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I, Zhen Li, hereby submit this original work as part of the requirements for the degree of Doctor of Philosophy in Environmental Engineering.

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The Transport and Fate of Metal and Metal Oxides Nanoparticles under Different Environmental Conditions

A dissertation submitted to the Graduate School of the University of Cincinnati in partial fulfillment of the requirements for the degree of

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Environmental Engineering Program,

Department of Biomedical, Chemical, and Environmental Engineering,

University of Cincinnati

By

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Abstract

Engineered Nanoparticles (NPs) have been widely used in various industrial processes and consumer products. While there seems to be unlimited potential that nanotechnology would improve the quality of our lives, it is inevitable that these manufactured materials will find their way to enter the environment. This study systematically studied the transport, retention and deposition of several industrially important metal and metal oxides NPs (CeO$_2$, TiO$_2$, ZnO and Ag) under different environmental conditions in the aquatic systems.

The stability, transport and deposition of engineered CeO$_2$ nanoparticles through water-saturated column packed with sand were studied by monitoring effluent CeO$_2$ concentration. The influence of solution chemistry such as ionic strength (1–10 mM) and pH (3–9) on the mobility and deposition of CeO$_2$ nanoparticles was investigated by using a three-phase (deposition-rinse-reentrainment) procedure in packed bed columns. The results show that water chemistry governs the transport and deposition of CeO$_2$ nanoparticles. A mathematical model was developed based on advection-dispersion-adsorption equations and it successfully predicts the transport, deposition and re-entrainment of CeO$_2$ nanoparticles through a packed bed. There is strong agreement between the deposition rate coefficients calculated from experimental data and predicted by the model.

This study also studied the role of natural organic matter (NOM) in the transport and fate of NPs in the aquatic environments. Unlike other studies which used synthesized or standardized NOM samples, this study used NOM that was obtained from OhiO River, which has more practical relevance. The influence of this NOM on the surface charge, transport and retention of Ceria NPs was investigated in packed columns. Results indicated that the properties of Ohio River NOMs (OR-NOMs) differ from Suwannee River Humic Acid (SRHA), which is
commonly used as standard NOM in similar researches. OR-NOMs showed a distinct effect in stabilizing and mobilizing CeO$_2$, and the summer NOM had a higher stabilizing effect than winter NOM. The stabilizing effect is attributed to both electrostatic effect and steric effect.

This study also characterized, experimentally and theoretically, the transport and retention of engineered NPs through slow sand filters at drinking water treatment plants (DWTPs) under realistic conditions. The transport of four commonly used NPs (ZnO, CeO$_2$, TiO$_2$, and Ag, with bare surfaces and coated with capping agents) through filter beds filled with three different sand surfaces were investigated. The results have shown that capping agents have a determinant importance in the colloidal stability and transport of NPs through the different filter media. The effort of the biofilm was less significant. The data was used to build a mathematical model which was used to simulate the performance of a scale-up slow sand filter and the effects on filtration cycle of traditional sand filtration system used in DWTPs. Finally, the study took a further step to examined and compared industrially coated and lab-coated NPs in the biofilm coated porous media and confirmed that The role of steric repulsion between electrostatically stabilized NPs and biofilm is a prevalent force against NPs retention in saturated porous media.
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Chapter 1. Introduction

1.1 Statement of the problems

Engineered nanoparticles (NPs) are particles with sizes smaller than 100 nm in at least one dimension. Recently NPs have received a lot of attention and concern recently due to their rapidly increasing applications in various areas (Domingos et al. 2009). Nanoparticles (NPs) have been widely used in a variety of areas such as electronic, biomedical, pharmaceutical, cosmetic, energy, environmental, catalytic and material applications (Aitken et al. 2006a). NPs have become an indispensable material for industries because of their unique size dependent properties such as electrical, magnetic, mechanical, optical and chemical properties, which largely differ from those of their bulk (Aitken et al. 2006a, Meng et al. 2009, Nowack and Bucheli 2007). For example, Ceria (CeO$_2$) has been used as an oxygen sensor and as a fuel additive to increase fuel efficiency (Zhang 2002). Recently, Ceria NPs have been used to reduce oxidative stress in biological systems as a free radical scavenger (Matheswaran 2007). Titanium (TiO$_2$) NPs have been used in paint, consumer products, catalysts, and also have been successfully used in environmental technology for the treatment of waste water and groundwater, the removal of benzothiophene from diesel fuel and the degradation of air pollutants, specifically nitrogen oxide, sulfur oxides and volatile organic compounds (Dalton 2002, Jung 2005, Toma 2006); ZnO NPs have been used in a variety of products and applications such as semiconductors, catalysts, and paints and increasingly are found in consumer products such as sunscreen because of the strong ultraviolet absorption properties of ZnO. Ag NPs are known to have significant antibacterial properties, and are used in fabrics and cosmetic and have medical uses. Ag is used
in dental resin composites (Sun 2002), synthetic zeolites (Faghihian and Kamali 2003), and in coatings of medical equipment such as catheters, infusion systems and medical textiles (Abou El-Nour 2010, Markarian 2006).

While it seems to be unlimited potential that nanotechnology would improve the quality of our lives, it is inevitable that these manufactured materials will find their way to enter the environment (Fadeel et al. 2007). Releases of NPs may come from point sources, such as factories or landfills, and from nonpoint sources, such as wet deposition from the atmosphere, storm-water runoff, and attrition from products containing NPs (Colvin 2003). After entering the water body, the fate of these NPs will depend on the transport (aggregation, deposition, adsorption, and bioaccumulation) and transformation (oxidation, reduction, dissolution, and biodegradation) processes. The knowledge of these processes, which determines the fate of the NPs in aquatic systems, is developing but yet limited. Therefore, there is a critical need for laboratory studies addressing the stability and transport of NPs under various environmental conditions.

In addition, while the behavior of some NPs in the environment and their ecotoxicology have been reviewed individually under specific conditions, currently no systematic description engineered NPs and their occurrence, fate and effects on the environment is yet available. Moreover, little is known of the interaction of engineered NPs with water treatment plants (WTPs). There is no conclusion if the WTPs are able to remove the engineered NPs once they occur in the source, which directly determines the exposure and hazard of NPs for human health.

The transport of colloids and NPs in porous media is impeded by two processes, 1) straining or physical filtration where the particle is larger than the pore and is trapped and 2) true filtration where the particle is removed from solution by interception, diffusion and
Experimental studies will be conducted to better understand the influence of solution and colloid-surface chemistry, porous media texture, flow rate, presence of natural organic matter, the mass and size distribution of NPs on their transport. The research was intended to provide contribution for summarizing the behavior of metal and metal oxide NPs in the aquatic environment and understanding the physiochemical interactions, which govern the movement, and how the current technology used in WTPs, interact with the engineered NPs. The followings questions were intended to be answered: What will happen to NPs when they enter the aquatic environment, whether deliberately or accidentally? How do specific particle and environmental properties affect deposition, aggregation and transport? Do NPs change in composition or structure as they go through the environment, or do they accumulate as pollutants in the environment? What is the combined effect of the water chemistry; natural organic matter (NOM) and what are the mechanisms behind it? Are we able to predict the transport and fate of certain NP based on mathematics model? Can sand filtration system in WTPs successfully remove the NPs in the water?

1.2 Potential hazard of engineered nanoparticles

Although the specific knowledge of toxicity of NPs to humans and ecosystems is still developing and no consistent agreement about the antimicrobial mechanism of NPs has been reached, there are preliminary evidence that widespread utilization of metal and metal oxides NPs present potential human and ecosystem hazard. The unique properties of NPs, such as high specific surface area abundant reactive sites on the surface as a consequence of a large fraction of atoms located on the exterior rather than in the interior of NPs, as well as their mobility, could potentially lead to unexpected health or environmental hazards (Baun et al. 2008, Bello and Isaacs 2010, Handy and Shaw 2007).
For Ceria NPs, it is of concern due to its distribution widely in the environment from diesel exhausts (Park 2008). The evidence suggests that toxicity is low in humans and that positive effects occur, such as reduction in the particle number concentration of ultrafine particles form diesel combustion, but further work is required to give more definitive responses (Park et al. 2008). Negative effects of CeO$_2$ on E. coli has been reported (Rodea-Palomares et al. 2011), where the NPs can be adsorbed on the E coli outer membrane. For TiO$_2$ NPs, study show that microorganisms in the presence of light are adversely affected by TiO$_2$ NPs due to the production of reactive oxygen species (ROS) (Oberdörster 2007). For ZnO, there are experimental evidence suggesting that ZnO NPs can produce oxidative stress in aquatic organisms (Wang 2005). A number of detailed studies have investigated Ag toxicity to bacteria (Morones 2005, Rai 2009, Shahverdi 2007, Sondi 2004). Ag NPs have been shown to increase antibacterial activity of antibiotics such as vancomycin and amoxicillin when used on S. aureus and E. coli (Shahverdi 2007). Both size and shape have been shown to affect antibacterial properties, with smaller sized NPs having more effect (Morones 2005, Pal 2007). A number of these studies also observed aggregation of Ag nanoparticles and larger effects on bacteria on agar plates compared with bacteria grown in a culture medium. This effect was most likely due to the increased dose and certain experimental conditions such as, temperature, pH, and mixing speed (Pal 2007).

Biochemical cycling of NPs may involve physicochemical reactions in the atmosphere; aggregation, or uptake, accumulation, transformation, and degradation in organisms. Uptake of NPs into the aquatic biota is a major concern. (Aitken et al. 2006a, Balbus 2007, Auffan et al. 2009). Organisms, and especially those that interact strongly with their immediate environment such as algae, plants, and fungi, are expected to be affected as a result of their exposure to NPs.
Accidental spillages or permitted release of industrial effluents in waterways and aquatic systems may result in direct exposure to NPs of humans via skin contact, inhalation of water aerosols and direct ingestion of contaminated drinking water or particles adsorbed on vegetables or other foods (Seaton et al. 2009). Thus, it is possible that NPs will enter human body through food chain.

When addressing environmental and health risk analysis of NPs, understanding the mechanism of colloid and colloid facilitated transport in porous media is critical. NPs with higher dispersion imply a higher mobility can be transported longer distances and impose a greater potential for risk of exposure. Higher mobility of NPs can potentially be involved in particle-facilitated contaminant movement (Kanti Sen 2006). Knowledge of the processes that control NPs transport and fate is required to efficiently manage and remediate many environmental contaminants. Thus, it is particularity important to achieve a better understanding of the transport in the aquatic system, which directly determines their bio-availability and toxicity.

1.3 The stability and transport of NPs in the aquatic systems

There are two aspects that determine the behaviors of engineered NPs: their characteristics, and the surrounding environment. The characteristics include size, shape, chemical composition, surface charge, and coating, particle state (free or matrix incorporated), and how these adsorb to or associate with larger biotic and non-biotic particles in the suspended and deposited, and the solution environment pH, ionic strength, ionic composition, surface charge, NOM content, and the hydrodynamic conditions. Such factors are important in determining whether particles aggregate with other particles or deposit onto various environmental surfaces (Oberdörster 2007). Changes in particle size and shape resulting from
aggregation may significantly alter transport potential as well as nanomaterials reactivity and toxicity. Whereas nanoparticle transport through aquatic environments is expected to be dominated by random Brownian diffusion, an increased particle size imparted by aggregation may result in particle-surface collisions due to gravitational sedimentation and interception. In addition, NPs may associate and aggregate with other naturally occurring substances, such as organic matter and naturally occurring colloidal matter. It is essential to recognize which interactions particles experience under different conditions to predict their fate in environment and their likelihood of exposure.

1.3.1 **The effect of water chemistry**

Water chemistry (pH, electrolyte type and concentration) plays an important role in the aggregation and transport. The deposition/aggregation process is determined by the NPs’ surface properties, which are mainly dependent on parameters such as temperature, ionic strength, pH, particle concentration and size, etc. (Elimelech and O'Melia 1990, Gotovac et al. 2006) (Filella and Buffle 1993) (Kretzschmar and Sticher 1997) (Lecoanet and Wiesner 2004). Generally, an increase in the ionic strength compresses the electric double layer, thus decreasing the electrostatic repulsion between two objects with the same charge (Jeong and Kim 2009) (Saleh et al. 2008) (French et al. 2009) Increase of the ionic strength diminishes the magnitude of the electrostatic repulsion, the energy barrier will then decrease and the attachment probability becomes closer to unity. It was observed that as the pH of NP dispersions approached the point of zero charge, aggregates were observed and the size the aggregates increased while the mobility of the NPs decreased. The formation of the aggregates is due to the significantly decreased repulsive forces between NPs, which was caused by the surface ionization of the NPs.
It was observed that the morphology and aggregation rate of TiO$_2$ NPs is a function of the ionic strength and electrolyte solution characteristics (French et al. 2009).

Although the effect of solution chemistry was extensively studied on various NPs, including metal and metal oxides such as TiO$_2$, ZnO, Ag, and carbon based NPs such as C$_{60}$ and carbon nanotubes, such investigation is very limited on certain NPs, such as CeO$_2$, which greatly hampers researchers’ capability to predict and access the potential risk and hazard of CeO$_2$ NPs in the environment. Thus it is necessary conduct experiments to continue gathering data on how the water chemistry influence metal and metal oxides NPs, especially for those less studied such as CeO$_2$.

1.3.2 The effect of natural organic matters

The stability and transport of NPs in the aquatic and subsurface environments is also impacted by the presence of NOMs. The origin of NOM is the breakdown of plant and animal tissue in the environment. Therefore, it varies in composition and concentration depending on the source and location of a water system. Generally, the main constituents of NOM are humic acids, fulvic acids, and a hydrophilic fraction (Hong and Elimelech 1997).

NOM has long been known to adsorb onto colloidal particles and influence their colloidal stability and to reduce the coagulation of particles in waste water treatment (Xie et al. 2008). It has been shown more recently that similar interactions presents between NOM and carbon nanotubes, fullerenes as well as several metal and metal oxides, which indicates that NOM enhance the stability and mobility of NPs in porous media (Chen and Elimelech 2007, 2008, Wang et al. 2008a). NOM can adsorb at the surface of NPs and colloids, which modifies the physico-chemical properties of the underlying solid and impact the stability and behavior of the particles. (Franchi and O'Melia 2003, Mylon et al. 2004, Pelley and Tufenkji 2008) The
adsorbed NOM layer on the surface have shown to enhance the transport of both natural and engineered colloids and NPs in saturated porous media. (Akbour et al. 2002) (Franchi and O'Melia 2003, Deshiikan et al. 1998)

The stabilization effect of NOM can be explained by two mechanisms: electrostatic and steric repulsions. Most studies have shown increased electrostatic repulsion due to adsorption of NOM fractions to the particle surface (Brown and Jaffé 2001, Tiraferri and Sethi 2009, Lin et al. 2010). This causes stabilization at moderate ionic strengths due to an absolute increase in the particle charge. Another mechanism is that the adsorbed fraction of NOM is thought to cause steric hindrance, which reduces aggregation irrespective of particle charge and ionic strength (Tian et al. 2010). The increase in colloidal stability is generally thought to affect the exposure of organisms in the aquatic environment to NPs. (Quik et al.)

There are some limitations of the current studies: (1) many of the studies cited above have used commercial, homogenized NOM isolates, typically, Suwannee River Humic Acid (SHRA), to represent NOM. Although SHRA well serves as a standardized material, in reality, the characteristics of NOM is highly heterogeneous regarding to collection location and seasonal change. The transport, fate, and bioavailability of NPs are highly dependant on the environment that they are exposed to. Even relatively subtle changes can significantly affect their morphology, hydrophobicity and charge. Therefore, it is absolutely necessary to assess the impacts of NOM using NOM that is isolated from a relevant origin. (2) While there are increasing studies on the stability and mobility of NPs in the aquatic systems, very few of them have chosen CeO₂ NPs as a model material, which seriously hampers our ability to describe and predict their potential exposure and bioavailability. Thus, to better predict the stability and transport of CeO₂ in water, it is necessary to study the influence of a local NOM that has more relevance in water treatment.
1.3.3 The effect of surfactants

Surfactants are compounds that lower the surface tension of a liquid, allow easier spreading and lowering of the interfacial tension between two liquids or between a liquid and a solid. Surfactants are useful in a number of household, industrial, and scientific applications, including oil recovery, drug delivery, chemical warfare decontamination, cleaning, waterproofing, and lubricating, or as additives for food, cosmetics, paint, and so forth (Rosen 2004).

Surface modification of NPs is one of the mostly accepted methods to improve the dispersion stability of nanoparticles. When surfactants are used to disperse and stabilize engineered NPs to achieve the desired stabilized effect, they also make NPs highly mobile in saturated sandy porous media, which potentially facilitate their transport and enhance their hazard. Surfactants are also widely present in water environments with the concentration up to 20–70 mg L$^{-1}$ in municipal wastewaters (Han et al. 2008) and can likely interact with the released NPs and influence their mobility in the soil/sediment environment. Surfactants may also sorb onto the surfaces of porous media and affect its hydraulic properties (Van Hoecke et al. 2011) (Brown and Jaffé 2001) (Wiel-Shafran et al. 2006); thus affect the interaction energy between the surface and NPs.

Various surfactants have been used to make NPs suspensions and can thus be discharged with the NPs. Non-ionic and ionic surfactants are commonly used to coat nano-TiO$_2$ to remain dispersed during the fabrication of paints and cosmetics. It was found that hydrophobic interaction has important role in the processes of stabilization of suspensions for nonionic surfactant, and for anionic surfactant (Tkachenko et al. 2006). Polyvinylpyrrolidone (PVP) is known to have an excellent wetting property and readily forms films, which makes it good as a
coating or an additive to coatings. It is a commonly used polymer dispersant to stabilize NPs (e.g. Ceria, Titanium, silver, iron, etc) in preparation and synthesis (A et al. 2007, Huang et al. 1996, Tamami et al. 2011, Zhang et al. 2009). Studies show that NPs suspended by different surfactants presented different breakthrough curves in sand columns (Abu-Zreig et al. 2003, Petryshyn et al. 2010) (Lu et al. 2013) (Zhao et al. 2012), and generally capped/coated NPs will travel farther than un-coated NPs and have more bioavailability; thus, will have potential impact on groundwater and plants. However, it remains unclear if surfactants would play similar role in the transport and retention in natural waters and in drinking water treatment facilities.

1.3.4 Removal of nanoparticles in water treatment facilities

Studies have suggested that NPs can remain in the environment for long periods and can be toxic to aquatic life(Mueller and Nowack 2008). Treated water from sewage plants and waste industrial processes is frequently discharged into aquatic systems, and there is concern that residual NPs present in these effluents could harm aquatic life. Studies have been conducted on metal oxides NPs after it reaches the wastewater treatment facilities(Limbach et al. 2008, Kaegi et al. 2011). In a laboratory-scale model of a water treatment plant, which contained activated sludge taken from an actual wastewater treatment plant, analysis of both the sludge and wastewater collected from the model plant revealed that a significant number of the NPs had not been removed from the treated sludge. The suggested reason is that the ingredients found in the wastewater could act like surfactants, substances that bind to the outside of the NPs and prevent them from clustering together. However, no data is available on the NPs transport and deposition in drinking water treatment plant facilities, which more directly impacts NP exposure in drinking water and human health.
However, to date, no data is available on the removal of NPs from drinking water treatment facilities. Slow sand filters (SSFs) are very commonly used in drinking water treatment facilities. SSF is a simple technology but it has been successfully used for over 200 years in drinking water purification (Ellis and Wood 1985). It has been used as a particle and pathogen filter that combines biological, physical, and chemical processes. They operate at very low filtration rates, use very fine sand, and usually operate without pre-chlorination. The low filtration rates result in long detention times in the water above the filter sand, and within the bed of sand. The long detention time and the general absence of pre-chlorination result in substantial biological life in the slow sand filtration process. The purification of water in passing through such filters is principally the result of straining through the developing filter skin and the top few millimeters of sand, together with biological activity (Timms et al. 1995, Keijola et al. 1988). Currently there is no evidence that it can capture or retain NPs when they enter the source of drinking water treatment plant. Since the NPs would potentially transport in surface and ground water, it is particular important to investigate if the sand filters in the drinking water treatment facilities can capture and retain NPs.

1.4 Objectives

The goal of this research work is to study the fate and transport selected engineered metal and metal oxides NPs (Ceria, Ag, ZnO and TiO$_2$) in aqueous environment and mechanism of their transport in natural and engineered porous media by examining the fundamental physical interaction, including the impact of water quality, NOMs, NPs characteristics, and interaction with biofilm. Emphasis is being placed on the investigation of the interaction between NPs and the collector surfaces under realistic environmental conditions. The specific objectives of this research study are:
• To present experimental and modeling study to investigate the stability, transport and deposition CeO$_2$ NPs through water-saturated pre-cleaned sand columns. The emphasis of this objective is to evaluate the solution chemistry (ionic strength and pH) on the stability and mobility of CeO$_2$ NPs.

• To further study the behavior of CeO$_2$ after being released into the aquatic system by exploring the effect of NOMs, which are extracted from a drinking water source, on the stability, transport and retention of CeO$_2$ NPs in water-saturated columns;

• To study the transport and retention of selected engineered NPs (CeO$_2$, Ag, ZnO and TiO$_2$) in the sand filters at the same conditions as a drinking water treatment facility, and the combined effect of water solution, NOMs, collector surface properties and surfactants on the transport and retention of NPs;

• To investigate the role and mechanisms of surfactants in the stability, transport and retention of TiO$_2$ and ZnO NPs, and to compare the commercial and lab-synthesized NPs with surfactants.

• For each objective, the selected NPs will be thoroughly characterized by investigating the dimension, size distribution, shape, and morphology. Their stability and aggregation will be evaluated under the specific conditions by measuring the surface charge of the NPs and measuring the size change / UV-vis absorbance with time. The transport and retention will be evaluated through column studies where the NPs will be introduced into sand columns under various conditions and the effluent concentration will be monitored with time. Both experimental and theoretical calculations will be conducted based on the data, such as attachment efficiency, interaction energy between the NPs and the collector surface, and the predicted
transport profile. It is anticipated that this study will provide contribution in understanding the behavior of metal and metal oxides NPs in the aquatic systems under various environmental conditions.

In order to reach the study objectives, there are a number of specific sub-objectives that need to be met:

**The influence of water chemistry on the transport and retention of CeO2 NPs:** In order to study the influence of the water chemistry, the column study should be run under variable ionic concentration and pH level. This variability will offer a chance to study the factors affecting the behavior, attachment efficiency and interaction energy between the CeO2 NPs and the sand surface. There are two steps in this process:

First step: Screening study - The ionic concentrations will be varied at 1, 10 and 100mM of NaCl, and the pH will be varied at 3, 6 and 9. A 2x3 screening study will be conducted with total of 9 varying conditions for the column studies. This will provide general tendency of the behavior of CeO2 in a wide range of pH and ionic strength.

Second step, more columns studies will be run at pH 6, with more levels of ionic concentrations, based on the results from the first step. This will provide more details on the influence of ionic strength on CeO2 under a near neutral condition.

