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Investigation of Filtration Mechanisms Involved in the Removal of Engineering
Nanomaterial From Drinking Water

A Dissertation submitted in partial satisfaction
of the requirements for the degree of

Doctor of Philosophy

in

Chemical and Environmental Engineering

by

Chen Chen

March, 2018

Dissertation Committee:

    Dr. Sharon Walker
    Dr. David Jassby
    Dr. Wenwan Zhong

The Dissertation of Chen Chen is approved:

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Committee Chairperson

University of California, Riverside

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Dedication

This PhD dissertation is dedicated to my parents for their love, support, encouragements, and patience.

ABSTRACT OF THE DISSERTATION

Investigation of Filtration Mechanisms Involved in the Removal of Engineering
Nanomaterial From Drinking Water

by

Chen Chen

Doctor of Philosophy, Graduate Program in Chemical and Environmental Engineering
University of California, Riverside, March 2018
Dr. Sharon Walker, Chairperson

The overarching goal of this study was to systematically investigate how engineered

particles behave in engineered filters under a range of relevant solution chemistry

conditions. Specifically, the approach was to conduct a combination of fundamental and

applied experiments, looking at engineered particles transport in idealized conditions,

followed by those simulating actual scenarios in the filtration stage of drinking water

treatment. It was confirmed that the leading factors in engineered particles destabilization

which leads to their removal include the type and concentrations of salts in solution, and

the process operating conditions (ionic strength and coagulant residual). Ultimately,

through the systematic variation of these parameters in the proposed micromodel

experiments described below, the conditions for optimal engineered particles

destabilization and removal was determined.

This dissertation work has allowed for the following observations. In the 2D micromodel,

the removal efficiency of latex nanoparticles and food grade TiO_2 in filtration is sensitive

to the particle aggregate size, surface charge, and surface composition. The model was

built to show single collector removal efficiency as a function of particle size and ionic strength, as well as predict the behavior or deposition location on collector of any nanoparticles entering the filtration system in order to improve the field of environmental nanotechnology. Furthermore, the predictions generated from the present work parallel those of the constricted 3D model, for instance, the collector size and average velocity. Ultimately, this research could be applied in place of 3D columns when designing filters for water and wastewater treatment.

Finally, the role of coagulant residual, TiO_2 structure, and solution chemistry on the removal efficiency were studied as well in simulated water (AGW and ASW). Results from this study indicate that for all TiO_2 suspensions, the greater coagulant residual concentrations increased the removal efficiency up until 0.5 mg/L alum, above that threshold the effect of coagulant residual were negligible.

This collection of studies provides critical insights into the importance of understanding particles size and coagulant residual concentrations more impactful and in realistic environments. These studies demonstrate the need to update more tests such that they more accurately reflect real exposure scenarios simulating environmental conditions.

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Chapter 1

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Introduction

1.1 Motivation and Background

The global value of the metal oxide industry surpassed $10 trillion in 2017 (Roco 2005). Just some of the growing range of industries in which metal oxides have been applied include: agriculture (Khataee et al. 2016), catalyst (Higarashi and Jardim 2002), coating (Kiser et al. 2009), paint (Long et al. 2006), construction (Weir et al. 2012), electronics and optics (Weir et al. 2012; Kreyling et al. 2017), filtration and purification in water (Kimura et al. 2013), food (Asada and Errman 2010; R. J. B. Peters, Bemmel, et al. 2014; R. J. B. Peters, van Bemmel, et al. 2014), and medical (Long et al. 2006). However, with increased application comes a greater concern for the potential environmental impact of nanomaterial-based products (Nel et al. 2006). Even through appropriate usage of the micro and nano sized metal oxides, the particles have been found in municipal wastewater and drinking water treatment plants (Westerhoff et al. 2011; Arturo A Keller and Lazareva 2013). Worse, previous investigations have demonstrated that metal oxides can be discharged from wastewater treatment plants into natural water bodies (lakes, rivers, streams) (Bennett, Kwong, and Powell 2007; Wang 2012; Ahmed 2016), and remain in those aquatic systems for decades (Petosa et al. 2010). Recent life cycle predictions of nanomaterial loadings in the environment indicate an important role for drinking water treatment plants (Dharmappa, Hasia, and Hagare 1997) in nanomaterial removal. The analysis suggested that of the three types of nanoparticles studied, nano-silver, nano-TiO_2, and carbon nanotubes, only the predicted concentrations of nano-TiO_2 in drinking water treatment effluents (0.7-16 µg/L) were close to or higher than the predicted no effect concentration level (1 µg/L) (Mueller and Nowack 2008). For that reason, more

information is required on the sources, occurrence, and morphology of TiO$_2$ in drinking water treatment effluents, as well as the factors affecting TiO$_2$ removal in drinking water treatment plants.

An extensive number of studies have focused on the potential toxicity of micro and nano size particles to aquatic life and human health. Some recent examples that demonstrated the toxicity of specific metal oxides to living organisms include zinc oxide to zebrafish embryo and crustaceans (Bondarenko et al. 2013), copper oxide to rats (Beaudrie et al. 2015; Song et al. 2015), cerium oxide to human lungs (Rogers et al. 2010), food grade and industrial grade titanium dioxides to algae (Yang, Doudrick, Bi, Hristovski, Herckes, and Kaegi 2014), as well as silver oxides to fish (George et al. 2012). Other investigations demonstrated that micro sized iron oxide can exhibit targeted toxicity, dependent upon surface modifications and interactions, with proteins in the human body (Gupta and Gupta 2005). Given the vast number of products leveraging the benefits of engineered metal oxides that proliferate in the environment and may cause damage, it is critical to understand the fate and transport of the particles in order to determine the best practices for the removal of the micro and nano sized metal oxides from the environment.

This dissertation specifically focuses on removal strategies of the micro and nano sized metal oxides from municipal drinking water treatment. The current strategy employed to remove the particles before drinking water distribution is by using the conventional coagulation-filtration treatment process, including coagulation, flocculation and sedimentation. Coagulation and flocculation are often the first steps in drinking water treatment. After adding coagulants into water, the positive charge of coagulants neutralize

the negative charge of dissolved particles in the treated water. And the particles bind with the chemicals and form larger particles is referred as floc. The floc would settle to the bottom of the water supply because of its gravity. In these primary stages of treatment, chemical additives (re: coagulants) – iron chloride ($FeCl_2$), iron sulfate ($FeSO_4$), or alum ($KAl(SO_4)_2 \cdot 12H_2O$) are used to facilitate the destabilization of particles in the water, so that the particles coagulate and sediment in the treatment facility for easy removal. Previous studies have demonstrated the use of the first three primary stages to effectively remove biosolids, NOM, suspended solids, other inorganic constituents for water treatment (Van Benschoten and Edzwald 1990; Kimura et al. 2013; Khataee et al. 2016; Lazar, Varghese, and Nair 2012; Dharmappa, Hasia, and Hagare 1997). However they are designed only to remove particles greater than 500 micros (Gregory 2005; Crittenden et al. 2012; Safoniuk 2004), so it falls to a fourth stage of drinking water treatment to remove the micro- and nano- sized particles.

The final stage in drinking water treatment before distribution is the filtration stage, which is designed to remove the aggregate particles (greater than 500 micros). For filtration stage, once the floc has settled to the bottom of the water supply, the clear water on top will pass through filters of varying compositions (sand, gravel, and charcoal) and pore sizes, in order to remove dissolved particles, such as dust, parasites, bacteria, viruses, and chemicals. Research regarding the fate and transport of nanoparticles in filtration systems, including TiO_2 (A. A. Keller et al. 2010; Chowdhury et al. 2011; Akilbekova et al. 2015), has been conducted extensively with the use of 3D columns (saturated and unsaturated) (Grolimund et al. 1998; Walker, Redman, and Elimelech 2005; S. a Bradford, Torkzaban, and Walker

2007; Chrysikopoulos and Syngouna 2014). Based on the column experiments, useful information on fate and transport, such as ionic strength, nanoparticles breakthrough, retention, solution chemistry (pH, divalent ions, etc.) can be determined (Lanphere, Luth, and Walker 2013). However, details of the mechanisms in micro-nano scale information cannot be determined in these macroscale column. Another limitation of this methodology is the requirement of a large amount of particles for experiments, which makes 3D column a poor technique for usage of expensive novel particles (Grolimund et al. 1998; Walker, Redman, and Elimelech 2005).

Thus, this dissertation utilized a 2D micromodel system to visualize and model the fate and transport of micro and nano particles in engineered filtration systems [58,59]. The advantages of this system, when compared to the standard 3D column studies [47], include the ability to track individual particles, and directly image the pore scale phenomena of collector particles interactions. Moreover, this 2D system used 300 times less experimental particles per experiment than a 3D column system. The novelty of this dissertation is the application of the 2D micromodel in an experimental matrix with varying electrostatic interactions (as modified by ionic strength), chemistry of particles (food grade and industrial grade TiO_2), solution chemistries (AGW, ASW, $CaCl_2$, KCl), and coagulant residual (0-5 mg/L), to determine the removal efficiency of the particles under various environmentally relevant conditions in an engineered filtration system. To summarize, this doctoral research addresses the fundamental mechanisms and phenomena involving the removal of micro- and nano- sized metal oxides through conventional water treatment filtration processes in a 2D micromodel system.

1.2 Aim and Scope

The overarching goal of this study was to systematically investigate how model engineered micro- and nano- particles behave in engineered filters under a range of relevant solution chemistry conditions, in order to ascertain the best removal strategies from drinking water filtration. The first study conducted included a combination of fundamental and applied experiments investigating the effect of size in transport with ideal particles in simple monovalent suspensions. This study also validated the experimental design of using a 2D micromodel system as a model for drinking water filtration for micro and nano sized particles. The next study simulated actual scenarios in the filtration stage of drinking water treatment. Food grade titanium dioxide (TiO_2) particles were introduced into the 2D micromodel system, with industrial grade TiO_2, the most commonly studied nanoparticle, used as a control to study the factors that lead to greater filtration of the metal oxides. Finally, the effect of coagulant residual on micro and nano sized metal oxide particles, leftover from the primary stages of drinking water treatment, were studied in a variety of suspensions including artificial surface water (ASW) and artificial ground water (AGW), as well as four other control conditions were used to evaluate the influence of monovalent and divalent salts. Based on this dissertation research, the factors leading to metal oxide destabilization and their removal, include the type and concentrations of salts in solution, the presence of and chemical structure, and the process operating conditions (flowrates and coagulant residuals). Ultimately, through the systematic variation of these parameters in

the micromodel experiments, the conditions for optimal metal oxide destabilization and removal were determined.

The work presented herein was conducted in collaboration with the University of California Center for Environmental Implications of Nanotechnology (UC-CEIN), which is a multi-disciplinary research community that addresses the responsible use and safe implementation of nanomaterials. This dissertation addresses these topics in three core chapters: the impact of size and ionic strength on the removal of micro and nano sized particles within a 2D micromodel system (Chapter 2), the impact of ionic strength and molecular structure on the removal of food grade and industrial grade TiO_2 particle in filtration (Chapter 3), and the effect of coagulant residual on the removal efficiency with food grade and industrial grade TiO_2 in simulated aquatic conditions (Chapter 4). The aims of this investigation were developed based upon the hypotheses and objectives presented in the subsequent section.

1.3 Hypotheses and Specific Objectives

To achieve the overall goal of this doctoral research, the following hypotheses and specific objectives were developed and are presented below (it should be noted that each specific objective has been addresses in a chapter within this dissertation).

Hypothesis 1: Larger particles will have a greater removal efficiency in the 2D micromodel filtration system. Higher ionic strength will also lead to a greater removal of particles.

To test this hypothesis, different sizes of fluorescent spherical latex nanoparticles have been selected for this objective (20, 200, 2000 nm) with various IS (1, 3.16, 10, 31.6, 100mM KCl). These were selected based upon their broad use in consumer products and foods. Specifically, the following tests were used to characterize the fate and transport of the particles: zeta potential measurements of particles and collector surfaces, DLVO theory calculations, and COMSOL simulations. The purpose of this work was two-fold: (1) to identify if the particles size and ionic strength were eliciting measurable changes in removal efficiency and (2) if the changes could be identified by the 2D micromodel systems and the mechanisms caused this phenomenon. (Chapter 2). This is important to validate the 2D micromodel system used in the subsequent two objectives.

Hypothesis 2: The smaller the particle, the more difficult it will be to remove via filtration.

Food grade titanium dioxide nanoparticles (TiO_2, E171, Fiorio Colori Spa) were utilized as the model micro sized metal oxides in the transport experiment [26,27], while industrial grade TiO_2 was used as the model metal oxide nano sized particle. The particles were characterized by size and zeta potential when suspended in a range of ionic strength (1, 3.16, 10, 31.6, 100 mM KCl) and pH (3-9) conditions. The particles suspended in pH 5 and 7 and a range of ionic strength conditions were then tested in the 2D micromodel to determine the removal of the particles. Results reported in this work demonstrate that overall, the removal efficiency of food grade are all lower than industrial grade TiO_2 under all ionic strength conditions. Thus, food grade is removed 13-38 % less (as defined by η) than industrial grade across the conditions tested in this study, and the higher ionic strength,

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the less food grade were removed compared to industrial grade. This is because of the smaller aggregate size and lower surface charge values of the food grade TiO_2. The greater size of the industrial grade TiO_2 aggregates resulted in larger hydrodynamic forces, leading to a higher removal efficiency. In addition, the lower zeta potential would increase the DLVO forces resulting in food grade TiO_2 more likely to exit with the effluent into the environment, potentially leading to ecosystem damage (Pourzahedi, Vance, and Eckelman 2017; Reed et al. 2016; Stieberova et al. 2017; W. Jones et al. 2017).

Hypothesis 3: The greater the addition of coagulant residual to the model filtration system will lead to an increased removal efficiency.

To test this hypothesis, Food and Industrial grade TiO_2 were suspended in artificial ground water and artificial surface water. Residual coagulant, alum $(KAl(SO_4)_2 \cdot 12H_2O)$, was added to these suspensions in a range of concentrations that may be found in drinking water treatment facilities (0, 0.05, 0.5, 5 mg/L). These suspensions were tested for size, zeta potential, fractal dimension, and removal efficiency via the 2D micromodel to determine the most effective conditions to remove the particles from drinking water. Results from this study also indicate that for all TiO_2 suspensions, the greater coagulant residual concentrations increased the removal efficiency up until 0.5 mg/L alum, above that threshold the effect of coagulant residual were negligible. Additionally, AGW had the greatest removal efficiency for all coagulant residual concentrations, followed by $CaCl_2$, ASW, and KCl, respectively. This trend implies that the removal of FG and IG TiO_2 via filtration could be improved by adding divalent salts. Analysis from results of this study

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suggests that adding coagulant residual up to 0.5 mg/L alum and adding divalent salts to the filtration stage of water treatment will increase the removal of FG TiO_2 from drinking water. This study has incorporated many levels of complexity to simulate the complex conditions in environmental systems such as ASW, AGW and different level of coagulant residual (alum), and is the first to report their impact on the transport of FG and IG TiO_2 in porous media.

These three objectives are all based on the hypothesis that all of the following parameters – solution chemistry, particle size, and presence of coagulant residual– influence the removal of metal oxides in the filtration stage. Through this systematic and quantitative investigation of metal oxide removal, the goal is to identify the optimal conditions for micro- and nano- sized particles removal in the filtration stage of water treatment and decouple the contributions of the parameters tested.

1.4 Experimental Approach

This dissertation is composed of five chapters including the introduction (Chapter 1) and conclusion (Chapter 5). Following the introduction, Chapter 2 describes the effects of size and ionic strength on the removal efficiency within a 2D micromodel system. The experimental design included three different sizes particles (20, 200, 2000 nm) suspended in a range of environmentally relevant ionic strength concentrations (1, 3.16, 10, 31.6, 100 mM KCl). Results from this study were as predicted by the DLVO model, where larger particles and higher ionic strength lead to a greater removal. These results lead to a model framework for ionic strength and particle size effects in filtration of the presence of \

residual (0, 0.05, 0.5, 5 mg/L) were applied into the ASW and AGW. In addition, to better understand the impact of monovalent and divalent solutions, four other controlled solutions were applied under the same ionic strength conditions. This results from this study indicate that for all TiO_2 suspensions, the greater coagulant residual concentrations increased the removal efficiency up until 0.5 mg/L alum, above that threshold the effect of coagulant residual were negligible. Notably, AGW had the greatest removal efficiency for all coagulant residual concentrations, followed by $CaCl_2$, ASW, and KCl, respectively. Analysis from results of this study suggests that adding coagulant residual up to 0.5 mg/L alum and adding divalent salts to the filtration stage of water treatment will increase the removal of FG TiO_2 from drinking water.

Chapter 5, entitled "Summary and Conclusions" summarizes the findings from this PhD dissertation. Two of the three chapters of this work are currently undergoing the peer-review process with the anticipation of publication. Chapter three has been accepted in a peer-reviewed journal. All chapters are listed below.

1.5 Manuscripts Resulted from Research

The dissertation research and parallel projects conducted from 2014 to 2018 have resulted in the preparation of three manuscripts. The first three manuscripts listed are the three chapters within this dissertation and include the supplemental information within the corresponding chapter. Each of the dissertation chapters are either currently in the peer-review process or have been accepted for publication.

1. Chen, Chen, Travis Waller, and Sharon L. Walker. "Visualization of transport and fate of nano and micro-scale particles in porous media: modeling coupled effects of ionic strength and size." Environmental Science: Nano 4.5 (2017): 1025-1036.

2. Chen Chen, Ian M. Marcus, Travis Waller, and Sharon L. Walker. "Filtration Mechanisms of Food and Industrial Grade TiO_2 Nanoparticles." Analytical and Bioanalytical Chemistry, Submitted in Feb 2018.

3. Chen Chen, S. Drew Story, Ian M. Marcus, and Sharon L. Walker. "Influence of Coagulant Residual on Filtration of Food Grade and Industrial Grade TiO_2 in Water Treatment Systems." Water Research, in preparation.

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Chapter 2

Visualization of Transport and Fate of Nano and Micro Scale Particles in Porous Media: Modeling Coupled Effects of Ionic Strength and Size

Chen, Chen, Travis Waller, and Sharon L. Walker. "Visualization of transport and fate of nano and micro-scale particles in porous media: modeling coupled effects of ionic strength and size." *Environmental Science: Nano* 4.5 (2017): 1025-1036.

Abstract

In this investigation, single collector removal efficiency (η) of three different size latex nanoparticles (20, 200 and 2000 nm) are presented for a 2-D micromodel system. η for each collector grain as a whole and by quadrant has been evaluated. Fluorescent microscopy allowed for the direct visualization of latex nanoparticle transport under various ionic strengths and particle sizes. The single collector removal efficiency (η) was quantified as a function of location on the individual collector grains across a range of ionic strength (1-100 mM KCl). A rigorous numerical model was developed that incorporates DLVO forces (electrostatic and van der Waals interactions) and hydrodynamic forces utilizing COMSOL over the range of experimental conditions tested to calculate η. This expression, based on a modification of filtration theory, accounts for the observed variation in the single collector removal efficiency with respect to location (or quadrant) on the collector, as well as changes in the zeta potential and particle size. This work confirms visually and theoretically that the greatest deposition along the collector surface occurs at the rear stagnation region of an individual collector. The single collector removal efficiency increases with ionic strength as well as particle size. Furthermore, this work demonstrates critical nature of the hydrodynamic forces, size, and ionic strength in the ultimate interactions between particles and collectors.

2.1 Introduction

The rapid growth of the nanotechnology industry has been termed next "industrial revolution"(Sun et al. 2009) . The global value of nanotechnology surpassed $1 trillion in 2015 (Roco 2005; Gould 2015), up from $4.1 billion in 2005 (Roco 2005). Nanotechnology's diverse applications include agriculture (Ditta, Arshad, and Ibrahim 2015), catalysts (Linic et al. 2015; G. Chen and Walker 2012), coatings (Joerger, Klaus, and Granqvist 2000), paints (Hischier et al. 2015), construction (Hanus and Harris 2013; Elsabahy and Wooley 2015), electronics and optics (Gilbertson et al. 2015; Wu et al. 2015), filtration and purification in water (Alele and Ulbricht 2016; L. Liu et al. 2012), food (Weir et al. 2012; Jalbani and Soylak 2015; Hannon et al. 2015), medical (Ling, Lee, and Hyeon 2015), with the potential of innovative and beneficial future applications. Estimates of global environmental nanoparticle (NP) emissions from products during and after usage revealed that 63-91% would eventually reach landfills by attaching to biosolids within wastewater treatment plants (Keller and Lazareva 2013). Additionally, current estimates predict that 8 to 28% of released NPs would reach soils via application of biosolids to agricultural land (which will be discharged into water as well), while 0.4 to 7% would reach water bodies through direct and indirect pathways. Previous studies have demonstrated that NPs (TiO_2, CeO_2, Ag, ZnO, carbon-based NPs) can be discharged from wastewater treatment plants into natural water bodies (lakes, rivers, streams) (Maurer-Jones et al. 2013), and can remain in those aquatic systems for decades (Jiang, Oberdörster, and Biswas 2009; P. Zhang et al. 2012; Zhu, Chang, and Chen 2010). Although the tremendous economic value of nanomaterials is very promising, there still remains a

distinct need to identify the environmental implications and any potential damage associated with nanoparticles (Beaudrie et al. 2015).

