (1) Electrostatic interactions of AuNS dependent on the cation concentration; (2) conformational changes of the AuNS surface coatings resulting in enhanced aggregation; (3) The presence of non-
aggregating PA-SWNTS which increases the interparticle distance, thus limiting aggregation.

Although the Huynh and Afrooz studies have led to some important data aiding in the understanding of heteroaggregation in controlled systems, more research is needed for environmentally relevant systems. Both these studies focused on the heteroaggregation between two oppositely charged particles. More complex systems must be studied in order to better understand the transport of ENPs in the environment. This can be achieved by increasing the amount of NOCs studied in heteroaggregation experiments and through the testing of natural water sources.

2.2 Role of naturally occurring colloids in contaminant transport

In aquatic systems, naturally occurring colloids (NOCs) will be present in quantities that far exceed the concentration of MWCNTs. Therefore, it is important to account for interactions between MWCNTs and NOCs in order to understand and predict MWCNT transport. This section of the literature review will first describe the types of NOCs present in natural systems, focusing on the natural clay kaolinite. Then the findings from studies examining the interactions between CNTs and NOCs will be described, along with experimental findings from studies utilizing natural water sources.

2.2.1 Types of natural colloids

Colloids can be generally defined as particles between 1 nm and 1 \( \mu m \) in size. However, in order to better understand the roles colloids play in natural aquatic
environments, it is helpful to break down aquatic colloids into three classes as identified by Buffle et al: (1) compact inorganic colloids, such as kaolinite and smectite clays; (2) large biopolymers, including polysaccharides or peptidoglycans; and (3) soil-derived fulvic compounds and aquagenic refractory organic matter (AROM) (Buffle et al).

Clay minerals are key components in many natural sediments and soils and will therefore play a key role in the transport of ENPs in the environment. Clays are generally classified as having a 1:1 or 2:1 structure. 1:1 clay consists of one silica tetrahedral sheet and one alumina octahedral sheet, while a 2:1 clay mineral has one octahedral sheet in between two tetrahedral sheets. In a study by Han et al., it was found that clays can destabilize surfactant-suspended MWCNTs by two mechanisms: (1) removal of the surfactant by clay and (2) favorable interactions between the solid phase of the clay and the MWCNTs. (Han et al.) However, many studies have cited the difficulties in analytical CNT quantification as impeding the study of soil/sediment interactions with CNT (Petersen, Henry) (Zhang et al.).

### 2.2.2 Kaolinite as model colloid

The natural clay kaolinite \((\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O})\) was chosen to be the model NOC due to its widespread presence in the natural environment and unique charge heterogeneity. It is found in many locations throughout the world with large quantities found in United States (U. S. Geological Survey). Kaolinite consists of two layers: one silica tetrahedral and one alumina octahedral. In Figure 4, the 1:1 structure of kaolinite is shown (Gupta, Hamton and Stokes). The tetrahedral face
carries negative charge for a wide range of pH values (pH>4), but the surface charge on the alumina octahedral edge and face are highly pH dependent (Tombacz and Szekeres). This results in a heterogeneously charged surface in many aqueous solutions. One study determined that the silica face of the kaolinite was always negatively charged at pH>4, while the alumina face was negatively charged at pH>8 and positively charged at pH <6 (Gupta, Hamton and Stokes). However, there is no consensus on the surface charge distribution of this clay. Kaolinite can be found from different sources (subsurface, soil, and sediment) and geographies, which results in a wide range of possible characteristics. In a study by Khawmee et al., a wide range of surface charge properties were found in a sample of fourteen soil kaolinites from Thailand (Khawmee, Suddhiprakarn and Kheoruenromne). This demonstrates that even within a relatively focused sampling region, there can be a wide range of kaolinite surface properties.

### 2.2.3 Natural Water Sample Transport Studies

There have only been a few studies that examine aggregation and sedimentation of ENPs in a natural water sample. In an intensive study by Ottofuelling et al., the aggregation of TiO$_2$ nanoparticles was analyzed for a wide range of solution chemistries and in various natural water sources (Ottofuelling, Von Der Kammer and Hofmann). Colloidal stability tests demonstrated that there is
a key dependency for aggregation on pH, ionic strength, and the presence of specific divalent ions (i.e. Ca\textsuperscript{2+}). The presence of Ca\textsuperscript{2+} is thought to result in aggregation due to bridging effects and charge neutralization, which destabilize the system. A matrix-testing scheme combining the results of the synthetic water tests was able to generally match the results from the natural water samples. This methodology provides a valuable framework for intensive study of natural samples (Ottofuelling, Von Der Kammer and Hofmann). Another key insight provided by the Ottofuelling et al. study is that there are a few key parameters (such as pH and the presence of specific ions like Ca\textsuperscript{2+} that can function as “master” parameters that can help predict the sedimentation behavior of natural systems. For example, the behavior of the TiO\textsubscript{2} in the groundwater sample was similar to its behavior in lake water, despite variations in water chemistry.

In a more general study by Quik et al., the importance of NOCs in the transport of CeO\textsubscript{2} nanoparticles was shown (Quik, Hendriks and van de Meent). In this study, the sedimentation of CeO\textsubscript{2} nanoparticles in filtered (0.2 um) vs. unfiltered samples of the Rhine and Meuse Rivers were compared. It was demonstrated the unfiltered samples (containing more macromolecules than the filtered samples) settled at a much greater rate. This demonstrates the importance of natural water studies as the first step in understanding the complex interactions relating to the sedimentation and aggregation of ENPs with NOCs. Quik et al. also infer homoaggregation was more likely to transpire in systems dosed with higher concentrations of CeO\textsubscript{2} nanoparticles while heteroaggregation with natural colloids was more likely to happen at lower concentrations of CeO\textsubscript{2}. As it is more likely that
low concentrations of ENP will be present in aquatic systems, this observation
dicates the importance of studies quantifying heteroaggregation, as it is likely to
play an important role in the transport of ENPs in the environment.
3. Methods and Materials

3.1 MATERIALS

3.1.1 MWCNTs

COOH-MWCNT with an average diameter of 15 ± 5 nm and length 1-5 μm were obtained from Nanolab, Inc. (Newton, MA). As outlined by the manufacturer, the COOH-MWCNTs were synthesized by chemical vapor deposition (CVD) using a HNO3/H2SO4 mixture. The COOH-MWCNT are 2-7% wt COOH by titration, as reported by the manufacturer.

An aqueous stock suspension of COOH-MWCNT was prepared by adding 5 mg COOH-MWNCT to 100 mL ultrapure water and dispersed by a sonicating probe (Vibra-Cell, VCX 500, Sonics and Material, Newton, CT) for at 50 W for 10 min, 75 for 10 min, and 100 W for 10 min (total 30 min). An ice bath was used to prevent overheating.