**The influence of NOMs on the stability and transport of CeO2 NPs:** In order to investigate the influence of NOMs with practical relevance, NOMs will be extracted from Ohio River, which is a local drinking water source. The NOMs will be extracted in both winter and summer to compare the seasonal variations. The NOMs will be characterized and compared with a standard commercial NOM sample. The stability and transport of the CeO2 will be conducted
under the presence of NOMs from both seasons by monitoring the surface charge and their transport in column studies.

**To investigate NPs with dispersant through biofilm coated drinking water sand filters:** In order to understand the combined effect of natural ions and NOMs in the raw water, the surface of the filter sand, as well as the dispersants and coatings in the NPs suspension, the pre-filtration water and filter sand used in this study will be obtained from a local drinking water plant. Laboratory columns studies will be conducted at the same conditions as the actual operational conditions in the drinking water treatment plant. Results of the column studies will be used to determine the breakthrough time and the attachment efficiency of different NPs. A mathematical model will be developed to simulate and predict the performance of a full-scale system and comparing actual treatment scenarios.

**To investigate the role of dispersants on the stability and transport of NPs:** Finally, the most dominant factor, surfactants of the NPs, will be investigated via column breakthrough studies. NPs will be coated with commonly used surfactants in the lab, and will also be compared with commercial NPs, which are coated for industrial application purposes.

### 1.5 Dissertation Structure

The dissertation has four main chapters, which are manuscripts published (Chapter 2 and 4) or submitted in peer reviewed journals and (Chapter 3) and in preparation for submittal to a peer reviewed journal (Chapter 5). The dissertation thus contains 6 chapters including the introduction and background (Chapter 1) and conclusions and future work (Chapter 6). The structure of the dissertation is described in Figure 1-1 Structure of Dissertation.

Chapter 2 is entitled *Transport and deposition of CeO2 nanoparticles in water-saturated porous media*; it was published in *Water Research* by Zhen Li, with co-authors Endalkachew
Sahle-Demessie, Ashraf Aly Hassan and George A. Sorial. This manuscript describes experimental results conducted to evaluate the stability and transport of CeO$_2$ over a wide range of ionic concentration and pH levels. A mathematical model was developed based on advection-dispersion-adsorption equations and it successfully predicts the transport, deposition and re-entrainment of CeO$_2$ nanoparticles through a packed bed. This chapter established main experimental methods and theoretical approaches, thus provided the foundation for the following work.

Chapter 3, *The Transport and Deposition of CeO2 Nanoparticles in the presence of Natural Organic Matters Extracted from Ohio River*, was submitted to *Water Research*, and is authored by Zhen Li, Endalkachew Sahle-Demessie, Ashraf Aly Hassan and George A. Sorial and Jonathan Pressmen. As an extension of the first manuscript, this manuscript further investigated the effect of NOMs, which is another important factor on the transport and fate of CeO$_2$. The experiments were conducted under the near neutral condition, which simulates natural water, with varying seasons and concentrations of NOMs, and ionic concentrations. The mechanism of the stabilizing effect was quantitatively discussed.

Chapter 4, *Transport of nanoparticles with dispersant through biofilm coated drinking water sand filters*, was published on *Water Research* by Zhen Li, Endalkachew Sahle-Demessie, Ashraf Aly Hassan and George A. Sorial. This chapter takes the first step to evaluate the behavior of NPs in a complex matrix and the potential removal of NPs in a drinking water treatment facility. This chapter studied the combined effect of NPs surface properties and surfactants, collector surface properties, as well as the solution chemistry. Filtration of engineered NPs in drinking water supplies was studied, and mathematical model simulation indicated that NPs could reduce water quality and shortens the filtration cycle.
Chapter 5, *The Transport and Deposition of Surface-modified TiO2 and ZnO Nanoparticles through Biofilm Coated Drinking Water Sand Filters*, is a manuscript by Zhen Li, Endalkachew Sahle-Demessie, and George A. Sorial and to be submitted to Chemosphere. The effect of dispersants was studied in Chapter 5. This study is based on the results of chapter 4, which concluded that the existence of dispersants is the dominant factor in the removal of NPs from the sand filters. Thus the role of the surfactants was further studied in this chapter, and lab-coated NPs were compared with commercial NPs that are coated for industrial applications.

And finally, the conclusions of this study and recommendations for future work are summarized in Chapter 6.
Chapter 1. Introduction

Chapter 2. Study the effect of solution chemistry (ion and pH)
Chapter 3. Study the effect of NOMs (origin and seasons)
Model NP: Ceria

Chapter 4. Study the transport of NPs in WTP sand filters: combined effect of solution chemistry, NPs surface properties and collector surface properties
Model NP: Ceria, ZnO, Ag, and TiO2

Chapter 5. Further study the effect of dispersants coating
Model NP: ZnO and TiO2

Chapter 6. Conclusions and Recommendations

Figure 1-1 Structure of Dissertation
1.6 References


2 Chapter 2. Transport and Deposition of CeO$_2$ Nanoparticles in Water-Saturated Porous Media

2.1 Abstract

Ceria nanoparticles are used for fuel cell, metal polishing and automobile exhaust catalyst; however, little is known about the impact of their release to the environment. The stability, transport and deposition of engineered CeO$_2$ nanoparticles through water-saturated column packed with sand were studied by monitoring effluent CeO$_2$ concentration. The influence of solution chemistry such as ionic strength ($1–10$ mM) and pH ($3–9$) on the mobility and deposition of CeO$_2$ nanoparticles was investigated by using a three-phase (deposition-rinse-reentrainment) procedure in packed bed columns. The results show that water chemistry governs the transport and deposition of CeO$_2$ nanoparticles. Transport is significantly hindered at acidic conditions (pH 3) and high ionic strengths ($10$ mM and above), and the deposited CeO$_2$ particles may not be re-entrained by increasing the pH or lowering the ionic strength of water. At neutral and alkaline conditions (pH 6 and 9), and lower ionic strengths (below $10$ mM), partial breakthrough of CeO$_2$ nanoparticles was observed and particles can be partially detached and re-entrained from porous media by changing the solution chemistry. A mathematical model was developed based on advection-dispersion-adsorption equations and it successfully predicts the transport, deposition and re-entrainment of CeO$_2$ nanoparticles through a packed bed. There is strong agreement between the deposition rate coefficients calculated from experimental data and predicted by the model. The successful prediction for attachment and detachment of nanoparticles during the deposition and re-entrainment phases is unique addition in this study.
This work can be applied to access the risk of CeO$_2$ nanoparticles transport in contaminated ground water.

2.2 Introduction

Manufactured nanoparticles have been developed and used in a diverse range of products and industries in the past few decades due to their unique and novel physicochemical properties. While their applications can benefit medicine, textiles, electronics, agriculture, cosmetics, new materials and environmental remediation; the potential impact of engineered nanomaterials on human health and aquatic animals is not fully understood once they are released to the environment (Nowack and Bucheli 2007, Baun et al. 2008, Aitken et al. 2006b, Bystrzejewska-Piotrowskaa et al. 2009, Dunphy Guzmán et al. 2006, Navarro et al. 2008)

Several researchers have investigated the transport and retention of nanomaterials through water-saturated porous media in packed–bed columns, which represents the behavior of nanomaterials in groundwater environments or engineered granular filtration systems. Experimental and mathematical modeling studies of the transport and deposition of Fullerene (C$_{60}$) nanoparticles have been conducted under varying flow conditions and electrolyte species in glass beads, quartz sands and Ottawa sand (Li et al. 2008). The mobility of Fullerene and metal oxides nanoparticles in aquatic system were evaluated and compared via column study, and the role of factors such as water velocity, electrolyte species and ionic strength was investigated (Lecoanet et al. 2004). In these studies, aqueous suspensions of nanoparticles were injected into columns packed with granular media and the behavior of the nanoparticles was commonly interpreted with clean-bed filtration theory, which describes the transport by mechanisms, interception on the particle by the media, sedimentation caused by gravity, and diffusion due to Brownian motion (Yao et al. 1971).
CeO$_2$ nanoparticles are used to make novel nanomaterials, and are widely applied for polishing materials (Kosynkin et al. 2000a), automobile exhaust catalysts (Fu et al. 2001), fuel cell materials (Corma et al. 2004), and additives in glass and ceramic application (Livingston and Helvajian 2005). However, CeO$_2$ nanoparticles have significant chronic toxicity for algae (Thill et al. 2006) and large uptake of nanoscale cerium was found in the liver of zebrafish exposed via ingestion (Johnston et al. 2010), and human lung fibroblast cells fast absorb nano CeO$_2$ even at a low concentration (100 ppb – 100 ppm) (Limbach et al. 2005). CeO$_2$ nanoparticles produce significant oxidative stress in human lung cells, indicating lipid peroxidation and cell membrane damage (Lin et al. 2006). On the other hand, there is limited work on the stability, mobility, transport and deposition of CeO$_2$ nanoparticles, which determines their potential exposure and bioavailability of environmentally released particles. Hence, understanding the transport and fate of CeO$_2$ nanoparticles is of particular interest to fill this knowledge gap.

In this study, we explored the transport and deposition of CeO$_2$ nanoparticles in water saturated sand columns, a process that is relevant to both ground water movement and the treatment of potable water by sand filtration methods. The objective of the present experimental and modeling study is to investigate the stability, transport and deposition of commercial manufactured CeO$_2$ nanoparticles through water-saturated pre-cleaned sand columns, and to evaluate the effect of solution chemistry (ionic strength and pH) on the mobility of CeO$_2$ nanoparticles.

2.3 Theoretical consideration

For steady-state fluid flow, the transport and retention of CeO$_2$ nanoparticles in a homogeneous porous medium can be described by the traditional 1-dimensional advection-dispersion-sorption/ desorption kinetics (Eq.2-1). The kinetics of CeO$_2$ attachment was expressed
similar to the clean bed filtration theory (Li et al. 2008, Saiers et al. 1994, Kuhnen et al. 2000) as a function of two coefficients: One is \( k_{\text{mod}} \), which is the modeled rate of nanoparticle attachment along the depth, while the other \( K_{\text{det}} \) estimates the detachment rates. \( S_{\text{max}} \) is the maximum retention capacity of CeO\(_2\) nanoparticles within the bed. Equations (2-1) and (2-2) given below are solved according to the initial and boundary conditions given in equation 2-3.

\[
\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - \nu_p \frac{\partial C}{\partial x} - \frac{\rho_b}{\theta_w} \frac{\partial S}{\partial x} \quad \text{(Eq. 2-1)}
\]

\[
\frac{\partial S}{\partial t} = \frac{S_{\text{max}} - S}{S_{\text{max}}} k_{\text{mod}} C - \frac{\rho_b}{\theta_w} k_{\text{det}} S \quad \text{(Eq. 2-2)}
\]

I.C. \( C(x, t=0) = 0 \)

B.C. \( S(x, t \rightarrow 0) = 0 \)

\[
C(x = 0, t) = C_0
\]

\[
\frac{\partial C}{\partial x} (x = L, t) = 0 \quad \text{(Eq. 2-3)}
\]

where, \( C \) is the concentration of CeO\(_2\) nanoparticles in solution, \( S \) is the concentration of CeO\(_2\) nanoparticles associated with the solid phase, \( t \) is time elapsed, \( x \) is the distance parallel to the flow, \( \rho_b \) is the sand bulk density, \( D \) is the hydrodynamic dispersion coefficient, \( \theta_w \) is the volumetric water content and \( \nu_p \) is pore water velocity.

Prior to the introduction of CeO\(_2\) nanoparticles, a nonreactive tracer test was conducted to assess water flow and hydrodynamic dispersion in the columns (data not shown). The hydrodynamic dispersion coefficient, \( D \), used later in the model was calculated using the tracer study. The deposition and detachment rate coefficients can be estimated by fitting the transport equations (1) and (2) and initial and boundary conditions, equation (3), to the experimental
breakthrough curve using a nonlinear least square technique. The mathematical model was solved by using Mathematica software (Wolfram, 1991).

The deposition of nanoparticles in porous media is limited, by the frequency of collision between the colloids and the matrix surface, and by the collision efficiency. The frequency of collision is controlled by the characteristics of nanoparticles and the matrix, and hydrodynamics of the flow. The collision efficiency is the fraction of collisions resulting in the attachment and sorption of the nanoparticles on the matrix surface. In the analysis of experimental data, attachment efficiency, $\alpha$, is defined as the ratio of the rate of particle deposition on a collector to the rate of collisions with that collector that has been used. For column studies, $\alpha$ can be expressed as a function of the relative effluent concentration $C/C_0$, where $C$ is the effluent concentration at time $t$, and $C_0$ is the influent concentration, shown in Eq. 2-4 (Yao et al. 1971):

$$\alpha = -\frac{2d_c}{3(1-\varepsilon)\eta_0 L} \ln(C/C_0) \quad \text{(Eq. 2-4)}$$

Where $d_c$ is the median diameter of the porous media, $\varepsilon$ is the bed porosity, $L$ is the length of the bed, and $\eta_0$ is the theoretical clean bed single collector efficiency, which describes the particle transport to an individual collector before particle accumulation alters the collector geometry. Single collector efficiency can be calculated as the sum of individual contributions each transport mechanism, and the overall correlation equation (Tufenkji and Elimelech 2003). The experimental particle deposition rate coefficient, $k_{exp}$, which represents the rate of physical chemical filtration, is related to the single-collector efficiency, $\eta_0$, when the transport of colloids in saturated porous media is within the advection-dispersion range. The expression for particle deposition rate is given as (Tufenkji and Elimelech 2003):
\[ k_{\text{exp}} = \frac{3}{2} \frac{(1 - \varepsilon)}{d c \varepsilon} U \alpha \eta_0 \] (Eq. 2-5)

Where \( U \) is the Darcy velocity of flow.

2.4 Experimental methods

2.4.1 Preparation and characterization of CeO\(_2\) nanoparticles

High grade CeO\(_2\) nanoparticles were obtained from Alfa Aesar (Ward Hill, MA) in suspension form (18 wt% in water with dispersants and polishing additives) and were used as is. Stock solutions of CeO\(_2\) nanoparticles were prepared by diluting the original suspension. The electrolyte concentration and pH of stock solutions were adjusted to the desired levels by adding appropriate amount of standard solutions: NaCl solution (1M), NaOH (1M), and HCl (1N).

Both laser diffraction particle size analyzer (Beckman Coulter LS230) and dynamic light scattering (DLS) system (ZetaSizer Nano ZS, Malvern) were used to determine the size distribution of CeO\(_2\) nanoparticles. Laser Doppler velocimetry in conjunction with phase analysis light scattering (ZetaSizer Nano, Malven) was used to measure the zeta potential of CeO\(_2\) nanoparticles. For size and zeta potential measurements, CeO\(_2\) nanoparticles suspensions were prepared with various initial ionic strengths (1 to 100 mM) over a pH range of 2.83 to 10.23. Transmission electron microscopy (JEOL, JEM-2010) images were obtained to confirm the primary size distribution of the particles. Suspended CeO\(_2\) nanoparticles were sonicated for 20 min before deposited onto a copper mesh grid and left to air-dry prior to TEM analysis. Powder XRD analysis was performed to determine the chemical composition and crystallographic structure of the nanoparticles. XRD data were collected with Cu K\(\alpha\) radiation (\(\lambda = 0.15059\) nm) with a 0.02 2\(\theta\) step size at the speed of 2\(^\circ\) min\(^{-1}\). UV-vis absorbance spectroscopy of CeO\(_2\)
nanoparticles were measured by HP 8453 over wavelength range of 200-800 nm. Calibration was based on maximum absorbance of \( \lambda = 309 \) nm.

2.4.2 Transport and Deposition Study

Glass columns (45cm length \times 2.54 cm diameter) were packed with the 20\times30 mesh size fraction (geometric mean diameter = 0.717 mm) of industrial mineral silica sand that contains 98.2% SiO\(_2\) and trace amount of metal oxides (AGSCO Co., IL). To remove metal and organic impurities the packing sand was thoroughly cleaned by sequential washing (1M HNO\(_3\)) water rinsing, and oven-drying (55 °C, 12 h). The columns were packed with pretreated sand using a wet packing method by adding 1cm depth at a time, yielding a bed porosity of 0.34. Schematic diagram of experimental setup is shown in appendix A (Fig. A-1). A three-phase procedure was applied to evaluate the role of solution chemistry on the transport, deposition and retention of CeO\(_2\) nanoparticles following the procedure reported earlier (McDowell-Boyer 1992). In Phase I (Deposition Phase), six pore volumes of CeO\(_2\) nanoparticle suspension was introduced continuously to the column, followed by Phase II (Rinse Phase), during which the column was rinsed with four pore volumes of the particle free solution which has the same solution chemistry as the nanoparticle suspensions used in Phase I. The ionic strength and pH was kept the same during these two phases but varied for different tests. In Phase III (Reentrainment Phase), MilliQ water was fed to the column to lower the ionic strength. The flow rate was kept constant at 20 mL/min for all three phases, providing \( N_{Re} \) of 0.844. A sample of 3 mL was collected from the effluent stream every 1 minute and was analyzed by UV-vis spectrometer at the wavelength of \( \lambda = 309 \pm 1 \) nm. Calibration of UV-vis spectrometer based on multi-concentration standard samples of CeO\(_2\) nanoparticles were used for quantitative analysis as shown in Fig. A-2 in Appendix A.
2.5 Results

2.5.1 Characterization of CeO\textsubscript{2} nanoparticles

The particle size distribution of the CeO\textsubscript{2} NPs in 1mM NaCl solution was measured by both DLS and laser diffraction particle analyzer (Fig. 2-1a). DLS intensity based The average hydrodynamic diameter as determined by DLS analyzer was 152.7 nm, and the laser diffraction particle analyzer provided a mean diameter of 62.6nm. DLS measurements also gave a wider size distribution. This difference can be accounted to differences in the techniques of the two methods. DLS measures the hydrodynamic diameter, which refers to how a particle diffuses in fluid, where a laser beam measures time-dependent fluctuations in scattered intensity caused by particles undergoing Brownian motion. The intensity fluctuations are autocorrelated by particle size distribution according to Doppler Effect. Whereas, for laser diffraction particle analyzer, particle size distribution is obtained by measurements of low angle light scattering intensity as a function of the scattering angle, the wavelength and polarization of light measured based on applicable scattering models. Correlations for both measurement techniques are based on the assumption that the particles are spherical. For a monodispersed, spherical latex particle standard (Standard, L300, Nominal 300 nm Latex Particles, Beckman Coulter), the two techniques give identical size distribution. Hence the difference in size distribution of the two techniques (Fig 2-1.a ) indicates that the CeO\textsubscript{2} used in this study are non-spherical particles, which is confirmed by TEM image. A representative TEM image of CeO\textsubscript{2} nanoparticles is shown in Fig. 2.1-b, which shows the variance in shape and size of the primary particles and provides evidence for aggregation. The images show that the 2-dimensional projects of the primary particles range from ca.5 nm diameter to ca.60 nm diameter and appear to have triangle,
pentagonal and hexagonal shapes similar to self-assembled CeO$_2$ nanostructure reported in literature (Wang and Feng 2003).

XRD analysis verified the purity and crystallinity of CeO$_2$ (Fig. 2-1 b). The peaks of diffraction angle (28.6°, 33.1°, 47.6°, 56.5°, 76.9°, 79.2°, and 88.3°) match the maximum diffraction angles and relative intensities of ceria from the Trace database (PDF number 75-0390) with primary particle size of 54nm, confirming the CeO$_2$ nanoparticles are ceria particles with nanocrystalline structure.

2.5.2 Stability of CeO$_2$ nanoparticles

The electrophoretic stability of CeO$_2$ was studied by measuring the zeta potential across a range of pH (2.83 to 10.23) at ionic strength of 1 and 10 mM NaCl (Fig. 2-2 a). These data show decrease in the magnitude of the zeta potential with increasing ionic strength due to the compression of electrical double layers. As the pH increased from 2.8 to 10.23, zeta potential changed from 4.41 mV to -28.8 mV in 1 mM NaCl solution, and from -1.98 mV to -39.7 mV in 10 mM NaCl solution. Aggregation of CeO$_2$ nanoparticles was studied by measuring the hydrodynamic size distribution after adding electrolyte or changing pH followed by sonication for 15 minutes and samples were left undisturbed up to 24 hours. At pH 6, the size distribution of CeO$_2$ nanoparticles did not show significant change, indicating little aggregation occurred (Fig. 2-2 b). However, at pH 3, which approaches the point of zero charge (pH$_{ZPC}$), size distribution become wider with multiple peaks, indicating that aggregation and polydispersity occurred due to the formation of bi- and trimodal systems.

2.5.3 Transport and deposition of CeO$_2$ nanoparticles in porous media

Screening study
A factorial screening experimental design was first conducted to study the influence of water chemistry (NaCl concentration of 1, 10 and 100 mM, and pH 3, 6, and 9). Effluent stream concentration of CeO$_2$ nanoparticles were monitored and breakthrough curves are presented in Fig. 2-3. The normalized effluent nanoparticle concentration (C/C$_0$) is shown as a function of cumulative volume normalized to pore volume. The breakthrough curves of CeO$_2$ nanoparticle suspensions through porous media differ distinctively for different solution chemistry. The results are summarized into three cases. Case (1) Breakthrough during deposition phase, where sharp breakthrough curves were observed at one pore volume for two of the test conditions at pH = 6, 1 mM NaCl, and pH 9, 10 mM NaCl. The normalized value of C/C$_0$ showed a step increase from the initial value of zero to a plateau of 0.9 ± 0.5. During the rinse phase, the normalized effluent stream concentration decreased sharply to almost zero when particle free solution was fed to the column, indicating little or no deposition occurring at these two conditions. Case (2) No breakthrough was observed during deposition phase, but peaks were observed during re-entainment phase: For test runs operated at conditions of pH=6, 10 or 100 mM NaCl, pH=9, 10 or 100 mM NaCl, no breakthrough occurred during deposition phase, indicating all the nanoparticles were captured by the sand. However, sharp peaks were observed during the re-entainment phase, when the ionic strength of the column was lowered by introducing Milli Q water and the pH was gradually brought back to 5.6 ± 0.5 (the pH of MilliQ water). This indicates the detachment of weakly attached nanoparticles that were previously captured during the deposition phase by the porous media. Case (3) There were no breakthrough during deposition phase and no peaks were observed during re-entainment phase. For test runs at pH of 3, no CeO$_2$ nanoparticles were detected in the effluent streams during deposition phase or re-
entrainment phase, indicating stronger attachment of CeO$_2$ to sand bed at lower that was not reversed at neutral pH or lowering the ionic strength.