An extensive number of studies have focused on the potential toxicity of nanoparticles to aquatic life and human health. Some researchers revealed that certain metal, engineered NPs such as, zinc oxide (Suman, Rajasree, and Kirubagaran 2015), copper oxide (Beaudrie et al. 2015; Song et al. 2015), cerium oxide (Rogers et al. 2010), and silver NPs (Kaduková et al. 2015), were toxic to crustaceans, algae, and fish (Bondarenko et al. 2013). Other investigations demonstrated that carbon nanotubes caused DNA damage to the epithelial cell line of the human lung in a very low concentration , while iron oxide NPs can exhibit targeted toxicity dependent upon surface modifications and interactions with proteins in the human body (Gupta and Gupta 2005). Given the vast number of products leveraging the benefits of nanotechnology, proliferating in the environment, and causing damage, it seems prudent to understand removal mechanisms of nanoparticles from environment in advance.

The current strategy is to remove NPs using the first three stages of traditional water treatment: coagulation, flocculation, sedimentation (Beyazit et al. 2010; Nason, McDowell, and Callahan 2012; Dunphy Guzman, Finnegan, and Banfield 2006; De Bleecker, Bogaerts, and Goedheer 2006). The fourth stage of water treatment, filtration, has mainly been considered in natural systems (Pelley and Tufenkji 2008; Lanphere, Luth, and Walker 2013; Buddrick, Cornell, and Small 2015). Engineered filters have mostly been studied with 3-D columns (Weber Jr, McGinley, and Katz 1991; Jardine et al. 1999; Darlington et al. 2009),

which require massive amount of particles for experiments as well as lack of the knowledge for particles movement in filtration. The majority of transport experiments have been conducted in a 3D porous medium (e.g. sand column) that indirectly monitors removal by evaluating the particle concentration at the inlet and outlet of the column (Wan and Wilson 1994). However, in these previous studies the calculation of single collector efficiency could only be achieved by taking average over multiple collectors and did not account for the distribution of hydrodynamic forces around the collectors. Additionally, this 3 D approach lacks resolution to identify for where on the collector the interaction occurs. Thus, in order to more rigorously evaluate the contributions of various transport, particle and chemical variables, a 2D approach has been undertaken.

Diffusion, interception, and sedimentation are the main mechanisms related to the mass transfer of NPs into collector surfaces at the solid-water interface(Yao, Habibian, and O'Melia 1971). As the particles approach the collector surfaces, they experience a combination of forces which effectively determine the subsequent attachment scenario (Cushing and Lawler 1998; Bergendahl and Grasso 1998; Li et al. 2005). These forces include gravity, buoyancy, hydrodynamic forces (drag and lift forces), electrical double layer interactions (repulsive or attractive forces), and van der Waals interactions (S. a Bradford, Torkzaban, and Walker 2007). In addition, recent experimental research has illuminated that pore structure and surface roughness also have an impact on the deposition behavior (Cushing and Lawler 1998; Tufenkji and Elimelech 2004; Foppen, Mporokoso, and Schijven 2005).

This investigation utilized a novel 2-D micromodel system to visualize and model the fate and transport of nanoparticles in engineered filtration systems (Willingham, Werth, and Valocchi 2008; C. Zhang et al. 2011). The advantages of this system when compared to the standard 3-D column studies (Jardine et al. 1999) include the ability to track individual particles, and directly image the pore scale phenomena of collector particles interactions. This approach is the first of its kind to depict a single collector grain as it interacts with nanoparticles under flow. Previous studies used this methodology more broadly to evaluate the deposition kinetics of bacteria (Yuan, Pham, and Nguyen 2008; Y. Liu et al. 2009); however, the role of size, ionic of strength, and hydrodynamics was not calculated. The novelty of this present study is the application of the micromodel in an experimental matrix with varying electrostatic interactions (as modified by ionic strength) and hydrodynamic interactions (as influenced by nanoparticle size) such that experimental results may be compared to a force balance model. These results provide insight into the detail that not only can calculate the single collector removal efficiency (average for individual collector or for a single quadrant), but also can calculate the force balance of each point along the collector grains and within the pore throat. This paper is the first to apply this experimental system for engineered nanomaterials.

2.2 Experimental Protocols

2.2.1 Fluorescent latex nanoparticles

Fluorescent latex nanoparticles (yellow-green carboxylate microspheres; λ_{ex}, 505nm; λ_{em}, 515 nm; 2% w/v) with different sizes were purchased from Thermofisher scientific

(Carlsbad, CA). Their sizes were 20, 200, and 2000 nm in diameter, and the uniformity of the particle size was verified by inspections of suspensions under the Olympus BX51 epifluorescent microscope (excitation filter wavelength of 460 nm and emission filter wavelength of 510 nm). Particle suspensions were made by mixing stock particle solution (4.55×10^9, 4.55×10^{12}, 4.55×10^{15} microspheres/mL of 20, 200, 2000 nm stock particle solutions, respectively) with deionized water, and diluted into constant concentration of 4.55×10^7 particles/mL. The same suspension concentration was applied in varied ionic strength (IS) electrolyte solutions (1-100 mM KCl in deionized water) at constant pH of 4.

2.2.2 Electrokinetic measurements

The primary component of the silica wafer micromodel is quartz. Relative surface charge of the micromodel was determined by conducting streaming potential measurements on quartz using an electrokinetic analyzer (EKA; SurPASS; Anton Paar, Graz, Austria) equipped with clamping cell (55 mm × 25 mm). After the clamping cell with quartz was mounted, the system was filled and then rinsed with 0.5L background solution (Tang, Kwon, and Leckie 2007). The measurements were performed over a wide range of IS (1-50 mM KCl) at 25ºC. Acid titration (0.05 M HCl) was used to evaluate the streaming potential until pH 3 was reached, then increased by adding NaOH (0.05 M) to approximately 10. Based on Helmholtz–Smoluchowski equation (Smoluchowski 1921) and Fairbrother Mastin approach (Fairbrother and Mastin 1924), the streaming potentials were converted to zeta potentials (Walker et al. 2002). Measurements were repeated four times for each pH increment value.

The electrophoretic mobility of the latex microspheres were measured using a ZetaPals instrument (Brookhaven Instruments Cooperation, Holtsville, NY) across the same range of solution conditions, and from this, the zeta potential (ζ) was calculated using the Smoluchowski equation (Smoluchowski 1921). Hydrodynamic diameter was measured using dynamic light scattering (DLS) (Brookhaven model BI-9000AT, Holtsville, NY) at a wavelength of 661 nm and scattering angle of 90°. The average diameter was determined from 10 runs for three identical samples; each run lasted 30 seconds. All solutions were made with ACS reagent grade chemicals (Fisher Scientific, Pittsburgh, PA).

2.2.3 Quantitative analysis of transport experiments in a 2D micromodel

Porous media micromodels were fabricated from a silicon wafer based on a standard procedure that has been previously developed and applied (Y. Liu et al. 2012; Lu et al. 2013). Each micromodel had a total of 1471 well uniformly distributed cylindrical collectors with 100 µm diameter, 20 µm in pore throat, 70 µm in pore body and 10 µm in depth, respectively. The porosity was 0.41, which is similar to packed bed column (Y. Liu et al. 2012; Elimelech et al. 2000).

The micromodel experimental setup included a 5 mL plastic syringe (BD, Franklin Lakes, NJ) with 1 mm external diameter polyethylene tubing and a three-valve adapter horizontal connecting the syringe to the inlet of micromodel. The velocity of infusion syringe pump (KDS 220, KD Scientific Inc., Holliston, MA) was set at 1 µl/hr (converted to 1.68×10^{-4} m/s in 2D micromodel), to remove all the air bubbles and reach fully-saturated condition. Before the transport experiment was performed, the micromodel was hydrated with 20 mL

of the electrolyte solution (corresponding to the particular IS of that experiment) in the absence of particles at pH 4. Then the corresponding samples were injected into the well saturated micromodel under steady state flow (Auset and Keller 2004). The samples were examined quantitatively with an Olympus BX51 epifluorescence microscope connected to a charge-coupled device (CCD) camera (Q-imaging RETIGA Exi, Fast 1394) and visualized using Image Pro 8.0 software. The movement of the particles was observed under a LMPlanFI 20x/0.40na objective lens (Olympus America Inc., Cypress, CA) and recorded every 30 s for tracking the location at which the particles deposited on the collector surfaces. The size of the viewing area was 420 by 340 microns. For each view, six random collectors (in the central position of micromodel) were counted.

For the purpose of enumerating the number of particles depositing in the forward, rear and side regions of the collector, each collector was divided into four quadrants and the number of particles depositing on each quadrant was manually counted over time Figure 2.1). For each of these quadrants, as well as the entire collector, the single collector removal efficiency (η) was calculated. The removal efficiency is the fraction of particles approaching collector that actually collide, described as

$$\eta = \frac{4I}{\pi d_c v c_p}$$

[1]

where I is number of attachment per collector (or per quadrant), d_c is the collector diameter (m), v is the velocity (m/s), and c_p is the particle concentration. These collector removal

efficiencies allow for a point of comparison for filter performance as a function of particle size and solution conditions.
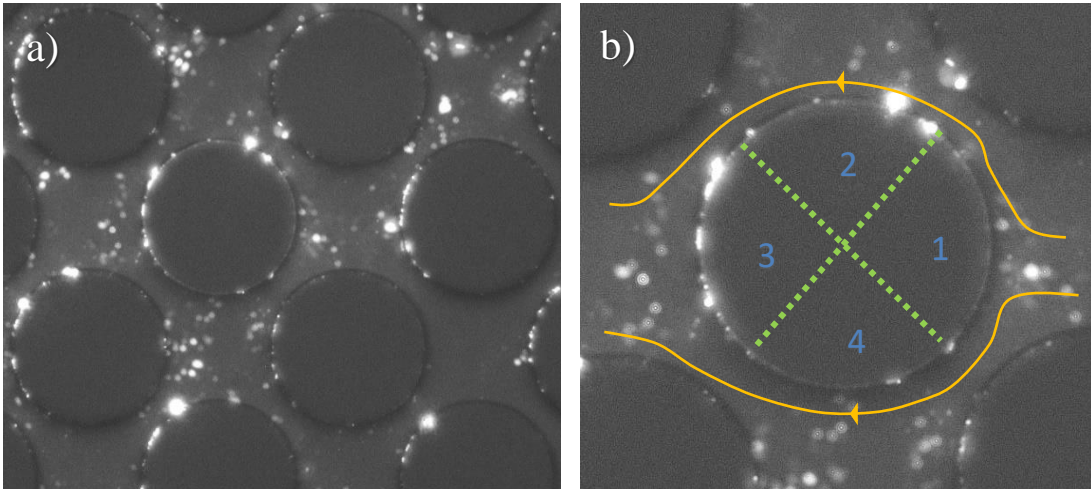
Figure 2.1 Diagram of micromodel under different lenses: a) 20X, six collector in sight where the number of particles depositing on each collector were manually counted; b) 40X, one collector in sight where collector was divided into quadrants.

2.2.4 Analysis of hydrodynamic and DLVO interaction forces

DLVO theory was applied to calculate the total interaction energy (sum of London-van der Waals attraction and electrostatic double-layer forces) (Derjaguin and Vlashenko 1948) for particles upon close approach to the collector surface as a function of separation distance (Derjaguin and Vlashenko 1948) (definitions and equations in ESI). The hydrodynamic force models are based on the conditions of fluid flow regime when entering the micromodel system. Nine points were chosen for force balance calculations to capture the phenomena occurring at three different quadrants. The range from 0-45° represents half of quadrant 1, 45-135° represents quadrant 2 (which has identical conditions to quadrant 4) and 135-180° represents quadrant 3.

Hydrodynamic forces, a combination of drag and lift forces, must also be accounted for when considering the forces involved in the transport of the particles. The expression of F_{lift} on a sphere is given by Saffman (Saffman 1965; Bergendahl and Grasso 1998) as

$$F_L = \frac{81.2\mu r_c^3 (\partial v / \partial r)^{3/2}}{v^{1/2}}$$

[2]

Where μ [M L^{-1} T^{-1}] is the dynamic viscosity of the flow, r_c [L] is the radius of the particles, $\partial v/\partial r$ [L T^{-2}] represents the acceleration of the particles around the collector surface, v [L T^{-1}] is the velocity of the particles around the collector surface. F_{lift} is a function of the collector radius, velocity distribution, as well as, acceleration to a magnitude of 1.5.

The expression of drag force has been defined previously as (Bergendahl and Grasso 2000)

$$F_D = 10.205\pi\mu(\partial v / \partial r)r_c^2 \qquad\qquad [3]$$

Based on equation 3, the fluid drag is proportional to the projected area of the particle and thus roughly to the square of the particle size.

On the other hand, the total interaction force F_{DLVO} acting on the particle as it approaches the surface, separate from the hydrodynamic force, is defined as

$$F_{DLVO} = \frac{\Phi_{total}(h)}{h} \qquad\qquad [4]$$

where ϕ_{total} (h) (calculated by Supporting Information equation S1) is the total interaction energy as a function of separation distance, h is the distance between particles and collector surface.

Due to the difficulties in applying three types of forces on the same axis of coordinate, a theory based on a force balance applied to coordinate direction changing with flow rate is now circumscribed. A simplified geometry is illustrated in Figure 2.2. The axial (drag) force on a sphere resting on a plane surface has been evaluated in equation 3. Another axial (lift) force perpendicular to the plane surface can be expressed in 2. The interparticle attraction and repulsion forces (DLVO force) are on the direction between center of collector and particle. Accordingly, the force in x and y direction are represented in the following two equations.

$$F_x = -F_{DLVO} \times \sin\theta - F_D \qquad\qquad [5]$$

$$F_y = F_{DLVO} \times \cos\theta + F_L \qquad\qquad [6]$$

As demonstrated in Figure 2.2, F_y is the force that determines the resulting repulsive or attractive force, while the F_x only shows the extent of particle "rolling" around the collector surface. It may be concluded that positive F_y values suggest repulsive conditions; whereas, negative F_y indicates attractive ones.
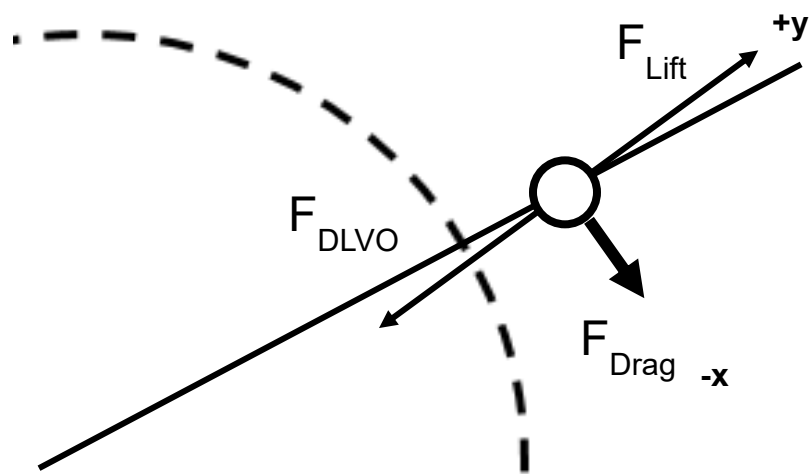
Figure 2.2 Schematic of the combination of DVLO and hydrodynamic (lift and drag) forces interacting on the particle. The X axis represents the forces on the particle resulting from the oncoming velocity flow acting in the positive x direction while the drag force is always on the negative X axis. Perpendicular to the velocity flow is the Y axis where the lift component of the hydrodynamic force acts in the positive Y direction while the DLVO forces can act in either the positive or negative Y direction representing attraction or repulsion, respectively. Experiments were conducted at pH 4 under conditions of 10^8 particles/mL and a flow rate of 1μL/hr.

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2.3 Results and discussion

2.3.1 Characterization of micromodel and latex nanoparticles

The influence of pH, particle size, as well as, ionic strength on the zeta potentials of latex microspheres is presented in the Figure 2.3. In DLVO theory (Derjaguin and Landau 1941),the interaction between the particles and micromodel are determined by the sum of van der Waals force and electrical double layer force. The zeta potential and thickness of the electrical double layer are the main properties of electrical double layer (Morrison and Ross 2002). Furthermore, zeta potential is dependent on the electrical double layer thickness (Benjamin et al. 1996). The thickness of electrical double layer is a function of ionic strength, with a greater ionic strength causing reduction in the double layer thickness. The zeta potential becomes more negative with increasing size (Figure 2.3) is expected bases on the solution for Poisson-Boltzmann equation at low potentials for spherical double layer (Borukhov, Andelman, and Orland 2000). The zeta potential of latex nanoparticles are shown in Figure 2.3a as a function of pH at a constant ionic strength (10 mM KCl). The measured isoelectric point for latex nanoparticles is ~ pH 3.5, which is consistent with previous work (Ouyang et al. 1996; Vie et al. 2015). The magnitude of the negative zeta potential indicates that latex nanoparticles above pH 4 are stable in suspension as the negative surface charge reduces nanoparticles aggregation (Mohanraj and Chen 2006). The role of pH on influencing the zeta potential of the nanomaterials is attributed to the hydrolysis of surface carboxylic groups (Schuetzner and Kenndler 1992; Jayaweera, Hettiarachchi, and Ocken 1994).

The zeta potential measured for quartz (simulating the charged behavior of the quartz -

based micromodel) in KCl solution is given as a function of pH with IS ranging from 1 to

100 mM in Figure 2.3b. In this figure, the zeta potential of the micromodel is plotted versus

the pH through 2.5 to 5.3. In general, an increase in the ionic strength of the aqueous

solution passing through the micromodel results in reduced zeta potential of the

micromodel surface because of electrical double layer compression (Benjamin et al. 1996).

As the isoelectric point of quartz is around pH 3.5, the observed inverse relationship

between ionic strength and zeta potential shows consistency with other studies (Cuddy,

Poda, and Brantley 2013; White and Monaghan 1936).
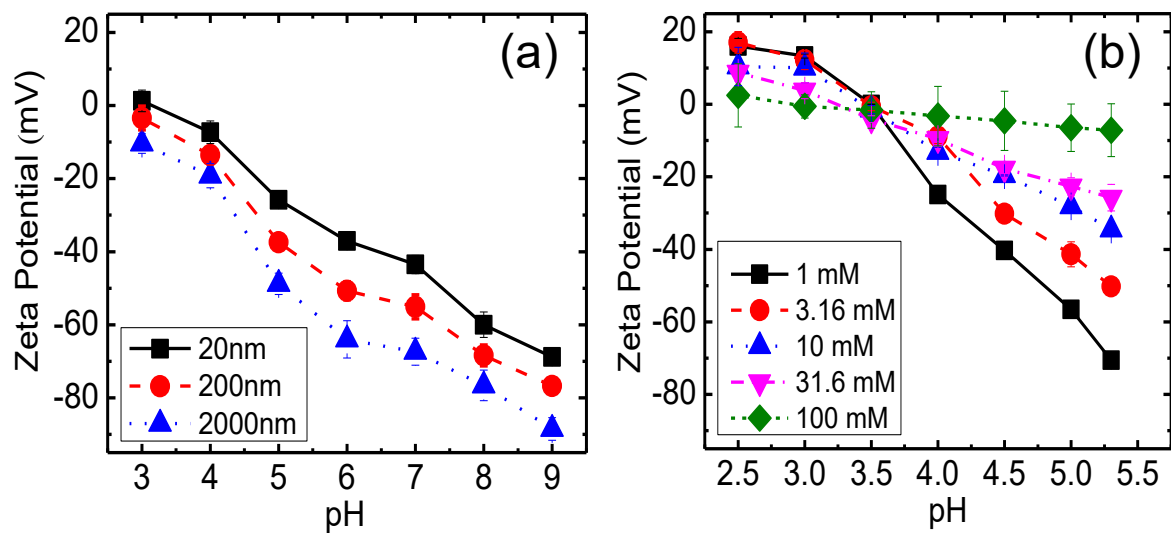
Figure 2.3 Zeta potentials of (a) latex microspheres (20, 200, 2000 nm) at a concentration of 10^8 particles/ mL in 10 mM KCl between a pH range of 3-9 and (b) the micromodel as a function of both ionic strength (1, 3.16, 10, 31.6, and 100 mM KCl) and pH (2.5-5.5). Errors bars indicate one standard deviation of triplicate measurements.