The NH₂-MWCNT with an average diameter of 15±5 nm and length 1-5 μm was obtained from Nanolab, Inc. (Newton, MA). As detailed by the manufacturer, the NH₂-MWCNT were prepared by reacting COOH-MWCNTs with ethylene diamine (H₂N-CH₂-CH₂-NH₂) resulting in a primary amine group added to the carbon chain. The stock suspension was sonicated by a sonicating probe at 50 W (Vibra-Cell, VCX 500, Sonics and Material, Newton, CT) for an hour before experimental use.

The solution of NH₂-MWCNT was challenging to disperse and only used in the pH 3 sedimentation experiments. Several attempts were made in dispersing the NH₂-MWCNT for experimental use. The pH was varied from 5.5 to 3 and various
sonication techniques were employed. The NH$_2$-MWCNT was dispersed by a sonicating probe (Vibra-Cell, VCX 500, Sonics and Material, Newton, CT) for at 100 W for 30 min increments for up to 2 hours in varied attempts to better stabilize the solution. Both a microtip sonication probe (1/8” tip diameter) and standard sonication probe (1/2” tip diameter) were used in attempts to better disperse the NH$_2$-MWCNT. Little difference in dispersal success was seen throughout each trial.

3.1.2 Kaolinite

The kaolin clay (kaolinite) was purchased from EMD Chemicals (Gibbstown, NJ). The average diameter of the kaolinite was 0.5 μm as reported by the manufacturer and validated by DLS (see section 3.2.1 for details concerning kaolinite characterization). Before use, the kaolinite powder was presettled for 24 hours. The top 80% of the supernatant was collected from a highly concentrated mixture and a 100 mg/L solution was prepared by diluting the concentrated solution. Reagent-grade NaCl, HCL, NaOH with a purity of 90% or above were used throughout the experiments for ionic strength and pH adjustments. A Barnstead Epure water system (Dubuque, IA) was used to produce the deionized water used in the preparation of all solutions.

3.1.3 Natural Water Samples

Two natural water samples were collected from the City of Houston’s East Water Purification Plant (EWPP). The EWPP has a design capacity of 360 MGD and an average daily flow of 275 MGD. The source waters of the EWPP consist of inflow from the Trinity River, Lake Houston, and Lake Conroe. Samples from the Trinity
River and Lake Houston inlets were sampled in 500 mL amber glass jars. The pH of the natural water samples was 7.4 ± 0.5. A portion of all samples was filtered through a 0.2 μm cellulose acetate membrane (Whatman, Austria). All samples were stored in the dark at 4°C.

3.2 METHODS

3.2.1 COOH-MWCNT, Kaolinite, and Natural Water Sample Characterization

The COOH-MWCNT and kaolinite were characterized by UV-Vis spectrophotometry and dynamic light scattering (DLS). A high-resolution dual beam UV-Vis spectrophotometer (UV-2550, Shimadzu Scientific Instruments, Columbia, MD) was used for all experiments. Quartz crystal cuvettes with a path length of 1 cm were used for all experiments. A Zen 3600 Zetasizer Nano (Malvern, Worcestershire, UK) with a fixed wavelength of 633 nm with a He-Ne laser was used for all experiments. The intensity of the light scattering was measured at 173°. Folded capillary cells (Malvern, Worcestershire, UK) were used to measure the mobility of the COOH-MWCNT and kaolinite by phase analysis light scattering (PALS). The pH range for the mobility measurements was 1.5 – 7.5. Each sample was measured three times at 23°C. The particle size of the COOH-CNT and kaolinite was also measured. Each measurement duration consisted of 20 runs with an equilibration time of 5 minutes. The results of the characterization experiments are shown in section 4.1.

The natural water samples collected from the EWPP plant were analyzed for a wide range of compounds within 24 hours of sampling. The EWPP plant conducts
daily testing of both the Trinity River and Lake Houston feed waters using standard EPA testing methods. The detailed water analysis report is listed in section 4.1.

3.2.2 Screening Experiments

Initial screening experiments were conducted to choose the appropriate ionic strength to identify conditions under which heteroaggregation can be detected and distinguished from homoaggregation. At higher ionic strength, the increased potential for homoaggregation would obscure any evidence of heteroaggregation. Nine 20 mL scintillation vials with 5 mg/L COOH-MWCNT and 10 mg/L kaolinite were dosed with varying amounts of NaCl (1 mM – 100 mM). The solutions were mixed for 1 hr and visually inspected for evidence of aggregation. The solution with 1 mM NaCl showed visual aggregates, and was therefore chosen as the ionic strength to be used throughout the remaining experiments. This ionic strength is within the range of electrolyte concentrations seen in the natural environment, as typically freshwater salinity is less than 0.5 ppt (US Navy Office of Research).

3.2.3 Sedimentation Experiments

The objective of the sedimentation experiments was to determine the effect different ratios of CNT-NOC at varied pH values had on the sedimentation behavior of the COOH-MWCNT. UV-Vis spectrophotometry was used to measure the change in absorbance over 42 hour periods. Several 20 mL samples of differing ratios of CNT:NOC were prepared. The concentration of kaolinite as the NOC was held constant at 10 mg/L throughout all experiments. The CNT concentration was changed to create suspensions of varying CNT:NOC ratios of 0.5, 0.1, 0.02, 0.01, and
0.005. This captures a wide range of possible CNT:NOC concentrations. The ionic strength of each sample was increased to 1 mM by the addition of NaCl. Samples of the CNT-Kaolinite mixture, CNT control of the corresponding CNT concentration for each ratio (5 mg/L, 1 mg/L, 200 µg/L, 100 µg/L, and 50 µg/L, respectively), and a kaolinite control were compared to determine the effect differing ratios of CNT:NOC had on the sedimentation behavior of CNT. 50 µg/L was the lowest concentration of MWCNT's able to register above the detection limit of the instrument (± 0.002 abs). After testing different mixing times, a 1 hr mixing time at approximately 400 rpm was chosen to enhance opportunities for aggregation. A high-resolution dual beam UV-Vis spectrophotometer (UV-2550, Shimadzu Scientific Instruments, Columbia, MD) was used for all experiments. Absorbance was measured at 255 nm initially, after 1 hr mixing, at 20 hrs, and 42 hrs. During the 42 hour experiment, the samples were not disturbed or moved. 3 mL were sampled from the middle of the scintillation vial for each measurement. A quartz crystal cuvette was used for all measurements.