**The role of ionic strength**

The results of rigorous test runs made at pH 6 with ionic strengths of 1, 2, 3, 5, and 10 mM for understanding the effects of ionic strength are presented in Fig 2-4. During the deposition phase, fast and complete breakthrough curves were observed at ionic strength of 1mM and 2mM, where the normalized effluent concentration rapidly reached to $0.96 \pm 0.4$. Whereas partial breakthroughs and gradual increase in $C/C_0$ were observed with decreasing slope and plateau values as the ionic strength changed from 2, to 3 and 5 mM. Instead of fast, steep breakthrough as observed before, the normalized nanoparticle concentrations increased gradually to a plateau. The specific shape of the partial breakthrough can be explained by the blocking effect (Kuhnen et al. 2000, Chen et al. 2002, Song and Elimelech 1994). As seen in Fig 2-2, at pH 6, CeO$_2$ NPs were negatively charged from 1 to 10 mM NaCl, and the size distribution of CeO$_2$ NPs didn’t widen for 24 hrs duration, indicating that stable particle-particle interaction predominates in these conditions. In this case, only a monolayer of deposited particles is formed on the sand surface and multi layer deposition could be neglected. Decrease in ceria deposition rate was reflected by the gradual increase in $C/C_0$ with time, forming partially breakthrough. The maximum surface coverage was increased due to the increased screening of particle surface charge as could be seen in table with values of $S_{max}$ of 0.1, 0.2, 1.2 mg/g corresponding to increased ionic strength of 3, 5 and 10 mM in runs 11, 12 and 6, respectively.

During the rinse phase, $C/C_0$ values decreased sharply to zero as particle free solution was fed to the column and during the re-entrainment phase a pulse increased with narrow, sharp
peaks were observed. The peak height increased with increase in ionic strength of the influent nanoparticle suspensions.

The attachment efficiency, $\alpha$, and the deposition rate coefficient $k_{\text{exp}}$ were determined using equation 4 and 5 for each transport experiment. Mathematical expressions based on mass balance were developed to evaluate the mass fraction of nanoparticles recovered during the rinse phase, phase 2, and the re-entrainment phase, phase III (Franchi and O'Melia 2003). The fractions of nano-CeO$_2$ recovered during the two phases, $FRC_2$ and $FRE_3$ are defined as:

$$FRC_2 = \frac{\sum \text{Mass of NPs Recovered during Phase 2}}{\sum \text{Mass of NPs Deposited during Phase 1}}$$

(Eq. 2-6)

$$FRE_3 = \frac{\sum \text{Mass of NPs Recovered during Phase 3}}{\sum \text{Mass of NPs Deposited during Phase 1} - \text{Mass of NPs Recovered during Phase 2}}$$

(Eq. 2-7)

Fig 2-5a shows attachment efficiency versus ionic strength at two distinct regions. At low ion concentrations (1-5mM), where the attachment efficiency and deposition rate coefficient increased proportionally with increasing NaCl concentration, whereas at high ion concentrations above 10 mM deposition rate coefficient and the attachment efficiency were independent of NaCl concentration. Fig 2-5b presents logarithmic values of $FRC_2$ and $FRE_3$ as a function of log concentrations of NaCl. $FRC_2$ values are in the range of 0.803~0.946 at ionic strength of 3 mM and lower, indicating almost complete detachment of nanoparticles during the rinse phase without changing the water chemistry. When the ionic strength increase to 5 mM and higher, there was a sharp drop in the $FRC_2$ value from 0.9 to 0.105, indicating large retention of nanoparticles occurred in Phase 1. The values of $FRE_3$ decreased as ionic strength increased. When the ionic strength was 1 mM and 2 mM, the corresponding values of $FRE_3$ were 0.694 and
0.390, respectively, indicating the nanoparticles deposited in phase 1 were subsequently re-entrained. As ionic strength increased to 3 mM and above, FRE_3 values dropped to below 0.033.

Batch CeO_2 nanoparticle suspensions left undisturbed showed little aggregation even after 24 hrs at pH 6, 1-100mM NaCl. This suggests that, although particle aggregation and deposition kinetics are closely related, the hindered transport at higher ionic strength in this study is not caused by nanoparticle aggregation. Unlike other similar studies, such as fullerence C_60 nanoparticles (Brant et al. 2005), where deposition is related to particle aggregation induced by the screening effect of electrolyte concentration, these effects were less obvious with CeO_2 nanoparticles. The increase of electrolyte concentration, at pH of 6, significantly increased nanoparticles attachment and deposition to the bed matrix, although there are limited aggregation of CeO_2 nanoparticles.

Derjaguin-Landau-Verwey-Overbeek (DLVO) theory (Derjaguin and and Landau 1941, Verwey and Overbeek 1948) was used to explain the particle-sand grain interaction energy at each ionic strength. The classical DLVO theory of colloidal stability describes the total interaction energy experienced by nanoparticles when approaching a collector surface as the sum of van der Waals (VDW) and electrical double-layer (EDL) repulsion. Theoretical analysis was conducted with a sphear-plate interaction to calculate the total interaction energy as a nanoparticle approaches sand surface (Elimelech and O'Melia 1990, Derjaguin and and Landau 1941, Gregory 1981, Healy and White 1978, Hogg et al. 1966). The variation of the DLVO interaction energy with separation distance at different ionic strengths at pH 6 is shown an insert in Fig 2-4.
Transport behavior of CeO$_2$ nanoparticles at various levels of ionic strength is in qualitative agreement with the DLVO theory (DLVO theory calculation is provided in the Appendix A). At low ionic strength, diffusion layer surrounding nanoparticles and collector surfaces cause the screening effect of the salt is smaller than the electrostatic repulsion between particles and sand surface. For solutions with ionic strength of 1 and 2 mM, calculated values predict the presence of a substantial repulsive energy barrier to deposition ranging from 33 to 19 kT at 1 mM and 2 mM, respectively. The high-energy barrier suggested that only a small fraction of the particles can overcome the primary energy barrier and deposit onto sand surface. At conditions when complete breakthrough was observed, the attachment efficiency and deposition rate constants increased with the increase of ionic strength and strong electrostatic repulsion effectively hindered attachment of nanoparticles to the sand surface. Low attachment efficiency results smaller deposition rate and the deposition kinetic becomes reaction-limited. As the ionic strength increased, the diffuse layers of sand surface and nanoparticles are progressively compressed and consequently, electrostatic repulsion is reduced. At solution ionic strength of 3 to 5 mM, the interaction energy calculations indicate small energy barrier to deposition, also the secondary minimum is deeper and located at a closer distance of separation between sand surface, suggesting that mechanism can be a combination of disposition in both primary minimum and secondary minimum. This is supported by the observation that only a portion of the particles remaining in the porous media after Phase 2 attached to the sand surface. Partial breakthrough of the column studies suggests as CeO$_2$ nanoparticles approach silica sand, they experience attractive force and deposition occurred at the shallow secondary-minimum well, where the nanoparticles are continuously captured and released by the sand surface. The slope and plateau value of the breakthrough curves decrease with the increase of the ionic strength because the
depth of decreasing secondary-minimum. The deposition rate coefficient and the attachment efficiency increased when ionic strength increased from 3 to 5 mM, and became independent of ionic strength at 10 mM and above. The deposition rate coefficient is independent of the ionic strength at high ion concentrations due to the reduction of electrostatic repulsion between nanoparticles and porous matrix surface. At these conditions, more collisions result in attachment, and the process was fast and the kinetic is limited by mass transfer.

Analysis of effluent stream during Phase 2 indeed deposited in secondary energy-minimum. During Phase 3, sharp peaks of pulse release of nanoparticles were observed, which is evident of the deposition in secondary-minimum. The introduction of MilliQ water to the column during Phase 3 eliminated the presence of secondary minimum, resulting rapid release of nanoparticles previously deposited at higher ionic strengths from sand surface. Fig 2-5b shows the fraction of deposited particles that was eluted during Phase 3, given as FRE3, decreased with the increase of ionic strength. This indicates that as the ionic strength increased, the contribution of secondary-minimum became smaller and more fraction of nanoparticles were deposited in the primary energy well.

While the role of the calculated secondary minimum provided theoretically explanation for the deposition and reentrainment of CeO2, it needs to be noted that certain limitations of the DLVO calculation here. For instance, the zeta potential was used in the calculation as estimation for surface charge. Also sphere-to-plate interaction energy profiles are sensitive to changes in particle size. The height of the repulsive energy barrier and the depth of the secondary energy well both change with changing particle diameter. In this study the energy barrier height and the depth of secondary minimum calculation are based on the average diameter of the NPs. Due to
the wide size distribution and polydispersivity of the NPs, as mentioned before, the energy interaction profile can only represent the majority of the NPs in the suspension and a small fraction of NPs that are either very small or large cannot be represented here. Calculations of the theoretical predictions assume that the particles are spherical, while both the particles and collectors selected for this study are likely to be considerably more spherical than the majority of those encountered in realistic situations, neither the CeO$_2$ NPs nor the sand grains are perfectly spherical. The angularity of the collector grain shape could also contribute to the removal of NPs by physical straining effect. These limitations could cause the deviation between the DLOV theoretical prediction and the actual deposition behaviors.

2.5.4 Predicting transport of CeO$_2$ nanoparticles with Mathematical model

The mathematical model for the transport and retention of CeO$_2$ nanoparticles was optimized to estimate the breakthrough under corresponding experimental conditions. The values of $k_{mod}$ and $S_{max}$ were determined by solving Eq.2-1 and Eq.2-2 and the necessary initial and boundary conditions, Eq.2-3, for the Deposition Phase, while assuming $k_{det}$ is negligible. The effect of $k_{det}$ was then considered for the whole column run while optimizing the value of $k_{det}$ in the Re-entrainment Phase. The initial conditions presented in Eq.2-3 apply only for the first phase. For the second and third phases, the initial conditions used are the final distributions calculated for both CeO$_2$ concentrations in solution ($C$) and associated to the solid phase ($S$) from the earlier phase.

The model successfully captured the sharp increase and decline of the CeO$_2$ concentration in the first two phases. There was a strong agreement of the deposition rate coefficients calculated from transport experimental data, $k_{exp}$, and predicted by the model, $k_{mod}$ (see Fig 2-5a), confirming successful simulation of the deposition process. The dispersion
term in Equation 1 accounts for broadening the elution curve. For conditions where breakthrough of the nano-CeO$_2$ occurred this term was insignificant (Chen et al. 2006). The volumetric water content was determined independently from physical measurements in the column. The results are plotted together with the experimental data in Fig 2-3 and 2.4. Model predictions of effluent concentration fitted well with experimental data for Phases 1 and 2, however, the model parameter optimization failed to converge and did not fully capture the sharp increases and drop of effluent curve during Phase 3. Although, previous studies have shown steady state condition of the first deposition phase (Liu et al. 2009) both first phases (Li et al. 2008, Hydutsky et al. 2007) or a pulse injection in the column (Hanna et al. 2010), the modeling effort for attachment and detachment of nanoparticles with changes in the fluid chemistry during the deposition and re-entrainment phase is a unique contribution of this study. The mathematical modeling efforts have the advantage in predicting the amount and distribution of CeO$_2$ held within the columns during all the phases. Particle deposition continues to grow within the column during the test run of pH 6, and ionic strength of 3mM. As shown in Table 1, the maximum attachment concentration occurred at the column inlet and the amount increased during the deposition phase. The attachment distribution continued to grow linearly along the length of the column with the highest deposition observed near the inlet. Deposition within the column redistributed suspended particles to sand surface during Phase 2. The same behavior was observed in run 12 (pH 6, ionic strength 5 mM), where higher deposition rates were observed. The maximum attachment at the inlet calculated for this run was 0.085 mg/g maintaining a ratio of 10% of the maximum deposition $S_{\text{max}}$ (0.2 mg/g) similar to the previous run. For the runs without breakthrough the deposition was also maximum near the inlet. The deposited mass of nanoparticles dropped rapidly by an order of magnitude at half the length of the column. For
instance, in run 9 the maximum attachment calculated was 0.35mg/g which is 35% of the total $S_{\text{max}}$. On the other hand, with full breakthrough, i.e. run 2, the deposition was almost negligible. Experimental effort was made to validate the distribution of deposited nanoparticles in the column by taking portions of the bed along the length of the column, washing and sonicating in MilliQ water to detach deposited nano-CeO$_2$. Unfortunately, desorbed silica interfered strongly with the analysis. A selective and quantitative technique is needed that can give 3-D distribution of deposited particles.

2.6 Conclusions

Accidental or deliberate introduction of CeO$_2$ nanoparticles into subsurface environments may lead to contamination of drinking water supplies and can act as colloidal carriers for sorbed contaminants. This study highlights the implication of CeO$_2$ nanoparticle and provides important insights to confirm the mobility of CeO$_2$ nanoparticle under typical groundwater movements. It is not straightforward to precisely predict the behavior of CeO$_2$ nanoparticle upon their environmental release because of the compliance of various environmental parameters. However, the values of attachment efficiency, deposition rate coefficients, fraction recovered/re-entrained at varying ionic strength and the modeling results provided in this study can be used to further estimate the relative mobility and evaluate the potential exposure and risk of CeO$_2$ nanoparticles.

Results of column studies clearly showed that the water chemistry governs the transport, deposition and re-entrainment of nanoparticles. The increase of ionic strength decreased the mobility of CeO$_2$ nanoparticles due to the compression of electrostatic double layer repulsion, which is in general agreement with DLVO theory prediction. The three phase flow method allowed better understanding of the influence of ionic strength in determining the condition whether the capture-release dynamics is reaction-limited or transport limited. A mathematical
model was developed and successfully simulates both complete and partial breakthrough and re-entrainment of the CeO$_2$ breakthrough curves. The model is also capable of predicting the distribution of nanoparticle deposition within the porous media.

2.7 References


### Table 2-1: Attachment and detachment coefficients at different operating conditions

<table>
<thead>
<tr>
<th>Ionic Strength</th>
<th>pH</th>
<th>Initial CeO₂ Concentration (mg/L)</th>
<th>S&lt;sub&gt;max&lt;/sub&gt; (mg/g)</th>
<th>k&lt;sub&gt;att&lt;/sub&gt; (1/Hr)</th>
<th>k&lt;sub&gt;exp&lt;/sub&gt; (1/Hr)</th>
<th>k&lt;sub&gt;det&lt;/sub&gt; (1/Hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Run 1</td>
<td>10mM</td>
<td>9</td>
<td>10</td>
<td>0.1</td>
<td>24.5</td>
<td>26.1</td>
</tr>
<tr>
<td>Run 2</td>
<td>1mM</td>
<td>6</td>
<td>10</td>
<td>1.0</td>
<td>0.3</td>
<td>0.70</td>
</tr>
<tr>
<td>Run 3</td>
<td>100mM</td>
<td>9</td>
<td>50</td>
<td>1.2</td>
<td>34.9</td>
<td>30.7</td>
</tr>
<tr>
<td>Run 4</td>
<td>1mM</td>
<td>9</td>
<td>50</td>
<td>1.0</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>Run 5</td>
<td>10mM</td>
<td>3</td>
<td>50</td>
<td>1.0</td>
<td>27.0</td>
<td>30.7</td>
</tr>
<tr>
<td>Run 6</td>
<td>10mM</td>
<td>6</td>
<td>50</td>
<td>1.2</td>
<td>25.1</td>
<td>23.37</td>
</tr>
<tr>
<td>Run 7</td>
<td>1mM</td>
<td>3</td>
<td>10</td>
<td>0.9</td>
<td>20.2</td>
<td>22.5</td>
</tr>
<tr>
<td>Run 8</td>
<td>100mM</td>
<td>6</td>
<td>50</td>
<td>1.1</td>
<td>25.6</td>
<td>27.6</td>
</tr>
<tr>
<td>Run 9</td>
<td>100mM</td>
<td>3</td>
<td>50</td>
<td>1.0</td>
<td>27</td>
<td>31.4</td>
</tr>
<tr>
<td>Run 10</td>
<td>2 mM</td>
<td>6</td>
<td>50</td>
<td>1.0</td>
<td>0.5</td>
<td>0.77</td>
</tr>
<tr>
<td>Run 11</td>
<td>3mM</td>
<td>6</td>
<td>50</td>
<td>0.1</td>
<td>2.3</td>
<td>1.91</td>
</tr>
<tr>
<td>Run 12</td>
<td>5mM</td>
<td>6</td>
<td>50</td>
<td>0.2</td>
<td>8.4</td>
<td>11.62</td>
</tr>
</tbody>
</table>
Figure 2-1 Characterization of CeO$_2$ nanoparticles (a) Size distribution of CeO$_2$ in MilliQ water, measured by DLS and Laser Diffraction pattern, with TEM image inserted, (b) XRD of CeO$_2$ nanoparticles.
Figure 2-2 Zeta potential and size distribution of CeO$_2$ nanoparticles (a) Zeta potential and electrophoretic mobility of CeO$_2$ nanoparticles as a function of pH at two levels of ionic strength (1 mM and 10 mM) (b) Intensity-weighted size distribution of CeO$_2$ in suspension
Figure 2-3 A profile of breakthrough curves of CeO$_2$ NPs on an experimental design of 9 runs under three ionic levels (1mM, 10mM, and 100mM) and three levels of pH (pH 3, 6, and 9). The lines represent model prediction.
Figure 2-4  Effects of ionic strength on deposition and reentrainment of CeO$_2$ nanoparticles, showing (a) attachment efficiency $\alpha$, rate constant, and $k_{exp}$, (b) mass fractions of recovered CeO$_2$ during phase II (FRC$_2$) and Phase III (FRE$_3$)
3 Chapter 3. The Transport and Deposition of CeO$_2$ Nanoparticles in the Presence of Natural Organic Matter Extracted from the Ohio River

3.1 Abstract

The presence of natural organic matter (NOM) in aquatic environment plays an important role on the stability, mobility and bioavailability nanoparticles (NPs) in water and sediment. NOM can mobilize and facilitate the transport of NPs, increasing their potential hazard. The complex and heterogeneous chemical structure and reactivity of NOM complicates the study of NPs. Furthermore, drinking water relevant whole NOM sources have not previously been available, resulting in research using NOM sources less representative of drinking water. In this study, water from the Ohio River was concentrated using reverse osmosis membranes and lyophilized to obtain a whole drinking water relevant NOM. Two NOM samples obtained during winter and summer seasons were characterized by thermal analysis and FTIR techniques. The influence of this NOM on the surface charge, transport, and retention of Ceria NPs was investigated in packed columns. Results indicated the properties of Ohio River NOM (OR-NOM) differ from Suwannee River Humic Acid (SRHA), which is commonly used in similar research. OR-NOM showed a distinct effect in stabilizing and mobilizing CeO$_2$, with the summer NOM resulting in a higher stabilizing effect than winter NOM. The stabilizing effect is attributed to both electrostatic and steric effects.

3.2 Introduction

Developments in nanotechnology are leading to the increase of a large number of new consumer goods incorporating of nanoparticles (NPs). As the result of normal use or accidental
releases some portions of these materials would enter the environment where they may pose a potential risk to aquatic and sediment organisms (Kolokassidou et al. 2007) and drinking water supply. There is increasing effort in understanding the environmental implications of NPs (Lecoanet and Wiesner 2004). Cerium oxide NPs (CeO$_2$NPs) are used as a fuel additive, for UV blocking and ceramic polishing (Saleh et al. 2008, Masui et al. 2000), catalysis (Jeong and Kim 2009) and fuel cells (Franchi and O'Melia 2003). CeO$_2$ is one of the manufactured NPs garnering attention by the NPs have shown significant chronic toxicity for algae (Thill et al., 2006), affect the liver of zebrafish (Johnston et al., 2010), and it is readily absorbed by human lung fibroblast cells at low concentrations (100 ppb) (Limbach et al., 2005). It causes significant oxidative stress in human lung cells, indicating lipid peroxidation and cell membrane damage (Lin et al., 2006).

NOM exists ubiquitously in the environment and is known to modify the physiochemical properties and morphologies of colloids including stability, mobility, aggregation and deposition properties of NPs. Adsorption of NOM to NPs surfaces increase electrostatic repulsion (Pelley and Tufenkji 2008, Akbour et al. 2002, Deshiikan et al. 1998, Brown and Jaffé 2001, Lin et al. 2010, Tian et al. 2010). The effects of water chemistry (pH and dissolved ions) on the stability and mobility of NPs have been observed to follow Derjaguin-Landau-Verwey-Overbeek theory (DLVO theory), which states that the interaction energy between two surfaces consists of electrostatic repulsion and van der Waals attraction (Lin et al. 2010). However, in the presence of NOM or other stabilizing agents, non-DLVO forces such as hydrogen bonding, hydration pressure, and steric forces also play important roles but are not as well understood (Brown and Jaffé 2001, Petryshyn et al. 2010).
Several limitations exist with past studies investigating interactions between NOM and NPs. First, many of studies used commercially available fractionated NOM isolates such as Suwannee River Humic Acid (SRHA) to represent whole drinking water NOM. Because the Suwannee River natural NOM content is so high, and because of the heterogeneous nature of NOM with respect to source location, seasonal change, and extraction/isolation processes, fractionated SRHA, while standardized, does not provide for a good representation of drinking water relevant NOM. Even relatively subtle changes can significantly affect NOM morphology, hydrophobicity and charge. Therefore, it is necessary to assess the impacts of a whole NOM that is isolated from a relevant source and validated with respect to characteristics of drinking water interest (McCurry et al. 2012, Pressman et al. 2012a, Pressman et al., 2012b).

Second, while there are increasing studies on the stability and mobility of NPs in aquatic systems, very few have chosen CeO$_2$ NPs as a model material, which seriously hampers our ability to describe and predict their potential exposure and bioavailability. The strong adsorption of NOM to Fe$_2$O$_3$, TiO$_2$, Al$_2$O$_3$, and ZnO surfaces was reported previously (Mosley et al., 2003 and Yang et al., 2009). Previous studies show the effect of water chemistry on the transport and retention of CeO$_2$ NPs (Wiel-Shafran et al. 2006) and the potential removal using drinking water filter treatment (Li et al. 2013). With respect to NOM and CeO$_2$ interactions, a few aggregation and settling studies have been conducted (Quik et al. 2010; Seaton et al. 2009; Zhao et al. 2012; Zhang et al., 2009), indicating that the adsorption of NOM onto CeO$_2$ significantly reduces their aggregation and stabilizes them under many conditions. Liu et al. (2012) studied the deposition of CeO$_2$ to a collector surface in both Quartz Crystal Microbalance with Dissipation Monitoring (QCM-D) and column experiments. Finally, previous research has attributed the stability of NOM coated NPs to enhanced electrostatic effects and steric effects (Gosh et al., 2008).
However, while the electrostatic effects were demonstrated by an increase in the absolute value of zeta-potential of CeO$_2$ NPs, the enhanced steric forces were not fully demonstrated.

The objective of this research is to provide a better understanding of the behavior of CeO$_2$ NPs in the presence of NOM in saturated porous media under simulated conditions of drinking water treatment relevance. NOM was concentrated and lyophilized from a local drinking water source during both winter and summer seasons using recently validated drinking water relevant methods (Pressman et al. 2010, McCurry et al. 2012, Pressman et al. 2012), which ensure the reconstituted NOM is similar to the original source NOM. The characteristics of the NOM were studied and compared with SRHA via thermogravimetric analysis (TGA) and Fourier transfer infrared (FT-IR) spectroscopy. The transport of CeO$_2$ in the presence of NOM was studied in packed bed columns and the effect of NOM was compared at different concentration, ionic strength, and seasonal change. Modified-DLVO modeling was performed to analyze the stabilizing effect of the NOM by demonstrating the steric repulsion. This work assesses the impact of NOM on the transport and fate of CeO$_2$ NPs in porous medium from a drinking water treatment point of view. We believe this is the first research to provide quantitative information on the transport of CeO$_2$ NPs in the presence of NOM from a local drinking water source collected over multiple seasons.