2.3.2 Removal efficiency in 2-D micromodel

NP removal is of primary interest during filtration; therefore, the goal of the experimental measurements was to identify the dependence of size and ionic strength on removal efficiency. This has been achieved by quantitatively examining the transport and removal of latex nanoparticles in a saturated silica micromodel. In Figure 2.4, the removal efficiency is plotted against the log of the ionic strength for the three model particle sizes (20, 200, 2000 nm). Based on data from transport experiments, the removal efficiency of a single collector divided into four quadrants was calculated using eq 1 (Figure 2.4a). The removal efficiency for the entire "single" collector and each of the quadrants is discussed below.
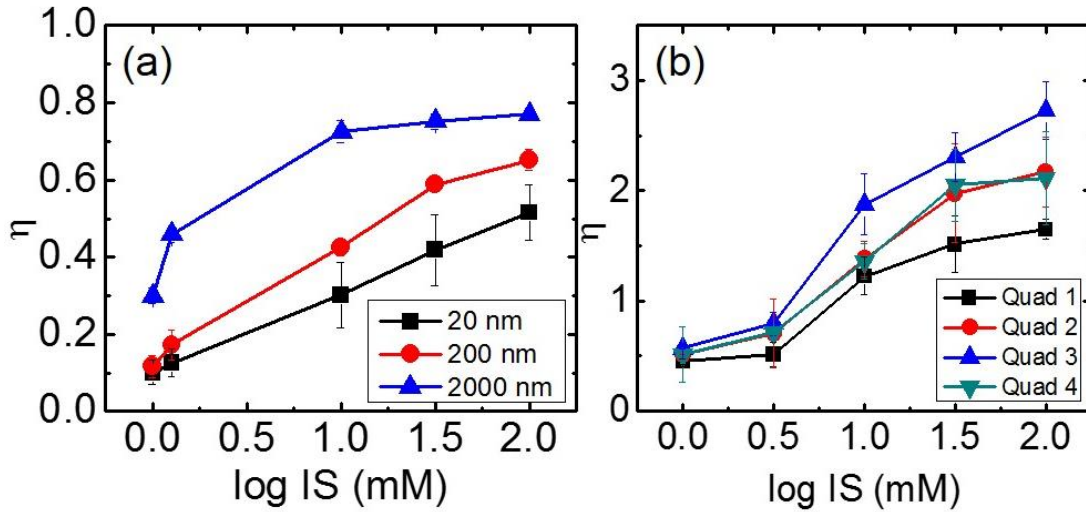
Figure 2.4 Removal efficiency of latex particles as a function of ionic strength for (a) the whole collector using 20, 200, 2000 nm latex microspheres and (b) each of the four quadrants using 200 nm particles. Experiments were conducted at pH 4 under conditions of 10^8 particles/mL and a flow rate of 1μL/hr. Error bars indicate one standard deviation of triplicate measurements.

In general, the single collector removal efficiency is proportional to $d_p^{-0.796}$ and was observed to increase with both ionic strength and latex nanoparticle size (more regarding these calculations are found in the Supporting Information). Figure 2.4a displays the experimental data which demonstrates this increased efficiency with size. Linear shear flow was observed from quadrant 1 to 2 while a rear stagnation zone was existed at quadrant 3 showing good agreement with previous quasi-stagnation flow studies (Lanphere, Luth, and Walker 2013). Although it is well established that hydrodynamic forces become more pronounced as particle size increases, this did not result in an increasing removal efficiency for the 2000 nm particles (Figure 2.4a). Figure S2.1 shows colloid deposition was predominant in impingement zones of collector surface, and one grain there is a relative paucity of colloids at the leeward flow stagnation zone at 180 degree. It appears possible that imprecations in the flow field created eddies that caused flow to impinge on the near boundaries of quadrants 2-3 and 3-4 (Johnson, Li, and Yal 2007). Moreover, DLVO interaction calculations revealed the presence of an energy barrier that would likely inhibit deposition limiting removal efficiency (even as promoted by hydrodynamic and van der Waals forces). This primary maxima was found to increase with particle size. An additional reason for the plateau in removal efficiency appearing above ionic strength 31.6 mM (Figure 2.4a: log IS= 1.5) may be the dimensions of the particle's electrostatic double layer (EDL). Bigger particles generally possess larger electrostatic double layer dimensions. Consequently, although the surface of the collector has not been fully covered with deposited particles, the EDL of the larger particles already effectively screens the collector to additional particles transporting near to the surface. Therefore, less attachment

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on the collector may occur due to repulsive interaction between suspended and attached particles. Another possible explanation for the plateau phenomenon observed with 2000 nm latex particles could be based on the single collector removal efficiency equation (equations S1-S6) (Pazmino, Trauscht, and Johnson 2014). Particles above 1 micron begin to be significantly impacted by the sedimentation mechanism (Brodsky et al. 2003; C. Chen et al. 2010; Rosso et al. 2003). Moreover, around 1 micron, particles experience the lowest single collector removal efficiency due to the dominance of diffusion and advection (Tufenkji and Elimelech 2004; Ma, Pazmino, and Johnson 2011). These phenomena may explain why the 2000 nm particles behavior is different from the other two smaller sized nanoparticles.

To further investigate the removal along the surface of the collector grains, each quadrant's removal efficiency was calculated and plotted versus ionic strength (Figure 2.4b). The removal efficiency trends were as follows: quadrant 3 > quadrant 2 ≈ quadrant 4 > quadrant 1. P-values obtained from the student's t-tests indicated that the difference between the removal efficiency of quadrant 2 and 4 are statistically insignificant at a 98% confidence interval. The flow rate distribution pattern has been simulated (Figure S2.2) to determine the fluid velocity field; this allowed for application of the convective diffusion equation to quantify the hydrodynamic forces acting on the particle. As demonstrated in previous studies, quadrants 1 and 3 exhibit forward and rear stagnation points, respectively, where the combination of removal forces acting on the particle are the least while quadrants 2 and 4 are regions of parallel flow where the hydrodynamic forces acting on the particles are the greatest (Torkzaban, Bradford, and Walker 2007). Good agreement was found between

the simulated flow pattern and measured deposition trends. This suggests that by simulating flow pattern for different particles, one can indirectly predict the relative removal efficiency during the micromodel filtration.

2.3.3 Contribution of DLVO-type interaction and hydrodynamic forces

An increasing deposition trend with ionic strength has been observed (Figure 2.3a). To shed light on the mechanisms associated with this phenomenon, DLVO theory has been introduced to evaluate the chemical interaction forces (electrostatic interactions and van der Waals forces) (Russel, Saville, and Schowalter 1989) involved. Characterization of both latex nanoparticles and the silicon micromodel indicate these surfaces have negative zeta potentials under the scenarios tested in this study (Figure 2.3) and the application of DLVO theory predicts the presence of a repulsive energy barrier (Figure 2.5). Notably, calculations of the interaction forces used equations S2.1-S4.In Figure 2.5, the total interaction energy is plotted as a function of separation distance between the particle and collector at different ionic strength (1-100 mM KCl) and latex microspheres sizes (20, 200, 2000 nm). As illustrated, the DLVO profiles predict the presence of a repulsive energy barrier where the magnitude of the primary energy maxima increases with a reduction in the ionic strength.

In particular, the depth of the primary maxima for 20 nm particles (Figure 2.5a) ranges from 0.01 kT at 100 mM to 3.25 kT at 1 mM. Similarly, for 200 nm particles (Figure 2.5b), negligible primary maxima exist between the quartz collector and the nanoparticle. The height of this energy barrier was reduced with increasing ionic strength (the primary

minimum for 1 and 100 mM was 17.7 and -0.01 kT, respectively). Additionally, by comparing three sizes of latex microsphere at 10 mM KCl and pH 4, it can be seen that the total interaction energy increases with the particle size (Figure 2.5d). Further, the depth of the secondary energy minimum also increases with particle size (Table S2.2), as well as, ionic strength due to compression of the double layer (S. a Bradford, Torkzaban, and Walker 2007). Since the thermal energy of latex is on the order of 0.4 kT, theoretically, the primary maxima heights and secondary minima depths shown in Figure 2.5 should be sufficient as to prevent the particles retention in the porous media. Interestingly, the experimental measurements agree with these DLVO results only for IS less than 10 mM and size smaller than 200 nm. This suggests that the extent of particles deposition in the micromodel can be predicted, but only for these lower ionic strength and particle size scenarios.
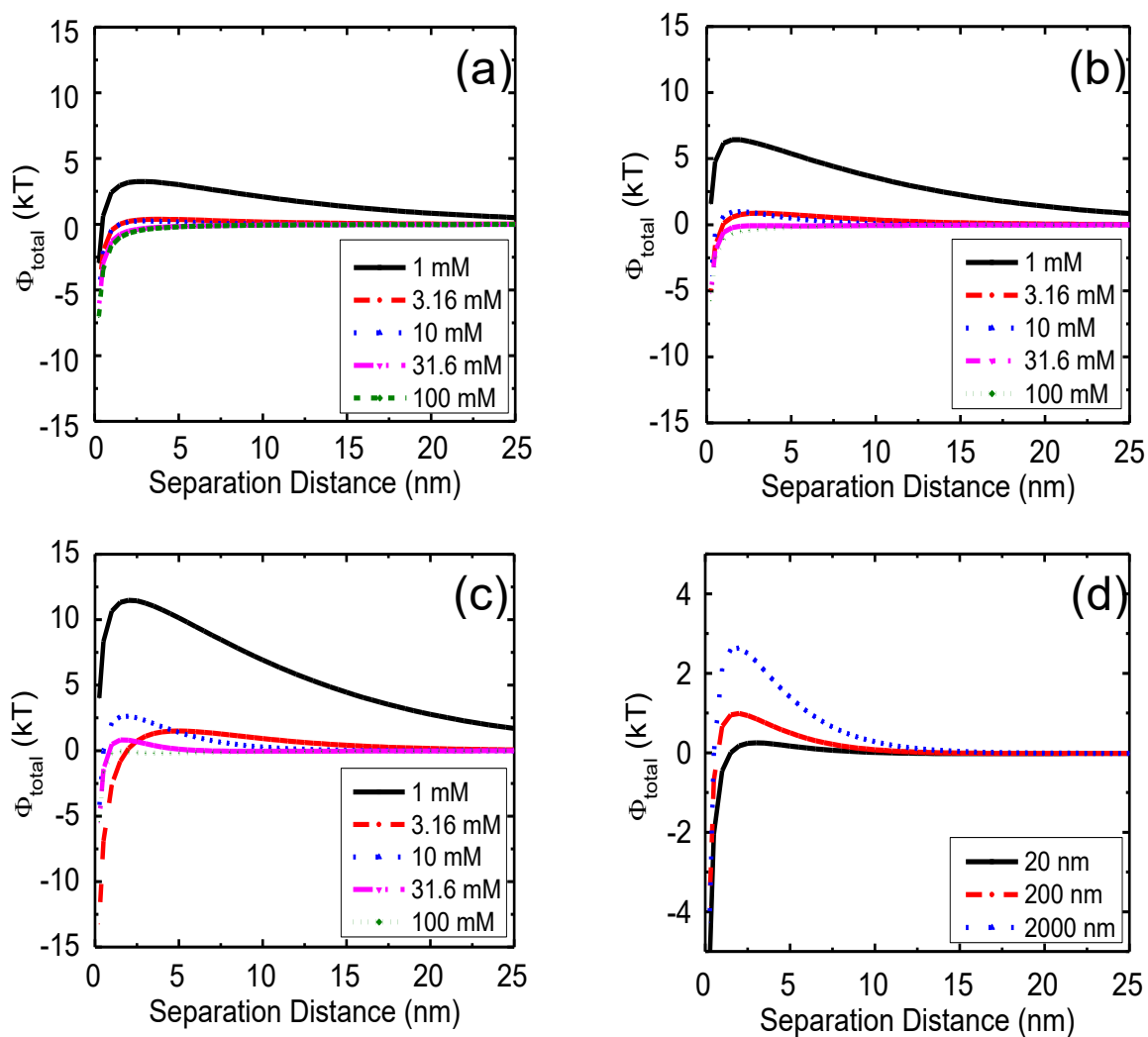
Figure 2.5 DVLO total interaction energy profiles generated for latex microspheres as a function of separation distance. Latex particle sizes of (a) 20 nm, (b) 200 nm, and (c) 2000 nm are presented for varied ionic strengths (1, 3.16, 10, 31.6, 100 mM KCl) at pH 4 using particle concentrations of 10^8 particles/ mL, and (d) compares total interaction energy of three latex particle sizes (20, 200, 2000 nm) at constant ionic strength (10 mM KCl).

DLVO-type forces are not the only forces at play. Rather, a combination of hydrodynamic forces (drag and lift forces) (Saffman 1965; Bergendahl and Grasso 2000) and DLVO forces must be accounted for (Torkzaban et al. 2008). To quantify the hydrodynamic forces across the surface of the collector, the distribution of flow velocity was required. The approach for calculating distribution and the extent to which the fluid is accelerating (thus contributing to hydrodynamic forces) was modeled by COMSOL and reported in the supporting information (in Figure S2.2). The schematic of the combination of DVLO and hydrodynamic (lift and drag) forces model interacting on the particle is demonstrated in Figure 2.2. The x axis represents the forces on the particle resulting from the oncoming velocity flow acting in the positive x direction, while the drag force is always on the negative x axis. Perpendicular to the velocity flow is the Y axis where the lift component of the hydrodynamic force acts in the positive y direction while the DLVO forces can act in either the positive or negative y direction representing attraction or repulsion, respectively. One notable trend is that the magnitude of both the drag and lift forces increases with the particle size (Table S2.2.) It can be observed that for 20 nm, the DLVO forces prevail over the hydrodynamic forces under same ionic strength while the hydrodynamic forces only play a role at an angle of 180°. This result indicates that hydrodynamic forces have a minimal effect on the removal efficiency under chemically favorable conditions. "Favorable" refers to the most suitable conditions for particle deposition to occur where DLVO attractive forces are sufficiently strong enough to overcome any inhibitory fluid forces (S. A. Bradford et al. 2004). As drag forces are lower near the rear stagnation point (180°) and highest around 30°, quadrant 3 is the first to

become favorable for removal efficiency. In contrast, quadrant 1 is last region for deposition. Another interesting tendency is that at constant size, removal increases with ionic strength due to the greater magnitude of DLVO forces as it overcomes the larger value of drag force (Table S2.2). Alternatively, for larger particles size (i.e. 2000 nm) DLVO and hydrodynamic forces have same magnitude contributing equally to particle deposition. It is also interesting to observe that total force, either in the x or y direction of the coordinates, increases with ionic strength (Figure 2.6b). As demonstrated in the diagram (Figure 2.2), recall that the interaction force in the negative y direction corresponds to an attractive force, and vice versa. In Figure 2.6, when ionic strength is held constant, the force in the y direction is positive between 0 and 100°(corresponding to quadrants 1, 2, and 4), whereas beyond 100°, the force is acting in the negative direction. The observed agreement between experimental and theoretical results is satisfactory for the entire range of sizes and ionic strengths tested. This agreement between the experimental and theoretical results shown in Figure 2.6 confirms the validity of the combination force analysis solution for determining the variation of the removal efficiency along the surfaces of the quadrants in the 2D micromodel. Also, the experimentally determined sized dependence for the two types of forces (hydrodynamic and DLVO) were found to be a quantitative agreement with theoretical predictions. Therefore, the 2D micromodel proved useful for quantitative studies of filtration mechanisms. The results obtained in this work also suggest that particle deposition studies can be utilized as a powerful technique for determining force distribution in micromodel.
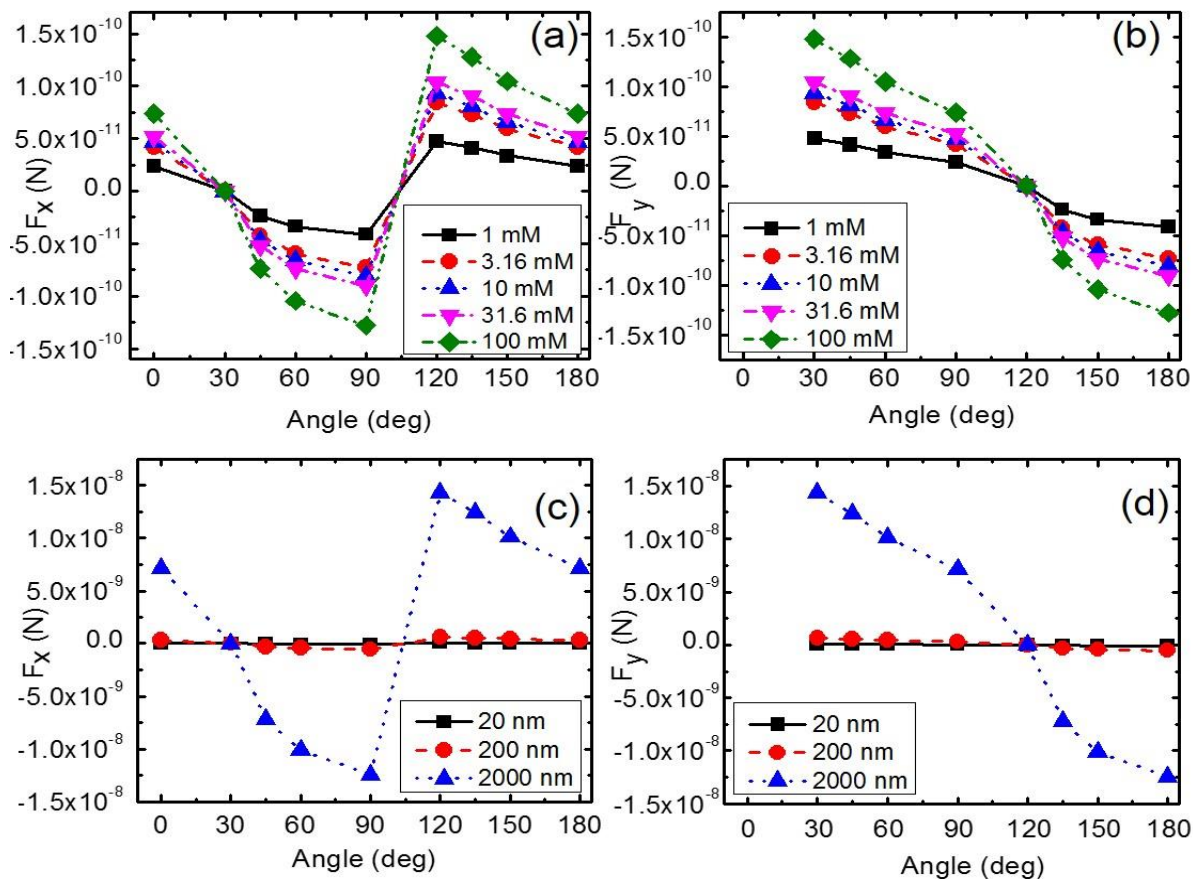
Figure 2.6 Total forces acting on the latex particle in the x and y directions between 0 and 180° of the collector surface. Figures (a) and (b) present changes in total force (x and y direction) as a function of ionic strength using 1, 3.16, 10, 31.6, and 100 mM KCl for 20 nm particles while (c) and (d) show changes in total force (x and y direction) as a function of particle size for 20, 200, 2000 nm latex particles in 10 mM KCl. Each point represents an average of 3 runs and the error bars indicate one standard deviation of those triplicate measurements.

2.4 Conclusions

In general, nanoparticle single collector removal efficiency has been shown to increase with particle size and ionic strength. Under the conditions tested, larger particles result in greater interactions with the collector due to the contribution of hydrodynamic forces. Interestingly, when it comes to statistically analyzing the removal efficiency at the quadrant level, the greatest removal efficiency was observed for the rear stagnation points (quadrant 3), while the least occurred in quadrant 1. It may be deduced that particles under these conditions were because of the leeward flow stagnation zones; thus, the hydrodynamic forces decreased due to the viscous shear.

The highest contribution of attached nanoparticles to the increase in removal efficiency is shown for the combination of largest size particles (2000 nm) and highest ionic strength (100 mM), where it was shown the hydrodynamic forces and DLVO force dominate equally. Lower and similar contribution to the increase in removal efficiency is shown for the combination of the 20 nm and 1 mM; for this condition, the study shows that only DLVO force dominate.

A model framework for ionic strength and particle size effects in filtration of the presence of different sizes of nanoparticles has been developed through this investigation. It is concluded that for any nanoparticle, the single collector removal efficiency is sensitive to the ionic strength and particle size. The model is built to show single collector removal efficiency as a function of particle size and ionic strength, as well as predict the behavior or deposition location on collector of any nanoparticles entering the filtration system in

order to improve the field of environmental nanotechnology. Furthermore, the predictions generated from the present work parallel those of the constricted 3D model, for instance, the collector size and average velocity. Ultimately, this research could be applied in place of 3D columns when designing filters for water and wastewater treatment.

2.5 Acknowledgements

2.6 References

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Supplementary Information for Chapter 2:

Visualization of Transport and Fate of Nano and Micro Scale Particles in Porous Media: Modeling Coupled Effects of Ionic Strength and Size with Force Analysis

Materials and Methods
DLVO Calculations

DLVO theory was applied to calculate the total interaction energy (sum of London-van der Waals attraction and electrostatic double-layer forces)[1] for particles upon close approach to the collector surface as a function of separation distance[1,2].

$$\Phi_{total}(h) = \Phi_{el}(h) + \Phi_{vdW}(h)$$

[1]

where Φ_{total} [M L^2 T^{-2}], Φ_{el} [M L^2 T^{-2}], and Φ_{vdW} [M L^2 T^{-2}] are the total, electrostatic, and van der Waals interaction energies, respectively, and h [L] is the separation distance between the latex microspheres and the surface of quartz collectors. Values of Φ_{total}, Φ_{el}, and Φ_{vdW} are commonly made dimensionless by dividing by the product of the Boltzmann constant ($k_B = 1.38 \times 10^{-23}$ J K^{-1}) and the absolute temperature (T_K).