Three pH ranges were tested. A low pH of 3.0±0.5, the unadjusted pH of 5.5±5, and a neutral pH of 7.0±0.5 were chosen in order to capture both the sedimentation behavior for both a wide range of pH values and at environmentally relevant levels. Higher pH values were not chosen as the CNT and kaolinite suspensions will be very stable in the upper pH range. The pH was adjusted by adding 1 N, 0.1 N, or 0.01 N HCL or NaOH dropwise as needed.
3.2.4 Aggregation Experiments

Aggregation Experiments were performed to track the aggregation of the CNT-NOC suspensions. Dynamic light scattering (DLS) was used to measure change in particle size over time. A Zen 3600 Zetasizer Nano (Malvern, Worcestershire, UK) with a fixed wavelength of 633 nm with a He-Ne laser was used for all measurements. The intensity of the light scattering was measured at 173°. Each sample was measured three times at 23°C. Each measurement duration consisted of 20 runs with an equilibration time of 5 minutes. Vials identical to the samples prepared for the sedimentation experiments were prepared and a 1 mL sample volume was analyzed. The vial was gently mixed before each sampling to suspend any settled particles to account for any large aggregates that may have formed over time. A disposable polystyrene cuvette (Sarstedt, Germany) was used in all experiments. Particle size (intensity mean in nm) was measured initially, after 1 hr mixing, and at 42 hours to track changes over the same timeframe tracked in the sedimentation experiments. The high polydispersity of the solutions limited the applicability of the z-average diameter calculations.

In order to optimize the DLS measurements of the diameter of the CNT-NOC heteroaggregates, low concentrations of COOH-MWCNTs were used compared to the kaolinite. This allowed the light scattering to be primarily due to the kaolinite particles, which minimizes the interference due to non-aggregated MWCNTs. A similar approach is used by Huynh et al., to measure the heteroaggregation of MWCNTs with positively charged hematite nanoparticles and Ferretti et al. to track
the hydrodynamic diameter of hematite nanoparticles and extracellular polysaccharides (Huynh, McCaffery and Chen), (Ferretti, Zhang and Buffle).

While the Huynh group was able to use concentrations of MWCNTs that were low enough to result in a scattered light intensity 20 times lower than the accompanying hematite particles, this study was limited by the detection limit of the UV-Vis, which limited the concentrations of MWCNTs in this study. Figure 5 shows the scattered light intensities of the kaolinite and MWCNTs in a 1 mM NaCl solution at the same laser intensity. Although the scattered light intensity of the MWCNTs was still lower than the kaolinite particles (approximately 6 times lower for 200 μg/L) the contribution of the MWCNTs to the light scattering will not be as negligible as in previous studies.

![Figure 5: Derived count rate (kcps) of 10 mg/L kaolinite and 200 ug/L COOH-MWCNT in 1 mM NaCl solution](image)

Therefore, the applicability of the particle size measurements for this study will be limited.
Time-resolved DLS measurements were also performed. Instead of 42 hr timelines, the vials of CNT-NOC mixtures were prepared and then immediately sampled for DLS analysis over a period of 2 hrs. Each vial was briefly shaken before sampling, and a 1 mL volume was analyzed every 5 min for two hours.

Time resolved, 30 min aggregation experiments were also performed at lower concentrations of COOH-MWCNT in additional attempts to minimize the scattering caused by CNT. Additional DLS trials were conducted for concentrations of COOH-MWCNT ranging from 20 µg/L to 5 µg/L. The scattering caused by the 10 µg/L and 5 µg/L was low enough to produce an insufficient signal from the Zetasizer, indicating that the light scattering at these low concentrations is negligible. Therefore, time resolved experiments were repeated at these low concentrations in attempts to minimize the error of the measurements. In order to preserve the original CNT-NOC ratios tested, the kaolinite concentration used in this set of experiments was 1 mg/L, resulting in CNT-kaolinite ratios of 0.01 and 0.005.

3.2.5 Natural Water Experiments

The sedimentation experiments were repeated using natural water samples collected from the Houston East Water Purification Plant to study the effect natural water chemistry has on the aggregation of MWCNTs. Samples were prepared in the same manner as the initial sedimentation experiments, although the natural water sample was used in the preparation of the 20 mL vials rather than DI water. A portion of all natural water samples was filtered through a 0.2 µm filter to examine the effect larger macromolecules and colloidal particles have on the sedimentation
behavior of MWCNTs in natural systems. A quartz crystal cuvette was used for all measurements.

### 3.2.6 Cryo-TEM

In order to better study the morphology of the CNT-Kaolinite heteroaggregates, a protocol for the imaging of the samples was developed. In order to preserve the original heteroaggregate structures, transmission electron microscopy enabled with a cryogenic sample holder was chosen. A cryo-enabled transmission electron microscope (Cryo-TEM) operating at 100 kV (JEM-2010F FasTEM, JEOL USA, Peabody, MA) was used to examine the CNT-NOC heteroaggregate structures formed at the ratios 0.5, 0.02, and 0.01. Copper Quantifoil TEM grids (Ted Pella, Redding, CA) were used for all experiments. Suspensions were prepared using the same protocol as the sedimentation experiments with an ionic strength of 1 mM NaCl at pH 3, 5.5, and 7. The CNT and kaolinite concentrations were tripled from those previously used in order to optimize the number of heteroaggregates seen on each grid. The samples were mixed for 1 hr at approximately 400 rpm immediately before the vitrification process.

The TEM grids were ionized in a high vacuum evaporator for 30 s to increase the hydrophilicity of the grid surfaces before analysis. The ionized grid was then placed into a temperature chamber of an automated vitrification robot (Vitrobot™) for specimen vitrification. The temperature and relative humidity of the chamber was maintained at approximately 22 °C and > 90%, respectively. 10 µL of the CNT-
Kao suspension was then placed on the prepared grid. The sample is then transferred in liquid nitrogen to the cryo holder and placed in the TEM for imaging. The cryo holder keeps the sample at a temperature below -160 °C for the duration of imaging. 15-20 minutes are needed for the sample to stabilize before imaging. The imaging of the CNT-Kaolinite suspensions is currently ongoing and the results from these trials are pending.

4. Results and Discussion

4.1 Characterization of COOH-MWCNT, Kaolinite, and Natural Water Samples

The COOH-MWCNT was characterized by UV-Vis spectrophotometry and DLS. The UV-Vis spectra of the COOH-MWCNT is shown in Figure 6.

![UV-Vis absorbance spectra for 10 mg/L COOH-MWCNT](image)

Figure 6: UV-Vis absorbance spectra for 10 mg/L COOH-MWCNT

The absorbance in the sedimentation experiments was measured at 255 nm corresponding with the peak absorbance found in the COOH-CNT spectra. This
wavelength was also chosen due to the absorptivity of the MWCNTs relative to kaolinite. This also allowed for the testing of lower, more environmentally relevant concentrations of COOH-MWCNTs. The electrophoretic mobility is shown for the COOH-CNTs plotted against that of kaolinite in Figure 7. A concentration of 10 mg/L of kaolinite and 5 mg/L solutions of COOH-MWCNT were used in the electrophoretic mobility analysis.

![Figure 7: Electrophoretic mobility of COOH-MWCNT and kaolinite](image)

The UV-Vis spectrum of the kaolinite is shown in Figure 8. The absorbance of the kaolinite is not negligible at 255 nm, so a kaolinite control was analyzed for all experiments to account for the kaolinite's contribution to the CNT-NOC mixture's absorbance.
Figure 8: UV-Vis absorbance spectra for 10 mg/L kaolinite

The electrophoretic mobility is shown plotted against that of the COOH-MWCNTs in Figure 7. Although the reported range of the isoelectric point (IEP) for many reference kaolinite samples is around 2.5-3, the inability for this sample to reach a positive value within this pH range is not unprecedented. In the study by Khawmee et al., only one out of the fourteen kaolinite samples tested was able to reach an IEP value (Khawmee, Sudhiprakarn and Kheoruenromne). This demonstrates that there is a net negative charge present on the kaolinite surface.