3.3 **Theoretical Consideration**

The deposition of nanoparticles in porous media is limited by the frequency of collision between the colloids and the matrix surface and by the collision efficiency. The frequency of collision is influenced by the characteristics of nanoparticles and the matrix, and hydrodynamics of the fluid flow, and the collision efficiency is the fraction of collisions results in the attachment and sorption of the nanoparticles on the matrix surface. The attachment efficiency, $K_{att}$, is
defined as the ratio of the rate of particles deposition on a collector to the rate of collisions with that collector. The attachment efficiency of the bed can be expressed as a function of the relative effluent concentration \( C/C_0 \), where \( C \) is the effluent concentration at time \( t \), and \( C_0 \) is the influent concentration, shown in Eq. 3-1 (Mylon et al. 2004):

\[
K_{att} = -\frac{2d_c}{3(1-\varepsilon)\eta_0 L} \ln(C/C_0) \quad \text{(Eq. 3-1)}
\]

Where \( d_c \) is the median diameter of the porous media, \( \varepsilon \) is the bed porosity, \( L \) is the length of the bed, and \( \eta_0 \) is the theoretical clean bed single collector efficiency, which describes the particle transport to an individual collector before particle accumulation alters the collector geometry. Single collector efficiency can be calculated as the sum of individual contributions each transport mechanism, and the overall correlation equation (Tufenkji and Elimelech 2003)

### 3.4 Material and Methods

#### 3.4.1 Concentration, lyophilization, and reconstitution of Ohio River NOM samples

Raw water from a full-scale drinking water treatment plant was first pumped through two 19P37-30 Membralox ceramic ultrafiltration (UF) membranes (0.02-μm pore size, Pall Corp., Port Washington, NY), which removed particulates and was analogous to typical drinking water treatment processes, allowing the deliberate study of dissolved NOM (Pressman et al. 2010). Following UF, ion exchange resin (Ambersep 200H hydrogen-form, Rohm and Haas, Philadelphia, PA) was used to remove calcium, magnesium, and sodium ions to reduce membrane fouling and osmotic pressure. Then, three Filmtec BW30-4040 reverse osmosis (RO) membranes (in-series operation) (Dow, Midland, MI) were used for concentration (165× by volume). The concentrate was then collected for further processing and the permeate was
discarded. Barium chloride was added to the concentrate in a multiple stage treatment process (barium-to-sulfate molar ratio of 0.9:1) to precipitate and remove sulfate (McCurry et al. 2011). The dissolved NOM was then lyophilized in a VirTis VirTual EL pilot scale freeze-dryer (SP Industries, Warminster, PA), following a multistep protocol with control over the shelf temperature, chamber pressure, and step length developed in previous research (McCurry et al. 2011). The solid NOM was stored in an airtight container in the dark until reconstitution.

Reconstitution was also performed following procedures developed in previous research (McCurry et al. 2012). Briefly, NOM was dissolved in DI water for desired concentrations (1, 5, 10 ppm) and the solutions were mixed for 1hr to ensure a homogeneous solution. The pH of the NOM solution was adjusted to a near neutral pH of 6.8 using NaOH to simulate natural water. NOM produced with these procedures was validated as representative of the source NOM with respect to water quality parameters typically measured in drinking water systems, including TOC, UV$_{254}$, and a suite of disinfection byproducts (Pressman et al. 2012). In this study, the NOM samples were collected from January (OR-NOM-Jan) and July (OR-NOM-July) to show seasonal variations. For comparison to other literature reports, SRHA from the International Humic Substances Society was selected as a standard reference.

3.4.2 Characterization of NOM

Thermal gravimetric analysis (TGA) was applied to evaluate the thermal stability of NOM by measuring the amount and rate of weight change of a material as a function of temperature. About 5 mg NOM sample was weighed on an alumina crucible and kept at isothermal conditions of 30 °C for 10 min under air flow (20 L/min) and then heated from 30 to 800 °C in air atmosphere at 10 °C/min. Attenuated total reflection FTIR (Perkin-Elmer model
200) spectroscopy equipped with a Nicolet 752 spectrophotometer and a 45-degree ZeSe flat plate crystal was used to determine functional groups.

TOC was sampled in triplicate and measured in a non-dispersive infrared gas SHIMADZU Analyzer (TOC-5000A). TOC samples were analyzed according to USEPA method 415.3 (USEPA, 2005) with a combustion catalytic TOC analyzer (TOCVcph, Shimadzu Corporation, Columbia, MD). UV254 absorbance was measured according to SM5910 (APHA, 1998) with a Nicolet Evolution 300 spectrophotometer (Thermo Scientific, Waltham, MA). A UV-spectrophotometer (Agilent) was used to determine the absorbance at a wavelength of 254nm.

3.4.3 Characterization of CeO$_2$ nanoparticles

High-grade CeO$_2$ nanoparticles were obtained from Alfa Aesar (Ward Hill, MA) in suspension form (18% by wt. in water) and were used as received. The NPs were characterized using dynamic light scattering (DLS), transmission electron microscopy (TEM), and powder X-ray diffraction as described previously (Li et al., 2011).

3.4.4 Zeta potential measurements of CeO$_2$ in the presence of OR-NOM

Laser Doppler velocimetry in conjunction with phase analysis light scattering (Zeta-Sizer Nano, Malven) was used to measure the $\zeta$-potential of CeO$_2$-NPs. CeO$_2$-NPs suspensions were prepared with various initial ionic strengths of NaCl (3, 10, 50 and 100 mM) and NOM concentrations (0, 1, 5 and 10 ppm).

3.4.5 Stability, transport and deposition of CeO$_2$ Nanoparticles

Glass columns (7.5 cm length ×2.54 cm ID) were packed with industrial mineral silica sand of 20 ×30 mesh size fraction (geometric mean diameter= 0.717 mm) that contains 98.2%
SiO₂ and trace amount of metal oxides (AGSCO Co., IL). The treatment and packing of porous media was described previously (Wiel-Shafran et al. 2006). Prior to starting column test runs and introducing NP suspension, the column was pre-conditioned with NOM solutions (without additional ions) for at least 10 pore volumes. At the onset of a test, the deposition phase consisted of CeO₂ NP suspension with NaCl (3, 10, 50 and 100 mM) and NOM concentrations (0, 1, 5 and 10 ppm) introduced to the column for 30 pore volumes. The rinse phase followed, in which the flow was switched back to particle-free NOM solutions with the same ionic concentration as the deposition phase. The NaCl and NOM concentration were kept constant during each experiment but varied for different tests. Finally, the re-entrainment phase consisted of NOM solution with no additional ions. The NP concentration was monitored at the effluent of the column using an on-line UV-visible spectrophotometer. Temporal changes in effluent concentration were presented as breakthrough curves using normalized effluent concentration versus pore volume.

3.5 Results and Discussion

3.5.1 Characterization of CeO₂ NPs

The average hydrodynamic diameter of CeO₂ NPs was 152.7 nm as determined by DLS based on laser intensity and 62 using laser diffraction analyzer. A representative TEM image of CeO₂ nanoparticles shows the variability in shape and size of the primary particles. The crystallographic phases of CeO₂ nanoparticles observed by XRD analysis shows Figure B2 (b) in Appendix B. X-ray diffraction patterns fitted well with crystalline pattern of CeO₂ phase, confirming purity of the particles.
3.5.2 Characterization of NOM

The UV-254 absorption and TOC of NOM are shown in Table B-1 (Appendix B), which shows that TOC level SRHA > NOM-July > NOM-Jan. The ICP-AES analysis was performed with an iCAP 6000 spectrometer (Thermo Scientific, Waltham, MA) following USEPA method 200.7 (USEPA, 1994). IC analysis was performed according to USEPA method 300.1 (USEPA, 1997). Elemental analysis with ICP-AES analyses of Oho River NOM are shown in Table B-2, B-3 indicating that OR-NOM-July has higher sulfur, Ca, and Mg than OR-NOM-Jan.

3.5.3 Thermogravimetric Analysis

Thermal analysis curves (TGA and DTG) have furnished important information concerning the structural composition of NOM and coal from different environments (Seo et al. 2011) (Young and LeBoeuf 2000). The results of TGA analysis of OR-NOM and SRHA are shown in Figure 3-1. The TGA-DTG curves of all samples show an initial weight loss between 2.4% and 8.1% as temperature increased from 30 to 100°C, corresponding to sample dehydration. The OR-NOM and SRHA TGA resulted in different thermal degradation patterns, indicating differences in composition. The TGA data for OR-NOM-Jan (Fig.3-1a) and OR-NOM-July (Fig.3-1b) both showed significant mass loss over the range of 150-570°C with two successive stages. For OR-NOM-Jan the weight loss was 34%, and for OR-NOM-July the weight loss was 54%. In contrast, the thermo-gravimetric study of SRHA (Fig.3-1c, SRHA-DTG) only showed one stage demonstrated by a sharp deep valley in the DTG curve in the 390-473 °C region, with weight loss between 31.1% and 62.3%.

The TGA of both OR-NOM samples showed two significant changes in weight. The moderate change of weight for OR-NOM-Jan was at 246°C, and for OR-NOM-July was at 220°C. Weight changes at these temperatures can be caused by thermal combustion of
polysaccharides, decarboxylation of acidic groups, dehydration of hydroxylate aliphatic structures (Pietro and Paola 2004), or transformation and oxidation of small molecules (Kolokassidou et al. 2007). Comparatively, the SRHA did not have a weight change near these temperatures. OR-NOM-Jan and OR-NOM-July reached their minimum DTGs at 458°C and 472°C, respectively, which were close to the 448°C minimum DTG of SRHA. These minima correspond well with the range 450-480°C, which is related to the combustion of aromatic structures, the cleavage of C-C bonds (Peuravuori et al. 1999), and which leads to depolymerization, cyclization reactions, and thermal cracking of higher molecular weight polynuclear systems, such as carboxylic and phenolic groups (Shurygina et al. 1971). For DTG losses around 450°C, thermal degradation can also involve the presence of long chain hydrocarbons and Nitrogen compounds (Iordanidis et al. 2001). SRHA has a more significant DTG weight loss at a narrower temperature range at this region compared to the OR-NOM samples. The difference in DTG response in this region may be explained by the difference in processing between the samples, whereas the SRHA is fractionated by XAD resin adsorption and the OR-NOM samples consist of whole NOM which contains fulvic substances and other smaller molecules. The ash content of the OR-NOM-Jan, OR-NOM-July and SRHA, which are determined from the minimum of the TG curve at high temperature, are 54%, 34% and 37%, respectively. High ash has been previously reported in reverse osmosis isolation of some winter and spring NOM samples that could be result of high Si content (Sun et al. 2002) The difference in the thermal degradation of the three NOM samples strongly suggests that differences in composition, structure, and functional groups are caused by preparation methods used where SRHA was fractionated and OH was whole.
3.5.4 Fourier Transfer Infrared Spectroscopic analysis of NOM

The FT-IR spectrum of the Ohio River NOM samples is summarized in Fig. 3-2, and the FT-IR spectra of SRHA was obtained from IHSS. While the spectra of the OR-NOM samples look similar there are distinctive differences compared to the SRHA. OR-NOM samples showed strong peaks at 1726 cm\(^{-1}\), which were not observed in the SRHA and may be attributed to the carboxyl C=O stretching absorption peak. This may be because of the higher content of fulvic acid in OR-NOM that contributes to higher carboxyl group content. The C-H stretch of the aliphatic group was shown to exist in the 1470~1410 cm\(^{-1}\) range. For OR-NOM-July the peak observed at 1410 cm\(^{-1}\) was higher than that of the OR-NOM-Jan, implying the higher water temperature and the more degraded organic matter in July led to a more hydrophilic characteristic. The peak in the range 1250 ~ 1000 cm\(^{-1}\) indicates C-O stretching and the presence of hydrophilic neutral compounds. Comparatively, the peak in the 880 ~ 750 cm\(^{-1}\) range (795 cm\(^{-1}\) for OR-NOM-July and 802 cm\(^{-1}\) for OR-NOM-Jan) indicates an O-H functional group attached to a carboxyl group and the presence of hydrophobic substances. These results indicate that the OR-NOM consists of both hydrophobic and hydrophilic substances. The FTIR spectrum of SRHA showed higher intensity and saturation in the range of 3600-3200 cm\(^{-1}\) with two peaks at 23398 and 3265 cm\(^{-1}\), while both OR-NOM samples resulted in only a broad absorption spectrum and no distinct peaks in this range. The SRHA peak at 1620 cm\(^{-1}\) can be attributed to aromatic C=C double bond stretching, conjugated with C=O and/or COO-, which was found to be around 1640 cm\(^{-1}\) (Morrison and Boyd, 1995). The peak at 1387 cm\(^{-1}\) can be attributed to –CO–CH\(_3\) and possibly nitrate. The 1207 cm\(^{-1}\) peak indicates nitrates (R–O–NO\(_2\)), =C–O–C groups, and possibly C–O of phenolic groups (Baes and Bloom 1989).
The composition difference between SRHA and OR-NOM comes from the origin and the method used to recover them from environmental matrices. To create SRHA, the IHSS concentrated the NOM using reverse osmosis followed by isolating the humic substances from natural water using XAD-8 resin adsorption. In this method, the dissolved organic matter was initially fractionated into hydrophobic and hydrophilic fractions. Subsequently, the hydrophobic fraction was eluted from the resin by an alkaline extraction, followed by precipitation of humic acid at low pH and a desalting step to obtain fulvic acid. The humic acid and fulvic acid that are isolated in this method thus contain only hydrophobic organic acids. Comparatively, the OR-NOM was concentrated using reverse osmosis membrane technology and directly lyophilized, maintaining a whole mixture of the hydrophobic and hydrophilic acids in addition to the other soluble organic solutes that are present in natural waters. These differences between SRHA and OR-NOM confirmed that using SRHA to study the effect of NOM might not be sufficient to represent the natural conditions of the environment.

3.5.5 The influence of OR-NOM on the \( \zeta \)-potential of CeO\(_2\) NPs

The effect of NOM on the electrophoretic stability of CeO\(_2\) was studied by measuring the \( \zeta \)-potential in the presence of increasing concentrations of OR-NOM (1, 5, 10 ppm) at various ionic strengths (3, 10, 50 and 100 mM NaCl)(Fig.3-3). The \( \zeta \)-potential of CeO\(_2\) NPs became less negative with increasing ionic strength because of the compression of electrical double layers, while increasing NOM concentration resulted in a more negative surface of the. The CeO\(_2\) NPs were more sensitive to the presence of summer collected NOM, resulting in lower \( \zeta \)-potential.

At the same NOM level, CeO\(_2\) NPs are generally more stable in the presence of OR-NOM-July compared to OR-NOM-Jan, reflected by a bigger absolute value of \( \zeta \)-potential. For example, at the concentration of 1 ppm, for OR-NOM-Jan, the absolute magnitude of \( \zeta \)-potential
of CeO₂ decreased from -43 mV at 1 mM NaCl to -32 mV at 100 mM NaCl; while for OR-NOM-July, it was from -46 mV at 1 mM NaCl to -35 mV at 100 mM NaCl. When increasing the NOM concentration, a general increase in the absolute value of CeO₂ ζ-potential was observed at most ionic values. However, the increase was more significant from 1 ppm to 5 ppm, than from 5 to 10 ppm. This may be because at the higher NOM concentrations the adsorption of NOM to the NPs surface reached saturation, so further NOM increase does not contribute a significant change.

3.5.6 Transport of CeO₂ NPs in porous media in the presence of OR-NOM

The transport breakthrough curves and retention profiles of CeO₂ NPs at pH 6.8, increasing ionic strength (3, 5, and 10 mM), and increasing NOM concentration (1, 5, and 10 ppm) are shown in Fig. 3-4 (A, B and C) for OR-NOM samples. From our previous study (Lu et al. 2013), in the absence of NOM and near-natural solution pH, the breakthrough profile of CeO₂ was partial when the ionic concentration was greater than 1 mM, reflected by a normalized breakthrough concentration (C/C₀, where C is the effluent concentration and C₀ is the effluent concentration) plateau value less than 1. However in the presence of NOM, CeO₂ quickly reached full breakthrough (C/C₀=1) in a 3 mM ionic concentration, even at the low NOM concentration of 1 ppm, confirming the stabilizing effect of dissolved NOM (Fig3- 4A).

At 5 mM ionic concentration and the 5 and 10 ppm OR-NOM concentrations, CeO₂ NPs gradually reach full breakthrough at pore volume 12. At 1 ppm NOM concentration, CeO₂ NPs reached partial breakthrough with a plateau of approximately 0.48 for both OR-NOM-Jan and OR-NOM-July. For 3 and 5 mM ionic concentration and a given NOM concentration, the type of NOM (Jan or July) did not affect the plateau of the breakthrough, but only affected the shape and rate of the initial breakthrough. The CeO₂ breakthrough occurred after 1-3 pore volumes, where the initial breakthrough rate increased with increasing NOM concentration. Also, the
breakthrough of CeO$_2$ was somewhat faster in the presence of OR-NOM-July as compared with OR-NOM-Jan. At a 10 mM ionic concentration, CeO$_2$ NPs had a partial breakthrough, starting around 1 pore volume and slowly reaching a plateau. The plateau concentration increased with increasing NOM concentration. Furthermore, the two higher NOM concentrations resulted in a higher plateau in the presence of the OR-NOM-July compared to the OR-NOM-Jan. Sharp peaks were observed for CeO$_2$ NPs during the rinse phase at approximately 35 pore volumes. The rinse peak intensity was higher when the plateau value of the breakthrough curve was lower in the deposition phase indicating that loosely adsorbed NPs washed out when the water chemistry changed.

Generally, the maximum effluent concentration normalized with the input concentration decreased with increasing ionic strength, and increased with increasing NOM concentrations when other conditions remained the same. The two Ohio River NOM samples resulted in differences in the transport of CeO$_2$ NPs that were more significant at higher ionic and NOM concentrations. OR-NOM-July showed a higher stabilizing effect for CeO$_2$ NPs, which can be explained by the higher organic carbon content. OR-NOM-July also has more C-H stretch of the aliphatic group, which contributes in stabilizing CeO$_2$ NPs.

At ionic strength of 3 and 5 mM, the breakthrough profile of CeO$_2$ NPs is in agreement with the ζ-potential measurements. For instance, in 5 mM ionic strength solution, when OR-NOM-July concentration increased from 1 to 5 ppm, the ζ-potential of the CeO$_2$ NPs decreased from -41.5 mV to -53.6 mV and the plateau value of the breakthrough curves of CeO$_2$ increased from 0.48 to 0.98. The same trend was observed for OR-NOM-Jan. This behavior is believed to result from an increased electrostatic repulsive interaction which prevents the CeO$_2$ particles from attaching within the column and therefore they exit in the effluent. This phenomenon is in
qualitative agreement with the DLVO theory of colloidal stability. On the other hand, the ζ-potentials of the CeO₂ NPs at 10 mM NaCl concentration changed only minimally with the increase in NOM from 5 to 10 ppm, while the maximum normalized effluent concentration of the breakthrough curve increased from 0.23 to 0.45 in the presence of OR-NOM-July and from 0.20 to 0.36 in the presence of OR-NOM-Jan. These results cannot be explained in the framework of the classic DLVO theory.

The transport and retention profile of CeO₂ NPs through porous media in the presence of SRHA is included in Appendix B in Fig B-3 (A, B and C). The effect of SRHA on the transport of the CeO₂ NPs is similar to the OH-NOM samples but generally results in less particle stabilization and higher maximum normalized effluent concentrations. For example, at the same ionic concentration and NOM concentration, the breakthrough curves for CeO₂ NPs showed higher maximum normalized effluent concentrations in the presence of SRHA as compared to OR-NOM, consequently yielding higher θ values. This indicates using SRHA as a model NOM to study the transport and retention of NPs in drinking water relevant sand filters may over-estimate the facilitating effect of NOM.

3.5.7 Modified DLVP theory and the attachment efficiency of CeO₂ NPs in the presence of OR-NOM.

The breakthrough curves of CeO₂ NPs were used to calculate the attachment efficiency (θ) in packed beds, which was experimentally determined for each of the test conditions following a previously described procedure (Li et al, 2011) and also provided in the Appendix B. Figure 3-4 (E, D, and F) summarizes θ as a function of NOM concentration at each ionic strength. The presence of increasing NOM concentrations decreased the attachment efficiency of CeO₂ NPs, becoming more pronounced as the ionic strength increased above 3 mM NaCl.
Therefore, the mobility and transport of the CeO$_2$ NPs was increased due to the adsorption of NOM to the NP surface. The stabilizing and mobilizing effect of OR-NOM-July is more pronounced than the OR-NOM-Jan. As a result, the stability and mobility of CeO$_2$ was largely dependent on the aqueous concentration of NOM, and the seasonal change of NOM, especially at higher ionic strength.

In order to better understand the impact of NOM on the transport and deposition behavior of CeO$_2$ NPs, the interaction energy between the CeO$_2$ NPs and the sand surfaces must be calculated for each experimental condition. Since the traditional DLVO theory was insufficient to describe the transport and deposition of CeO$_2$ in the sand filters at 10 mM NaCl, as discussed previously, a steric repulsive energy was added to the total interaction energy to better describe the energy profile between NOM coated CeO$_2$ NPs and sand surfaces. Steric repulsion between two surfaces results from volume restriction and osmotic effects. The former takes place from the reduction of space in the zone between particle surfaces; the later arises from the high concentration of adsorbed charged macromolecules in the region between the surfaces as they approach each other. Electrostatic and steric repulsion forces inhibit deposition of particles to grain surfaces.

The modified DLVO interaction energy profile for CeO$_2$ NPs at 3 mM NaCl, in the presence of 5 ppm and 10 ppm OR-NOM-July is shown in Fig.3-5. The results show that for the traditional DLVO theory, which includes only double layer repulsion and van der Wall attraction, the interaction energy profile for 5 ppm NOM (A) and 10 ppm NOM (B) were very close. The DLVO theory demonstrates the existence of a repulsive energy barrier at 12 kT where the DLVO curve peaks around 5 nm and a shallow secondary minimum of 6 kT, implying moderate deposition conditions. However, the enhanced breakthrough when the NOM concentration was
increased to 10 ppm is not reflected in the DLVO curve. Adding the steric repulsive energy to the DLVO theory resulted in a shallower secondary minimum and a greater energy barrier because of the adsorption of OR-NOM to the CeO$_2$ NPs. A clear increase in the primary energy barrier is shown for 10 ppm NOM (27 kT) compared to 5 ppm NOM (18 kT), indicating that it is less likely for CeO$_2$ NPs to overcome the primary energy barrier and be deposited onto the sand surface, which explains the enhanced breakthrough that was observed in the transport column studies.