For a sphere-plate interaction, the electrostatic double layer interactions can be determined with the constant surface potential interaction expression of Hogg[3] as

$$\Phi_{el}(h) = \frac{\pi r_1 r_2}{(r_1 + r_2)} \left\{ 2\phi_1\phi_2 \ln\left[\frac{1 + \exp(-\kappa h)}{1 - \exp(-\kappa h)}\right] + \left(\phi_1^{\ 2} + \phi_2^{\ 2}\right) \ln\left[1 - \exp(-2\kappa h)\right] \right\}$$

[2]

where r_1 [L] is the radius of a latex microsphere, r_2 [L] is the radius of the collector, ϕ_1 [M $L^2 T^{-3} A^{-1}$] is the surface potential of the latex microsphere, ϕ_2 [M $L^2 T^{-3} A^{-1}$] is the surface potential of the collector, and κ [L^{-1}] is the Debye–Huckel parameter. Measured zeta potentials were used in place of surface potentials in Eq. [1].

The van der Waals interaction energy Φ_{vdW} was determined using the expression by Gregory[2] as

$$\Phi_{vdW}(h) = \frac{A_{123} r_1}{6h} \left\{ 1 + \frac{14h}{\lambda} \right\}^{-1}$$

[3]

where A_{123} [M $L^2 T^{-2}$] is the Hamaker constant in this system, and λ [L] is the characteristic wavelength that is often taken as 100 nm (Gregory, 1981). A value of 4.04×10^{-21} J for the Hamaker constant of the latex-quartz-water system was determined by using

$$A_{123} = (\sqrt{A_{11}} - \sqrt{A_{33}})(\sqrt{A_{22}} - \sqrt{A_{33}})$$

[4]

where A_{11}, A_{22}, and A_{33} is the Hamaker constant of latex, quartz and water in vacuum, respectively. The value of these Hamaker constants was gained from the results of the theoretical calculation approximation for Hamaker constants[4,5].

Correlation Equation for Predicting Single Collector Efficiency

The transport and deposition of particles in saturated porous media is described by the convective-diffusion equation. Under steady-state condition, the dimensionless convection-diffusion equation can be expressed as[6,7]:

$$\eta_0 = \eta_0(N_R, N_{Pe}, N_{vdW}, N_{gr}) \tag{5}$$

The definitions of these parameters are provided in Table S1. Based on the additivity assumption previously presented[6,8], the overall single collector removal efficiency can be decided by summing each transport mechanism (including diffusion, interception and gravitational transport mechanisms). The methodology for each transport mechanisms correlation equations is shown as follows:

For diffusion, the correlation has been determined as:

$$\eta_D = 2.4 A_S^{1/3} N_R^{-0.081} N_{Pe}^{-0.715} N_{vdW}^{-0.052} \tag{6}$$

It is interesting to find that based on the eq S6, $\eta_D \sim d_p^{-0.796}$ (compared to $\eta_D \sim d_p^{-0.666}$ of classic method[9]), which indicates the significant influence of hydrodynamic interactions on particle deposition.

Similarly, for interception, the expression was shown as:

$$\eta_I = 0.55 A_S N_R^{1.55} N_{Pe}^{-0.125} N_{vdW}^{-0.125} \tag{7}$$

For gravitational transport mechanism,

$$\eta_G = 0.475 N_R^{-1.35} N_{Pe}^{-1.11} N_{vdW}^{0.053} N_{gr}^{1.11} \tag{8}$$

The overall single collector removal efficiency for deposition in saturated porous media can now be written as the sum of each transport mechanism (eqs S6-S8):

$$\eta_0 = 2.4 A_S^{1/3} N_R^{-0.081} N_{Pe}^{-0.715} N_{vdW}^{-0.052} + 0.55 A_S N_R^{1.55} N_{Pe}^{-0.125} N_{vdW}^{-0.125}$$
$$+ 0.475 N_R^{-1.35} N_{Pe}^{-1.11} N_{vdW}^{0.053} N_{gr}^{1.11}$$

[9]

Velocity Distribution Calculation with COMSOL

COMSOL was used to simulate the velocity distribution around the collector. The assumption was made that the bulk solution in the 2D micromodel system is stationary with no pressure drop in the system. Therefore, the relevant expressions are as follows:

$$\rho(u \cdot \nabla)u = \nabla \cdot [-pI + \mu(\nabla u + (\nabla u)^T - \frac{2}{3}\mu(\nabla \cdot u)I] + F$$

[5]

$$\nabla \cdot (\rho u) = 0$$

[6]

Boundary conditions:

u=0 at the position x=1, when solution first entered the 2D micromodel system,

u= =-U$_0$ n, bulk solution velocity at the position x=35 µm.

Specifically, the velocity of each point around the collector surface was determined through simulations using COMSOL (results of the simulation are presented in Figure S2b). These values of velocity were then used for the calculation of the lift and drag forces (eq. 2-4) at every point from the collector surface to the bulk fluid in the 2-D system. Additionally, the lift and drag forces at a few representative points around the collector surface have been

calculated and are presented in the manuscript (Figure 5). With these calculated fluid forces, a force balance was done on individual nanoparticles as they travel along the collector grain and within the pore throat.

Results and Discussion
Velocity and Acceleration Distribution

In order to calculate the hydrodynamic forces (lift force and drag force), the velocity distributions and acceleration as a function of x position as well as distance from surface are pictured in Figure S2. COMSOL has been used to simulate the velocity distribution (shown in Figure S2a) where the red arrow indicates the flow direction.

According to Figure S2a, the corresponding velocity distribution as a function of distance around the collector surface has been plotted in Figure S2b. The velocity of each point around the collector surface was determined through simulations using COMSOL (results of simulation are presented in Figure S2b). These values of velocity were then used to calculate the lift and drag forces (eq. 2-4) at every point from the collector surface to bulk fluid in the 2-D system. Additionally, lift and drag forces at a few representative points around collector surface have been calculated and are presented in the manuscript (Figure 5). With these calculated fluid forces, a further force balance was done for individual moving nanoparticles as they travel along the collector grain and within the pore throat.

Calculations were done either for the entire collector surface or for a portion of the surface identified as quadrants 1-4. The portion of surface contained in quadrant 1 represents an

X position ranging from 355 to 330 µm. Quadrants 2 and 4 are represented by X values from 330 to 265 µm and similarly, quadrant 3 is represented by X values from 265 to 250 µm. For a given X position, the velocity increases with the distance from the collector due to lower shear forces compared to the non-slip conditions at the surface.

Figure S3b shows that at distances from the collector surface between 0.5-10 nm, velocity decreases as expected as the fluid flows along quadrant 1 before becoming relatively constant at quadrants 2 and 4. Upon reaching quadrant 3, a slight increase in velocity was observed. Alternatively, at a 50 nm distance from collector surface, the flowrate represents the bulk flow in the micromodel. Generally, velocity increases with greater particle distance from the collector surface; however, for the closest surface distances of 0 and 0.1 nm, the velocity at an x position of 280 µm is greater than the distances farther from the collector. This observation potentially results from a decrease in the pore throat depth between collector grains causing an acceleration of the fluid flow according to Bernoulli equation[10]

Based on the velocity distribution (Figure S2b), acceleration as a function of distance from the collector surface has been plotted against x position (Figure S2c). Quadrant 3 recorded the greatest acceleration while quadrants 2 and 4 are relatively low. The velocity and acceleration data has been used to calculate the hydrodynamic forces by equations 2 and 3, respectively.

Contribution of DLVO-type Interaction and Hydrodynamic Forces

Figure S3 (b) and (d) show that at the same ionic strength, F_y approaches zero as the angle increases between 0~120° representing quadrant 1 entirely (0-45°) and a portion of quadrant 2 (45-135°). It can be observed that positive F_y forces (repulsive, see Figure 2) dominate at angles up to 120° before negative F_y (attractive) forces take control. After 120⁰, the magnitude of the negative forces increases with the angle accounting for the remainder of quadrant 2 (120-135⁰) and quadrant 3, each controlled by attractive forces.

Moreover, the force on the x axis (F_x; eq5) in Figure S3 (a) and (c) remains negative (drag) between 0-100° indicating that for all of quadrant 1(0-45°) and part of the quadrants 2 and 4 (45-100°), the particles are inclined to roll backwards from quadrants 2 and 4 to quadrant 1. For 100-120°, which represents quadrants 2 and 4, F_x became positive and increased with the angle. This indicates that the particles tend to move from quadrant 2 and 4 towards to quadrant 3 in the flow direction. Within the range of 100 to 180⁰, F_x remained positive, however decreased as the angle became greater demonstrating that particles were still prone to move with the fluid streamlines (from 2 to 3), yet with a declining magnitude. The agreement between experimental and theoretical results is acceptable for the entire range of ionic strengths with the collector surface (all four quadrants). Compliance of the experimental and theoretical results shown in Figure S3b seems to confirm the applicability of the hydrodynamic and DLVO force solutions for particle deposition in the micromodel. It should be mentioned that the significant change (positive or negative) in forces of x and y axis with fluid streamlines, is particularly due to the flow distribution around the collector surface. The influence of particle size on deposition has also been systematically studied.

Comparison plots of total forces in x and y directions as a function of particles size (20, 200, 2000 nm) was pictured against with angle (0 to 180°) at an ionic strength of 10 mM (Figure S3c and d, respectively). Magnitude of both F_x and F_y increase with size which illustrates that more deposition around the collector would occur with larger particles. Specifically, shown in Figure S3d, the F_y increases significantly with size after 120° and remains negative meaning 2000 nm particles are more likely to attach in quadrant 3 than the smaller particles. This suggests that the experimental results obtained in the micromodel can be used as useful reference measurements for prediction of particle deposition onto the collector surface. This work can also shows that hydrodynamic and DLVO force analysis can be exploited as powerful methods for determining filtration parameters in porous media.

Table S2.1 Summary of dimensionless parameters governing particles in filtration

Parameter	Definition	Physical interpretation
N_R	$\dfrac{d_p}{d_c}$	Aspect ratio
N_{Pe}	$\dfrac{U d_c}{D_\infty}$	Peclet number: ratio of convection transport to diffusive transport
N_{vdW}	$\dfrac{A}{kT}$	van der Waals number: ratio of van der Waals interaction energy to the particle's thermal energy
N_{gr}	$\dfrac{4}{3}\dfrac{\pi a_p^4 (\rho_p - \rho_f)g}{kT}$	Gravitational number: ratio of particle's gravitational potential when located one particle radius from collector to particle's thermal energy
N_A	$\dfrac{A}{12\pi\mu a_p^2 U}$	Attraction number: combined influence of van der Waals attraction forces and fluid velocity on particles deposition rate due to interception
N_G	$\dfrac{2}{9}\dfrac{a_p^2(\rho_p - \rho_f)g}{\mu U}$	Gravity number: ratio of Stokes particle settling velocity to approach velocity of the fluid

The parameters in various dimensionless groups are as follows: d_p is the particle diameter, d_c is the collector diameter, U is the fluid approach velocity, D_∞ is the bulk diffusion coefficient (Stokes-Einstein equation), A is the Hamaker constant, k is the Boltzmann constant, T is fluid absolute temperature, a_p is particle radius, ρ_p is the particle density, ρ_f is the fluid density, μ is the absolute fluid viscosity, and

g is the gravitational acceleration.

Table S2.2 Summary of hydrodynamic forces and F_x, F_y as a function of size and ionic strength

				1 mM			3.16 mM			10 mM			31.6 mM			100 mM		
Size (nm)	Angle (°)	F_L (N)	F_{D20nm} (N)	F_{DLVO} (N)	F_x (N)	F_y (N)	F_{DLVO} (N)	F_x (N)	F_y (N)	F_{DLVO} (N)	F_x (N)	F_y (N)	F_{DLVO} (N)	F_x (N)	F_y (N)	F_{DLVO} (N)	F_x (N)	F_y (N)
	30	1.11E-30	2.19E-23	-4.80E-11	2.38E-11	-4.10E-11	-8.40E-11	4.21E-11	-7.30E-11	-9.30E-11	4.67E-11	-8.10E-11	-1.00E-10	5.21E-11	-9.00E-11	-1.50E-10	7.39E-11	-1.30E-10
	45	1.23E-29	1.20E-22	-4.80E-11	3.37E-11	-3.40E-11	-8.40E-11	5.95E-11	-5.90E-11	-9.30E-11	6.60E-11	-6.60E-11	-1.00E-10	7.37E-11	-7.40E-11	-1.50E-10	1.04E-10	-1.00E-10
	60	1.89E-33	2.95E-25	-4.80E-11	4.12E-11	-2.40E-11	-8.40E-11	7.29E-11	-4.20E-11	-9.30E-11	8.09E-11	-4.70E-11	-1.00E-10	9.03E-11	-5.20E-11	-1.50E-10	1.28E-10	-7.40E-11
20	90	9.83E-35	-3.20E-26	-4.80E-11	4.76E-11	-2.90E-27	-8.40E-11	8.41E-11	-5.20E-27	-9.30E-11	9.34E-11	-5.70E-27	-1.00E-10	1.04E-10	-6.40E-27	-1.50E-10	1.48E-10	-9.10E-27
	120	2.72E-31	9.53E-24	-4.80E-11	-4.10E-11	2.38E-11	-8.40E-11	-7.30E-11	4.21E-11	-9.30E-11	-8.10E-11	4.67E-11	-1.00E-10	-9.00E-11	5.21E-11	-1.50E-10	-1.30E-10	7.39E-11
	135	9.83E-35	-3.20E-26	-4.80E-11	-3.40E-11	3.37E-11	-8.40E-11	-5.90E-11	5.95E-11	-9.30E-11	-6.60E-11	6.60E-11	-1.00E-10	-7.40E-11	7.37E-11	-1.50E-10	-1.00E-10	1.04E-10
	150	1.52E-30	9.98E-24	-4.80E-11	-2.40E-11	4.12E-11	-8.40E-11	-4.20E-11	7.29E-11	-9.30E-11	-4.70E-11	8.09E-11	-1.00E-10	-5.20E-11	9.03E-11	-1.50E-10	-7.40E-11	1.28E-10
	180	2.19E-31	-2.00E-23	-4.80E-11	1.97E-23	4.76E-11	-8.40E-11	1.97E-23	8.41E-11	-9.30E-11	1.97E-23	9.34E-11	-1.00E-10	1.97E-23	1.04E-10	-1.50E-10	1.97E-23	1.48E-10
	30	1.11E-27	2.19E-21	2.55E-10	-1.30E-10	2.21E-10	-5.80E-10	2.88E-10	-5.00E-10	-6.30E-10	3.13E-10	-5.40E-10	-1.30E-09	6.59E-10	-1.10E-09	-1.50E-09	7.39E-10	-1.30E-09
	45	1.23E-26	1.20E-20	2.55E-10	-1.80E-10	1.81E-10	-5.80E-10	4.08E-10	-4.10E-10	-6.30E-10	4.43E-10	-4.40E-10	-1.30E-09	9.32E-10	-9.30E-10	-1.50E-09	1.04E-09	-1.00E-09
	60	1.89E-30	2.95E-23	2.55E-10	-2.20E-10	1.28E-10	-5.80E-10	4.99E-10	-2.90E-10	-6.30E-10	5.42E-10	-3.10E-10	-1.30E-09	1.14E-09	-6.60E-10	-1.50E-09	1.28E-09	-7.40E-10
200	90	9.83E-32	-3.20E-24	2.55E-10	-2.60E-10	1.56E-26	-5.80E-10	5.76E-10	-3.50E-26	-6.30E-10	6.26E-10	-3.80E-26	-1.30E-09	1.32E-09	-8.10E-26	-1.50E-09	1.48E-09	-9.10E-26
	120	2.72E-28	9.53E-22	2.55E-10	2.21E-10	-1.30E-10	-5.80E-10	-5.00E-10	2.88E-10	-6.30E-10	-5.40E-10	3.13E-10	-1.30E-09	-1.10E-09	6.59E-10	-1.50E-09	-1.30E-09	7.39E-10
	135	9.83E-32	-3.20E-24	2.55E-10	1.81E-10	-1.80E-10	-5.80E-10	-4.10E-10	4.08E-10	-6.30E-10	-4.40E-10	4.43E-10	-1.30E-09	-9.30E-10	9.32E-10	-1.50E-09	-1.00E-09	1.04E-09
	150	1.52E-27	9.98E-22	2.55E-10	1.28E-10	-2.20E-10	-5.80E-10	-2.90E-10	4.99E-10	-6.30E-10	-3.10E-10	5.42E-10	-1.30E-09	-6.60E-10	1.14E-09	-1.50E-09	-7.40E-10	1.28E-09
	180	2.19E-28	-2.00E-21	2.55E-10	1.97E-21	-2.60E-10	-5.80E-10	1.97E-21	5.76E-10	-6.30E-10	1.97E-21	6.26E-10	-1.30E-09	1.97E-21	1.32E-09	-1.50E-09	1.97E-21	1.48E-09
	30	1.11E-24	2.19E-19	-2.40E-09	1.22E-09	-2.10E-09	-9.10E-09	4.53E-09	-7.80E-09	-1.40E-08	7.16E-09	-1.20E-08	-1.00E-08	5.00E-09	-8.70E-09	-1.50E-08	7.40E-09	
	45	1.23E-23	1.20E-18	-2.40E-09	1.73E-09	-1.70E-09	-9.10E-09	6.40E-09	-6.40E-09	-1.40E-08	1.01E-08	-1.00E-08	-1.00E-08	7.07E-09	-7.10E-09	-1.50E-08	1.05E-08	-1.00E-08
	60	1.89E-27	2.95E-21	-2.40E-09	2.12E-09	-1.20E-09	-9.10E-09	7.84E-09	-4.50E-09	-1.40E-08	1.24E-08	-7.20E-09	-1.00E-08	8.66E-09	-5.00E-09	-1.50E-08	1.28E-08	-7.40E-09
2000	90	9.83E-29	-3.20E-22	-2.40E-09	2.45E-09	-1.50E-25	-9.10E-09	9.05E-09	-5.50E-25	-1.40E-08	1.43E-08	-8.80E-25	-1.00E-08	1.00E-08	-6.10E-25	-1.50E-08	1.48E-08	-9.10E-25
	120	2.72E-25	9.53E-20	-2.4E-09	-2.1E-09	1.22E-09	-9.1E-09	-7.8E-09	4.53E-09	-1.40E-08	-1.20E-08	7.16E-09	-1.00E-08	-8.70E-09	5.00E-09	-1.50E-08	-1.30E-08	7.40E-09
	135	9.83E-29	-3.2E-22	-2.4E-09	-1.7E-09	1.73E-09	-9.1E-09	-6.4E-09	6.40E-09	-1.40E-08	-1.00E-08	1.01E-08	-1.00E-08	-7.10E-09	7.07E-09	-1.50E-08	-1.00E-08	1.05E-08
	150	1.52E-24	9.98E-20	-2.4E-09	-1.2E-09	2.12E-09	-9.1E-09	-4.5E-09	7.84E-09	-1.40E-08	-7.20E-09	1.24E-08	-1.00E-08	-5.00E-09	8.66E-09	-1.50E-08	-7.40E-09	1.28E-08
	180	2.19E-25	-2E-19	-2.4E-09	1.97E-19	2.45E-09	-9.1E-09	1.97E-19	9.05E-09	-1.40E-08	1.97E-19	1.43E-08	-1.00E-08	1.97E-19	1.00E-08	-1.50E-08	1.97E-19	1.48E-08

Figure S2.1

Hydrodynamic diameter of latex particles (20, 200, 2000 nm) at ionic strengths of 1, 3.16, 10, 31.6, and100 mM KCl at pH 4.
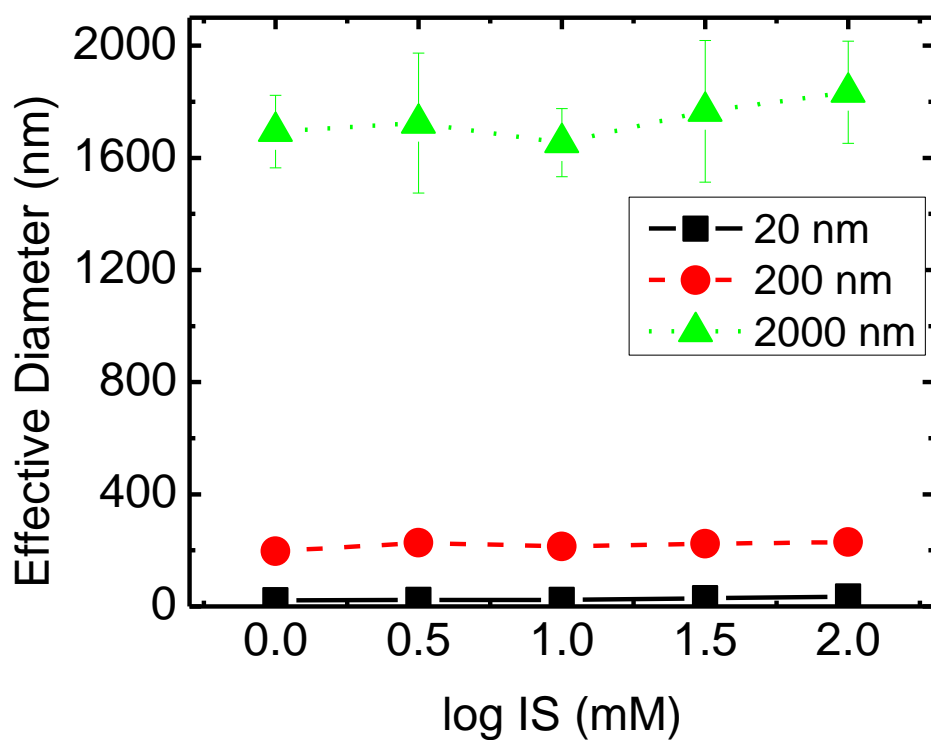
Figure S2.2