The characterization data for the natural water samples is below in Table 1. This data falls into a similar range of values reported for other natural bodies of water. A comparison of other natural water bodies is seen in Table 2. These results will influence the discussion of the natural water data in section 4.12.
Table 1: Water quality characteristics for the Trinity River and Lake Houston inflow to the EWPP plant

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Trinity River</th>
<th>Lake Houston</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>mg/L</td>
</tr>
<tr>
<td>Alkalinity</td>
<td>90</td>
<td>84</td>
<td></td>
</tr>
<tr>
<td>Bromide</td>
<td>0.16</td>
<td>&lt;0.10</td>
<td>mg/L</td>
</tr>
<tr>
<td>Calcium</td>
<td>39</td>
<td>22</td>
<td>mg/L</td>
</tr>
<tr>
<td>Chloride</td>
<td>38</td>
<td>41</td>
<td>mg/L</td>
</tr>
<tr>
<td>Conductivity</td>
<td>412</td>
<td>348</td>
<td>μmhos/cm</td>
</tr>
<tr>
<td>Iron (Fe)</td>
<td>0.57</td>
<td>0.16</td>
<td>mg/L</td>
</tr>
<tr>
<td>Magnesium</td>
<td>3.9</td>
<td>2.6</td>
<td>mg/L</td>
</tr>
<tr>
<td>Manganese (Mn)</td>
<td>0.06</td>
<td>0.11</td>
<td>mg/L</td>
</tr>
<tr>
<td>Nitrate</td>
<td>0.11</td>
<td>&lt;0.04</td>
<td>mg/L</td>
</tr>
<tr>
<td>Nitrite</td>
<td>&lt;0.04</td>
<td>&lt;0.04</td>
<td>mg/L</td>
</tr>
<tr>
<td>Potassium</td>
<td>6.1</td>
<td>5.7</td>
<td>mg/L</td>
</tr>
<tr>
<td>Silica (SiO₂)</td>
<td>5.2</td>
<td>3</td>
<td>mg/L</td>
</tr>
<tr>
<td>Sodium</td>
<td>23</td>
<td>27</td>
<td>mg/L</td>
</tr>
<tr>
<td>Sulfate</td>
<td>43</td>
<td>12</td>
<td>mg/L</td>
</tr>
<tr>
<td>Total Hardness (CaCO₃)</td>
<td>115</td>
<td>66</td>
<td>mg/L</td>
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<tr>
<td>TOC</td>
<td>5.7</td>
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<td>mg/L</td>
</tr>
<tr>
<td>Total Phosphate</td>
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<td>mg/L</td>
</tr>
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<td>Total Residual Chlorine</td>
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<td>0.1</td>
<td>mg/L</td>
</tr>
<tr>
<td>TSS</td>
<td>13</td>
<td>13</td>
<td>mg/L</td>
</tr>
<tr>
<td>TDS</td>
<td>227</td>
<td>191</td>
<td>mg/L</td>
</tr>
<tr>
<td>Turbidity</td>
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<td>NTU</td>
</tr>
<tr>
<td>UV 254</td>
<td>0.132</td>
<td>0.163</td>
<td>cm⁻¹</td>
</tr>
</tbody>
</table>

Table 2: Comparative water quality values from different source waters. Rain water (adapted from Ottufoelling).

<table>
<thead>
<tr>
<th></th>
<th>Rain water</th>
<th>Lake Water</th>
<th>River Water</th>
<th>Sea Water</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na+2</td>
<td>1.1</td>
<td>0</td>
<td>3.1</td>
<td>11145</td>
</tr>
<tr>
<td>K+</td>
<td>0.3</td>
<td>0</td>
<td>0.9</td>
<td>414</td>
</tr>
<tr>
<td>Mg+2</td>
<td>0.4</td>
<td>6</td>
<td>8.7</td>
<td>1339</td>
</tr>
<tr>
<td>Ca+2</td>
<td>1</td>
<td>45.6</td>
<td>43</td>
<td>429</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>1.1</td>
<td>2.5</td>
<td>2.8</td>
<td>20065</td>
</tr>
<tr>
<td>HCO₃⁻</td>
<td>1.2</td>
<td>12.6</td>
<td>9.4</td>
<td>1787</td>
</tr>
<tr>
<td>SO₄⁻₂</td>
<td>4.2</td>
<td>15</td>
<td>53</td>
<td>230</td>
</tr>
</tbody>
</table>
4.2 Sedimentation Experiments, COOH-MWCNT at pH 5.5

At pH 5.5, the COOH-MWCNTs appear to remain stable for most of the ratios tested. Figure 9 shows the results of sedimentation experiment at pH 5.5. At ratio 0.5, the absorbance of the CNT-NOC mixture remains constant throughout the experiment. For the 0.5 ratio in Figure 9, the combined absorbance of the 5 mg/L CNT control and the 10 mg/L NOC control is approximately the total absorbance of the mixture. This correlation implies that the two particles are not interacting heavily; there is no notable shift in the absorbance of the mixed solution when compared to the stable controls. However, this sample was the only vial in this experimental set to show visual signs of sedimentation. However, since there is no notable shift between the CNT-NOC mixture and the sum of the controls, the sight of black aggregates could be due to the slight sedimentation of the COOH-MWCNT. Other than the visual evidence of a few dark, black particles, there is no further evidence of enhanced sedimentation or aggregation due to the presence of kaolinite for this concentration of COOH-MWCNT.

In Figure 9, a CNT:NOC ratio of 0.1 (1 mg/L COOH-MWCNT, 10 mg/L kaolinite) is shown to behave similarly to the previous ratio. Again, each sample (both the CNT-NOC mixture and the corresponding controls) remains stable throughout the experiment. There is a slight discrepancy in the absorbance of the mixed solution and the combined controls, but it is not indicative of any strong particle-particle interactions. The sum of the controls is slightly less than the absorbance of the mixture, indicating a potential stabilizing effect due to the
presence of kaolinite. However, the stabilizing effect at this ratio is not as prevalent as it is in the 0.02 and 0.01 CNT:NOC mixtures.

For the ratios 0.02 and 0.01, the sum of the controls falls below the mixture’s absorbance. Again, this could imply a stabilizing effect due to the interactions between the kaolinite and COOH-MWCNT. As the ratio increases, the stabilizing effect of the kaolinite addition on the COOH-MWCNT becomes more prevalent for the ratios 0.02 and 0.01. Additional DLS measurements were made in order to further examine this potential stabilization effect.