The presence of NOM in the NP suspensions clearly affected the maximum normalized effluent concentrations in the transport study as well as the attachment efficiency and maximum transport distance. OR-NOM clearly increased the stability of CeO$_2$ NPs in water as the absolute $\zeta$-potential increased with an increasing NOM concentration. However, there was a difference in the magnitude of the $\zeta$-potential depending on the whether NOM was from January or July, resulting in a different breakthrough profile at a 10 mM ionic strength. This difference in $\zeta$-potential is related to the proportion of humic acid to fulvic acid present in these two NOM types and the TOC level. An absolute increase in the magnitude of $\zeta$-potential increased the electrostatic repulsion, which in turn reduced aggregation and enhanced transport of nanoparticles through the sand column. The adsorption of NOM stabilized CeO$_2$ NPs against van der Waals attractive forces. The repulsive forces were a combination of electric particle surface charge or electrostatic double layer repulsions, and the steric repulsion forces generated from the adsorption of long-chain-charged NOM molecules on the surface of NPs.

3.6 Conclusion

Overall, this study characterized Ohio River NOM and demonstrated the effects of NOM on stability and transport of CeO$_2$ NPs in saturated porous media. OR-NOM characterized by
thermal analysis and FT-IR was shown to have significant differences compared to SRHA. OR-NOM was observed to enhance the breakthrough and facilitate the transport of CeO$_2$ NPs in moderate (1-10 mM) ionic strength solutions. The enhancement is dominated by the altered electrokinetic properties of the CeO$_2$ NPs. Increasing NOM concentrations, as measured by zeta potential, increase the electrostatic repulsive interaction between CeO$_2$ NPs. As the concentration of NOM increases, combinations of elevated electrostatic and steric interaction provide further repulsive forces to stabilize and mobilize CeO$_2$ NPs in the aquatic environment. A modified DLVO theory presented in this study can qualitatively interpret the general trends of the CeO$_2$ NPs transport and retention behavior under such conditions. The effect was also compared between summer and winter collected NOM samples. Summer collected NOM showed a stronger effect in stabilizing and facilitating the transport of CeO$_2$ NPs. The difference in chemical and physical properties between SRHA and OR-NOM suggests that SRHA may only be used to determine qualitative effects of NOM, since SRHA might not represent the composition of natural organic matter of a specific environment.

3.7 References


Figure 3-1 Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) of natural organic matter (NOM), (A) Winter collection from Ohio River, OR-NOM-Jan, (b) for July collection Ohio river, OR-NOM-July, and (c) SRHA. Sample average weight was 5 mg, Initial temperature = 30 oC, Air flow was 20 ml/min, for heating rate =10 oC/min Pan Type: Platinum.
Figure 3-2 Fourier transfer infrared spectra of Ohio River extracted NOM (OR-NOM) that were collected during the months of January (OR-NOM-Jan), and July (OR-NOM-July).

Figure 3-3 Zeta potential of CeO2 as a function of ionic concentration in the presence of Ohio River NOM samples, (A) OR-NOM-Jan, and (B) OR-NOM-July for concentration: 3, 5 and 10 ppm.
Figure 3-4 Breakthrough of CeO2 nanoparticles in the presence of Ohio river NOM (OR-NOM) at concentrations 1, 5 and 10 ppm having selected ionic concentration of (A) 3 mM NaCl, (B) 5 mM NaCl, (C) 10 mM NaCl, and the corresponding attachment efficiency for ionic concentration, (D) 3mM NaCl, (E) 5mM NaCl, (F) 10mM NaCl
Figure 3-5 Modified DLVO interaction energy when CeO2 NPs approaching sand surface at the ionic concentration of 10 mM NaCl, in the presence of (A) 5 ppm OR-NOM-July, and (B) 10 ppm OR-NOM-July
4 Chapter 4. Transport of Nanoparticles with Dispersant through Biofilm Coated Drinking Water Sand Filters

4.1 Abstract

This chapter characterizes, experimentally and theoretically, the transport and retention of engineered nanoparticles (NP) through slow sand filters at drinking water treatment plants (DWTPs) under realistic conditions. The transport of four commonly used NPs (ZnO, CeO$_2$, TiO$_2$, and Ag, with bare surfaces and coated with capping agents) through filter beds filled with sands from either acid washed and calcined, freshly acquired filter media, and used filter media from active filter media, were investigated. The study was conducted using water obtained upstream of the sand filter at DWTP. The results have shown that capping agents have a determinant importance in the colloidal stability and transport of NPs through the different filter media. The presence of the biofilm in used filter media increased adsorption of NPs but its effects in retaining capped NPs was less significant. The data was used to build a mathematical model based on the advection-dispersion equation. The model was used to simulate the performance of a scale-up slow sand filter and the effects on filtration cycle of traditional sand filtration system used in DWTPs.

4.2 Introduction

As the utilization of nanoscale materials in many commercial products increases, engineered nanoparticles (NPs) are becoming emerging contaminant of concern with the potential for wide-spread distribution in the aquatic environment (Baun et al. 2008). Determining the fate of NPs in drinking source water has important significance for health risk assessment and regulatory interest (Navarro et al. 2008, Thomas et al. 2006, Hassellöv et al. 2008).
Many experimental studies and mathematical modeling were performed to better understand the stability on NPs in aqueous system and their transport and deposition through porous media (Petosa et al. 2010). In these studies, aqueous suspensions of NPs were injected into columns packed with granular porous media, and the transport and retention of NPs were evaluated under varying conditions such as media type, water chemistry the presence of natural organic matter (NOM), and flow velocities (Lecoanet and Wiesner 2004, Chen and Elimelech 2008, Liu et al. 2009, Jaisi et al. 2008, Chen and Elimelech 2006, Wang et al. 2008b, Fang et al. 2009, Wang et al. 2008c). It was generally observed that NPs can change their behavior depending on the surrounding media, and it was commonly agreed that their flow behavior can be explained using classic Derjaguin-Landau-Verwey-Overbeek (DLVO) theory (Derjaguin and Landau 1941, Verwey and Overbeek 1948) and clean-bed filtration theory. However, predicting the fate of NPs in the aquatic environment from the transport studies is far from simple. The conditions in these studies were artificial and simplified, thus they are far from the actual conditions of natural water matrix and collector surfaces.

Drinking water treatment plants (DWTP) can be directly impacted by accidental or routine release of NPs to source waters. Earlier research on the effectiveness of DWTP facilities has shown that NPs coagulate with alum resulting in only 20 to 60% removal by sedimentation (Zhang et al. 2008). Tong et al. (Tong et al. 2010) have shown that an extracellular polymer substance of E-Coli biofilm can increase the breakthrough of C60 NPs in the biofilm-covered sand columns. However, these studies are not adequate to predict the capability of DWTP removing NPs.

Suspended solids and waterborne pathogens are removed by slow sand filtration (SSF) via both physical processes (such as absorption, diffusion, screening and sedimentation) and
biological processes (such as predation, natural death, and metabolic breakdown) (Ellis and Wood 1985, Keijola et al. 1988, Haarhoff J 1991, Fogel D 1993, Bahgat et al. 1999). The biological zone, also known as “Schmutzdecke”, is where the highest biomass concentration occurs, and it is the region where most biological treatment is achieved (Haarhoff J 1991). These characteristics of SSF sand bed are not reflected on the lab-designed columns in the studies summarized previously. Thus the previous studies could not be used to fully predict the capability of the retention of NPs in SSF.

The present research investigated the transport and retention of NPs under realistic environmental conditions of actual pre-filtration drinking water taken prior to SSF system. The study provided comparison on the effects of water matrix and the difference in filter bed filled with pretreated clean sand and biofilm coated sand. The pre-filtration water and filter sand were provided by Great Cincinnati Waterworks (GCWW), a local DWTP. The test conditions replicate the actual operating conditions of the SSF of GCWW. To our knowledge, currently no such research has been conducted before.

This study aims at investigating the stability, transport, and deposition of selected engineered NPs through SSF. The effectiveness of biofilm coated sand in SSF in removing NPs from natural waters was studied by replicating actual DWTP operations in laboratory settings including water and the water-saturated porous media used in the DWTP. Column runs were conducted in three different media to compare sand samples obtained from a DWTP with the same unused sand type and with acid treated sand. Water used in the experiments was obtained from the influent stream of the SSF in the DWTP. The removal efficiency, breakthrough time, and other results obtained from lab-scale column tests were used to develop mathematical
simulation and predicting the performance of a full-scale system and comparing actual treatment scenarios.

4.3 Theoretical Considerations

The theoretical analysis of the filter bed subsystem leads to a coupled system of equations that describes local fluid flow within the control stream and adsorption and desorption within individual collector elements comprising the packed bed. A one dimensional advection-dispersion-sorption/desorption kinetics (Eq.4-1) describes the transport and retention of NPs on a homogeneous porous medium in steady-state flow. The clean bed filtration theory expresses the kinetics as a function of the rate of NP attachment along the depth $k_{mod}$, the detachment rate, $k_{det}$, and $S_{max}$ the maximum retention capacity of NPs within the bed. The coupled transport and retention equations (Eq.4-1 and Eq. 4-2) and boundary and initial conditions (Eq.3) are as follows:

\[
\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x} - \frac{\rho_b}{\theta_w} \frac{\partial S}{\partial t} \quad \text{(Eq.4-1)}
\]

\[
\frac{\rho_b}{\theta_w} \frac{\partial S}{\partial x} = S_{max} C - \frac{\rho_b}{\theta_w} k_{det} S \quad \text{(Eq.4-2)}
\]

I.C \hspace{1cm} C(x,t=0)=0 \hspace{1cm} S(x,t \to 0)=0

B.C \hspace{1cm} C(x = 0,t) = C_0 \hspace{1cm} \frac{\partial C}{\partial x} (x = L, t) = 0 \quad \text{(Eq. 4-3 )}

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where, C is the concentration of NPs in solution, S is the concentration of NPs associated with the solid phase, t is time elapsed, x is the distance parallel to the flow, $\rho_b$ is the sand bulk density, D is the hydrodynamic dispersion coefficient, $\theta_w$ is the volumetric water content and $V_p$ is pore water velocity. The details of the modeling was described in our earlier publication (Li et al. 2011).

In the analysis of the experimental data, the attachment efficiency, $\alpha$, is defined as the ratio of the rate of particle deposition on a collector to the rate of collisions with that collector that has been used. For column studies, $\alpha$ can be expressed as a function of the relative effluent concentration $C/C_0$, where C is the effluent concentration at time t, and $C_0$ is the influent concentration, and as following:

$$\alpha = \frac{2d_c}{3(1-\varepsilon)\eta_0 L} \ln \left(\frac{C}{C_0}\right) \quad \text{(Eq. 4-4)}$$

Where $d_c$ is the median diameter of the porous media, $\varepsilon$ is the bed porosity, $L$ is the length of the bed, and $\eta_0$ is the theoretical clean bed single collector efficiency, which describes the particle transport to an individual collector before particle accumulation alters the collector geometry. Single collector efficiency can be calculated as the sum of individual contributions each transport mechanism, and the overall correlation equation. The experimental particle deposition rate coefficient, $k_{exp}$, which represents the rate of physical chemical filtration, is related to the single-collector efficiency, $\eta_0$, when the transport of colloids in saturated porous media is within the advection-dispersion range. The expression for particle deposition rate is given as following:
\[ k_{\text{exp}} = \frac{3}{2} \frac{(1 - \varepsilon)}{d \varepsilon} U \alpha \eta_0 \]  
(Eq. 4-5)

Where \( U \) is the Darcy velocity of the flow.

4.4 Material and Methods

4.4.1 Nanoparticles

Industrialy important NPs: CeO\(_2\), TiO\(_2\), ZnO and Ag NPs were selected as model NPs. Physico-chemical properties and vendors of these NPs are summarized in Table C-1 (Appendix C). Silver NPs were synthesized in the laboratory following a previously reported technique (El Badawy et al. 2010) coated with citrate and Polyvinylpyrrolidone (PVP). Other NPs were received from commercial vendors and known concentrations of NP suspensions were prepared by adding NPs stock solution in appropriate volume of water. NP suspensions were sonicated for 15 min at 20 KHz at intensity of 20W/L prior to their use in the experiments.

4.4.2 Porous Media

Three types of sands were used to make the porous media for this study. First, the Used Filter Sand that was acquired from the top layer of filter sand cake in the backwashed SSF of GCWW. Second, Fresh Filter Sand, i.e., the same type as the Used Filter Sand, was obtained from Northern filter Media Inc. (Muscatine, IA). It has mesh size of 30 x 40 with an effective size of 0.5 mm and a uniformity coefficient of 1.65. Third, Treated sand was obtained from American Graded Sand Company (AGSCO Co, Wheeling IL). It was thoroughly cleaned by sequential washing with 1M HNO\(_3\) solution and repeat rinsing with water, followed by oven
drying at 550 °C for 12 hr. The Treated sand had mesh size 20 x 30 with an effective size of 0.7 mm and the uniformity coefficient was < 2.5. Thermogravimetric analysis (TGA) (Pyris 1, PerkinElmer Co.) was conducted to determine the total organic mass on filter media. The size and morphology of the biofilm on the sand was examined by ultrahigh resolution field emission scanning electron microscopes (SEM). The biofilm growth on used filter sand was also analyzed with a Confocal Laser Scanning Microscopy (Zeiss LSM 510, Plan-Neofluar 40×/0.3) after biofilm staining with the LIVE/DEAD BacLight viability kit (L7012, Molecular Probes, Inc.).

4.4.3 Water Samples

Raw water used in this study was collected from the upstream of the sand filter after the final settling stage at GCWW which gets its water from the Ohio River. Samples were collected in the month of February and all samples were stored at 4 °C under dark conditions until needed. The pH of the collected raw water was measured by an Oakton pH meter (Ion 510 series, Fisher Scientific); the turbidity of suspended particle density was evaluated using turbidity meter (Hach® 2100N Laboratory Turbidity Meter), the conductivity and resistivity was measured by a Fisher Scientific Traceable* Conductivity and Resistivity Meter (Fisher Scientific). Volatile suspended solids (VSS) was measured using Standard Method 2540 E, American Water Works Association, Water Environment Federation. Total organic carbon (TOC) was obtained in triplicate, measured in a non-dispersive infrared gas SHIMADZU Analyzer (TOC-5000A). The concentrations of 18 dissolved ions in the raw water were determined by inductively coupled plasma atomic emission spectrometry (ICP-AES) (Optima 2100 ICP-AES Optima PerkinElmer Inc.). Concentrated acids, HNO₃ (69%) and HCl (36%) (Trace Metals Grade, Fisher Chemical,) were used to acidify all solutions. All calibration solutions and quality control solutions were prepared from single element standards or multi-element solutions (SPEX CertiPrep).
4.4.4 Measuring Surface charge zeta potential of NPs and porous media

The $\zeta$-potential of the NPs-to-solution interface was measured with a laser Doppler velocimetry setup (Malvern Instruments Ltd.). For the porous media, SurPASS Electrokinetic Analyzer (Antone Parr) was used to investigate the $\zeta$-potential based on a streaming potential and streaming current measurement. An integrated titration unit using two syringe pumps enabled the automatic change of electrolyte pH, conductivity, or concentration, which enabled non-destructive measurements of the large samples. The $\zeta$-potential was related to the surface charge at a solid/liquid interface and is a powerful indicator for the surface chemistry (pH titration) and liquid phase adsorption processes.

4.4.5 Measuring NP Aggregation in Raw water

The NPs were dispersed in raw water and in DI water. The size distribution of NP suspensions were measured as a function of time via dynamic light scattering (DLS) using a Zetasizer Nano ZS (Malvern Instruments Worcestershire, UK). Quantitative measurement of NP concentration was measured by UV-visible spectrometer (Agilent 8453) at the maximum wavelength of each NP based on multi-concentration calibration which was previously established. The aggregation process was also monitored by measuring the concentration change of the suspensions using UV-Visible Spectrophotometer at a 5 min time interval for 120 min.

4.4.6 Transport of NPs in sand filters under GCWW operation conditions

The transport studies were intended to simulate the slow sand filtration process of the GCWW, where supernatant water reservoir maintains a constant water head providing the driving pressure through the filter. A low pressure peristaltic pump (Master Flex-Cole-Palmer) provided equivalent pressure at the same flux with a flow rate of 19 mL/min. The transport study
was performed using cylindrical glass columns with internal diameter of 2.5 cm and 15 cm long (Ace Glass). The columns were packed with specific sands using a wet packing method by adding 5 mm depth at a time, yielding a bed porosity of 0.34. Prior to starting column test runs and introducing NPs suspension, the column was flushed with GCWW raw water for at least 10 pore volumes. At the onset of the test, a stream of NP suspension was introduced to the column for 30 pore volumes, after which the flow was switched back to raw water. The NPs concentration was monitored at the effluent of the column using an on-line UV-visible spectrophotometer. Temporal changes in effluent concentration were presented as breakthrough curves using normalized effluent concentration versus pore volume (V<sub>p</sub>).

4.5 Results and Discussion

4.5.1 Characterization of Nanoparticles

The characteristics of the NPs selected in this study are summarized in Table C-1 (Appendix C). The average particle size of NPs and their ζ- potential varied significantly between DI water and raw water matrix due to the dissolved ions and natural organic matter. Particles aggregated in raw water where the size of ZnO increased by a factor of 2 from DI water to raw water, and for Ag-Citrate it increased by a factor of 9. Particles also exhibited poly-disperse system where most particles remained in the original state while a small portion formed large cluster structures. The surface charge was more negative for most of the NP when dispersed in raw water except for CeO<sub>2</sub> with no dispersant and ZnO with dispersant; however, the difference of two waters is not significant. The NOM in the raw water absorbs onto the bare surface of the NPs, and the negatively charged functional groups counterbalance the VDWL attraction between the NPs. For NPs with a strong dispersant, this effect is not significant.
4.5.2 Characterization of water samples

The water obtained from GCWW had turbidity of 0.268 NTU, pH of 7.8, total organic carbon (TOC) level of 2.56 ppm, and total hardness of 133 mg/L as CaCO₃ and may have contained microbiological growth. The ICP-OES analysis shows that the main ions were Mg²⁺, K⁺, Na⁺ and Ca²⁺ (Figure C-2, Appendix C). The conductivity was measured at 344.9 µs/cm corresponding to ionic strength of ca. 5.5 mM using the Russell approximation equations (Chris 2011).

4.5.3 Characterization of the Filter Media

Optical microscope (Figure 4-1 a-c) and scanning electron microscopy (Figure 4-1 d-f) images of samples show the shape, roughness, and physical homogeneity of the sand particles. Treated sand had smooth clean surface, while the Fresh filter sand has irregular rougher shape and a coarser surface. The extended use period has resulted in polished smooth shape particles covered with biofilm containing a diverse microbial population and extracellular matrix. Scanning electron micrographs show the surface of the biofilm on used sand particles. Rod-shaped gels embedded in an extracellular fibrillary material structure indicating predominance of filamentous micro-organisms at the surface of the filter sand. Extracellular polymeric substance of the fresh and used sand samples containing biofilm were qualitatively measured using confocal laser scanning microscope (CLSM) after staining cells with a fluorescent dye specific for nucleic acids. The lateral CLSM images of the fresh sand and used sand are shown in Figure 4-1 h-j. The CLSM images show the used filter sand was covered with a thick mass of microorganisms, bacteria, bacteriophages, and protozoa. Crystalline clean quartz sand has a negative charge and attracts positively charged particles of colloidal matter and metal cations.
Hence, the $\zeta$-potential of mineral grains plays an important role in the initial deposition kinetics of colloidal particles (Elimelech et al. 2000).

All three sands were negatively charged at the operating condition for the column studies at pH ranges from 7 to 8. The used filter sand has a markedly lower negative $\zeta$–potential average of -18 mV than the fresh sand (-45 mV) and treated sand samples (-66 mV). This agrees with reported average $\zeta$-potential of microalgae other unicellular algae and -30 mV for green alga *Dunaliella parva* at pH 7.6 in a glycerol buffer (Rosenhahn et al. 2009). Unused filter sand has an isoelectric point at pH ~ 2.7, and treated sand has an isoelectric point even lower at pH ~ 2.0 (when extrapolated). This is an indication of the presence of possible acidic surface chemistry. The isoelectric point of used filter sand was ~ 4.0 indicating a more inert surface and a lower concentration of acidic surface groups. Metal oxides NPs are negatively charged (Table C-1 Appendix C) and would be consequently repelled by sand particles. The treated sand were more negatively charged at the pH ranges investigated (Figure 4-2), and the $\zeta$–potential was less negative for unused filter sand and used filter sand. This could determine NP deposition kinetics onto the charged surfaces during the initial ripening process.

4.5.4 **Aggregation Kinetics and Stability of Nanoparticles in Filter Water**

The change in the average particle size of the four NPs with and without dispersant were studied in DI and Raw water. When NPs without capping agents or dispersants were suspended in raw water followed by sonication, they quickly form large aggregates with highly poly-dispersed clusters (Figure 4-3 and Figure C-3, Appendix C). Similar fast formation of ZnO and TiO$_2$ aggregates in water were observed by other researchers (French et al. 2009, Zhou and Keller 2010). Adding dry NP powder to water could result in high local initial concentrations
that enhanced collision frequency, hence particles reduce their surface energy, which leads to rapid initial aggregation forming larger clusters. However, for ZnO with dispersant, the initial average hydrodynamic diameter in raw water was $141.8 \text{ nm}$ where the size remained at $198 \pm 2 \text{ nm}$, with little aggregation during the following hour. For Ag NPs, both with citrate and PVP, the particle size distribution remained at $80 \pm 5 \text{ nm}$ in raw water and no cluster aggregation was observed.

The stability of NPs in raw water was also studied by measuring the change in bulk concentration of NPs over time using UV-visible spectrometer (supplemental C). Quantitative analysis was done using a calibration of a UV-visible spectrometer based on multi-concentration standard samples of NPs tested. Particle aggregation is dependent on the presence of dispersant, the water type and initial concentrations as shown for TiO$_2$ (Figure 4-3). Higher concentrations of dissolved ion and initial NPs increased aggregation. In raw water, CeO$_2$ NPs without dispersant, had fast aggregation from 44nm to a poly-dispersed system of more than 1µm during 75 min. The high ion concentrations in the raw water samples compressed the electron double layer hence reducing the electrostatic repulsion and decreased surface charges and electrophoretic mobility EPM. However, the influence of ionic strength is less significant than the presence of polymer dispersant. Aggregation for TiO$_2$ particles was faster under the same conditions, without dispersant.