Velocity distribution simulated in COMSOL as a function of (a) x position, and a function of (b) distance from surface. Acceleration was plotted as a function as x position as well as distance from collector surface (c). The portion of surface for quadrant 1 is represented a range of x position from 355 to 330 µm. Surface portions of quadrants 2 and 4 are represented by x values from 330 to 265 µm. Surface portions of quadrant 3 are represented by x value from 265 to 250 µm.
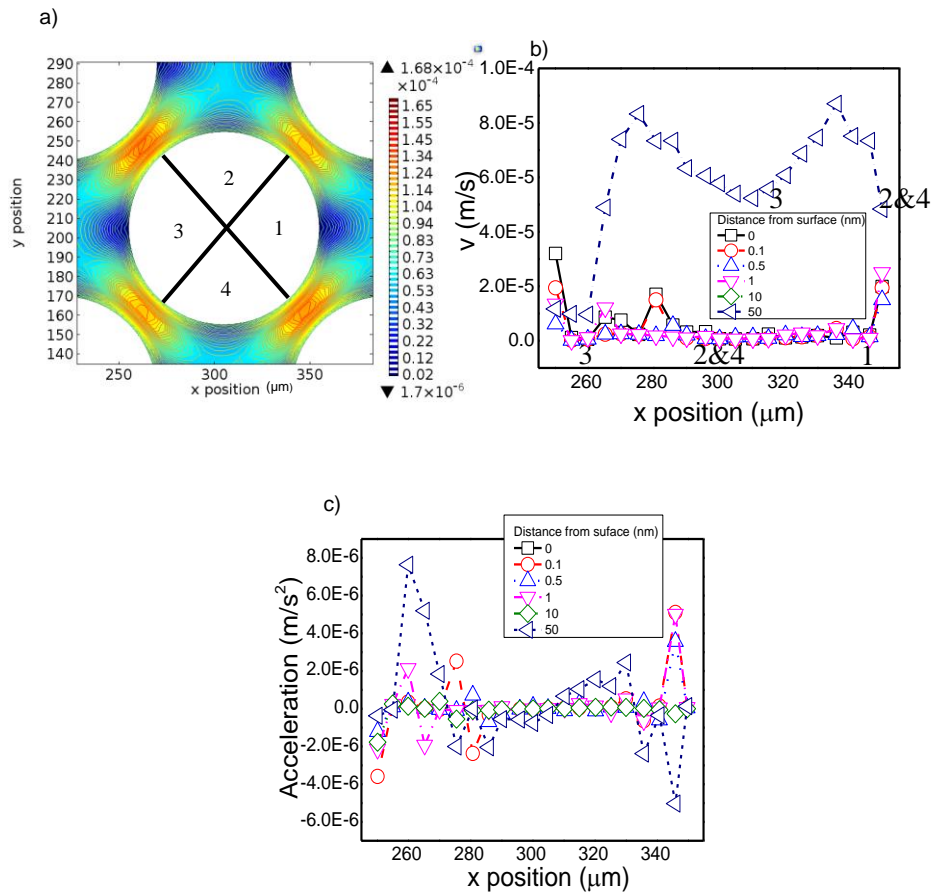
Figure S2.3 .

Total forces on 200 and 2000 nm particles in the x and y directions as a function of ionic strength (1, 3.16, 10, 31.6, and100 mM KCl) at collector surface angles between 0-180°. Forces on 200 nm particles in (a) F_x and (b) F_y, as well as, 2000 nm particles; (c) F_x and (d) F_y are presented. ,
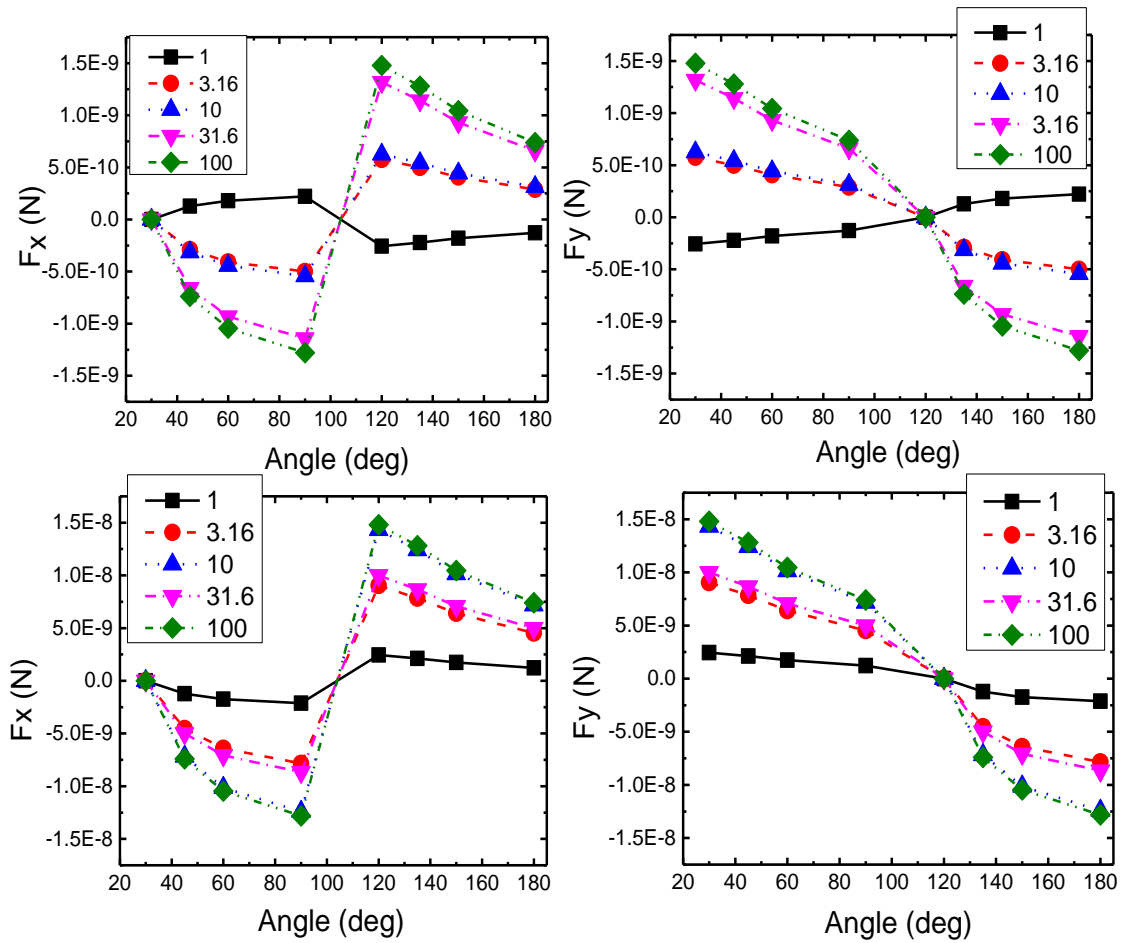
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Chapter 3

Filtration mechanisms of food and industrial grade TiO$_2$ nanoparticles: Do all TiO$_2$ particles act the same?

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Abstract

The removal of food and industrial grade titanium dioxide (TiO_2) particles through drinking water filtration was assessed via direct visualization of an *in situ* 2D micromodel. The goal of this research was to determine whether variances in surface composition, aggregate size, and ionic strength result in different transport and deposition processes in porous media. Food and industrial grade TiO_2 particles were characterized by measuring their hydrodynamic diameter, zeta potential, and zero point of charge before introduction into the 2-D micromodel. The removal efficiency as a function of position on the collector surface was calculated from direct visualization measurements. Notably, food grade TiO_2 had a lower removal efficiency when compared with industrial grade. The difference in removal efficiency between the two particle types could be attributed to the higher stability (as indicated by the larger zeta potential values) of the food grade particles, which lead to a reduced aggregate size when compared to the industrial grade particles. This removal efficiency trend was most pronounced in the rear stagnation point, due to the high contribution of hydrodynamic forces at that point. It could be inferred from the results presented herein that particle removal strategies should be based on particle aggregate size, surface charge, and surface composition.

3.1 Introduction

In the last decade, nanoparticles (NPs) have developed to such an extent that it is now possible to fabricate, characterize, and tailor the functional properties of NPs for a variety of industry scale applications. Nanomaterials are applied in industrial, agricultural, consumer, medical, manufacturing, and military sectors (Masciangioli and Zhang 2003; Long et al. 2006) due to their enhanced electronic, optical, thermal, and photoactive capacities (Petosa et al. 2010). The global value of NPs surpassed $1 trillion in 2015 (Roco 2005), up from $4.1 billion in 2005 (Gould 2015). This astounding growth of the NP industry has led to their greater proliferation and distribution in the environment (Arturo A Keller et al. 2013).

Nano titanium dioxide (TiO_2) was chosen as the NP of focus for this investigation for its wide use in manufacturing (Nel et al. 2006; Allen et al. 2005), decontamination capacity for air (T. Jones and Egerton 2012), soil (Choi, Stathatos, and Dionysiou 2006; Konstantinou and Albanis 2004), and water applications (Balasubramanian et al. 2004; Esterkin et al. 2005), as well as popular consumer products like paint (Khataee et al. 2016), toothpastes (Rompelberg et al. 2016), sunscreens (Higarashi and Jardim 2002; Wolf et al. 2003)·(Weir et al. 2012), and cosmetics (Weir et al. 2012; Kreyling et al. 2017). The aforementioned food and consumer products that contain TiO_2 may potentially discharge into the environment through the sewage system, before entering wastewater treatment plants (Kiser et al. 2009; Arturo A Keller and Lazareva 2013). However, even after treatment, studies have demonstrated that TiO_2 particles are still found in wastewater

effluent (Kiser et al. 2009; Arturo A Keller et al. 2013; Kaida et al. 2003; Eisenberg et al. 2015), suggesting that these particles will end up in receiving surface water, or in biomass, impacting downstream ecological environments (Bennett, Kwong, and Powell 2007; Wang 2012; Ahmed 2016).

The unique properties of NPs, such as high specific surface area (Bonso et al. 2012), abundant reactive sites on the surface (Fenoglio et al. 2009), and their electrophoretic mobility (Guan et al. 2012; Jagadale et al. 2013), could potentially lead to unexpected health or environmental hazards (Hamidi-Asl et al. 2016; Maynard 2006; Wiesner et al. 2006). TiO_2 has a high tendency to bio-accumulate in aquatic organisms (Sze and McKay 2012). This implies that TiO_2 particles could be bio-concentrated from one species to another, and hence posing the greatest risk to human beings through food chain transport. Indeed, some studies found that TiO_2 NPs were accumulating and in gill, liver, heart, and brain tissue, while causing DNA damage in fish (Johnston et al. 2010; Zhu, Zhou, and Cai 2011; George et al. 2012; Reeves et al. 2008). A study in terrestrial mammals demonstrated that both anatase and rutile nano forms of TiO_2 particles (<100 nm) lead to epithelial inflammation of the lung in rodents (Bermudez et al. 2002). In addition, bio-distribution experiments showed that nano TiO_2 particles are retained in liver, spleen, kidneys and lung tissues after oral ingestion in adult mice (Warheit et al. 2006). There is a consensus amongst stakeholders that removal mechanisms of TiO_2 from diverse ecosystems need to be explored (T. Tong et al. 2015; Ge et al. 2013; X.-Y. Li et al. 2017).

Even though food grade TiO_2 represents the majority of TiO_2-containing materials that enter the ecosystem today (Xin-Xin Chen et al. 2013; Weir et al. 2012; R. J. B. Peters, van

Bemmel, et al. 2014; R. Peters et al. 2015; Yang, Doudrick, Bi, Hristovski, Herckes, Westerhoff, et al. 2014; Skocaj et al. 2011) , most researchers have utilized industrial grade nano forms of TiO_2 when studying the molecule (e.g. Evonik Degussa P25) (Chowdhury et al. 2011; Marcus et al. 2012; Godinez and Darnault 2011; Prakash et al. 2009). This is because industrial grade (IG) TiO_2 is a commonly used photocatalyst (Herrmann 1999), catalyst carrier (Braun, Baidins, and Marganski 1992), and heat stabilizer, due to the primary crystals being relatively uniform (Xiaobo Chen et al. 2011) and less than 50 nm in size (Weir et al. 2012). Previous studies have demonstrated that the transport of industrial grade (IG) nano TiO_2 are influenced by multiple factors including solution chemistry (Chowdhury et al. 2011) (e.g., pH and ionic strength), flow velocity (Godinez and Darnault 2011), surfactant concentration (Domingos, Tufenkji, and Wilkinson 2009), and the presence of natural organic matter (NOM) (Bhatnagar and Sillanpää 2017; Zhang et al. 2009; Chowdhury, Walker, and Mylon 2013; Lecoanet, Bottero, and Wiesner 2004). However, information about the transport – as well as size and surface properties – of food grade (FG) TiO_2 is limited.

The aim of this paper is to address a knowledge gap for nano food grade TiO_2 transport and filtration by evaluating the mechanisms involved in the removal of food and industrial grade TiO_2. The research presented herein is the first to study food grade TiO_2 in an engineered filtration system, and by direct visualization in a 2-D micromodel system (C. Chen, Waller, and Walker 2017). Outcomes from this research demonstrate that the variances in surface composition and aggregate size due to ionic strength, results in

different transport and deposition processes in porous media, impacting the removal of particles from the environment.

3.2 Materials and methods

3.2.1 TiO$_2$ sample selection and preparation

3.2.1.1 TiO$_2$ selection

Two forms of nano-TiO$_2$ were studied individually during transport experiments. An industrial grade TiO$_2$ (Aeroxide TiO$_2$ P25; Evonik Degussa Corporation, NJ) was selected as it is commonly used in environmental toxicity, fate, and transport studies (Maness et al. 1999; Sun et al. 2009; X. Lin et al. 2014; Z. Chen et al. 2014). The industrial grade TiO$_2$ samples used in this study consists of a 75% / 25% anatase/rutile TiO$_2$ crystal structure mixture. According to the manufacturer, nanomaterials were >99.5% pure with a primary particle size of 21 nm (Weir et al. 2012; Lankoff et al. 2012).

The other type of TiO$_2$ used in this study, designated as food grade TiO$_2$ (E171), is a European Union classification for a white food color additive (CI 77891, Pigment White 6). For this research, the food grade sample was acquired from Arizona State University to represent a form likely to be utilized in food and personal care products (Weir et al. 2012). Particle size was determined to be 122 ± 48 nm using TEM (Calzolai, Gilliland, and Rossi 2012) and 98% / 2% anatase / rutile crystal structure mixture.

3.2.1.2 TiO$_2$ sample preparation

The TiO$_2$ particles were prepared for study by first suspending them in a range of solution chemistry conditions. The ionic strength (IS) of these suspensions were 1, 3.16, 10, 31.6, and 100 mM KCl. Then, for the particle characterization experiments, each of the aforementioned ionic strength solutions were adjusted to a counting number pH value between 3-9 using 0.1 M HCl or 0.1 M KOH for a total of 35 solution chemistry conditions (5 ionic strengths, 7 pH values). While the transport experiments were all conducted at pH 5. After suspending the TiO$_2$ samples in one of the solution chemistry conditions, the suspension was sonicated for 30 minutes in a water bath (Transsonic 460/H, Barnstead/Lab-line, Melrose Park, IL) before subsequent experiments described in the following sections.

3.2.1.3 Particles fluorescent coating procedure

The particles were fluorescently labeled with fluorescein isothiocyanate (FITC, Sigma, USA) particles to observe them in the micromodel (J. Lu et al. 2007). First, 20 mg of TiO$_2$ particles were suspended into 150 ml DMF (Dimethylformamide, Sigma, USA), and 100 µl APTS ((3-Aminopropyl) triethoxysilane, Sigma, USA) was suspended into 5 ml DMF. Then the aforementioned solutions were combined and stirred for 10 min under a pure nitrogen environment. The solution was then covered with aluminum foil, sonicated for 30 min, and stirred for 20 hr. The APTS modified particles samples in DMF was then washed by centrifuging, decanting the DMF, and re-suspending the particles in DMF 3 times at 3700 g for 15 min. Then, 50 mg FITC was mixed into the 25 ml DMF suspension and

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vortexed for 30 s. The suspension was then covered with aluminum foil and stirred for 4 hr. To collect the FITC labelled nanoparticles, the suspension was washed by centrifuging, decanting the DMF, and suspending the particles in DMF 3 times at 3700 g for 15 min. After decanting the DMF, the FITC labelled nanoparticles were dried under vacuum for 24h then stored at 4 °C in the refrigerator. The florescence coverage was confirmed by using a fluorometer (Turner Quantech, Barnstead/Thermolyne, Dubuque, IA; excitation 490 nm and emission 515 nm) to be about 5% for food grade and 7% for industrial grade, respectively.

3.2.2 Particle characterization

The primary particle size and crystal structure of the TiO_2 NPs were determined from X-ray diffraction measurements (Philips PW1800 diffractometer, Weversbaan, Netherlands). The sizes of the TiO_2 NPs were further confirmed via transmission electron microscopy (TEM, FEI-PHILIPS CM300, Hillsboro, OR). More than 200 nanoparticles from 10 different images were used for size determination. Specific surface areas were determined using nitrogen adsorption–desorption measurements (Model ASAP2020, Micromeritics Instrument Corporation, USA).

The isoelectric points (IEPs) of food grade and industrial grade TiO_2 were determined for all of the aforementioned suspensions (Section 2.1.2) by conducting electrokinetic characterization using a ZetaPALS analyzer (Brookhaven Instruments Corp., Holtsville, NY) from pH 3 to 10. Hydrodynamic diameter of the two types of TiO_2 nanoparticles were

measured using dynamic light scattering (DLS) (Brookhaven model BI-9000AT Holtsville, NY) at a wavelength of 661 nm and scattering angle of 90 °. The average diameter was determined from the arithmetic average of 10 runs for three separate samples, with each run involving an average of measurements taken over 30 s.

The relative charge of the silica micromodel used for the investigation of particle transport in this study was determined by conducting streaming potential measurements on a compositionally identical quartz slide using an electrokinetic analyzer (EKA; SurPASS; Anton Paar, Graz, Austria) equipped with clamping cell (55 mm × 25 mm) (Walker et al. 2002). The streaming potential measurements of the silica collector were performed over a range of IS (1-50 mM KCl) at 25 °C, as described in previous research (N. M. Kinsinger et al. 2017). Based on Helmholtz–Smoluchowski equation (Smoluchowski 1921) and Fairbrother Mastin approach (Fairbrother and Mastin 1924), the streaming potential for the quartz was converted to zeta potentials (Elimelech, Chen, and Waypa 1994). Measurements were repeated four times for each pH increment value (3-9) at all tested ionic strengths (Section 2.1.2). All solutions were made with ACS reagent grade chemicals (Fisher Scientific, Pittsburgh, PA) and pH was controlled with HCl or KOH.

3.2.3 Transport experiments in a 2D micromodel

In this study, porous media was simulated using a 2-D micromodel that was fabricated from a silicon wafer based on a procedure that has been previously developed and applied (C. Chen, Waller, and Walker 2017; Liu et al. 2012). Each micromodel had a total of 1471 uniformly distributed cylindrical collectors with a 100 µm diameter, 20 µm pore throat, 70

μm pore body and 10 μm depth. The porosity was 0.41, which is similar to packed bed column (Elimelech et al. 2000).

The micromodel experimental setup included a 60 mL plastic syringe (BD, Franklin Lakes, NJ) with 0.8 mm internal diameter polyethylene tubing and a three-valve adapter horizontal connecting the syringe to the inlet of micromodel. The velocity of infusion syringe pump (KDS 220, KD Scientific Inc., Holliston, MA) was set at 1 μl/hr, this volumetric flowrate corresponds to a linear velocity of 1.68×10^{-4} m/s, and a Peclet number of 0.8. Before the transport experiment was performed, the micromodel was fully saturated with 20 mL of the electrolyte solution in the absence of particles at pH 5 or 7, with an ionic strength ranging from 1-100 mM (the pH and IS selected to be identical to the solution chemistry of the NP suspension used in the experiment). Then the corresponding particle suspensions were injected into the fully saturated micromodel under laminar flow rate, as was done in previous studies (Chowdhury et al. 2011; Auset and Keller 2004). The particles were observed using an LMPlanFI 20x/0.40na objective lens (Olympus America Inc., Cypress, CA) and images were recorded every 30 s for tracking the time and location at which the particles deposited on the collector surfaces. The size of the viewing area was 420 μm x 340 μm and included particles in the vicinity of six random collectors (in the central position of micromodel). The number of nanoparticles depositing on the collectors within the flow cell were captured using an Olympus BX51 epifluorescence microscope (Q-imaging, Surrey, Canada) connected to a charge-coupled device (CCD) camera (Q-imaging RETIGA Exi, Fast 1394, Surrey, Canada) and counted using Image Pro 8.0 software (Q-imaging, Surrey, Canada).