In the final ratio tested, 0.005, there is a slight difference between the two controls and the mixed solution. However, at this low ratio, the measurement limit of the instrument begins to limit the accuracy of the data. Since the UV-Vis is accurate to ± 0.002 abs, this is not considered a significant difference. Therefore, there is no indication of enhanced sedimentation due to the heteroaggregation of CNT and kaolinite at this pH and low ratio.
Figure 9: Absorbance of COOH-CNT-Kaolinite mixture ("CNT:NOC"), COOH-CNT alone ("CNT Control"), and Kaolinite alone ("NOC control") at pH 5.5 and ionic strength 1 mM over 42 hours

There are several notable limitations to this form of analysis. The main problem is the inability to measure the MWCNT concentration in a polydisperse mixture. The absorbance due to the kaolinite present in the mixed solution was
significant enough to prevent the MWCNT concentration in the mixture to be calculated. This is problematic, as the environmentally relevant concentrations of CNT in the environment fall in a low concentration range. UV-Vis spectrophotometry would not be suited to examine any lower ratios than 0.005. Other methods of analysis such as fluorescently tagging the CNT for analysis could provide useful data at lower concentration ranges. Another useful method is radioactive tagging using C14.
4.3 Aggregation Experiments, COOH-MWCNT at pH 5.5

In Table 3 below, the intensity mean (nm) measured by DLS for the COOH-MWCNT at pH 5 is shown. The CNT:NOC mixture and the NOC control remain stable after 1 hr mixing, but both show signs of aggregation after 42 hours. The kaolinite control has greater variability compared to the other samples tested, which introduces error into the measurements. Because both samples behave similarly, this data does not indicate evidence of enhanced aggregation of the CNT:NOC mixture at this ratio. There is also no evidence of steric stabilization, as the NOC control also shows signs of aggregation. This does not support the enhanced stabilization as indicated in the corresponding sedimentation experiments at this ratio.

However, it is important to again point out the limitations of this method. Although it is assumed that the COOH-MWCNT’s contribution of light scattering is negligible, it is possible that there is some interference caused by the presence of the non-aggregated COOH-MWCNTs. This could lead to underestimating the intensity mean, as the smaller-sized MWCNTs could cause the mean to shift towards a smaller value than the actual diameter. One method to overcome this limitation would be to preserve the ratio of CNT:NOC but drop the concentrations of both materials. As the concentration of COOH-MWCNTs decreases, the accuracy of the DLS measurements of the CNT:NOC mixture will increase. However, the detection
limit of the spectrophotometer used in the sedimentation experiments limited the possible concentrations of MWCNTs used in this study.

Table 3: Intensity Mean (nm) for 0.01 CNT:NOC ratio for COOH-MWCNT at pH 5.5 (± 1 SD)

<table>
<thead>
<tr>
<th>Time (hrs)</th>
<th>CNT:NOC</th>
<th>NOC Control</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>677 ± 189</td>
<td>773 ± 250</td>
</tr>
<tr>
<td>1</td>
<td>523 ± 87</td>
<td>747 ± 251</td>
</tr>
<tr>
<td>42</td>
<td>1015 ± 264</td>
<td>1570 ± 342</td>
</tr>
</tbody>
</table>

4.4 Sedimentation Experiments, NH2-MWCNT at pH 3

The NH2-MWCNTs could not be dispersed at pH 5.5 or pH 7. Therefore, sedimentation experiments were only feasible to perform at low pH levels where a greater level of dispersal was reached. However, the solution of NH2-MWCNT could not completely be cleared of pre-formed homoaggregates, even after extensive sonication. Therefore, the results from this data set are not as useful in understanding the potential for heteroaggregation between the CNT and kaolinite.

At pH 3, all samples quickly settled out of solution. At ratio 0.5, the absorbance of the CNT-NOC mixture and both controls settle out of solution within the first few hours. In Figure 10, for the 0.5 ratio, the combined absorbance of the 5 mg/L CNT control and the 10 mg/L NOC control is approximately the total absorbance of the mixture. This correlation implies that the two particles are not interacting heavily; there is no notable shift in the absorbance of the mixed solution when compared to the stable controls. However, the presence of large NH2-MWCNTs homoaggregates could have increased the rate of the kaolinite settling due to differential settling. However, there is not enough evidence from sedimentation
experiments alone to justify this explanation. There is no evidence of enhanced sedimentation or aggregation due to the presence of kaolinite for this concentration of NH$_2$-MWCNT.

The CNT:NOC ratio of 0.1 also quickly settles out of solution. There is a slight discrepancy in the absorbance of the mixed solution and the combined controls, but it there is not enough supporting evidence to interpret this difference as significant.

Similarly, for the ratios 0.02, 0.01, and 0.005, all mixtures quickly settle out of this solution at this low pH. The effect the positive surface charge of the NH$_2$-MWCNTs has on the interactions with the negatively charged NOC cannot be deduced, as the preformed aggregates prevent the NH$_2$-MWCNTs from interacting freely with the surrounding particles. However, if the NH$_2$-MWCNTs were stabilized using a surfactant, as is common practice, the positive charge would also be neutralized in the process. Intense, lengthy sonication also effects the surface composition of the NH$_2$-MWCNTs and leads to further difficulty in interpreting the results. More efforts are needed in the stabilization of NH$_2$-MWCNTs before they will work as a viable experimental subject without surfactant-enabled stabilization.
Figure 10: Absorbance of NH2-MWCNT-Kaolinite mixture ("CNT:NOC"), NH2-MWCNT alone ("CNT Control"), and Kaolinite alone ("NOC control") at pH 3 and ionic strength 1 mM over 42 hours.
4.5 Sedimentation Experiments, COOH-MWCNT at pH 3

At pH 3, the COOH-MWCNTs begin to show evidence of enhanced sedimentation at specific ratios. At ratio 0.5, the absorbance of the CNT-NOC mixture, CNT control, and NOC control remain generally constant throughout the experiment, and slightly drops after 20hrs. In Figure 11, for the ratio 0.5, the combined absorbance of the mixture and the controls is very similar. This correlation implies that the two particles are not interacting heavily; there is no notable shift in the absorbance of the mixed solution when compared to the stable controls. There is no evidence of enhanced sedimentation or aggregation due to the presence of kaolinite for this concentration of COOH-MWCNT.

The CNT:NOC ratio of 0.1 begins to show a shift from the control values after 20 hrs. Although it is a slight change when compared to the 0.5 ratio, it does mark the beginning of the ratio-dependant behavior at this pH. After the 20 hr mark, the CNT:NOC mixture begins to behave differently than the combined controls. This implies that there are some ongoing interactions between the COOH-MWCNT and the kaolinite at this pH.

These differences begin to become more apparent at the lower ratios tested. In the ratios of 0.02, 0.01, and 0.005, there is evidence of enhanced sedimentation due to the interactions between the COOH-MWCNT and kaolinite. Here, the behavior of the mixed solution varies greatly with the two controls. This demonstrates that the particles are not acting independently from one another and are enhancing the
sedimentation of both particles. This could be due to the decreasing electrophoretic mobility of the kaolinite and CNT at lower pH.