4.5.5 **Transport and Retention of Nanoparticles in Filter Media**

The breakthrough data was used to determine the mathematical model constants. Figure 4-4, shows experimental results as symbols and the model predictions as solid lines. The normalized effluent concentration was dependent on the type of coating of NPs and the packing media. Breakthrough curves of dispersant coated NPs, flowing through columns packed with
treated sand, fresh sand and used sand are shown in Figures 4-4a, 4-4b and 4-4c, respectively. For the NPs without dispersant, the sand columns were capable of retaining bare-surface NPs and no breakthrough was observed (Figures 4-4d, 4-4e and 4-4f). PVP coated Ag had full breakthrough within 2 pore volume flow, whereas the citrate coated Ag took 30 pore volume for the effluent to $C/C_0$ reach to 1. For ZnO, a fast partial breakthrough occurred and the $C/C_0$ reached a plateau value of 0.7 and remained unchanged. The breakthroughs of Ag-PVP and ZnO were similar in the treated and unused filter sand, after breakthrough NPs rapidly reached a plateau value of 0.9 and 0.7, respectively. The retention times for NPs through biofilm coated used sand was higher than the other porous media tested (Figure 4-4c).

Sharp peaks were observed for CeO$_2$ NPs during the rinse phase following the deposition phase, which were more significant for the column packed with treated sand and unused filter sand, but not for the used sand. This indicates that the attachment forces of CeO$_2$ NPs to the treated sand and unused filter sand were rather weak, but the existence of a biofilm on the used filter sand inhibited the release of deposited NPs. For all of the sand types, NP concentrations dropped back to 0 immediately after the NPs feed. The initial breakthrough $C/C_0$ value for Ag-Citrate NPs was 0.3, and it gradually increased to 0.6 at the end of the deposition phase, indicating that used filter sand has more potential of retaining Ag-Citrate NPs.

The breakthrough curves were used to estimate the attachment efficiency and deposition rate coefficient for the three filter media. Attachment efficiency, the ratio of the rate at which NPs strike the collector divided by the rate of at which particles flow toward the collector is usually used to estimate filter efficiency. The biofilm coated sand increased the attachment efficiency by 75%, averaged for all NPs, as compared to acid treated sand. However, the presence of dispersants dramatically increases the attachment efficiency of NPs to the porous
media, confirming that dispersant plays the most significant role in the occurrence of the breakthrough (Table 4-1). The attachment efficiency decreased by an average of 35 to 41 times in presence of dispersant compared to bare surface NPs. It shows that, for the three types of sand tested, the NPs with dispersant showed little or no retention compared to bare surface NPs. The order of the retention for NPs is: ZnO and TiO$_2$, CeO$_2$, Ag with Citrate, ZnO with dispersant, CeO$_2$ with dispersant, and Ag with PVP.

4.5.6 Effects of Dispersant

The dispersants that were added during the manufacturing process of engineered NPs act as a key factor in their stability, transport and deposition. The dispersants can attach macromolecules to the surfaces of the NPs, significantly promoting the stability of the NPs. When dispersed in raw water, even in the presence of divalent ions, NPs with dispersant remains stable. The DLVO theory describes aggregation behavior of colloids in water as sum of the van der Waals attraction between particles and repulsion due to overlap of the ion clouds surrounding the particles interaction (Israelachvili 1992). The theory explains the influence of many factors that control colloid aggregation behavior of NP including pH, ionic strength, solution composition, particle size, surface chemistry, and the concentration of suspended particles. Dispersants play a significant role since they modify the inter-particle interactions by chemically or physically attaching polymers to the particle surface, sterically stabilizing the particles and altering the transport characteristics of the colloids (Verwey and Overbeek 1948).

Temporal change in hydrodynamic diameter has been considered as an important measure in evaluating the stability of the NPs. Polymer coated or capped NPs could form stable colloidal suspensions despite the increase of hydrodynamic diameter. Polymer bridging, where a segment of polymers from chains would attach on the unoccupied particle surface, forming large
structures in the suspension, but not necessarily lead to sedimentation. In this study, CeO$_2$ with dispersant have excess polymers in the system covering all the NPs and leaving no bare surface or means for the attachment of the particles to collector surface. In this case, the particle size did not increase and steric repulsion plays an important role for the stabilization of the particles. This also applied to Ag-PVP, Ag-Citrate, and ZnO with dispersant. Citrate or PVP coating of Ag had different stabilizing effects. Citrate is weakly bound to the core Ag and stabilizes Ag NPs by charge repulsion; whereas PVP strongly binds to the core and sterically stabilizes NPs (Henglein and Giersig 1999). Huynh and Chen (Huynh and Chen 2011) evaluated the aggregation of Ag NPs and found out that the Ag-PVP were significantly more stable than Ag-Citrate in both monovalent and divalent ions, due to steric repulsion imparted by the large, non-charged polymers; and the addition of humic acid resulted in the adsorption of the macromolecules on both citrate and PVP coated Ag NPs. Our results further confirmed this finding in the column transport study. The zeta potential of Ag-PVP didn’t show much difference in DI water and raw water (-10.2 to -6.2 mV), while the zeta potential Ag-Citrate decreased dramatically from DI water to raw water (-36.1 to -6.82 mV) (Table B.1 Appndx C). In raw water, the attachment efficiency of Ag-PVP is ten times smaller than Ag-Citrate, and this applies to the three types of sands (Table.4-1). This indicates that in raw water which contains mono divalent ions and NOM, the steric repulsion of the capping agent is still the leading effect for the NP stability. However, the high ionic strength of raw water matrix and the heterogeneous biofilm coated collector surfaces showed strong interaction even with polymer capped NPs and the classical DLVO theory may not be sufficient to explain or predict the breakthrough behavior. Although, the dispersant were critical in affecting the breakthrough curves, they had little effects on the ζ-potential of the NPs in Raw water. The slow aggregation of the NPs in Raw water did not affect
the breakthrough or the plateau values. The hydrated particle surface of biofilm coated used sand formed a hydrophilic surface, where the strong hydration hindered the true contact between surfaces, hence increasing the free energy of the system. At higher ionic strengths, the hydration forces have a stronger effect on colloid stability as compared to the double layer compression. The inability of filter beds to retain polymer capped NP is significant since PVP-coated Ag-NP show high cellular uptake if they get in blood streams and induce production of reactive oxygen species (Foldbjerg et al. 2009, Huang et al. 2010)

During the initial state of the breakthrough tests with CeO$_2$-NPs with dispersant through used sand packed column, sharp overshoot peaks were observed in the UV-visible absorbance of the effluent stream. This suggested that the dispersant interacted with the biofilm, causing the washing or peeling of the biofilm from the used filter sand surface.

4.5.7 Modeling Deep-Bed Filtration

Simulation parameters obtained from NPs column breakthrough studies (Used filter sand) were combined with the model equations (1 -3) to predict the breakthrough of NPs in actual sand filters. The Cincinnati water facility has 47 divided square shaped filters (effective size = 0.5 mm, uniformity coefficient = 1.65, bed depth = 0.61 m, unit area=133.8 m$^2$). The equations for transport and adsorption in the columns were solved simultaneously to determine the attachment kinetics of NPs to sand grains based on the initial and boundary conditions of the column. The model accounts for the initial deposition of NPs covering filter grains with a monolayer deposition followed by the interaction of NPs with previously deposited ones. The model assumes the attachment of the suspended particles and their re-entrainment by the flow occurring in parallel. The objective is to investigate the model prediction for the transport and deposition of manufactured NPs through actual slow gravitational sand filters, of GCWW DWTP, and to
evaluate the effectiveness of the filter in retaining the NPs for two cases: a. a single spike of NPs and b. steady state feed of NPs.

The filter response to a pulse input of the NPs in a continuous flow of water with initial concentrations ranging from 50 to 250 ppm in the feed stream was simulated. The boundary condition replaced by a Dirac-delta function to ensure the immediate dampening and to avoid singularity shows the sand filter was able to redistribute the sharp influent peak (Figure C-4a, Appendix C). The maximum effluent peak observed was $0.21 \pm 0.01 \%$ of the influent. The breakthrough in terms of normalized concentration was found to be the same independent of the influent concentration. This scenario is more likely to occur if a DWTP receives an impulse of NP contaminated water. On the other hand full breakthrough was observed when NPs were supplied continuously to the filter bed at a concentration of 5 to 50 ppm. Again, the normalized concentration breakthrough is independent of the initial concentration. The breakthrough of CeO$_2$ and PVP coated Ag is two orders of magnitude faster than for ZnO and citrated coated Ag NPs (Figure C4-b, Appendix C). The simulation suggested that slow sand filters at DWTP have the capacity to retain single pulse injection of NPs in the feed stream, but steady constant influx cannot be retained.

4.6 Conclusion

The present study has undertaken a first step in investigating the potential removal of metal and metal oxides NPs in actual DWTPs using a laboratory-scale model unit. Additional experiments will be required for in-depth studies on the detailed mechanism of the interaction between NPs, the dispersants and the biofilm. Experimental and modeling results indicate a limited capability of the removal of metal and metal oxide NPs from the source of drinking water. For NPs with bare surfaces, the sand filters are capable of retaining them in the raw water,
however, for NPs with dispersants (Ceria, ZnO, Ag-Citrate and Ag-PVP), the steric repulsion due to the presence of dispersant became the dominant factor for their mobility, diffusion and transport with little or no measurable retention on NPs in the sand filters. The high mobility of NPs in DWTPs allowed particles to spread over larger distances and makes monitoring of environmental distribution rather a complex task. To fully evaluate the removal of NPs in the DWTPs, additional research is required to evaluate the capability of other process units in removing NPs, for example, coagulation and sedimentation.

4.7 References


Figure 4.8 Characteristics of filter media using optical microscope observed under 1000 magnification (Area = 90.0 × 67.2 μm²). (a) acid washed and calcined organic free sand (b) Unused filter sand (c) Used filter sand; SEM at 500, 5000 magnification of (d) acid washed and calcined organic free sand (e) Unused filter sand (f) Used filter sand, (g, h, i) Representative biofilms formed on SSF media examined by confocal laser scanning microscopy after being stained with a BacLight Live/Dead kit. Panels A and B
Figure 4-2 $\zeta$-potential measured streaming potential technique as a function of solution pH for treated sand grains (filled diamonds), fresh filter sand (filled triangles) and used filter sand with biofilm (squares) at 10-3 MKCl as a background electrolyte solution at room temperature.

Figure 4-3 Dynamic light scattering studies of the aggregation kinetics of Ag, TiO$_2$, ZnO and CeO$_2$ with and without dispersant in Pre-filtration water and Millipore waters.
Figure 4-4 Nanoparticle transport in three different porous medium. NP breakthrough curves are expressed as normalized NP concentration at the filter column effluent as a function of pore volume for NP with dispersant (a) Treated sand, (b) fresh sand, (c) used sand, and in absence of dispersant for three porous media (d), (e) and (f). NP concentrations were 10 mg/L in CWW water, at pH = 7.2 and room temperature (21 °C)
Table 4-1 Attachment efficiency and deposition rate coefficients of nanoparticles in different sand media, obtained from column breakthrough curves

<table>
<thead>
<tr>
<th>NPs</th>
<th>Attachment efficiency</th>
<th>deposition rate coefficient $k_{exp}$ (1/hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>clean</td>
<td>fresh</td>
</tr>
<tr>
<td>With dispersant</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ceria</td>
<td>0.012</td>
<td>0.022</td>
</tr>
<tr>
<td>Ag-PVP</td>
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<td>0.003</td>
</tr>
<tr>
<td>Ag-citrate</td>
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<tr>
<td>ZnO</td>
<td>0.034</td>
<td>0.026</td>
</tr>
<tr>
<td>No dispersant</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ceria</td>
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<td>0.617</td>
</tr>
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<tr>
<td>TiO$_2$</td>
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<td>0.926</td>
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</table>
Chapter 5. The Transport and Deposition of Surface-modified TiO$_2$ and ZnO Nanoparticles through Biofilm Coated Drinking Water Sand Filters

5.1 Abstract

This study investigates the role of different coatings in the transport, deposition and retention of commonly used nanoparticles (NPs) through slow sand filters at drinking water treatment plants (DWTPs) under realistic conditions. Two types of industrially important NPs (ZnO and TiO$_2$) with different coatings (ZnO coated with Silane coupling agent and TiO$_2$ with stearic acid) were used. Industrially coated NPs were received from vendors and were used as-is. NPs were also coated in the laboratory with polyvinylpyrrolidone (PVP). The transport of NPs through filter beds filled with sands acid washed and calcined, or freshly acquired filter media, or used filter media from active filter media, were investigated. Transport and deposition studies were conducted using water obtained upstream of the sand filter at Cincinnati water treatment plant. Artificially grown biofilms cannot adequately predict the slow-sand-filtration where biofilm has been accumulated and aged. Results have shown that surface modified NPs are more stable than the bare NPs in natural water and coated NPs passed through the sand columns rapidly and reached partial breakthrough with different plateau values. Type of coating methods used exhibited different mobility and traditional DLVO theory is limited to explain the interaction when both biofilm and polymer coatings are existed. The role of steric repulsion between electrostatically stabilized NPs and biofilm is a prevalent force against NPs retention in saturated porous media and present evidence that the presence of biofilm in an environment not
be interpreted as a necessarily retaining factor in the context of the deposition of sterically stabilized NPs.

5.2 Introduction

Engineered nanoparticles are increasingly combined with a large range of manufactured goods and consumer products due to novel properties that can improve the functionality of a range of commercial products. TiO$_2$ NPs are widely used in commercial products including photocatalysts, photovoltaics, sunscreens, cosmetics, coatings, paints, and pigments (Higarashi and Jardim 2002, Nagaveni et al. 2004, Quan et al. 2005) and are proven to be a superior photocatalyst characterized by large photo-stability, porosity, ion exchange capability and high specific surface area-to-volume ratio (Hoffmann et al. 1995). ZnO NPs are used in a variety of industrial and medical applications, including high-tech materials, plastics, paints and production of paper, and for cosmetics and sunscreen (Adams et al. 2006, Osman et al. 2010, Mu and Sprando 2010). However, there remain concerns regarding the impact of TiO$_2$ and ZnO NPs on environmental and human health. The potential environmental risks associated with NPs will largely depend on their behavior and fate following the release into natural environmental systems (Botta et al. 2011, Labille et al. 2010). Accumulated evidence has shown the adverse exposure effects on aquatic organisms including microbes, algae, invertebrates, and fish (Adams et al. 2006, Long et al. 2006, Trouiller et al. 2009). Research has demonstrated the toxicity of ZnO NPs on various living organisms such as plants (Lin and Xing 2008) and bacteria (Adams et al. 2006), as well as human cell line (Osman et al. 2010), which further heightened the general public attention. Consequently the environmental fate of NPs has become a great interest to researchers, regulatory agencies and policy makers.
Studies have shown that the transport and fate of TiO$_2$ and ZnO nanoparticles are potentially influenced and governed by environmental factors such as the complexity of the porous media matrix (e.g. grain and pore size distribution), solution chemistry (e.g. ionic strength, pH and the presence of natural organic matter or surfactants), the surface properties of NPs and the fluid dynamics characteristic of the column system (Chen et al. 2011); (Thio et al. 2011); (Godinez and Darnault 2011); (Jiang et al. 2012). Such studies are very often carried out in well-defined columns packed with homogeneous porous media. These experiments are generally conducted under relatively pristine conditions that do not represent the complexity or heterogeneity of natural and engineered aquatic (Lowry et al. 2012). For instance, slow sand filters (SSFs) are very commonly used in drinking water treatment plants (DWTP) for over 200 years (Ellis and Wood 1985). The process provides treatment through physical filtration of particles and biological removal of pathogens and organics in the upper biologically active layer of the sand bed, known as the Schmutzdecke. For slow-sand filter (SSF), Schmutzdecke is where the highest concentration of biomass exists, hence the region where most biological treatment is achieved (Datta and Chaudhuri 1991). These characteristics of SSF sand bed are not reflected on the lab-designed columns in the studies summarized previously. Thus, these studies may not be used to fully predict the capability of the retention of NPs in SSF.

The mobility of bare surface NPs was found to be quite low in typical aquatic environment (e.g., neutral pH and ionic strength = 10 mM in NaCl) (Jiang et al. 2012). Although bare surface TiO$_2$ and ZnO NPs are not expected to transport large distances in natural subsurface mainly because of aggregation and deposition to the natural collector surfaces, it remains unclear what the transport behavior of more stabilized TiO$_2$ and ZnO NPs. Considering that industrial formulations may increases the stability and mobility of these NPs, investigations
of the transport potential of industrially sourced NPs and their interactions with environmentally relevant surfaces becomes essential to assess the environmental risks of NPs.

Our previous studies took the first steps to investigate the transport and retention of engineered NPs sand columns that resemble the operation condition of SSF in drinking water treatment facilities (Solovitch et al. 2010). Results have shown that the existence of surfactants play a significant role in the transport and mobility of NPs under natural conditions. The present study expanded our previous efforts by investigating the transport and retention of TiO$_2$ and ZnO with different coatings in realistic environmental conditions of actual pre-filtration drinking water through sand bed that have been taken from SSF system. The study provided comparison between the type of commonly used polymer coatings and methods of industrial and laboratory coating methods. It also provided comparison on the effects of water matrix and the difference in filter bed filled with pretreated clean sand and biofilm coated sand. Great Cincinnati Waterworks (GCWW), a local drinking water treatment plant, provided the pre-filtration water and filter sand. The test conditions replicate the actual operating conditions of the SSF of GCWW.

This study aims at investigating the role of coatings or dispersants in the transport and retention of TiO$_2$ and ZnO NPs through SSF. For both TiO$_2$ and ZnO NPs, two types coating were used and compared in this study: (1) NPs that were procured from vendors, which are coated for better stability for industrial purpose. (2) NPs that were coated in the lab with Polyvinylpyrrolidone (PVP), which is a commonly used polymer to stabilize NPs. The effectiveness of biofilm coated sand in SSF in removing NPs from natural waters was studied by replicating actual drinking water treatment facility operations in laboratory settings including the actual water and the water-saturated porous media used in the DWTP. Column runs were
conducted in three different mediums to compare sand samples obtained from a drinking water treatment facility with the same unused sand type and with acid treated sand. Water used in the experiments was obtained from the influent stream of the SSF in the drinking water treatment facility.

5.3 Methods and Materials

5.3.1 Nanoparticles preparation and characterization

Nano-TiO$_2$ and ZnO obtained from vendor (Sun Innovations) were coated with PVP in the laboratory per the following procedure: Bare surface NPs were dispersed in ethanol and sonicated at 20 KHz at intensity of 20W/L for 20min. The suspension was heated to 70 °C under vigorous mechanical stir. PVP was dissolved in ethanol at the concentration of 2g/L, PVP solution was added drop-wise to NPs suspensions and the mixture was kept at 70 °C for 6 hours. After the mixture was allowed to cool to room temp, the NPs were recovered by centrifuge. Coated NPs were washed with ethanol 3 times to remove any unattached PVP. The NPs were then dried at 40 °C in vacuum. The PVP-coated NPs are referred as TiO$_2$-PVP and ZnO-PVP.

Industrially coated TiO$_2$ and ZnO were also obtained from a vendor (US Research Nanomaterials, Inc, TX). Zinc oxide nanoparticles coated with Silane coupling agent (3-Aminopropyltriethoxysilane, 1wt% C$_9$H$_{23}$N$_2$O$_3$Si) (ZnO-KH550) and titanium dioxide nanoparticles coated with Al, Si and stearic acid (TiO$_2$-SA) were selected. Bare-surface TiO$_2$ and ZnO were also purchased from vendor (Sigma Aldrich, MO) and used in all experiments as control references.
The zeta potential of the NPs-to-solution interface was measured with a laser doppler velocimetry setup (Zetasizer Nano SZ, Malvern Instruments Ltd.). Physico-chemical properties and vendors’ provided information of these NPs are summarized in Table 5-1.

Thermal gravimetric analysis (TGA) (Pyris 1, PerkinElmer Co.) was applied to confirm the coating by comparing the weight loss with bare surface NPs. About 5 mg of lyophilized NPs was weighed on an alumina crucible and kept at isothermal conditions of 30 °C for 10 min under air flow (20 L/min). The sample was then heated from 30 to 800 °C in air atmosphere at the rate of 10 °C/min. Thermogravimetric analysis (TGA) (Pyris 1, PerkinElmer Co.) was conducted to determine the total organic mass on filter media. The size and morphology of the biofilm on the sand was examined by ultrahigh resolution field emission scanning electron microscopes (SEM). The biofilm growth on used filter sand was also analyzed with a Confocal Laser Scanning Microscopy (Zeiss LSM 510, Plan-Neofluar 40×/0.3) after biofilm staining with the LIVE/DEAD BacLight viability kit (L7012, Molecular Probes, Inc.).

Attenuated total reflection FTIR (Perkin-Elmer model 2000) spectroscopy equipped with a Nicolet 752 spectrophotometer with a 45-degree ZeSe flat plate crystal was used to determine the functional groups.

Known concentrations of NP suspensions were prepared by adding NPs stock solution in appropriate volume of water. NP suspensions were sonicated for 15 min at 20 KHz at intensity of 20W/L prior to their use in the experiments.

5.3.2 Porous Media

Similar to our previous study, three types of sands were used to make the porous media: used filter sand, fresh filter sand, and treated sand. Used filter sand that was acquired from the top layer of filter sand cake in the backwashed SSF of Greater Cincinnati Water Works. Fresh
filter sand, the same type as the Used Filter Sand, was obtained from Northern filter Media Inc. (Muscatine, IA). It has mesh size of 30 x 40 with an effective size of 0.5 mm and a uniformity coefficient of 1.65. Treated sand was obtained from the American Graded Sand Company (AGSCO Co, Wheeling IL). Treated sand was thoroughly cleaned by sequential washing with 1M HNO$_3$ solution and repeat rinsing with water, followed by oven drying at 550 °C for 12 hr. The treated sand had mesh size 20 x 30 with an effective size of 0.7 mm and the uniformity coefficient was < 2.5.

5.3.3 Water Samples

Raw water used in this study was collected from the upstream of the sand filter after the final settling stage at GCWW which gets its water from the Ohio River. Samples were collected in the month of February and all samples were stored at 4 °C under dark conditions until needed.

The pH of the collected raw water was measured by an Oakton pH meter (Ion 510 series, Fisher Scientific); the turbidity of suspended particle density was evaluated using turbidity meter (Hach® 2100N Laboratory Turbidity Meter), the conductivity and resistivity was measured by a Fisher Scientific Traceable* Conductivity and Resistivity Meter (Fisher Scientific). Volatile suspended solids (VSS) was measured using Standard Method 2540 E, American Water Works Association, Water Environment Federation. Total organic carbon (TOC) was obtained in triplicate measured in a non-dispersive infrared gas SHIMADZU Analyzer (TOC-5000A).

The concentrations of 18 dissolved ions in the raw water were determined by inductively coupled plasma atomic emission spectrometry (ICP-AES) (Optima 2100 ICP-AES Optima PerkinElmer Inc.). Concentrated acids, HNO$_3$ (69%) and HCl (36%) (Trace Metals Grade, Fisher Chemical,) were used to acidify all solutions. All calibration solutions and quality control
solutions were prepared from single element standards or multi-element solutions (SPEX CertiPrep).