The single collector removal efficiency (η) was calculated by enumerating the number of particles depositing around the entire collector (Yao, Habibian, and O'Melia 1971; Ducker, Xu, and Israelachvili 1994). The removal efficiency is defined as the fraction of particles approaching the collector that actually collide (Tufenkji and Elimelech 2004).

$$\eta = \frac{I}{\pi d_c D v c_p}$$

[1]

where the overall rate of particle collisions with the collector(I) (particles/s) is obtained by integration of the particle flux over the collector surface area of interest (either entire surface or a representative quadrant of the spherical collector). The collector diameter is represented by d_c (m), D is depth of the collector, v is the velocity (m/s), and c_p is the particle concentration[77]. These collector removal efficiencies allow for a point.

3.3 Results and discussion

3.3.1 Contrasting of food and industrial grade TiO$_2$ characteristics

A comparison of representative physical and chemical properties known to influence environmental fate and transport of nanoparticles was conducted for food (FG) and industrial (IG) grade TiO$_2$ (Figure 3.1). The diameter of FG and IG TiO$_2$ samples derived from SEM images (Figure 3.1a and 1b) were calculated to be 128 ± 47 nm, and 25 ± 9 nm, respectively. Based on TEM image analysis (Figure S3.1A), the primarily particle size of food grade TiO$_2$ had a very broad size distribution (25 to 410 nm), with 38 % of the particles smaller than 100 nm. While the primarily size of the industrial grade TiO$_2$ (Figure S3.1B) were observed to have a narrow size distribution (20-40 nm), with 100 % of the

particles less than 100 nm. It should be pointed out that only one source for food grade TiO_2 was tested and further research is needed to determine the differences in sources of food grade TiO_2 as other proprietary samples may vary.

The zeta potential of food grade and industrial grade TiO_2, as a function of pH and ionic strength are presented in Figure 3.1E and 1F, respectively. The measured isoelectric point (IEP) for the FITC labeled food grade particles was pH ~4, while the FITC labeled
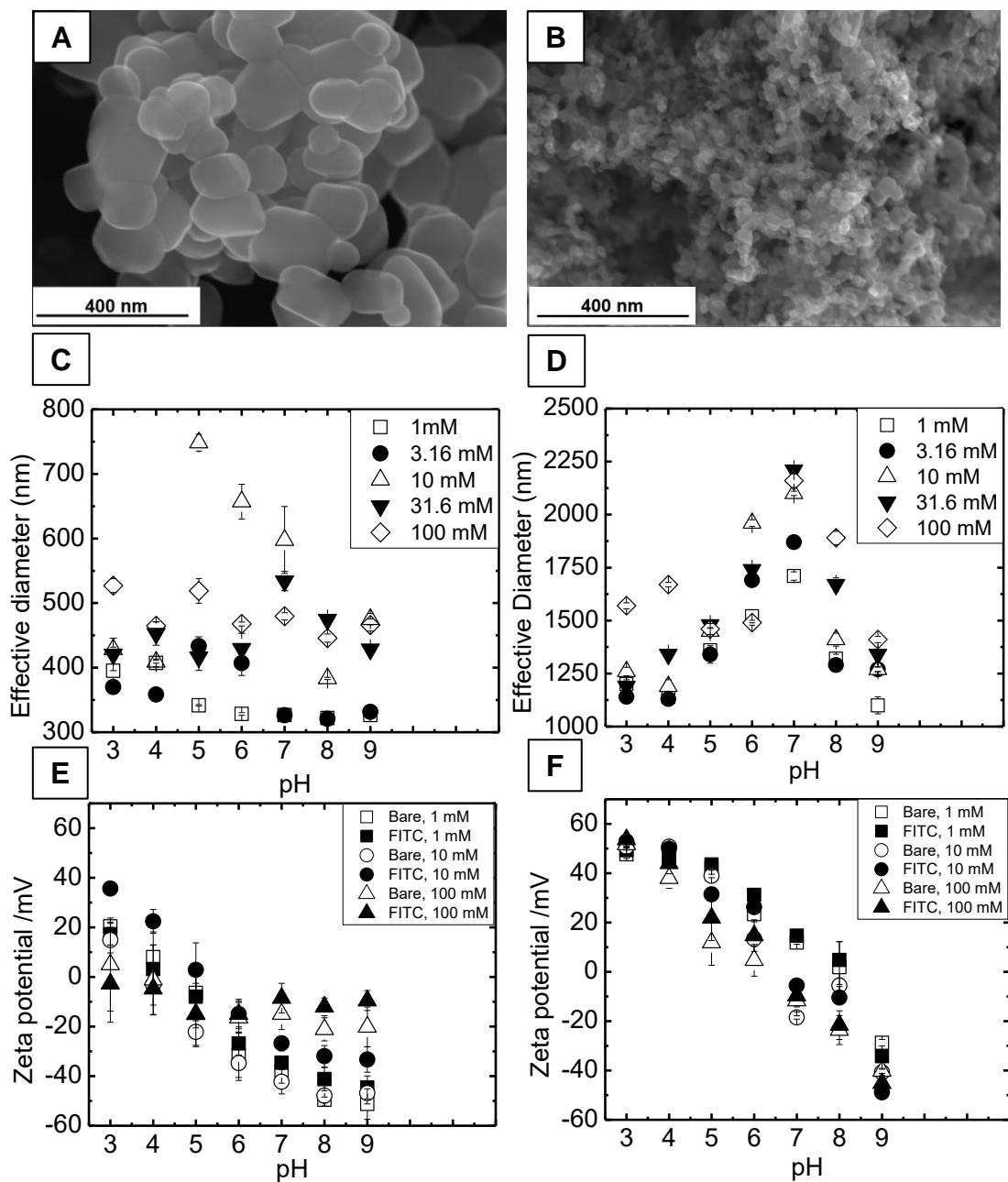
Figure 3.1 Representative properties of TiO_2 particles: SEM analysis of (a) food and (b) industrial grade TiO_2. Hydrodynamic diameter of (c) food and (d) industrial grade TiO_2 at ionic strengths of 1, 3.16, 10, 31.6, and 100 mM KCl from pH 3-9. Zeta potentials of (e) food and (f) industrial grade TiO_2 with and without FITC coating at a concentration of 5 ppm in 10 and 100 mM KCl across a pH range of 3-9. Errors bars indicate one standard deviation of triplicate measurements.

industrial grade TiO_2 was pH ~7, both values are consistent with previous work. The zeta potential (ZP) of FITC labeled FG particles at pH 5 were -5, 8, and -18 mV for suspensions of 1, 10, and 100 mM, respectively. This result is counter to previous research (Kosmulski and Dahlsten 2006; Nägele 1986; G. Chen, Liu, and Su 2011), where the lower ionic strength has a higher absolute value of ZP, as is the case for the FG particles at pH 7, and IG at pH 5. The ZP of FITC labeled IG particles at pH 7 were 15, -3, and -7 for suspensions of 1, 10, and 100 mM, respectively. Thus, in this case, as for FG at pH 5, the particles suspended in 10 mM KCl were the closest to neutral ZP. This is important since previous investigation have found that particle suspensions are less stable and have a greater tendency to form aggregates as they approach neutral ZP values (Gumy et al. 2006; McCafferty 2010; Jiang, Oberdörster, and Biswas 2009; Metin et al. 2011).

Dynamic light scattering (DLS) experiments were conducted to measure the aggregate size of both types of TiO_2 as a function of pH and IS (Figure 3.1C and 1D). The effective diameter of FG TiO_2 aggregates were between 300-800 nm for all tested water chemistries. While the effective diameter of the IG TiO_2 aggregates were higher at every water chemistry tested than the food grade with values between 1000-2300 nm, which is consistent with previous studies (Yang, Doudrick, Bi, Hristovski, Herckes, Westerhoff, et al. 2014; Weir et al. 2012; Ohno et al. 2001). Interestingly, the highest value for effective diameter for FG TiO_2 was when the particle was suspended in pH 5 and an IS of 10 mM solution (~800 nm). This result could be explained by the ZP for FG TiO_2 with FITC coating, which was close to neutral at 10 mM IS (Figure 3.1E). Contrarily, FG TiO_2 with FITC coating suspended in 100 mM at pH 7 was close to the IEP, but the effective diameter

was smaller than that of 10 mM. This may be due to other physical factors (grain size, orientation and configuration, and surface roughness) (S. A. Bradford et al. 2002) and chemical factors (i.e., pH, ionic strength, surface charge, etc.) (Ouyang et al. 1996), which were found in the previous studies to contribute to aggregate size. For IG particles suspended in pH 5, the effective diameter was not influenced by ionic strength, all aggregated to a size between 1300-1400 nm. IG particles suspended in pH 7 increase in aggregate size with respect to increases in IS, from 1700 nm at IS 1 mM to greater than 2200 nm for IS 10-100 mM. This range of aggregate sizes aligns with the ZP values for IG TiO_2 at pH 7, as this is approximately the IEP for the particles. To further investigate the effects of the charge and size of the particles under environmentally relevant conditions, the forces acting on the particles were calculated and discussed in the following section.

3.3.2 Removal trends of FG and IG TiO$_2$

The transport experiments were analyzed by calculating the total single collector removal efficiency (η of the nanoparticles. The calculated η values are plotted against the ionic strength for the two types of TiO_2 with FITC labeling at pH 5 and 7 (Figure 3.2). The transport experiments were conducted in triplicate under a range of ionic strength values (1, 3.16, 10, 31.6, 100 mM). In general, similar to previous studies, the η of both grades of TiO_2 were observed to increase with ionic strength (Gottschalk et al. 2009; G. Chen, Liu, and Su 2011). Another observation from Figure 3.2, was that the particles had a higher removal at pH 7 than 5 at all IS except for IG at 1 mM. Finally, a third observation in

Figure 3.2 is that FG TiO$_2$ has a lower removal efficiency than IG TiO$_2$ though all conditions.

For food grade TiO$_2$ at pH 5 and 7, the total removal efficiency, increased from 0.008 and 0.16 at 1 mM to 0.33 and 0.58 at IS 31.6 mM, respectively, before plateauing between 31.6 and 100 mM. The industrial grade TiO$_2$ at pH 5 had a similar trend, increasing from 0.26 at 1 mM to 0.51 at 31.6 mM IS, then plateauing. A potential explanation for the plateauing phenomena may be that the particle aggregate surface area is so large that due to electrostatic repulsion, the deposited particles may be inhibiting further nanoparticles approach and attachment from occurring (Elimelech, Gregory, and Jia 2013; Wiesner 1999). This phenomenon does not seem to effect IG TiO$_2$ particles suspended in pH 7, in that the removal efficiency linearly increases with IS from 0.22 at 1 mM up to 0.75 at 100 mM (Chrysikopoulos and Syngouna 2014; Baumgartl et al. 2009; Abele, Baeßler, and Westphal 2003; Han et al. 2016; Walker, Redman, and Elimelech 2004). The lack of plateauing for IG TiO$_2$ particles suspended in pH 7 could be explained by the rate of change of fluid velocity around the flow stagnation zone, which is significantly greater because the particles form the largest aggregates in suspension. In addition, the hydrodynamic forces increased exponentially with the rate of change of the fluid velocity (to the power of 1.5) (Elimelech, Chen, and Waypa 1994; C. Chen, Waller, and Walker 2017). Overall, it was observed that the contribution of hydronamic forces increased with aggregate size, leading to greater deposition on the collector. Other studies have also demonstrated that particle removal efficiencies are greater with increasing aggregate size in the presence of an energy barrier to deposition for particles aggregate size less than about 5 µm[59], due to

decreasing retention in flow stagnation zones (M. Tong and Johnson 2007; W P Johnson, Li, and Yal 2007; Ma, Pazmino, and Johnson 2011). In general, the removal efficiency of FG TiO2, were observed to be 20-35% lower than the removal efficieny for IG in similar suspensions. Thus, these findings highlight the importance of utilizing the type of particles most likely present within the system (notably food vs. industrial grade) to perform the most relevant environmental fate and transport studies.
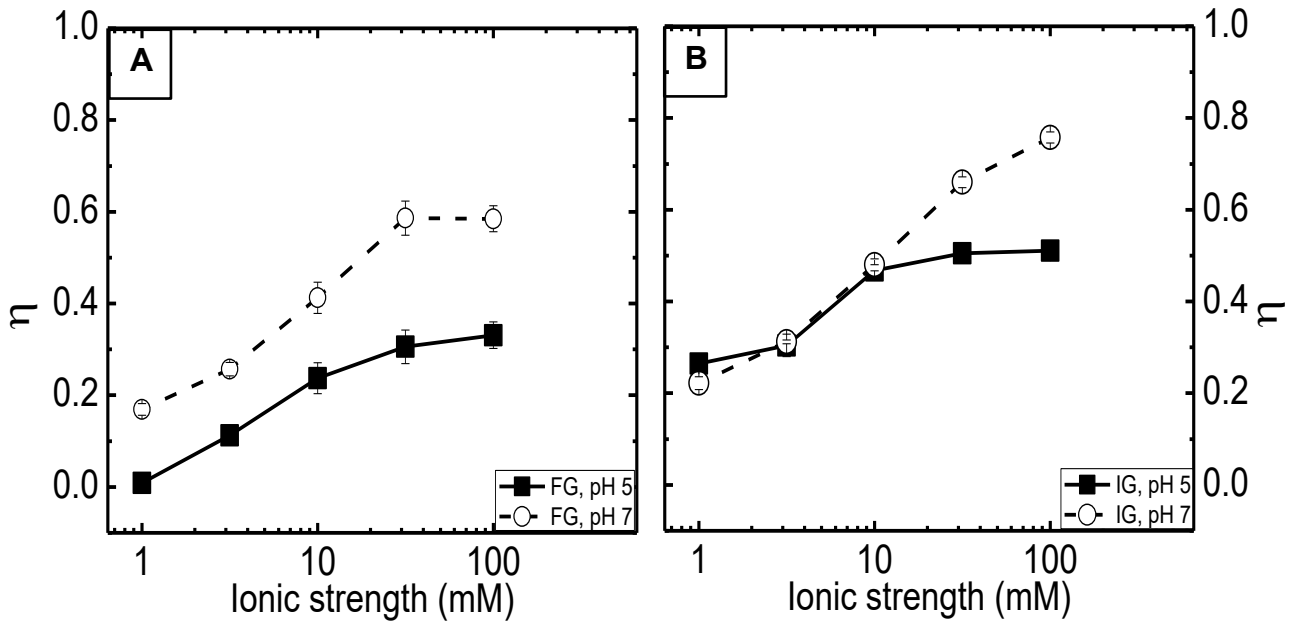
Figure 3.2. Removal efficiency η of both food (A) and industrial grade (B) TiO$_2$ as a function of ionic strength (1-100 mM) for the whole collector η. Experiments were conducted at pH 5 (represented by open shape) and pH 7 (represented by solid shape) under conditions of 5ppm and a flow rate of 1μL/hr. Error bars indicate one standard deviation of triplicate measurements.

3.4 Conclusions

Nanomaterials are becoming ubiquitous in the modern world and their discharge is accumulating in the environment (Nel et al. 2006; Roco 2005; Petosa et al. 2010; Arturo A Keller et al. 2013). Therefore, it is important to understand the fate and transport of any engineering particles that may enter and influence the quality of aquatic systems, such as TiO_2 particles present in common costumer items and food. Here multiple water quality conditions (varying ionic strength and pH) were applied to thoroughly compare the surfaces and removal efficiency of food and industrial grade TiO_2 in a 2-D micromodel system. Results reported in this work demonstrate that overall, the removal efficiency (η) of food grade are all lower than industrial grade TiO_2 under all ionic strength conditions. Specifically, food grade is removed 20-35 % less than industrial grade TiO_2 across the conditions tested in this study. The difference in removal becomes more pronounced with increasing ionic strength and is attributed to the FG particles forming smaller aggregate sizes and having lower surface charge values. As a result, food grade TiO_2 is more likely to accumulate in the environment, potentially leading to environmental and human health risks (Pourzahedi, Vance, and Eckelman 2017; Reed et al. 2016; Stieberova et al. 2017; W. Jones et al. 2017).

When studying approaches with the purpose of removing engineered nanoparticles from water, one representative type of particle is typically chosen to represent all of the engineered nanoparticles of that molecular structure (Donovan et al. 2016; Lazar, Varghese, and Nair 2012). For example, while FG TiO_2 represents the majority of TiO_2-containing materials

that enter the ecosystem today (Weir et al. 2012), most researchers utilize industrial grade nano form of TiO_2, as a surrogate for all forms of TiO_2 (Clemente et al. 2015; Zhu, Zhou, and Cai 2011). Thus, this study demonstrates that nuances in the particle type and behavior in aquatic environments (i.e. aggregate size, charge, and surface composition) are important to evaluate and consider, and importance of not simply relying on a single model material sample of the same molecular formula (e.g. TiO_2) when ascertaining the extent of removal and designing treatment strategies for nanomaterials.

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Chapter 4

Influence of Coagulant Residual on Filtration of Food Grade and Industrial Grade TiO$_2$ in Water Treatment Systems

Abstract

This investigation assessed the role the coagulant residual, TiO_2 structure, solution chemistry, and ionic strength (IS) have on the removal efficiency of TiO_2 nanoparticles from the filtration stage of drinking water treatment. Six solution conditions were tested in this study: two IS of KCl and $CaCl_2$ (1.83 and 10 mM), as well as artificial ground water (AGW) (10 mM), and artificial surface water (ASW) (1.83 mM). Coagulant (0, 0.05, 0.5, 5 mg/L $KAl(SO_4)_2 \cdot 12H_2O$) was added to each of the solution conditions to simulate the residual coagulant present in the filtration stage of water treatment through an open 2D micromodel with uniformly spaced cylindrical collectors. This system allowed for the calculation of the single collector removal efficiency for the particles suspended in simulated water treatment conditions using real-time visualization measurements. In addition, the TiO_2 particle were characterized in the various suspensions by measuring their hydrodynamic diameter, zeta potential, and zero point of charge before introduction into the micromodel. Results from this study indicate that for idential solution chemistries and residual coagulant concentrations, industrial grade TiO_2 (IG) had a higher removal efficiency than food grade TiO_2 (FG). This was due to the IG particles forming larger aggregates than the FG particles. In addition, particles suspended in divalent salts had a greater removal efficiency than particles suspended in KCl. Higher ionic strength suspensions also lead to greater removal of the TiO_2. For all TiO_2 suspensions, the greater coagulant residual concentrations increased the removal efficiency up until 0.5 mg/L alum, above that threshold the effect of coagulant residual were negligible. This study

demonstrates the limits that modification of solution chemistry has on the removal of TiO_2 particles.

4.1 Introduction

Currently, more than 80% of all the coagulants all around the world include aluminum (Al) ions(Sharp, Parsons, and Jefferson 2006). Al-based coagulants such as alum $(KAl(SO_4)_2 \cdot 12H_2O)$, are commonly used in drinking water treatment to enhance the removal of particulate, colloidal, and dissolved substances via coagulation processes(Sharp, Parsons, and Jefferson 2006). The treatment of surface water with alum has been in operation for hundreds of years all over the world (Srinivasan, Viraraghavan, and Subramanian 1999; Chowdhury et al. 2011; Jacobson and Delucchi 2011). It is an effective method for coagulation, because the aluminum ions act by forming surface-active hydrolysis products that adsorb on particle surfaces and reduce their stabilizing surface charge. This forms an aluminium hydroxide precipitate, which increases the rate of formation of particle aggregates. The particle aggregates can then be removed by separation processes such as sedimentation and filtration leading to drinkable water.