As seen in Figure 7, the electrophoretic mobility of the two solutions is at the value closest to neutral for the tested pH values. Although the mobility becomes less negative as pH decreases, it does not ever reach an IEP. This leads to a destabilizing effect, which causes the particles to be more likely to aggregate and settle out of solution. However, since the IEP is never reached, this implies that only part of the kaolinite surface may be positively charged, but retains a net negative charge. This leads to more unpredictable aggregation behavior. The data from this set implies that the ratio of CNT:NC plays an important role in determining the surface interactions between the CNT and kaolinite that would lead to aggregation. More research concerning the aggregate structure using microscopic techniques would provide valuable data on the mechanisms of aggregation for this complex system.

Because of this evidence of enhanced sedimentation, aggregation studies using DLS were performed for the ratios of 0.02, 0.01, and 0.005 in order to examine the potential for aggregation at this pH.
Figure 11: Absorbance of COOH-MWCNT-Kaolinite mixture ("CNT:NOC"), COOH-MWCNT alone ("CNT Control"), and Kaolinite alone ("NOC control") at pH 3 and ionic strength 1 mM over 42 hours
4.6 Aggregation Experiments, COOH-MWCNT at pH 3

Aggregation experiments following the same timeframe of the sedimentation experiments were performed for the ratios that demonstrated signs of enhanced sedimentation. For the ratios of 0.01 and 0.005 the CNT:NOC mixture showed an increase in the intensity mean over the course of 42 hours (Table 4). The 0.02 CNT:NOC mixture also provides some evidence of increasing particle size, but not to the extent of the lower ratios. The increasing size of the 0.01 and 0.005 CNT:NOC mixtures indicates enhanced aggregation of the COOH-CNT and kaolinite. However, the kaolinite control also shows signs of aggregation after 1 hr mixing. This corresponding increase in the kaolinite particle’s size makes it difficult to interpret the increasing size seen in the CNT:NOC mixtures. The large error in the 0.01, 0.005 and NOC control after 1 hour mixing also make it difficult to draw conclusions from this data.

Again, the usefulness of this method of analysis for the chosen system of kaolinite and MWCNTs is limited. The scattering of the smaller, non-aggregated MWCNTs can skew the intensity mean results, and the increasing size of the kaolinite control makes it difficult to separate the CNT-NOC aggregates from the potentially aggregating kaolinite in the mixture. It is difficult to rectify these results with the results of the sedimentation experiments, which clearly indicated enhanced sedimentation for the 0.02, 0.01, and 0.005 ratios at pH 3. Further particle size analysis is needed in order to clearly quantify the aggregation indicated by the sedimentation and DLS experiments.
Table 4: Intensity mean (nm) for 0.02, 0.01, and 0.005 CNT:NOC ratios for COOH-MWCNT at pH 3 (± 1 SD)

<table>
<thead>
<tr>
<th>Time (hrs)</th>
<th>0.02</th>
<th>0.01</th>
<th>0.005</th>
<th>NOC Control</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>506 ± 56</td>
<td>645 ± 49</td>
<td>810 ± 28</td>
<td>792 ± 30</td>
</tr>
<tr>
<td>1</td>
<td>537 ± 35</td>
<td>1061 ± 176</td>
<td>1058 ± 216</td>
<td>986 ± 165</td>
</tr>
<tr>
<td>42</td>
<td>591 ± 12</td>
<td>1171 ± 259</td>
<td>1161 ± 150</td>
<td>935.5 ± 163</td>
</tr>
</tbody>
</table>

4.7 2-Hour Aggregation Experiments, COOH-MWCNT at pH3

Additional aggregation experiments were performed for the 0.02, 0.01, and 0.005 ratios for the COOH-MWCNT and kaolinite mixtures at pH 3. In Figure 12, all three ratios demonstrate a general increase in particle size over time. The 0.005 ratio generally has the fastest increase while the 0.02 ratio shows the least amount of change over time. However, all three ratios are all increasing at around the same rate and do not exhibit a linear rate of change. This information can help in the determination of the aggregation kinetics for the COOH-MWCNT and NOC aggregate, although more information is needed before a quantitative analysis can be conducted. Additionally, the unpredictability of the kaolinite control limits the application of these results. It is unclear whether the increase in particle size is due to the formation of aggregates, or the interference of the larger kaolinite particles aggregating during the course of measurement.
Figure 12: Time-resolved, intensity mean (nm) measurements for 0.02, 0.01, and 0.005 CNT:NOC ratios and 10 μg/L NOC control. Measured every 5 min for 2 hrs.

4.7 30 min Aggregation Experiments, COOH-MWCNT at pH3

The time-resolved experiments repeated at the low concentrations of 10 μg/L and 5 μg/L COOH-MWCNT indicate that the aggregate formation happens during the 1 hr mixing period. In Figure 13 below, the spikes in the average intensity mean (nm) that occur in the first 5 minutes of analysis potentially show the formation of large aggregates followed by their sedimentation. However, similar behavior is seen in the kaolinite control, which impedes any clear indicators of heteroaggregation. The high polydispersity of the kaolinite used throughout these experiments makes monitoring particle size change through DLS analysis challenging. It is recommended that other methods of analysis such as advanced
microscopy techniques are employed to better understand the aggregation behavior of kaolinite and COOH-MWCNT.

Figure 13: Time-resolved intensity mean (nm) measurements for the kaolinite control, 0.01 and 0.005 CNT:NOC ratios. Measured every 15 seconds for 30 min.
4.8 Sedimentation Experiments, COOH-MWCNT at pH 7

At pH 7, the COOH-MWCNTs appear to remain stable for most of the ratios tested. At ratio 0.5, the absorbance of the CNT-NOC mixture remains constant throughout the experiment. In Figure 14, for the 0.5 ratio, the combined absorbance of the 5 mg/L CNT control and the 10 mg/L NOC control is approximately the total absorbance of the mixture. This correlation implies that the two particles are not interacting heavily; there is no notable shift in the absorbance of the mixed solution when compared to the stable controls. There is no evidence of enhanced sedimentation or aggregation due to the presence of kaolinite for this concentration of COOH-MWCNT. This combination of pH7 and ratio 0.5 lead to the greatest similarity between the controls and the CNT:NOC mixture out of all the experimental trials.