5.3.4  **Transport of NPs in sand filters under GCWW operation conditions**

The transport studies were intended to simulate the slow sand filtration process of the GCWW, where supernatant water reservoir maintains a constant water head providing the driving pressure through the filter. A low pressure peristaltic pump (Master Flex-Cole-Palmer) provided equivalent pressure at the same flux with a flow rate of 19 mL/min. The transport study was performed using cylindrical glass columns with internal diameter of 2.5 cm and 15 cm long (Ace Glass). The columns were packed with specific sands using a wet packing method by adding 5 mm depth at a time, yielding a bed porosity of 0.34. Prior to starting column test runs and introducing NPs suspension, the column was flushed with GCWW raw water for at least 10 pore volumes. At the onset of the test, a stream of NP suspension was introduced to the column for 30 pore volumes, after which the flow was switched back to raw water. The NPs concentration was monitored at the effluent of the column using an on-line UV-visible spectrophotometer (Agilent 8453). Temporal changes in effluent concentration were presented as breakthrough curves using normalized effluent concentration versus pore volume.

5.3.5  **Determination of Attachment Efficiency (k_{att})**

The fraction of particle collisions, with each other or with a sand grain, which may result in particle attachment, is referred to as the attachment efficiency. The attachment efficiency between NPs and collectors in particle-sand grain interactions (k_{att}) was calculated using colloid filtration theory. For column studies, α can be expressed as a function of the relative effluent
concentration \( C/C_0 \), where \( C \) is the effluent concentration at time \( t \), and \( C_0 \) is the influent concentration, and as following:

\[
k_{att} = -\frac{2d_c}{2(1-\varepsilon)n_0L} \ln(C/C_0) \quad \text{(Eq. 5-1)}
\]

Where \( d_c \) is the median diameter of the porous media, \( \varepsilon \) is the bed porosity, \( L \) is the length of the bed, and \( n_0 \) is the theoretical clean bed single collector efficiency, which describes the particle transport to an individual collector before particle accumulation alters the collector geometry. Single collector efficiency can be calculated as the sum of individual contributions each transport mechanism, and the overall correlation equation.

5.4 Results

5.4.1 Characterization of Nanoparticles

The characteristics of the NPs selected in this study are summarized in Table 5-1. The average particle size of all NPs and their zeta potential varied between distilled water and raw water matrix due to the dissolved ions and natural organic matter. Particles aggregated in raw water where size of all NPs increased 2 to 3 times. NPs also exhibited polydisperse system where most particles remained in the original state while a small portion formed large cluster structures. For TiO\(_2\), compared to bare surface particles, the surface charge was more negative when coated with PVP and stearic acid in both distilled water and CWW water. For ZnO bared surface particles, the zeta potential was more negative in CWW water (-18.1 mV) than in distilled water (-7.0 mV), however, for coated ZnO NPs, the zeta potential of the particles between distilled water and CWW water was not significant (ZnO-PVP: -8.35 mV in distilled and -8.64 mV in CWW; ZnO KH550: -6.35 mV in distilled and -6.70mV in CWW). For bare surface ZnO NPs, the NOM in the raw water absorbs onto the bare surface of the NPs, and the
negatively charged functional groups counterbalance the van der Waals-London attractive forces between the NPs. For NPs with strong dispersants (PVP and BH550), this effect is not significant.

TGA results in Figure 5-1 showed the thermal decomposition of the polymers for TiO$_2$ (Figure 5-1-a) and ZnO (Figure 5-1-b). The data shows that TiO$_2$-SA has 1.5% more weight loss compared to bare TiO$_2$, and ZnO has 6.2% more weight loss compared to TiO$_2$. BH-550 coated ZnO has 1.3% more weight loss and PVP coated has 6.5% more weight loss compared to uncoated ZnO. The grafting density can be calculated for the NPs according to the following (Abdolmaleki et al. 2012):

$$Grafting\ \text{Density} = \frac{(Wt\ \text{loss}+Na)}{(100+M_{n}\text{polymer}+S_{\text{particle}})} \times 10^6 [\mu\text{mol/m}^2] \ldots \ldots \text{(Eq. 5-2)}$$

where loss weight is the percent weight loss corresponding to the decomposition of polymer, $Na$ is Avogadro’s number, $M_{n}\text{polymer}$ molecular weight of polymer, $S_{\text{particle}}$ is the specific surface of NPs (m$^2$/g) calculated by the following relation: $6/(\rho \times d)$, with $\rho$ and $d$ are the volume (m$^3$) and mass (g) of the material, and the NP diameter, respectively. The results are shown in Table 1. The grafting density for TiO$_2$-PVP, TiO$_2$-SA, ZnO-PVP, ZnO-KH550 are 0.024, 0.019, 0.031, 0.069 chain/nm$^2$, respectively. Higher grafting density means more polymer brushes on the particle surface.

The FT-IR spectra of the NPs are shown in Figure 5-2. The TiO$_2$-SA NPs shows an absorption peak around 1715 cm$^{-1}$ (Figure 5-2-a). This absorption peak indicates the presence of the carboxylic acid groups that belongs to the stearic acid. Two peaks at about 1328 and 1525 cm$^{-1}$ were also observed. This is interpreted as a complexation of the TiO$_2$ with the carboxylates formed from the stearic acid. The FT-IR spectrum of ZnO-KH550 (Figure 5-2-b) gave a broad absorption band located at 3410 cm$^{-1}$, which is attributed to $–OH$ and $–NH_2$. The peaks at 2927 and 1052 cm$^{-1}$ can be assigned to the symmetric methylene stretch ($–CH_2$), and the Si–O stretch,
respectively. The absorption peaks presented at 1700 and 1648 cm\(^{-1}\) were relevant to the stretching vibration of conjugated esteric C=O and stretching vibration of C=C bonds, respectively. Absorption bonds of stretching vibrations of esteric C–O bond appeared at 1172 and 1017 cm\(^{-1}\). This result was consistent with previous researchers (Abdolmaleki et al. 2012) and it confirms that the surface of ZnO NPs was successfully grafted by Saline. In the FTIR spectrum of both TiO\(_2\)-PVP and ZnO-PVP (Figure 5-2- c and d) several peaks were observed and located at 1738, 1655, 1423, 1365, and 1220 cm\(^{-1}\). The absorbent peak at 1665 cm\(^{-1}\) belongs to C=O group of N-vinyl pyrrolidone. The peak obtained at 1655 cm\(^{-1}\) resulted from stretching mode of CN in PVP molecule. The 1423 cm\(^{-1}\) peak can be attributed to bending vibrations of \(\text{CH}_2\) group of PVP. The absorbent peak centered at 1220 cm\(^{-1}\) is due to C–N stretching vibration of PVP. These peaks indicated that both TiO\(_2\) and ZnO were successfully coated by PVP.

5.4.2 Characterization of water samples

The water obtained from GCWW had turbidity of 0.268 NTU, pH of 7.8, total organic carbon (TOC) level of 2.56 ppm, and total hardness of 133 mg/L as CaCO\(_3\) and may have contained microbiological growth. The ICP-OES analysis shows that the main ions were Mg\(^{2+}\), K\(^{+}\), Na\(^{+}\) and Ca\(^{2+}\) (Appendix D). The conductivity was measured at 344.9 µs/cm corresponding to ionic strength of ca. 5.5 mM by using the Russell approximation equations. The dissolved oxygen (DO) was relatively low at 0.065 mg/L, which might be due to biological activities during storage.

5.4.3 Characterization of the Filter Media

Optical microscope (Figure 5-3 a-c) and scanning electron microscopy (Figure 5-3 d-f) images of samples show the shape, roughness, and physical homogeneity of the sand particles.
Treated sand had smooth clean surface, while the Fresh filter sand has irregular rougher shape and coarser surface. The extended use period has resulted in polished smooth shape particles covered with biofilm containing a diverse microbial population and extracellular matrix. Scanning electron micrographs show the surface of the biofilm on used sand particles. Rod-shaped gels embedded in an extracellular fibrillary material structure indicating predominance of filamentous micro-organisms at the surface of the filter sand. Extracellular polymeric substance of the fresh and used sand samples containing biofilm were qualitatively measured using confocal laser scanning microscope (CLSM) after staining cells with a fluorescent dye specific for nucleic acids. The lateral CLSM images of the fresh sand and used sand are shown in Figure 5-3 h-j. The CLSM images show the used filter sand was covered with a thick mass of microorganisms, bacteria, bacteriophages, and protozoa. Crystalline clean quartz sand has a negative charge and attracts positively charged particles of colloidal matter and metal cations. Hence, the zeta-potential of mineral grains plays an important role in the initial deposition kinetics of colloidal particles(Elimelech et al. 2000).

5.4.4 Transports and Retention of Nanoparticles in Filter Media

Breakthrough profiles of coated NPs in three sand mediums are shown in Figure 5-4 A-D, which indicate that the normalized effluent concentrations \( \frac{C}{C_0} \) were dependent on the type of coating of NPs and the type packing media. Breakthrough studies were carried out with suspended bare-surface TiO\textsubscript{2} and ZnO but no breakthrough or minimum breakthrough \( (\frac{C}{C_0} < 0.1) \) was observed in the effluent thus the results are not shown in Figure 5-4. The minimum breakthrough curves of bare surface particles in different sands are included in figure D-1 and Figure D-2 in Appendix D. The results of limited transport for coated surface NPs (see Figure 5-4) indicate that NPs began to breakthrough from the column after 1-1.5 pore volume and
gradually reached a partial breakthrough, which occurred around after 7 pore volumes. The plateau value of each type of NP varies based on the surface coating, but the plateaus value did not show significant differences among the three types of sand columns used. This observation was in general agreement with our previous study (Li et al 2013). For ZnO-PVP, the NPs reached plateau value of 0.33, 0.34 and 0.35 in Filter sand, Fresh sand and Treated sand, respectively. For ZnO-KH550, the plateau values were 0.58, 0.58, and 0.61 in Filter sand, Fresh sand, and Treated sand, respectively. For TiO$_2$-PVP, the plateau value were 0.85 for Filter sand, 0.87 for Fresh sand, and 0.90 for Treated sand. For TiO$_2$-SA the plateau values were 0.54 for Filter sand, 0.56 for Fresh sand and 0.57 for Treated Sand. Filter sand has more slightly higher effectiveness in retaining NPs compared to sands that are not coated by biofilm. This trend also applies on the initial breakthrough (1-7 pore volume). NPs had a slightly faster breakthrough rate in the Treated sand than in the Fresh and Filter sand, but the difference was not significant. The breakthrough curves were used to estimate the attachment efficiency ($k_{att}$), and the $k_{att}$ of each NP in filter sand was presented in Table 1. Since the difference on the breakthrough curves between different sand media could be ignored, the $k_{att}$ of the same type of NP in three type of sands, which derived from the plateau values, are very close. Thus the $k_{att}$ of NPs in Fresh sand and Treated Sand are not shown.

5.5 Discussion

The presence of polymer coating did not significantly change the zeta potential for selected NPs in raw water; however, coating dramatically decreased the attachment efficiency of NPs to the porous media. The results confirmed that coating plays the most significant role in the occurrence of the breakthrough. The attachment efficiency decreased by an average of 35 to 41 times in presence of coating compared to bare surface NPs. For both TiO$_2$ and ZnO, the
attachment efficiency decreased with the increasing grafting density for the same NP. Although ZnO-PVP and ZnO-KH550 have higher grafting density than TiO$_2$-PVP and TiO$_2$-SA, both ZnO NPs have lower plateau values than TiO$_2$ NPs. The type of coatings has different influence for the two NPs. PVP coating reduced the attachment of TiO$_2$ much more than for ZnO even at a lower grafting density.

It is noted that all four NPs, the biofilm-coated Filter Sand did not show a significant increase in the retention and deposition of NPs. This finding differs from many previous research that used other biofilm in column studies, such as *Escherichia coli* (Tong et al. 2010, Jiang et al. 2013), *Pseudomonas aeruginosa* biofilm (Lerner et al. 2012), and *Bacillus spp* (Xiao and Wiesner 2013), which all reported remarkable increase in the deposition and retention of NPs in the biofilm-coated porous media. The key mechanism of the biofilm-NPs interaction was explained as pore clogging and resultant physical straining (Jiang et al. 2012). It was also reported that the surface potential of biofilm-covered sand was less negative thus the electrostatic repulsion was decreased compared to clean-surface sand, which enhanced the deposition (Tripathi et al. 2011).

There are two studies that also observed unchanged deposition for biofilm-covered sand: The retention of PVP stabilized silver nanoparticle was not enhanced by the attachment to biofilm to glass beads (Xiao and Wiesner 2013) and sand (Mitzel and Tufenkji 2014). It is mostly likely due to the use of sterically stabilized Ag NPs, coupled with a reduction in physical straining due to modified growth method of biofilm. Traditional DLVO theory describes aggregation and deposition behavior of colloids in water as sum of the van der Waals attraction between particles and repulsion due to overlap of the ion clouds surrounding the particles interaction (Israelachvili 1992). The theory explains the influence of many factors that control
colloid aggregation behavior of NP including pH, ionic strength, solution composition, particle size, surface chemistry, and the concentration of suspended particles. However, in the presence of polymer coating and dispersants, the steric repulsion becomes the dominant force. The polymer chains can attach macromolecules to the surfaces of the NPs, significantly promoting the stability of the NPs. When dispersed in raw water, even in the presence of divalent ions, NPs with dispersant remains stable. In this case, traditional DLVO theory fails to predict the deposition of NPs in the porous media. In the presence of biofilm and heterogeneous collector surface, DLVO theory is further limited. However, extended DLVO theory, which takes count of non-DLVO interactions, such as steric interactions, magnetic forces, and hydration forces, are being used to predict and simulated NP aggregation and deposition (Petosa et al. 2010). Hoek and Agarwal (Hoek and Agarwal 2006) performed simulations to study interfacial interactions between spherical particles and rough substrate surface. They found out that the magnitude of DLVO potential was reduced by the surface roughness because of significant interfacial separation. Grassian (Stebounova et al. 2011) applied an extended DLVO model calculation and showed that silver nanoparticles have a propensity to settle out in high ionic strength media independent of surface modification. Future effort should be made to elucidate the extended DLVO interaction between modified NP surface and natural, biofilm covered media.

5.6 Conclusions

This study explored the role of different NP coatings in the transport and retention of TiO$_2$ and ZnO NPs in sand columns under water treatment facility operation conditions. The study demonstrated that in the absence of a polymer coating, TiO$_2$ and ZnO NPs were rapidly retained by collector surfaces that are both clean and coated by biofilm. The suspension stability and transport behavior of the polymer-coated NPs was quite different from their bare surface
counterparts due to electrometric stabilization. The surface modified particles are more stable than the bare NPs in CWW water, which contains divalent ions. Both lab-coated NPs and industrially coated NPs passed through the sand columns rapidly and reached partials breakthrough with different plateau values. Overall, this work suggests that upon enter into slow sand filtration system in a water treatment facility, bare surface TiO$_2$ and ZnO NPs may experience limited mobility and largely be retained and removed by the sand filters, while the polymer-coated TiO$_2$ and ZnO NPs may exhibit far greater mobility and are less likely to be removed by the slow sand filters. Studies that used artificially grown biofilms cannot adequately predict the slow sand filtration where biofilm has been accumulated and aged for years. Lab-coated NPs and industrially coated NPs exhibited different mobility and traditional DLVO theory is limited to explain the interaction when both biofilm and polymer coatings are existed and the mechanism needs to be further elucidated. Given that a majority of commercially and industrially employed NPs will be surface-functionalized and stabilized, engineered NPs may present greater risks upon release and be more difficult to remove using contemporary drinking water approaches. Additional research ought to focus how to destabilize and removed polymer coated engineered NP in the water treatment system using current on innovative approaches.

5.7 References


### 5.8 Tables and Figures

#### Table 5-1 Physico-chemical characteristics of nanoparticles tested

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Figure 5-1 Thermogravimetric Analysis of TiO$_2$ NPs (A) and ZnO NPs (B) in air flow. Sample avg. wt = 5 mg, Air flow rate = 20 ml/min, Initial temperature = 30 °C, Pan Type: Platinum, Heating rate = 10 °C
Figure 5-2  FT-IR Spectra of coated and uncoated TiO$_2$ (A) and ZnO (B) with different polymer coatings (show axis)
Figure 5-3  Characteristics of filter media using optical microscope observed under 1000 magnification with an microscope (Area = 90.0 m2). Optical images of (a) acid washed and calcined organic free sand (b) Unused filter sand (c) Used filter sand; SEM at 500, 5000 magnification of (d) acid washed and calcined organic free sand (e) Unused filter sand (f) Used filter sand, (g, h, i) Representative biofilms formed on SSF media examined by confocal laser scanning microscopy after being stained with a BacLight Live/Dead kit. Panels A and B
Figure 5-4 Coated Nanoparticle transport in three different porous media. NP breakthrough curves are expressed as normalized NP concentration at the filter column effluent as a function of pore volume for NP with dispersant polymer coatings (A) ZnO-PVP, (B) TiO$_2$-PVP, (C) ZnO-KH550, and (D) TiO$_2$-SA, with NP concentrations were 20 mg/L in CWW raw water, at pH = 7.2 and room temperature (21 °C).
6 Chapter 6. Conclusions and Future Work

This work began by investigating the transport and retention of CeO$_2$ NPs in well-defined water saturated porous medium. Accidental or deliberate introduction of CeO$_2$ nanoparticles into subsurface environments may lead to contamination of drinking water supplies and can act as colloidal carriers for sorbed contaminants. CeO$_2$ NPs were studied in a relatively pristine environment: controlled water chemistry with a wide range of pH and ionic strength, and treated, clean collector surface. Results of column studies clearly showed that the water chemistry governs the transport, deposition and re-entrainment of nanoparticles. The three-phase flow method allowed better understanding of the influence of ionic strength in determining the condition whether the capture-release dynamics is reaction-limited or transport limited. A mathematical model was developed and successfully simulates both complete and partial breakthrough and re-entrainment of the CeO$_2$ breakthrough curves. The model is also capable of predicting the distribution of nanoparticle deposition within the porous media. This study highlighted the implication of CeO$_2$ nanoparticle and provides important insights to confirm the mobility of CeO$_2$ nanoparticle under typical groundwater movements. Although it was straightforward to precisely predict the behavior of CeO$_2$ nanoparticle upon their environmental release because of the compliance of various environmental parameters, it demonstrated that the role of water chemistry (pH and ionic strength) are in general agreement with DLVO theory prediction. The values of attachment efficiency, deposition rate coefficients, fraction recovered/re-entrained at varying ionic strength and the modeling results provided in this study can be used to further estimate the relative mobility and evaluate the potential exposure and risk of CeO$_2$ nanoparticles.
The second step of the study was to investigate the influence of natural organic matters which ubiquitously in the aquatic environment. This part of study characterized the NOMs extracted from Ohio River and demonstrated their distinctive effect in enhancing stability and transport of CeO$_2$ NPs in saturated porous media. OR-NOMs were characterized by thermal analysis and FT-IR, and the characterization showed obvious difference from SRHA. OR-NOMs were observed to enhance the breakthrough and facilitate the transport of CeO$_2$ in moderate (1-10 mM) ionic concentrations. The enhancement is largely dominated by the altered electrokinetic property of the CeO$_2$ NPs. The increase in the magnitude of zeta potential increases the electrostatic repulsive interaction between CeO$_2$ NPs. As the concentration of NOM increases, combinations of elevated electrostatic and steric interaction provide further repulsive forces to stabilize and mobilize CeO$_2$ NPs in aquatic environment. The results showed that in the presence of NOMs, traditional DLVO theory was not adequate to predict the transport and retention of CeO$_2$ NPs. A modified DLVO theory presented in this study can qualitatively interpret the general trends of the CeO$_2$ NPs transport and retention behavior under such conditions. The effect was also compared between summer and winter collected NOM samples. Summer collected NOM showed a stronger effect in stabilizing and facilitating the transport of CeO$_2$ NPs. In addition, the information presented here can be used for assessing the environmental exposure, risk, and ecological implications of CeO$_2$ NPs and eventually developing regulations for such nanoparticles.

The study moved on to investigate the potential removal of metal and metal oxides NPs in actual DWTPs using a laboratory-scale model unit. Experimental and modeling results indicate a limited capability of the removal of metal and metal oxide NPs from the source of drinking water. For NPs with bare surfaces, the sand filters are capable of retaining them in the raw water,
however, for NPs with dispersants (Ceria, ZnO, Ag-Citrate and Ag-PVP), the steric repulsion due to the presence of dispersant became the dominant factor for their mobility, diffusion and transport with little or no measurable retention on NPs in the sand filters. The high mobility of NPs in DWTPs allowed particles to spread over larger distances and makes monitoring of environmental distribution rather a complex task.

Lastly, the study explored the role of different coatings in the transport and retention of TiO$_2$ and ZnO NPs in sand columns under water treatment facility operation conditions. The study demonstrated that in the absence of a polymer coating, TiO$_2$ and ZnO NPs were rapidly retained by collector surfaces that are both clean and coated by biofilm. The suspension stability and transport behavior of the polymer-coated NPs was quite different from their bare surface counterparts due to electrometric stabilization. The surface modified particles are more stable than the bare NPs even in the presence of divalent ions. Both lab-coated NPs and industrially coated NPs passed through the sand columns rapidly and reached partials breakthrough with different plateau values. Overall, this work suggests that upon enter into slow sand filtration system in a water treatment facility, bare surface TiO$_2$ and ZnO NPs may experience limited mobility and largely be retained and removed by the sand filters, while the polymer-coated TiO$_2$ and ZnO NPs may exhibit far greater mobility and are less likely to be removed by the slow sand filters. Studies that used artificially grown biofilms cannot adequately predict the slow sand filtration where biofilm has been accumulated and aged for years. Lab-coated NPs and industrially coated NPs exhibited different mobility and traditional DLVO theory is limited to explain the interaction when both biofilm and polymer coatings are existed and the mechanism needs to be further elucidated. Given that a majority of commercially and industrially employed
NPs will be surface-functionalized and stabilized, engineered NPs may present greater risks upon release and be more difficult to remove using contemporary drinking water approaches.

As our understanding of the fate and transport of engineered nanoparticles has expanded greatly, there is much need to better understand the behavior of NPs in complex experimental systems such as river, ocean, and soil, and drinking water treatment facilities. To achieve the goal, future work is suggested as follows:

1- One important environmental implication of engineered NPs is that they might significantly alter the fate and transport of common environmental organic contaminants. In this research, it has been proven that naturally occurring organic matter can quickly absorb to the surface of NPs and significantly promote the transport of NPs. Thus it is expected that NPs will significantly affect the partition/distribution of hydrophobic organic contaminants among different phases. This will subsequently affect the mobility and transport properties of organic contaminants. Future studies are suggested to investigate the effect of metal and metal oxides NPs on the transport of nonionic, highly hydrophobic organic contaminants such as polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs) in saturated porous media. Batch adsorption and desorption experiments are recommended to understand the mechanisms controlling the mobilizing effect of NPs. Column studies need to be conducted under different flow velocities, pH and ionic strength, with different collector surface (both coated with biofilm or bare-surface silica) to fully understand how NPs will impact the transport and fate of hydrophobic organic contaminants. The results should be compared with dissolved natural organic matter that was previously studied in this research.