In a typical drinking water treatment process, coagulation is commonly referred to as the destabilization step. The next stage of water treatment, flocculation, refers to cases where the coagulant (such as alum) dominates through fluid motion (*i.e.* orthokinetic aggregation) and aggregates (flocs) tend to be larger (Benjamin 2002; Gregory 2005). The metal salts used as coagulants (i.e. aluminum, iron) are effective in removing

colloidal particles and dissolved organic substances through charge neutralization and sweep flocculation mechanisms (Duan and Gregory 2003). Specifically, the Duan and Gregory (2003) study found that charge neutralization can be effective in destabilizing colloidal particles at low dosages of aluminum and ferric salts (5 – 50 µM), bulk precipitation of metal hydroxide yielded larger flocs from sweep flocculation, and that optimum pH is important for the effectiveness of the coagulant. Sweep flocculation leads to faster aggregation than charge neutralization, and gives stronger/denser flocs (Gregory 2005). Moreover, an important phenomena involving the effectiveness of metal coagulants is from the pH change caused by hydrolysis of the metal cations (in this case, Al^{3+}); the change in pH of the solution governs the metal coagulants' effectiveness during coagulation since metal ion solubility will be affected (Crittenden and Harza 2005; Gregory 2005). Indeed, other researchers have demonstrated the use of conventional water treatment processes (i.e. coagulation, flocculation, sedimentation, and filtration) to effectively remove natural organic matter, suspended solids, and other inorganic constituents from water and wastewater (Duan, Wang et al. 2002; Domínguez, Beltrán de Heredia et al. 2005; Beltrán-Heredia, Sánchez-Martín et al. 2009; Zhao, Liu et al. 2009; Kim, Liu et al. 2012). However, even with an extensive body of literature on these stages of water treatment and a growing number of papers on micro and nano material stability, the capacity of conventional water to remove micro and nano particles has not yet been fully determined.

One proposed strategy to remove a greater number of micro and nano sized metal oxide particles would be to simply add more coagulant. However, previous studies have

demonstrated that a portion of the alum added to the raw water is not removed during

treatment and remains as residual aluminium in the treated water (Crapper McLachlan

and De Boni 1980; Vaidyanathan and Tien 1988; Van Benschoten and Edzwald 1990).

Indeed, there is considerable concern throughout the world over the levels of aluminium

found in drinking water sources (raw water) and treated drinking water. This has arisen

mainly for two reasons. First, acid rain has caused the aluminium level in many

freshwater sources to increase (Schecher and Driscoll 1988). This high (3.6 to 6 mg/l)

concentration of aluminium in treated water gives rise to turbidity, reduces disinfection

efficiency, and may precipitate as $Al(OH)_3$ during the course of distribution (Rahman

1992). Secondly, the possibility of an association between aluminium and

neuropathological diseases, including presenile dementia and Alzheimer's disease is

frequently hypothesized (Schecher and Driscoll 1988; Crapper McLachlan and De Boni

1980; Stauber et al. 1999). Therefore, standards have been established for the control of

residual Al in drinking water. The drinking water quality limit for Al according the

World Health Organization (WHO) guidelines is 0.2 mg/L, while the limit for Japan and

the USA are 0.1 mg/L (Kimura et al. 2013) and 0.05 mg/L(Kimura et al. 2013),

respectively. Thus, the quantity of coagulant used must be balanced with the potential

amount of particle removal to ensure drinking water safety.

Thus, the goal of this project was to shed light on the relationship between the coagulant

residual concentration and the removal efficiency in the filtration stage of water treatment

of micro and nano sized TiO_2 particles. This systematic study for the assessment of current

water treatment infrastructure in removing nano and micro sized particles prior to their

entering water distribution systems (Lecoanet and Wiesner 2004; Dunphy Guzman, Finnegan et al. 2006) was conducted in a 2D filtration micromodel. This micromodel was thus used to study the removal efficiency of two grades of TiO_2 suspended in standard drinking water influent by using a variety of environmentally relevant coagulant residual in order to give insight into potential removal strategies.

4.2 Methods and Materials

4.2.1 TiO_2 particles preparation

The food grade (FG) TiO_2 employed in this study was acquired from Arizona State University to represent the particles applied in food products. Particle size was determined to be 48 – 122 nm with a phase composition of 2% rutile and 98% anatase based on previous report (C. Chen, Waller, and Walker 2017). And a representative industrial grade (IG) TiO_2, as a comparison, employed in this study were P25 Evonik Degussa (Evonik Industries AG) with a phase composition of 18% rutile and 82% anatase of which purity of 99.5%. The average size reported by the manufacturer to be 21 nm (X-ray diffraction), however, is composed of fused aggregate particles that can aggregate to form larger secondary aggregates in suspension. Before transport test experiments, a stock suspension of for each grade of TiO_2 was prepared via a similar protocol by Chen et al. (2017). The TiO_2 particles were sonicated (Transsonic 460/H; Barnstead Lab-Line) for ~5 min to help break up aggregation immediately before transport experiments. Coated TiO_2 with FITC for each grade were prepared by a similarly reported procedure (Maurizi et al., 2009) by utilizing FITC as the coating agent for both grades if TiO_2.

4.2.2 Test Solutions

Six solution conditions were tested in this study: two ionic strengths (IS) of monovalent KCl and divalent $CaCl_2$, artificial groundwater (AGW), and artificial surface water (ASW). Two IS values were selected to control for the IS of ASW (1.83 mM) (Yip et al., 2011) and AGW (10 mM) (Bolster et al., 1999), respectively. The complete list of constituents for AGW and ASW can be found in previous research (Kinsinger, et al, 2014). All chemicals were ACS grade reagents (Fisher Scientific). For select experiments, to study the coagulant residual effect on removal efficiency, 4 concentrations of alum were applied to each suspension with the 2 different grades of TiO_2, including 0, 0.05, 0.5, 5 mg/L of alum (KAl $(SO_4)_2 \cdot 12H_2O$, Sigma-Aldrich). Those concentrations were selected to represent a typical average of the drinking water quality limit for Al. Specifically, 0 mg/L was used as the control, 0.05 mg/L is meant to represent the limit in the US, 0.5 mg/L represents the limit of the World Health Organization (WHO), while 5 mg/L represents a value in the range of treated wastewater effluent (<5 mg/L) (Crittenden and Harza, 2005).

4.2.3 Particles characterization in suspension

Electrophoretic mobility (EPM) and hydrodynamic diameter of the FG and IG TiO_2 particle suspensions were determined using a ZetaPALS Analyzer (Brookhaven Instruments, Holtsville, NY). Zeta potential was calculated from the EPM using the Smoluchowski equation, which is applicable when the Debye length (thickness of the

double layer) of a particle is much less than the particle size (Elimelech et al., 1998; Gregory, 2006). Hydrodynamic diameter was measured using the dynamic light scattering function of the same ZetaPALS Analyzer instrument. Particle suspensions were sonicated for 10 min before addition to respective media, where a final 30 s sonication was performed just before characterization. The zeta potential and hydrodynamic diameter were determined from the average of 5 runs, with each run lasting 2 min.

Multi-angle static light scattering (SLS) (BI-200SM, Brookhaven Instruments, Holtsville, NY) was used to determine the aggregate morphology of the food grade and industrial grade TiO$_2$ aggregates as a function of concentration of coagulant residual. A 5 mW HeNe Laser (Uniphase) was employed to provide a single-frequency output with a wavelength of 632.8 nm. For light scattering measurements borosilicate culture tubes (Fisher Scientific, PA) were used as the sample cuvette. Scattering angle was varied from 15° to 45°, for a total of ten discrete angles equally distributed on a logarithmic scale. Fractal dimension of the food grade and industrial grade TiO$_2$ aggregates was determined from scattering intensities utilizing Rayleigh-Gans-Debye (RGD) theory from the following equations:

$$I(q) \propto q^{-D_f} \qquad (1)$$

$$q = \frac{4\pi}{\lambda} \sin\frac{\theta}{2} \qquad (2)$$

Where θ = scattering angle; λ = wavelength of incident light; D_f = fractal dimension; q = scattering wave vector; $I(q)$ = scattering intensity.

4.2.4 Quantitative analysis of transport experiments in a 2D micromodel

2D micromodel transport experiments (Chen et al., 2017) were used to simulate conventional filtration process. Alum, $(KAl(SO_4)_2 \cdot 12H_2O)$ at a dosage of 0, 0.05, 0.5, 5 mg/L was used with the limit for drinking water of Japan, USA, and WHO, which is more commonly used for practical water treatment operations (Gregory, 2006). The TiO_2 concentration (bare and coated) was 5ppm for all experiments. 60 mL samples were prepared in the solution for 2D transport experiments. Samples collected were used to evaluate particle removal efficiency. The removal efficiency is the fraction of particles approaching collector that actually collide, described as

$$\eta = \frac{4I}{\pi d_c v c_p}$$

[1]

where I is the number of attachment per collector, d_c is the collector diameter (m), v is the velocity (m/s), and c_p is the particle concentration.

4.2.5 Statistical analysis

All characterization and transport experiments were performed in triplicate in order to have an average and standard error. To test for differences between water chemistry, fractal dimension, and removal efficiency in all experiments listed above, a t-test was conducted to determine statistically significant differences for confidence intervals of 95% and 99% ($p < 0.05$ and $p < 0.01$, respectively).

4.3 Results and Discussion

4.3.1 Effects of coagulant residual level and solution chemistry on zeta potential of FG and IG TiO_2

The zeta potential of food grade and industrial grade TiO_2, as a function of the concentration of the coagulant residual alum (0, 0.05, 0.5, 5 mg/L $KAl(SO_4)_2 \cdot 12H_2O$) are presented in Figure 1A-D, respectively. The zeta potential of food grade TiO_2 in the absence of the coagulant residual were highly negative in all of the suspensions tested. While the zeta potential of industrial grade TiO_2 were highly positive in all of the suspensions tested in the absence of alum. This is consistent with previous studies demonstrating that the isoelectric point of industrial grade TiO_2 was approximately pH 6.2 (Suttiponparnit et al. 2011; Kosmulski 2002). Particles have a positive zeta potential when pH is lower than 6, while the zeta potential is negative when pH is higher than 6 (Jiang, Oberdörster, and Biswas 2009).

The addition of the coagulant residual lead to the suspensions becoming more acidic due to the formation of sulfuric acid from the hydrolysis of alum to form hydrolyzed cationic species (N. Kinsinger et al. 2015). The dominate species was $Al(OH)^{4\,-}$, although a minor species of $Al(OH)^{4\,+}$ was also present. The positively charged hydrolyzed species strongly adsorbed to the negatively charged TiO_2 particles (IEP ~ pH 6.2) (Duan and Gregory 1998), leading to charge neutralization and particle destabilization. With a further increase in alum loading, the particles can develop an excess charge from the

positive species and this can lead to charge reversal, re-stabilizing the particles (Duan and Gregory 2003, 1998). It has been found that only ~5 µM Al/m^2 particle surface is required for charge neutralization at pH 6, assuming a complete available titanium surface area (P.-H. Lin, Lion, and Weber-Shirk 2010). Therefore, the observed positively charged particles (Fig. 1) are due to charge reversal from excess absorption of the positively charged Al species. This could explain the phenomenon of the zeta potential of the particle surfaces becoming more electrically neutral with increasing alum concentration, resulting in particles destabilization.

In general, the valence of the suspension lead to small, but significant differences in zeta potential for both grades of particles at each respective coagulant dosage and IS (P < 0.05). The monovalent suspensions tended to be the most stable (highest absolute zeta potential value), followed by the ASW or AGW (depending on IS), with the divalent cation suspension being closest to neutral (lowest absolute zeta potential value). Similar stability trends have been observed with regard to simple KCl and CaCl$_2$ systems (Chowdhury et al. 2011) and in more complex waters (A. A. Keller et al. 2010). Interestingly, the ionic strength of the suspension (between 1.83 and 10 mM) did not significant affect the zeta potential of either particle (Fig 1 A vs. C and B vs. D). This may be because precipitation began to be observed for FG TiO$_2$ with the addition of 5 mg/L alum. This is due to the solubility limit of the excessive coagulant dosage, which occurs when the concentration of Al (III) exceeds solubility limit (minimum at near pH 6)

(Dentel and Gossett 1988) and promotes precipitation of amorphous colloidal hydroxide

particles (homogeneous or heterogeneous) (Duan and Gregory 2003).
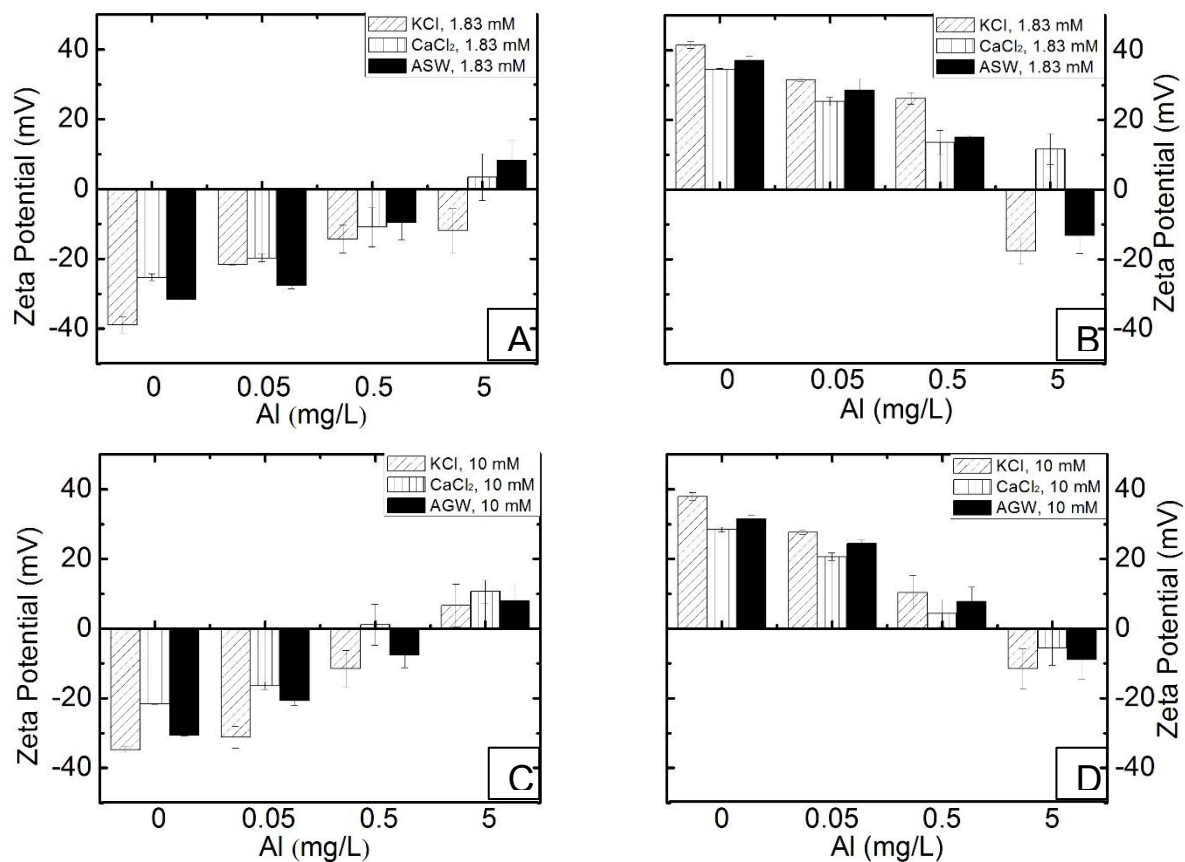
Figure 4.1. Zeta potentials of food and industrial grade TiO_2 with 0, 0.05, 0.5, 5 mg/L concentration of Alum in ASW with comparison group of 1.83 mM KCl and CaCl$_2$ (A,C) and in AGW with comparison group of 10 mM KCl and CaCl$_2$ respectively. Errors bars indicate one standard deviation of triplicate measurements.

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4.3.2 Effects of coagulant residual level and solution chemistry on DLS of FG and IG TiO$_2$

The particle size of food and industrial grade TiO$_2$, as a function of the concentration of the coagulant residual alum (0, 0.05, 0.5, 5 mg/L KAl(SO$_4$)$_2$·12H$_2$O) are presented in Figure 2A-D. In general, particles suspended in CaCl$_2$ formed the largest aggregates, followed by the simulated water suspensions, while the KCl suspensions lead to the formation of the smallest aggregates for both grades of particles, across all IS and alum concentrations. These results are in line with previous studies, which have reported that increased concentrations of multi-charged cations lead to greater metal-oxide aggregation (F. Lu et al. 2009; Chowdhury, Walker, and Mylon 2013; Lanphere, Luth, and Walker 2013). Specifically, Ca^{2+} ions lead to greater electrical double layer compression than monovalent ions due to the larger outer valence shell size (Hayes et al. 2011). This phenomenon is most likely due to charge screening and reduced Debye length (Redman, Walker, and Elimelech 2004). Previous studies have also demonstrated similar effects where calcium ions Ca^{2+} contributed to enhanced nanoparticle aggregation and larger particle sizes (X. Li et al. 2006; Zhang et al. 2009; Pelley and Tufenkji 2008; S. a. Bradford and Torkzaban 2013). It has been also reported previously that the Ca^{2+} ions can bind with the oxygen functional groups, which may explain the specific increase in aggregation observed in the AGW suspension when compared to the artificial surface water (ASW) suspensions (Chowdhury, Walker, and Mylon 2013; Zhang et al. 2007). Increased hydroxide precipitation is also a likely cause of the increased TiO$_2$ particle aggregate size, due to the presence of highly charged anions, such as sulfate, which promote the hydroxide precipitation that enmesh the smaller TiO$_2$ particles to form

significantly larger secondary particles that easily settle out of solution (Duan and Gregory 2003).

For both grades of TiO_2 the effective diameter significantly increases with the addition of alum ($P < 0.05$) up until 0.5 mg/L for each of the background solutions, while there is no increase between 0.5 and 5 mg/L. This may be because Al(III) species exert a profound effect on the isoelectric point of TiO_2 and on the coagulation of the TiO_2 colloid (Wiese and Healy 1975). For TiO_2 the critical coagulation concentration (CCC) and the critical stabilization concentration (CSC) shift from about pH 6 in the absence of Al(III) to about pH 9 as the concentration of Al (III) is increased. Since the pH of the DLS was ~ pH 6, one possible explanation would be between 0 and 0.5 mg/L, both types of TiO_2 were below the CCC, while higher than the 0.5 mg/L alum, it was above the CCC, and the aggregate size was no longer affected by the alum concentration.

The percent increase in aggregate size as a function of coagulant residual was significantly greater for the FG than IG TiO_2 particles (Figure 2 A and B, C and D), which was consistent with previous studies (Westerhoff et al. 2011).When comparing the FG TiO_2 particles suspended in two different ionic strengths (1.83 vs. 10 mM) the greater ionic strength lead to a significantly greater aggregate size ($P < 0.05$). The electrical double layer (EDL) theory explains a reduction in the thickness of the diffuse double layer with increasing ionic strength (Stankovich and Carnie 1996). This allows for a greater degree of particle-particle interaction resulting in an increase in the level of

aggregation and potential for particle settling. The lack of an effect of ionic strength on the solubility was also observed for IG particles (Figure 2B and 2D). Previous research has demonstrated that micro size particles (> 1µm) were stable at increased ionic strengths (0.15 M NaCl) (Jiang, Oberdörster, and Biswas 2009). Therefore, the changes in aggregate size and the measured zeta potential due to variations in ionic strength are expected to be negligible.