The CNT:NOC ratio of 0.1 is shown to behave similarly to the previous ratio. Again, each sample (both the CNT-NOC mixture and the corresponding controls) remains relatively stable throughout the experiment. There is a slight discrepancy in the absorbance of the mixed solution and the combined controls, which could imply some interactions, but it is very slight. The sum of the controls is slightly more than the absorbance of the mixture, indicating enhanced sedimentation. However this does not continue to develop for the lower ratios to the same extent in the lower pH range.
For the ratios of 0.02, 0.01, and 0.005 the sum of the controls is very similar to the absorbance of the mixture. This implies that the particles are not interacting very often, preventing any aggregation from occurring. However, the stabilizing behavior seen in the pH 5.5 experiments does not occur at pH 7. This implies that there are limited opportunities for the kaolinite and CNT to interact at this pH. At lower pH, the potential for interactions leading to either enhanced stability (pH 5.5) or enhanced sedimentation (pH 3) are more prevalent than at a neutral pH, which indicates limited interactions between CNT and kaolinite.
Figure 14: Absorbance of COOH-CNT-Kaolinite mixture ("CNT:NOC"), COOH-CNT alone ("CNT Control"), and Kaolinite alone ("NOC Control") at pH 7 and ionic strength 1 mM over 42 hours.
4.9 DLVO Calculations

Calculations using the established Derjaguin-Landau-Verwey-Overbeek (DLVO) theory of colloidal stability were done in order to compare the experimental results of the sedimentation and aggregation data to the expected theoretical interactions between the kaolinite and COOH-MWCNTs. The DLVO theory states that the stability of particles in an aqueous system can be expressed as the sum of the electrical double-layer (EDL) and van der Waals (VDW) interactions. The sum of the interaction energies of the EDL and VDW interactions will dictate the stability of two approaching particles. The main equations used were adapted from the original theory and shown below (Clark) (Petosa et al.) (Gregory 1975) (Gregory 1981):

\[ V_T = V_{EDL} + V_{VDW} \]  \hspace{1cm} (1)

\[ V_{EDL} = 64\pi\varepsilon_0\varepsilon_r \frac{a_1a_2}{a_1+a_2} \left( \frac{k_BT}{\varepsilon e} \right)^2 \Gamma_1 \Gamma_2 \exp(-\kappa h) \]  \hspace{1cm} (2)

\[ V_{VDW} = -A_{12} \frac{a_1a_2}{\kappa h(a_1+a_2)} \]  \hspace{1cm} (3)

Here, \( \varepsilon_o \) is the dielectric permittivity in a vacuum, \( 8.85 \times 10^{-12} \) F/m; \( \varepsilon_r \) is the relative dielectric permittivity of the solution (water); \( a_i \) is the particle radius; \( k_B \) is the Boltzmann constant, \( 1.3805 \times 10^{-23} \) J/K; \( T \) is absolute temperature; \( \Gamma_i \) is the dimensionless surface potential for particle or collector (\( \Gamma_i = \tanh \left( \frac{z e \psi_i}{4k_BT} \right) \) where \( z \) is the counterion valence, \( e \) is the electron charge, \( \psi_i \) is the surface potential); \( \kappa \) is the inverse Debye length; \( h \) is the surface-to-surface separation distance; and \( A_{12} \) is the Hamaker constant.
In order to compare each system, it was assumed that the CNT interactions could be modeled using the same particle-particle equations if the equivalent spherical diameter of the cylindrical CNT was calculated.

The relationship between the total interaction energies as a function of separation distance were established for each experimental system: kaolinite-kaolinite, CNT-CNT, and kaolinite-CNT interactions were calculated at pH 3, 5.5, and 7 to compare the experimental results with theory. Figure 15 shows the differing net interaction energy values for the three systems.

![interaction energy vs. separation distance](image)

**Figure 15:** Total Interaction Energy vs. Separation Distance for kaolinite-kaolinite, CNT-CNT, and kaolinite-CNT interactions.

As pH increases, the absolute value of the EPM of the kaolinite and CNT also increases. This indicates an increase in the surface potential due to the presence of the ionizable COOH- groups on the CNT surface. This increase in surface potential results in enhanced stability at higher pH. As shown in Figure 15, the total
interaction energy required to overcome the net repulsive forces between the particles decreases with decreasing pH for each system.
4.10 Importance of pH

The general trend throughout all the experiments found increasing signs of interaction between the kaolinite and CNT as pH decreased. Figure 14 compares the behavior of the 0.01 COOH-CNT:NOC ratio for all pH values tested. At the highest pH of 7, the sum of the controls behave very similarly to the mixed solution. This implies that the interactions between CNT and NOC are not affecting the stability of the solution. At pH 5.5, there is a shift in the relationship between the mixture’s absorbance and the combined controls. As seen in Figure 16, the CNT control at pH 5.5 and pH 7 remains constant. There are small shifts in the kaolinite control’s absorbance after 20 hours that lead to a shift in the control sum absorbance. The mixture also shows shifts in absorbance compared to values at higher pH. This implies that the CNT:NOC mixture is more stable at a pH 5.5 than at pH 7. However, this stabilizing effect is not very strong compared to the destabilizing effect seen at pH 3.

At pH 3, the kaolinite control and the CNT control remain quite stable. The mixture, however, shows significant sedimentation when compared to the controls. This implies that the CNT and kaolinite are aggregating and being removed from the bulk water. This implies that the mechanism for CNT removal for this solution chemistry is heteroaggregation of the CNT and NOC rather than homoaggregation, as the mixture behaves independently of the two controls.
As pH increases, the absolute value of the EPM of the kaolinite and CNT also increases. This indicates an increase in the surface potential due to the presence of the ionizable COOH- groups on the CNT surface. This increase in surface potential due to the dissociation of COOH- results in enhanced stability at higher pH. Additionally, this deprotonation of COOH- leads to a more hydrophilic surface on the CNT, leading to greater repulsive forces. At an acidic pH of 3, the value of the EPM is closer to 0 for both the CNT and kaolinite. This leads to more possible opportunities for collision.
Figure 16: Effect of pH on sedimentation behavior of 0.01 ratio of COOH-CNT:NOC.
4.11 Effect of CNT:NOC Ratio on Stability

In order to quantify the impact differing ratios had on the stability of the wide range of solutions tested throughout this study, the percent change in stability as indicated by change in absorbance was calculated. The percent change in stability was calculated using the following equation:

\[
\frac{\text{Abs}_{\text{CNT:NOC}} - \text{Abs}_{\text{Control}}}{\text{Abs}_{\text{Control}}} \tag{3}
\]

Where \(\text{Abs}_{\text{CNT:NOC}}\) is the absorbance of the CNT:NOC mixture after 42 hours and \(\text{Abs}_{\text{Control}}\) is the sum of the absorbance of the CNT control and NOC control after 42 hours. If the percent impact on stability is positive, then it indicates enhanced stabilization of the mixture. If the percentage is negative, that indicates that enhanced sedimentation occurred due to the destabilization of the mixed solution.

In figure 17, the percent impact on stability is plotted verses the five ratios tested (0.5, 0.1, 0.02, 0.01, and 0.005) at pH 3, 5.5, and 7. As seen by the arc in positive values at ratios 0.1 – 0.01 at pH 5.5, this demonstrates that increased stability was witnessed in this range of solutions. For the lowest and highest ratios (0.5 and 0.005), there is no indication of either enhanced stability or sedimentation, as both show approximately 0% impact on stability.
For pH 7, there is generally no ratio-dependent effect on stability. Overall, all ratios show little indication of any impact on stability, with very slight negative values calculated.