2- To fully evaluate the removal of NPs in the DWTPs, additional research is required to evaluate the capability of other processes of DWTP units in removing NPs, such as coagulation,
Aggregation kinetics of metal and metal oxides should be studied under the same condition of coagulation in the DWTPs. It would be interesting to observe if the NPs would deposit in activated carbon. It is also recommended to study that, when being deposited/loaded into the activated carbon, how do NPs impact the capacity and efficiency of the removal of other conventional organic contaminants by activated carbon, such as PCBs and PAHs. Factors that could affect this process includes the type of NPs, the surface of the NPs (coated vs. non-coated), pH, ionic strength, contact time, and adsorbent/NPs dosage.

Such studies will give us more information fully evaluate the transport and retention of engineered NPs in the drinking water treatment facilities, and also the impact of NPs on the WTP in removing organic contaminants.

3- Additional experiments will be required for in-depth studies on the detailed mechanism of the interaction between NPs and the biofilm. As mentioned in Chapter 5, previous studies have suggested that the presence of biofilms can alter the transport behavior of engineered NPs in natural and engineered aquatic environment, which contradicts the findings in this study. Biofilms are ubiquitous in aquatic environments, yet there is limited information on the influence of these microbial structures on the transport and fate of engineered NPs in granular porous media. The biofilm studied in this research was obtained from a drinking water treatment plant. Additional research needs to be conducted to compare the interaction of NPs with different biofilms, such as *Escherichia coli*, *Pseudomonas spp.*, or *Bacillus spp.* It is recommended to use experimental columns as a growth chamber and use sand to develop a biofilm through nutrient supply and incubation within the column. Column breakthrough studies need to be conducted to study the retention of NPs through biofilm-covered sand. Factors that could impact this process include water chemistry (ions and pH) and coatings of the NPs.
Appendix A: Supplementary Material for Chapter 2

1. Fig. A-1. Schematic diagram of the experimental setup

2. Detection Method of CeO₂ nanoparticles
A sample of 3 mL was collected from the effluent stream of the column and was analyzed by UV-vis spectrometer at the wavelength of $\lambda = 309 \pm 1$ nm. Four samples were collected for each pore volume. Calibration of UV-vis spectrometer based on multi-concentration standard samples of CeO$_2$ nanoparticles were used for quantitative analysis as shown in Figure A-2.

Figure A-2 Detection Method of CeO$_2$ nanoparticles with UV-vis spectrometer at the wavelength of $\lambda = 309$ $\mu$m

3. DLVO calculation of CeO$_2$ nanoparticle

Particle–collector interaction energy is estimated using classical and modified DLVO theory to account for steric repulsion provided by guar gum. The nanoparticles are assumed to be uniform spheres, small relative to the sand grains, i.e., sphere-to-plate interaction is calculated.
Equations of classical DLVO theory for bare particles–bare collector interactions (Healy and White 1978) (Elimelech and O'Melia 1990):

The equation for double layer interaction $V_{edl}$:

$$V_{edl} = \pi \varepsilon_0 \varepsilon_r R (2 \Phi_1 \Phi_2 \ln \left( \frac{1 + \exp(-\kappa h)}{1 - \exp(-\kappa h)} \right) + (\Phi_1^2 + \Phi_2^2) \ln(1 - \exp(-2\kappa h))) \quad (Eq. A-1)$$

The equation for Van de Wal force $V_{vdw}$

$$V_{vdw} = -\frac{AR}{6h(1+14h/\lambda)} \quad (Eq A-2)$$

Where

$$\kappa = \left( \frac{2000e^2N_A\lambda I_c}{\varepsilon_0 \varepsilon_r kT} \right)^{1/2} \quad (Eq. A-3)$$

And

$$A = \left( A_{11}^{1/2} - A_{22}^{1/2} \right) \left( A_{33}^{1/2} - A_{22}^{1/2} \right) \quad (Eq. A-4)$$

In the equations, $h$ is the separation distance between the particle surface and sand surface, $\lambda$ is the characteristic wavelength of the interaction (100 nm), $k$ is the Boltzmann constant, $\kappa$ is the Debye length, $R$ is the particle diameter, $T$ is the absolute temperature (298°K), $\varepsilon_0$ is the permittivity of a vacuum, $\varepsilon_r$ is the relative dielectric constant of water, $N_A$ is Avogadro's number, $I_c$ is the ionic strength, $R$ is the particle diameter (62.6nm, measured by particle analyzer) and $\Phi_1$ and $\Phi_2$ are surface potentials of particles and sand, respectively. Here zeta potentials were used as estimation for surface potentials.

In Eq.4, Hamaker constant $A$ is the overall Hamaker interaction parameter for the deposition of a CeO$_2$ NP onto sand surface when suspended in water. The Hamaker constants $A_{11}, A_{22}$, and $A_{33}$ are for sand surface, water and CeO$_2$ NP in vacuum, respectively. The values used were: $A_{11} = 6.5 \times 10^{-20}$ J, $A_{22} = 3.7 \times 10^{-20}$ J, and $A_{33} = 1 \times 10^{-20}$ J, which were obtained from literature (Israelachvili 1991).
The interaction profiles between sand surface and CeO$_2$ nanoparticles at pH 3, pH 6 and pH 9 at various ionic strength levels are demonstrated in Figure A-3a, b and c.

Figure A-3a. Interaction profiles between sand surface and CeO$_2$ nanoparticles at pH 3.
Figure A-3b. Interaction profiles between sand surface and CeO$_2$ nanoparticles at pH 6
Figure A-3c Interaction profiles between sand surface and CeO$_2$ nanoparticles at pH 9

**Literature Cited**


Appendix B: Supplementary Material for Chapter 3

1. Characterization of natural organic matter (NOM)

The chemical properties and elemental composition of natural organic matter tested are given below.

Table B-1. Characterization of NOMs use, total organic carbon (TOC), and UV$_{254}$ absorbance

<table>
<thead>
<tr>
<th>Parameter</th>
<th>OR-NOM-Jan</th>
<th>OR-NOM-July</th>
<th>SRHA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conc. (g/L)</td>
<td>1.53</td>
<td>1.15</td>
<td>1.05</td>
</tr>
<tr>
<td>TOC (ppm)</td>
<td>277</td>
<td>291</td>
<td>325</td>
</tr>
<tr>
<td>UV254</td>
<td>6.88</td>
<td>9.25</td>
<td>7.48</td>
</tr>
</tbody>
</table>

Table B-2. ICP analysis of Ohio River NOM conducted using an iCAP 6000 spectrometer

<table>
<thead>
<tr>
<th>(ppm)</th>
<th>SO4 (IC)</th>
<th>Ca</th>
<th>K</th>
<th>Mg</th>
<th>Na</th>
<th>P</th>
<th>S</th>
<th>Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>OR-NOM-JAN</td>
<td>54.22</td>
<td>26.89</td>
<td>2.10</td>
<td>8.92</td>
<td>22.69</td>
<td>0.30</td>
<td>18.09</td>
<td>2.43</td>
</tr>
<tr>
<td>OR-NOM-JUL</td>
<td>86.97</td>
<td>44.01</td>
<td>2.83</td>
<td>14.46</td>
<td>25.19</td>
<td>0.02</td>
<td>29.02</td>
<td>1.51</td>
</tr>
</tbody>
</table>

Table B-3 Elemental analysis of the lyophilized NOM solid. All values corrected for dry conditions and adjusted using

<table>
<thead>
<tr>
<th>Sample</th>
<th>C</th>
<th>H</th>
<th>N</th>
<th>O</th>
<th>S</th>
<th>O to C ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Jan. 2011</td>
<td>50</td>
<td>5.0</td>
<td>2.9</td>
<td>38</td>
<td>3.5</td>
<td>0.76</td>
</tr>
<tr>
<td>July 2011</td>
<td>55</td>
<td>4.1</td>
<td>3.1</td>
<td>36</td>
<td>2.5</td>
<td>0.84</td>
</tr>
</tbody>
</table>
2. Nanoparticle characterization

Figure B-1, Characterization of CeO₂ NPs, A) Size distribution measured using dynamic light scattering method, B) X-ray diffraction patterns, and C) Transmission electron microscope image showing polydispersed NPs
3. Transport of CeO2 NPs in porous media in the presence of SRHA

![Graph showing transport of CeO2 NPs in porous media in the presence of SRHA](image)

**Figure B-2.** Breakthrough of CeO2 nanoparticles in the presence of SRHA (1, 5 and 10ppm) under different ionic concentration: A, 3mM NaCl, B, 5mM NaCl, C, 10mM NaCl
In the presence of SRHA, CeO$_2$ NPs quickly reached full breakthrough (plateau value =1) at an ionic concentration of 3 mM, yielding very small values of $K_{att}$ ($\leq 0.1$). At ionic concentration of 5 mM, and SRHA concentration of 5-10 ppm, CeO$_2$ NPs gradually reached full breakthrough at pore volume 10, which is very similar with OR-NOMS but at a faster rate. At 1 ppm SRHA concentration, CeO$_2$ NPs reached partial breakthrough with plateau value of $\sim 0.58$, which is higher than in the presence of OR-NOMs ($\sim 0.48$). At ionic concentration of 10 mM, CeO$_2$ NPs had a partial breakthrough, starting around 1.5 pore volume, and slowly reached the plateau value. The plateau value generally increased with the increase of SRHA concentration. The corresponding attachment efficiency $k_{att}$ is shown in Figure S4, indicating that the facilitating effect of SRHA increases with the increasing SHRA concentration and decreasing ionic strength.
The role of SRHA is very similar with OR-NOMs in facilitating the transport of CeO2 NPs but the effect is much stronger.

4. DLVO calculation for CeO2 nanoparticle

Particle–collector interaction energy is estimated using classical and modified DLVO theory to account for steric repulsion provided by guar gum. The nanoparticles are assumed to be uniform spheres, small relative to the sand grains, i.e., sphere-to-plate interaction is calculated. Equations of classical DLVO theory for bare particles–bare collector interactions(Healy and White 1978) (Elimelech and O'Melia 1990):

The equation for double layer interaction $V_{edl}$:

$$V_{edl} = \pi\varepsilon_0\varepsilon_rR(2\varnothing_1 \varnothing_2 \ln \left(\frac{1+\exp(-k\varnothing)}{1-\exp(-k\varnothing)}\right) + (\psi_1^2 + \psi_2^2)\ln(1 - \exp(-2k\varnothing))$$

(Eq. B-1)

The equation for Van de Wal force $V_{vdw}$

$$V_{vdw} = -\frac{AR}{6h(1+14h/\lambda)}$$

(Eq. B-2)

Where

$$\kappa = \left(\frac{2000e^2N_A^{\varepsilon r}kI_c}{\varepsilon_0\varepsilon_r kT}\right)^{1/2}$$

(Eq. B-3)

And

$$A = \left(\begin{array}{c}
\frac{1}{2}A_{11} - \frac{1}{2}A_{22} \\
A_{11} - A_{22}
\end{array}\right)\left(\begin{array}{c}
\frac{1}{2}A_{33} - \frac{1}{2}A_{22} \\
A_{33} - A_{22}
\end{array}\right)$$

(Eq.B-4)

$$F_{steric}(h) = 2\pi a_p \left(\frac{T_k}{s^3}\right) \left\{\frac{4l}{5} \left[\left(\frac{l}{h}\right)^5 - 1\right] + \frac{4l}{7} \left[\left(\frac{h}{l}\right)^7 - 1\right]\right\}$$

(Eq. B-5)

$$\phi_{steric} (D) = -\int_0^D F_{steric} (h) dh \quad \text{for } h, D \leq 1$$

(Eq.B-6)

In the equations, $h$ is the separation distance between the particle surface and sand surface, $\lambda$ is the characteristic wavelength of the interaction (100 nm), $k$ is the Boltzmann constant, $\kappa$ is the Debye length, $R$ is the particle diameter, $T$ is the absolute temperature (298°K), $\varepsilon_0$ is the permittivity of a vacuum, $\varepsilon_r$ is the relative dielectric constant of water, $N_A$ is Avogadro's number,
\( I_c \) is the ionic strength, \( R \) is the particle diameter (62.6nm, measured by particle analyzer) and \( \phi_1 \) and \( \phi_2 \) are surface potentials of particles and sand, respectively. Here zeta potentials were used as estimation for surface potentials.

In Eq.4, Hamaker constant \( A \) is the overall Hamaker interaction parameter for the deposition of a CeO\(_2\) NP onto sand surface when suspended in water. The Hamaker constants \( A_{11}, A_{22}, \) and \( A_{33} \) are for sand surface, water and CeO\(_2\) NP in vacuum, respectively. The values used were: \( A_{11} = 6.5 \times 10^{-20} \) J, \( A_{22} = 3.7 \times 10^{-20} \) J, and \( A_{33} = 5.7 \times 10^{-20} \) J, which were obtained from literature (Israelachvili 1991).

References


Appendix C. Supplementary Material for Chapter 4

1. Characterizing Nanoparticles used for the study

Figure C-1. TEM images of the NPs
Table C-1. Physicochemical characterization of nanoparticles tested

<table>
<thead>
<tr>
<th>Parameter</th>
<th>CeO₂</th>
<th>CeO₂</th>
<th>ZnO</th>
<th>ZnO</th>
<th>Ag-Citrate</th>
<th>Ag-PVP</th>
<th>TiO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Description</td>
<td>18 wt% with dispersant in suspension</td>
<td>powder</td>
<td>50% wt with dispersant in suspension</td>
<td>Powder</td>
<td>In suspension</td>
<td>In suspension</td>
<td>powder</td>
</tr>
<tr>
<td>Vendor</td>
<td>Alfa Easar</td>
<td>Alfa Easar</td>
<td>Alfa Easar</td>
<td>Sigma-Aldrich</td>
<td>EPA Lab-produced</td>
<td>EPA Lab-produced</td>
<td>Degussa</td>
</tr>
<tr>
<td>Vendor reported sizes (nm)</td>
<td>30</td>
<td>30</td>
<td>20</td>
<td>20</td>
<td>N/A</td>
<td>N/A</td>
<td>20</td>
</tr>
<tr>
<td>DLS particle sizes in DI water (nm)</td>
<td>184±7.5</td>
<td>253±48</td>
<td>89.6±12</td>
<td>328±40</td>
<td>10</td>
<td>12</td>
<td>276±15</td>
</tr>
<tr>
<td>DLS particle size distribution</td>
<td>Mono-dispersed</td>
<td>Bimodal peaks 100 and 330 nm</td>
<td>Mono-dispersed</td>
<td>Bimodal peaks 140 and 525 nm</td>
<td>Mono-dispersed</td>
<td>Mono-dispersed</td>
<td>Mono-dispersed</td>
</tr>
<tr>
<td>DLS particle sizes in CWW water (nm)</td>
<td>515±43</td>
<td>1772±14</td>
<td>189.3±2.6</td>
<td>850.2±2</td>
<td>89.9±8.4</td>
<td>81.7±0.76</td>
<td>464±7.3</td>
</tr>
<tr>
<td>DLS particle size distribution</td>
<td>Mono-dispersed</td>
<td>Bimodal</td>
<td>Mono-dispersed</td>
<td>Bimodal peaks 446 and 5691 nm</td>
<td>Mono-dispersed</td>
<td>Bimodal peaks 6.8 and 93.5 nm</td>
<td>Mono-dispersed</td>
</tr>
<tr>
<td>Zeta potential (mV)</td>
<td>-17.6</td>
<td>0.863</td>
<td>-7.00</td>
<td>-6.18</td>
<td>-36.7</td>
<td>-10.2</td>
<td>-10.5</td>
</tr>
<tr>
<td>Parameter</td>
<td>CeO₂</td>
<td>CeO₂</td>
<td>ZnO</td>
<td>ZnO</td>
<td>Ag-Citrate</td>
<td>Ag-PVP</td>
<td>TiO₂</td>
</tr>
<tr>
<td>------------------</td>
<td>------</td>
<td>------</td>
<td>-----</td>
<td>-----</td>
<td>------------</td>
<td>--------</td>
<td>------</td>
</tr>
<tr>
<td>In CWW water</td>
<td>-11.7</td>
<td>-12.2</td>
<td>-18.1</td>
<td>-6.92</td>
<td>-6.82</td>
<td>-6.2</td>
<td>-7.2</td>
</tr>
</tbody>
</table>
2. Characteristics of water used for the study

Figure C-2. The ICP-OES analysis of CWW raw water

Figure C-3. Stability of NPs in CWW water using UV-vis absorbance.
The stability was evaluated by measuring the Uv-vis absorbance of NPs suspension in CWW water. NPs suspension was prepared in CWW water and sonicated for 10 min. Then the suspensions were left still and a sample of 3 mL was collected from the same depth of the flask and was analyzed by UV-vis spectrometer. Figure B.1 shows the absorbance of each NPs maximum wavelength was observed as the time change. The absorbance was correlated to concentrations of NPs using a calibration curve.

3. Model Parameters

Table C-2 Model parameters for the different transport and deposition of different nanoparticles through three types of sand.

<table>
<thead>
<tr>
<th>NPs</th>
<th>$S_{\text{max}}$ (µg/g)</th>
<th>deposition rate coefficient $k_{\text{att}}$ (1/hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>clean</td>
<td>fresh</td>
</tr>
<tr>
<td>With dispersant</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CeO$_2$-PVA*</td>
<td>5.8</td>
<td>192.3</td>
</tr>
<tr>
<td>Ag-PVP</td>
<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td>Ag-citrate</td>
<td>8.2</td>
<td>3.5</td>
</tr>
<tr>
<td>ZnO-PVA*</td>
<td>23.6</td>
<td>30.8</td>
</tr>
<tr>
<td>No dispersant</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ceria</td>
<td>30.7</td>
<td>18,000</td>
</tr>
<tr>
<td>ZnO</td>
<td>7.4</td>
<td>77.1</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>443.9</td>
<td>3,077</td>
</tr>
</tbody>
</table>
Figure C-4. Model Simulation of breakthrough behavior of NPs in slow sand filter and redistribution of the sharp influent peak for (a) steady-state flow with step-increase of NPs in the influent, (b) for a single spiked input
4. Determining Dispersant used for the commercial CeO$_2$ and ZnO

In this study, the silver nanoparticles had either citrate or PVP as dispersants, but ZnO and CeO$_2$ were obtained from a commercial vendor and the dispersant were proprietary. We performed various tests to determine the type of dispersant used with the suspended CeO$_2$ and ZnO nanoparticles with dispersants. These samples Suspended Cerium(IV) oxide, NanoTek® CE-6082, 18% in H$_2$O, colloidal dispersion with dispersant and Zinc oxide, NanoShield® ZN-5060, 50% in H$_2$O, colloidal dispersion with dispersant were obtained from Alfa Easar A Johnson Mattey Company. We dried both CeO$_2$ and ZnO colloidal dispersion samples and employed FTIR and $^1$H NMR studies on them to help identify the dispersant and blend behavior of PVA and ZnO or CeO$_2$. Fourier Transform Infrared Spectroscopy (FTIR) was used to characterize the presence of specific chemical groups in the materials. After screening test of FTIR of various possible dispersants poly vinyl alcohol (PVA) was confirmed to be the most likely dispersant with used. PVA powder and both ZnO, and CeO$_2$ with dispersant were analyzed by FTIR using Transmittance Mode. FTIR spectra were obtained in the range of wave number from 4000 to 650 cm$^{-1}$ during 64 scans, with 4 cm$^{-1}$ resolution (Spectrum 2000, Perkin-Elmer, USA). The FTIR spectra were normalized and major vibration bands were associated with chemical groups. All major peaks related to hydroxyl and acetate groups were observed. The large bands observed between 3550 and 3200 cm$^{-1}$ are linked to the stretching O–H from the intermolecular and intramolecular hydrogen bonds. The vibrational band observed between 2840 and 3000 cm$^{-1}$ refers to the stretching C–H from alkyl groups and the peaks between 1750–1735 cm$^{-1}$ are due to the stretching C-O and C=O from acetate group remaining from PVA.
We also run tests on the powder nanoparticles that didn’t contain any dispersant. The dried solids were extracted with dichloromethane for overnight and then the supernatant was dried and dissolved in deuterated chloroform, a common solvent used in NMR spectroscopy, in order to increase the polymer concentration. The dispersant was identified to be polyvinyl alcohol (PVA), which is a common dispersant used for nanoparticles.

The figure below shows the FTIR spectra of PVA and PVA-nanoparticle are presented. The intensity of the 1750–1735 cm$^{-1}$ is weak for PVAs with nanoparticles indicating that only few acetate groups are present in the polymer chain and very strong for PVAs. The interaction of the PVA with nanoparticles results in a reduction of the intensity of the O–H peaks a possible formation of acetal bridges. For instance, FTIR spectra of PVA-NP samples reveal two important bands at $\nu=2850$ and 2750 cm$^{-1}$ of C–H stretching related to aldehydes, a duplet absorption with peaks attributed to the alkyl chain (Maansur et al., Polymer, 2004). Also, strong band from carbonyl group was verified (C-O at $\nu=1720$–1740 cm$^{-1}$). These bands are overlapping and broadening PVA bands in these regions. In addition to that, by PVA-ZnO, the O–H stretching vibration peak ($\nu=3330$–3350 cm$^{-1}$) was relatively decreased when compared to pure PVA. (H.S. Mansur, R.L. Oréfice, A.A.P. Mansur, Polymer 45 (2004) 7193.)
Figure C-5 FTIR spectra of polyvinyl alcohol (PVA) and commercial ZnO and CeO$_2$ with dispersant use for this study.

Table shows the most characteristic bands of PVA and PVA with ZnO and CeO$_2$ and their assignment.

Table C-3 Comparison of FTIR and NMR vibrational assignments.

<table>
<thead>
<tr>
<th>FTIR Wave number (cm$^{-1}$)</th>
<th>NMR Chemical Shift (ppm)</th>
<th>Assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>430-760</td>
<td>1.3</td>
<td>CH$_2$ bend</td>
</tr>
<tr>
<td>1087</td>
<td>1.0</td>
<td>-CH$_3$ methyl</td>
</tr>
<tr>
<td>1141</td>
<td>4.7</td>
<td>CH-aldehyde stretch</td>
</tr>
<tr>
<td>1461</td>
<td>3.7</td>
<td>CH2</td>
</tr>
<tr>
<td>1731</td>
<td>4.7</td>
<td>C=O</td>
</tr>
<tr>
<td>2940</td>
<td>0.9</td>
<td>C-H alkyl group</td>
</tr>
<tr>
<td>3300</td>
<td>3.4 – 4</td>
<td>O-H</td>
</tr>
</tbody>
</table>
Figure C-6  Proton NMR spectrum of a) PVA, b) ZnO- PVA* and c) CeO$_2$- PVA*
Figure D-1, The ICP-OES analysis of CWW raw water
Figure D-2. TiO$_2$ Nanoparticle transport in three different porous media. NP breakthrough curves are expressed as normalized NP concentration at the filter column effluent as a function of pore volume for NP.
Figure D-3. TiO$_2$ Nanoparticle transport in three different porous media. NP breakthrough curves are expressed as normalized NP concentration at the filter column effluent as a function of pore volume for NP.