A strong correlation between the zeta potential and average size was observed. When the alum concentration is far from the isoelectric point, the absolute value of zeta potential was greater (Figure 1). The electrostatic repulsive force is then dominant over the van der Waals force; such that agglomeration is suppressed. Consequently, the average size was small, ~600 nm for FG TiO_2, and ~ 1600 nm for IG TiO_2 when alum concentration was 0 mg/L. When the alum concentration approached the isoelectric point, the repulsive force was weakened due to low surface charge, and the hydrodynamic size increased. Under these conditions, large flocs were formed, which settled out of the solution.
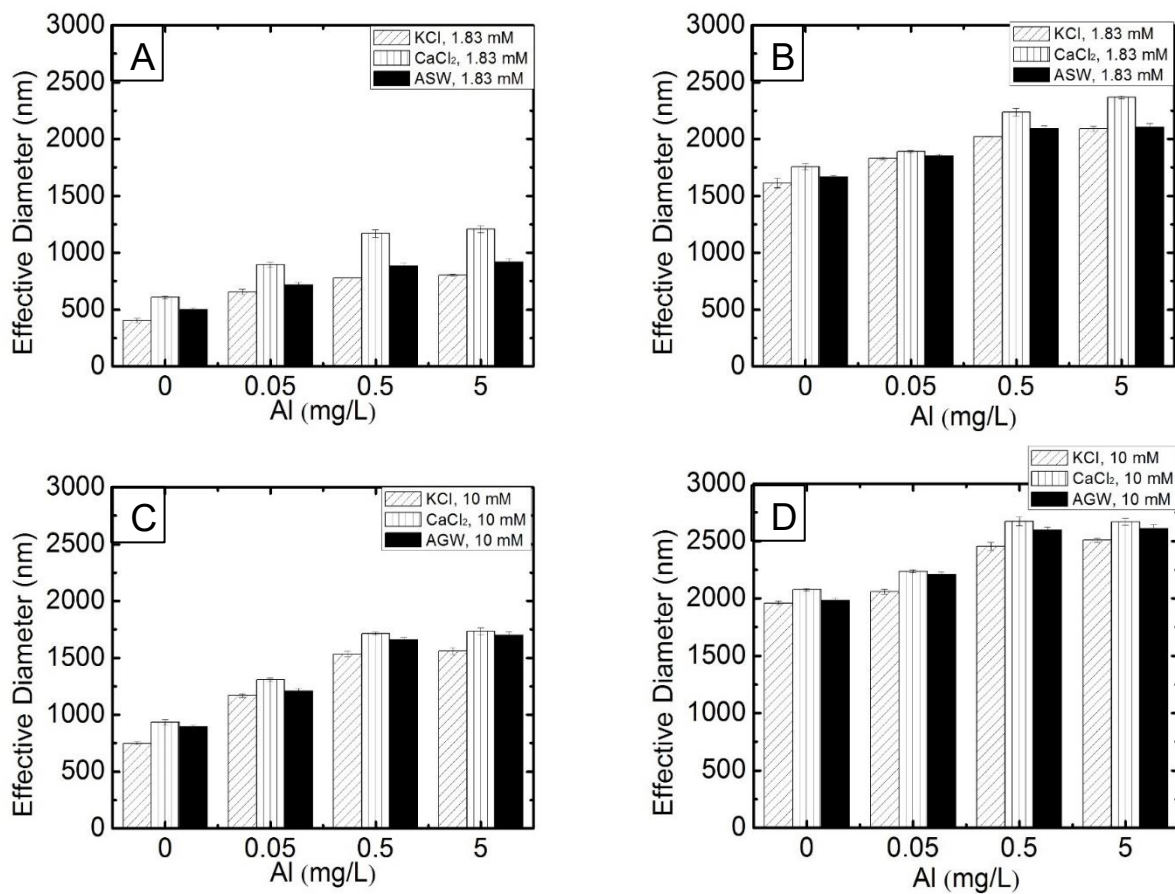
Figure 4.2. Effective diameter of food and industrial grade TiO$_2$ with 0, 0.05, 0.5, 5 mg/L concentration of Alum in ASW, with comparison group of 1.83 mM KCl and CaCl$_2$ (A,C) and in AGW with comparison group of 10 mM KCl and CaCl$_2$ (B,D) respectively. Errors bars indicate one standard deviation of triplicate measurements.
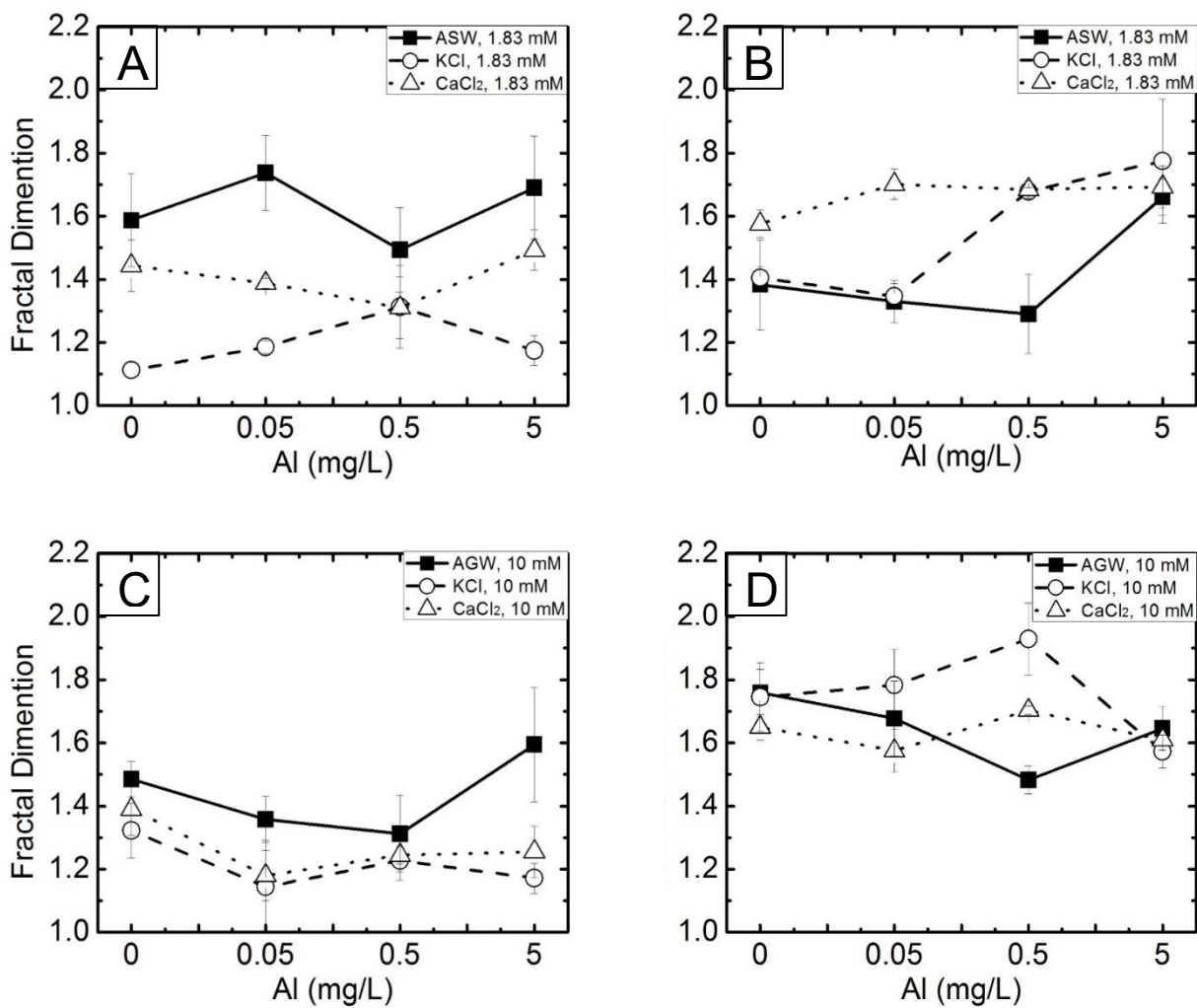
4.3.3 Effects of coagulant residual level and solution chemistry on aggregate morphology of FG and IG TiO$_2$

Fractal dimension of the food grade and industrial grade TiO$_2$ aggregates formed in the presence of residual coagulant (0, 0.05, 0.5, 5 mg/L KAl(SO$_4$)$_2$·12H$_2$O) was measured by static light scattering (SLS). To illustrate more clearly the observed trends with particle concentration and ionic strength, the fractal dimensions are plotted in Figure 3. In general, for FG TiO$_2$, fractal dimension was highest in the simulated water conditions (AGW and ASW), followed by a divalent solution (CaCl$_2$) of similar total ionic strength, and then monovalent solution (KCl). Contrarily, for IG TiO$_2$, fractal dimension in multivalent water conditions (AGW and ASW) were lower than in the same IS divalent (CaCl$_2$) and monovalent (KCl) suspensions. Interestingly, for FG TiO$_2$, changes in fractal dimension did not correlate with coagulant residual concentration, while for IG TiO$_2$, fractal dimension significantly increased between 0.5 and 5 mg/L coagulant residual concentration. These results indicate that FG TiO$_2$ aggregates were very stable. An increase in measured fractal dimension for IG TiO$_2$ aggregates at and above 0.5 mg/L coagulant residual concentration would indicate more tightly packed structures. Whereas slower aggregation rates are typically associated with higher fractal dimensions, it is possible that the coagulant residual in these conditions destabilized enough of the particles in suspension so as to cause the lower fractal dimension aggregates to settle out of suspension.

The electrolyte concentrations of the single salt solutions used in the experiments were 1.83 and 10 mM. This allowed observation of the behavior of the fractal dimension at

different coagulant residual concentrations. The fractal dimensions were found to range from 1.11 to 1.93, which corresponds well to known literature values of 1.0 and 2.1 for diffusion-limited cluster-cluster aggregation (Meakin and Jullien 1988; Heinson, Chakrabarti, and Sorensen 2015) and reaction-limited cluster-cluster aggregation (Fry et al. 2004; Heinson, Sorensen, and Chakrabarti 2010), respectively. Clearly, the structure of aggregates formed from the colloidal particles differs between the two types of TiO_2 particles evaluated, but the effect of coagulant residual concentration is minimal in these conditions. In 2012, Jassby *et al.* also reported that there was only a minor impact on the fractal dimension as a function of IS of TiO_2 aggregates due to the fused nature of their primary particle structure (Jassby 2011). Yet little else has been reported on the effects of coagulant residual concentration on the aggregate structure of colloidal systems.

Figure 4.3. Fractal dimension of both food and industrial grade TiO_2 as a function of coagulant residual concentration (0, 0.05, 0.5, 5 mg/L) for AGW and ASW, four relevant ionic strength with 1.83 mM KCl and $CaCl_2$ (A,C) and 10 mM KCl and $CaCl_2$ (B,D) environmental conditions were applied. Experiments were conducted at a flow rate of 1μL/hr. Error bars indicate one standard deviation of triplicate measurements.

4.3.4 Effects of coagulant residual level and solution chemistry on removal of FG and IG TiO$_2$

The removal efficiency of food grade and industrial grade TiO$_2$, as a function of the concentration of the coagulant residual alum (0, 0.05, 0.5, 5 mg/L KAl(SO$_4$)$_2$·12H$_2$O) are presented in Figure 4. Results from this study indicate that for all TiO$_2$ suspensions, the removal efficiency increased with greater coagulant residual concentrations up until 0.5 mg/L alum, above that threshold there was no increase in removal. The removal efficiencies measured in this study correlate well with the stability characterization results, as well as observations of nanoparticle transport reported in the literature (Godinez *et al.*, 2013; Wang *et al.*, 2013). For identical solution chemistries and residual coagulant concentrations, industrial grade TiO$_2$ had a significantly higher removal efficiency than food grade TiO$_2$ ($P < 0.05$). This was due to the IG particles forming larger (Figure 2) and thicker aggregations (Figure 3) than the FG TiO$_2$ particles. Increases in removal due to aggregate size is because the DLVO and hydrodynamic forces increases with the size (S. a Bradford, Torkzaban, and Walker 2007) and gravitational forces increases with both thicker and larger aggregate size (Ma, Pazmino, and Johnson 2011; G. Chen, Hong, and Walker 2010; Cai et al. 2015).

A larger removal efficiency was observed in the CaCl$_2$ compared with the KCl suspension across the same range of alum concentration for both types of FG and IG. This difference in removal recovery may be due to a higher degree of adsorption by alum onto the collectors in the presence of Ca^{2+} ions. Higher ionic strength also lead to a significantly greater removal for both grades of TiO$_2$, which could be attributable to the increases in

aggregate size. An interesting deviation from the direct link between aggregate size and removal efficiency is that there is no significant difference in the removal of either grade of TiO2 whether suspended in ASW and CaCl2 at 1.83 mM, as well as AGW and CaCl2 at 10 mM, when keeping alum constant.
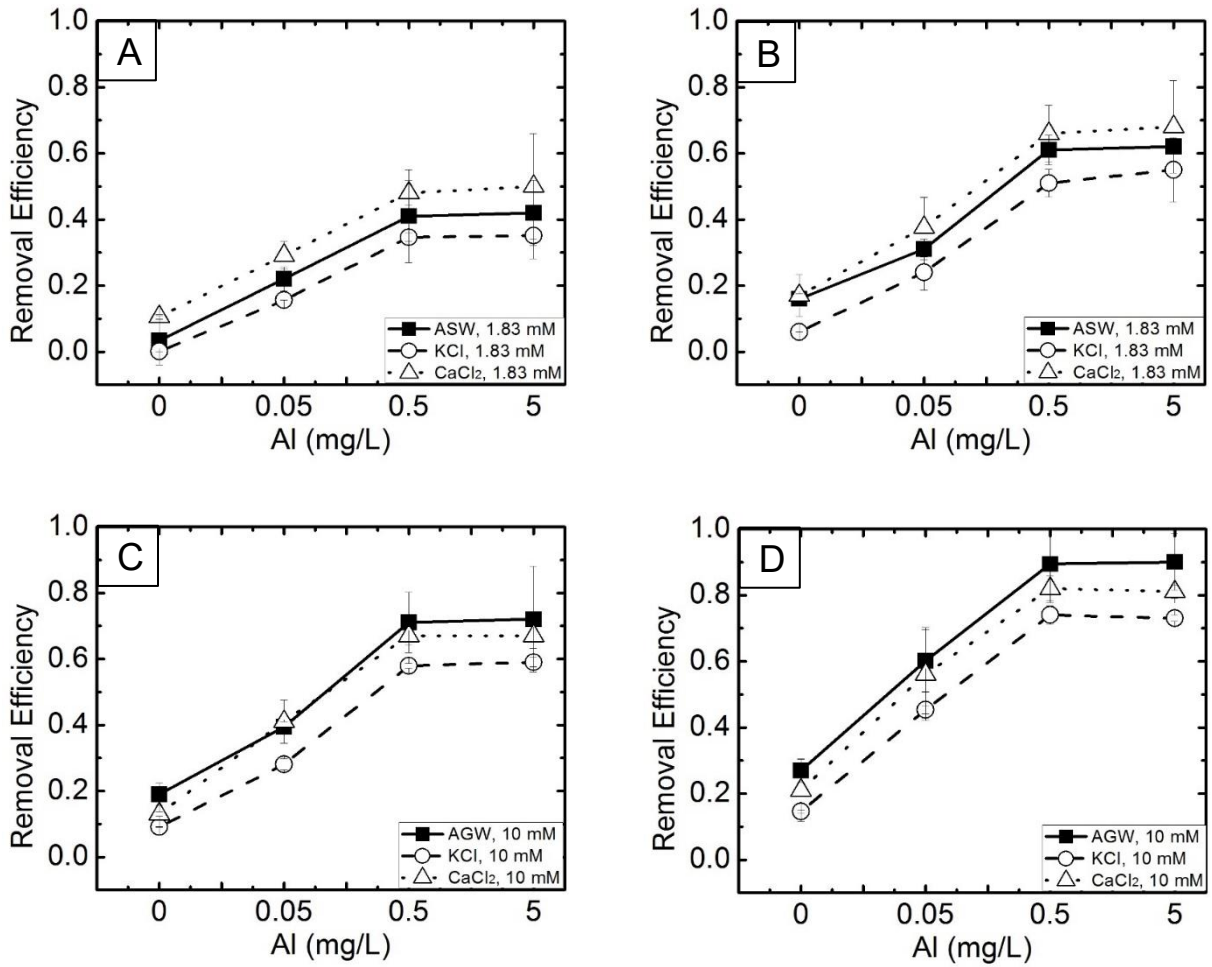

Figure 4.4. Removal efficiency η of both food and industrial grade TiO_2 as a function of coagulant residual concentration (0, 0.05, 0.5, 5 mg/L) for AGW and ASW, four relevant ionic strength with 1.83 mM KCl and CaCl2 (A,C) and 10 mM KCl and CaCl2 (B,D) environmental conditions were applied. Experiments were conducted at a flow rate of 1μL/hr. Error bars indicate one standard deviation of triplicate measurements.

4.4 Conclusions

In the past, studies have generally used simple monovalent systems to understand the fate and transport of industrial grade and food grade TiO_2 in porous media; therefore, more complex systems including the presence of divalent ions, monovalent ions, simulated water (AGW, ASW), and the presence of different concentration alum residual were evaluated in this study. The presence of alum for both monovalent and divalent cations, lead the FG and IG TiO_2 to become less stable and more easy to remove. The presence of divalent ions (e.g., Ca^{2+}, Mg^{2+}) resulted in FG and IG being less stable compared with monovalent ions at similar concentrations regardless of alum concentration.

The results indicate that there is a significant difference between the behavior of FG and IG in simulated water (AGW, ASW) systems. For identical solution chemistries and residual coagulant concentrations, industrial grade TiO_2 (IG) had a higher removal efficiency than food grade TiO_2 (FG). This was due to the IG particles forming larger aggregates than the FG particles. Since AGW have a higher concentration of divalent ions (e.g., Ca^{2+}, Mg^{2+}), IG will tend to become less stable and will eventually settle out or be removed in these subsurface environments. Conversely, for ASW, with the concentration of divalent ions typically lower, IG would remain more stable and their transport will be greater in the subsurface layers in natural water bodies.

Results from this study also indicate that for all TiO_2 suspensions, the greater coagulant residual concentrations increased the removal efficiency up until 0.5 mg/L alum, above that threshold the effect of coagulant residual were negligible. Additionally, AGW had the greatest removal efficiency for all coagulant residual concentrations, followed by

CaCl$_2$, ASW, and KCl, respectively. Analysis from results of this study suggests that having some coagulant residual, up to 0.5 mg/L alum, in the filtration stage of drinking water treatment will help remove micro and nano sized particles from drinking water. However, more work needs to be done to find the right balance in ensuring drinking water has both low levels of micro and nano particles, as well as low levels of coagulant residual.

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Chapter 5

Summary and Conclusions

The overarching goal of this study was to systematically investigate how model ENPs behave in engineered filters under a range of relevant solution chemistry conditions. Specifically, the study conducted a combination of fundamental and applied experiments, looking at ENP transport in idealized conditions, followed by those simulating actual scenarios in the filtration stage of drinking water treatment.

In Chapter 2, nanoparticle single collector removal efficiency has been shown to increase with particle size and ionic strength in gerneral. Under the conditions tested, larger particles result in greater interactions with the collector due to the contribution of hydrodynamic forces. Interestingly, when it comes to statistically analyzing the removal efficiency at the quadrant level, the greatest removal efficiency was observed for the rear stagnation points (quadrant 3), while the least occurred in quadrant 1. It may be deduced that particles under these conditions were because of the leeward flow stagnation zones; thus, the hydrodynamic forces decreased due to the viscous shear.

The highest contribution of attached nanoparticles to the increase in removal efficiency is shown for the combination of largest size particles (2000 nm) and highest ionic strength (100 mM), where it was shown the hydrodynamic forces and DLVO force dominate equally. Lower and similar contribution to the increase in removal efficiency is shown for the combination of the 20 nm and 1 mM; for this condition, the study shows that only DLVO force dominate.

A model framework for ionic strength and particle size effects in filtration of the presence of different sizes of nanoparticles has been developed through this investigation. It is concluded that for any nanoparticle, the single collector removal efficiency is sensitive to

the ionic strength and particle size. The model is built to show single collector removal efficiency as a function of particle size and ionic strength, as well as predict the behavior or deposition location on collector of any nanoparticles entering the filtration system in order to improve the field of environmental nanotechnology. Furthermore, the predictions generated from the present work parallel those of the constricted 3D model, for instance, the collector size and average velocity. Ultimately, this research could be applied in place of 3D columns when designing filters for water and wastewater treatment.

In Chapter 3, results reported in this work demonstrate that overall, the removal efficiency of food grade are all lower than industrial grade TiO_2 under all ionic strength conditions. Thus, food grade is removed 13-38 % less (as defined by η) than industrial grade across the conditions tested in this study, and the higher ionic strength, the less food grade were removed compared to industrial grade. This is because their smaller aggregate size and lower surface charge values. As a result, food grade TiO_2 is more likely to accumulate in the environment potentially leading to ecosystem damage (Pourzahedi, Vance, and Eckelman 2017; Reed et al. 2016; Stieberova et al. 2017; W. Jones et al. 2017).

The observed agreement between experimental and theoretical results is consistent for the entire range of sizes and ionic strengths tested. And when it comes to water treatment policy of removing engineered nanoparticles, one molecular structure is typically chosen to represent all the engineered nanoparticles of that metallic element (Donovan et al. 2016; Lazar, Varghese, and Nair 2012). For example, while FG TiO_2 represents the majority of TiO_2-containing materials that enter the ecosystem today (Weir et al. 2012), most researchers utilize industrial grade nano form of TiO_2, as a surrogate for all forms of TiO_2

(Clemente et al. 2015; Zhu, Zhou, and Cai 2011). Thus, this study demonstrates that nuances in the particles aggregate size and surface composition are important to consider, and not simply the molecular formula (e.g. TiO_2) when acertaining removal strategies for NPs. Additionally, it seems that for FG TiO_2, we need to test high IS for these transport experiments in the future to find the limitation like IG TiO_2. Finally, the approach of characterizing the particles before transport experiments to deduce aggregate size and surface charge should be utilized as a cost-effective way in determining the difficulty of removal of the various engineered particles in future experiments

In Chapter 4, results from this study indicate that for all TiO_2 suspensions, the greater coagulant residual concentrations increased the removal efficiency up until 0.5 mg/L alum, above that threshold the effect of coagulant residual were negligible. Additionally, AGW had the greatest removal efficiency for all coagulant residual concentrations, followed by $CaCl_2$, ASW, and KCl, respectively. This trend implies that the removal of FG and IG TiO_2 via filtration could be improved by adding divalent salts. Analysis from results of this study suggests that adding coagulant residual up to 0.5 mg/L alum and adding divalent salts to the filtration stage of water treatment will increase the removal of FG TiO_2 from drinking water. This study has incorporated many levels of complexity to simulate the complex conditions in environmental systems such as ASW, AGW and different level of coagulant residual (alum), and is the first to report their impact on the transport of FG and IG TiO_2 in porous media.

Through this research, it was confirmed that the leading factors in ENP destabilization which leads to their removal including the type and concentrations of salts in solution, the

presence of and chemical structure of the ENP capping agent, and the process operating

conditions (flowrates and coagulant residuals). Ultimately, through the systematic

variation of these parameters in the micromodel experiments, the conditions for optimal

ENP destabilization and removal were determined.