The highest impact on stability was seen for the ratios at pH 3. As the ratio of CNT:NOC decreased, the percent impact on stability increased in magnitude. The values became more negative, until all the mixture of the CNT and kaolinite completely settled out of solution at the 0.005 ratio. This demonstrates that low pH leads to enhanced sedimentation as the ratio of CNT:NOC decreases.

Similar to the findings of Huynh et al.’s heteroaggregation study, these results imply that there is an optimal ratio for heteroaggregation. As the ratio increases at pH 3, the magnitude of the % impact on stability increases. A possible reason for this could be the concentration of CNT is too high at a CNT:NOC ratio of 0.5, and the non-aggregated CNTs could impede any extensive aggregation. As the ratio decreases, the concentration of CNT is low enough to result in the formation of aggregates.

Figure 17: Ratio of CNT:NOC vs. Percent Impact on Stability at pH 7, 5.5, and 3
4.12 Natural Water Samples

Natural Water Samples for the Houston EWPP drinking water plant were analyzed to determine the impact natural colloids present in unaltered natural water samples effected the sedimentation behavior of the COOH-MWCNTs. Samples from the Trinity River and Lake Houston inflow to the plant were both tested. A portion of the natural water samples were filtered using a 0.2 um filter in order to determine the effects larger colloidal matter has on the sedimentation behavior of the COOH-MWCNTs.
4.12.1 Trinity River

The UV-Vis absorbance of the COOH-CNT in filtered and unfiltered Trinity River water samples was measured for 5 mg/L and 10 mg/L CNT solutions. Figure 18 plots the filtered and unfiltered samples against the absorbance of COOH-CNT of the corresponding concentrations dispersed in DI water at pH 7. From the figure, it is clear that the constituents present in the natural sample result in increased sedimentation of the CNT when compared to the controlled synthetic sample prepared in DI water. However, the filtered and unfiltered samples behave differently depending on the concentration of CNT present.

For the 5 mg/L sample, the filtered and unfiltered sedimentation behavior is very similar. Both settle out of solution by 20 hours and have similar rates of change. The unfiltered sample shows slight indication of enhanced sedimentation, as it decreases in absorbance at a slightly faster rate than the filtered sample.

At the lower concentration of 1 mg/L, the filtered and unfiltered samples behave quite differently. The filtered sample, although less stable than the DI water-dispersed sample, does not settle out of solution to the extent of the unfiltered sample. This implies that the unfiltered sample is much less stable than the filtered sample. For the 1 mg/L CNT concentration, the unfiltered sample registers at a negative absorbance, which implies that components of the natural water are removed along with the CNT through sedimentation.
Figure 18: Absorbance of filtered ("F") and unfiltered ("UF") 5 mg/L and 100 μg/L COOH-CNT in Trinity River water sample compared with same concentrations dispersed in DI water at pH 7.

4.12.2 Lake Houston

Similar results were found for the Lake Houston water sample. As shown in Figure 19, the 5 mg/L solution in the filtered and unfiltered natural water samples settled much quicker to the controlled DI sample. There is some slight evidence of enhanced sedimentation in the unfiltered sample compared to the filtered sample after 20 hours of settling. However, both the filtered and unfiltered samples behave very similarly.

In the 1 mg/L CNT experiment, a similar trend to the Trinity River sample is seen. The absorbance of the DI-prepared sample and the filtered sample remain steady during the 42 hour settling period. However, the absorbance of the unfiltered sample drastically decreases over time. This implies that the unfiltered Lake Houston water is less stable than the filtered sample, similar to seen in the Trinity Water experiments. Again, the negative absorbance readings for the 1 mg/L CNT
samples imply that the settling of the CNT results in the enhanced sedimentation of other components in the natural water sample.

Figure 19: Absorbance of filtered ("F") and unfiltered ("UF") 5 mg/L and 100 µg/L COOH-CNT in Lake Houston water sample compared with same concentrations dispersed in DI water at pH 7.

Both natural water samples behaved quite similarly. When the 100 µg/L experiments are compared, there is some evidence of enhanced sedimentation on the Trinity River water. However, all general trends in the settling of the CNT remain the same. Since both water samples were taken at similar locations, it is not surprising that they behave quite similarly. However, a wide range of natural water constituents is possible and will vary with each source. The makeup of the natural water will also change seasonally and with changing amounts of precipitation. These changes could drastically affect the CNT’s sedimentation rate.

As reported in Table 1 in Section 4.1, the significant concentration of Ca²⁺, silica, and the relatively high reported conductivity all could potentially aid in the destabilizing of CNT in the Lake Houston and Trinity River Systems. While distilled water has an average conductivity of 0.5 to 3 µmhos/cm, the two natural water samples have a conductivity of approximately 400 µmhos/cm (EPA). This increase in ionic strength could result in increased potential for homoaggregation as well as
heteroaggregation of the CNT. As discussed previously, the Ca$^{+2}$ can also aid in heteroaggregation, as it can result in a bridging effect between particles (Ottofuelling).

This potential for the enhanced sedimentation of other constituents in the natural water sample may indicate the COOH-MWCNTs potential to transport other contaminants. This could lead to changes in the distribution of contaminants in aquatic systems, as contaminants that would not typically settle out of solution may be affected by the presence of CNT in the environment. This could lead to unpredicted environmental hazards that are not currently accounted for in the fate and transport of nanomaterials in the environment.
5. Conclusion

The objective of this research was to characterize the potential for heteroaggregation between MWCNTS with NOCs in the aquatic environment. Carboxylated and amine functionalized MWCNTs were studied. Sedimentation experiments, aggregation studies, and the analysis of natural water samples were used to study the effect NOCs have on the behavior of MWCNTs in aquatic systems. A range of CNT:NOC ratios and pH were studied to determine the effect different solution chemistries had on the behavior of the MWCNTs in the natural environment. The sedimentation of the COOH-MWCNTs was found to be heavily dependent on pH and the CNT:NOC ratio. As the CNT:NOC ratio decreased, the CNT-NOC mixture demonstrated enhanced sedimentation behavior at pH 3. The stability of the solution has the highest at pH 5.5 and very low at pH 3. At neutral pH, the CNT:NOC mixture did not indicate any significant shift in stability compared to the CNT and kaolinite controls.

Filtered and unfiltered natural water samples from Lake Houston and the Trinity River were also analyzed and found to significantly enhance the sedimentation of the CNTs at neutral pH. The unfiltered samples exhibited enhanced sedimentation of the COOH-MWCNTs compared to the filtered samples. There was also evidence of enhanced removal of other particles present in the natural water sample due to the addition of CNTs. This indicates that the presence of CNTs could affect the transport of other contaminants in aquatic systems, altering the distribution of contaminants particularly at the sediment-water interface. These
results suggest that NOCs enhance the sedimentation of CNTs in the natural environment and are highly dependent on pH and the ratio of carbon nanotube to natural colloid.
Bibliography


