ABSTRACT

MAGNETIC SEEDING AGGREGATION
TO ENHANCE THE REMOVAL EFFICIENCY OF
TiO$_2$ NANOPARTICLES FROM WATER

By
Ashish Dhananjay Borgaonkar

Engineered nanoparticles, such as titanium dioxide (TiO$_2$), are important building blocks for the evolution of nanotechnology in industries and commercial products. Ever so increasing use of the engineered nanoparticles is bound to result in a substantial fraction of these nanoparticles ending up in wastewater; or surface water and groundwater, which are sources of intake for drinking water treatment. Removal of these engineered nanoparticles in wastewater and drinking water treatment processes is a very important step towards the protection of environmental and public health as well as protecting water treatment units from fouling and other issues.

Experimental studies showed TiO$_2$ removal efficiency of up to 75% using conventional coagulation and flocculation, but only with very high coagulant dosage and prolonged settling time. Clearly, conventional treatment will prove to be costly and impractical to treat TiO$_2$ in water. This research presents a method of using cationic surfactant-modified magnetite nanoparticles to enhance removal efficiency of TiO$_2$ nanoparticles in coagulation and flocculation. Magnetite nanoparticles can be recovered using an organic solvent (such as: cyclohexane) and recycled to minimize cost. Furthermore, effect of modeled parameters: pH, coagulant dose and type, settling time, and initial TiO$_2$ nanoparticle concentration on removal efficiency using the proposed method is also presented. Finally, the best operating ranges for values of modeled

parameters, which if maintained will maximize removal efficiency were obtained for both conventional and proposed method.

The method employed herein was able to increase the removal up to 90%+ at much lower coagulant dosage as compared to conventional coagulation and flocculation. The increase in removal efficiency is due to magnetic seeding aggregation. The outcome also indicated that the use of cationic surfactant-modified magnetite nanoparticles makes the coagulation and flocculation not only practical, but also cost efficient for removal of TiO_2 engineered nanoparticles. The results of this work will provide water and wastewater authorities with better understanding of the behavior of TiO_2 engineered nanoparticles in process streams and will help them come up with a better removal mechanism for TiO_2 engineered nanoparticles with least possible or no additional cost.

MAGNETIC SEEDING AGGREGATION
TO ENHANCE THE REMOVAL EFFICIENCY OF
TiO$_2$ NANOPARTICLES FROM WATER

By
Ashish Dhananjay Borgaonkar

A Dissertation
Submitted to the Doctoral Defense Committee
In Partial Fulfillment of the Requirements for the degree of
Doctor of Philosophy in Environmental Engineering

Department of Civil and Environmental Engineering
New Jersey Institute of Technology

May 2011

APPROVAL PAGE

MAGNETIC SEEDING AGGREGATION
TO ENHANCE THE REMOVAL EFFICIENCY OF
TiO$_2$ NANOPARTICLES FROM WATER

Ashish Dhananjay Borgaonkar

_____

Dr. Taha F. Marhaba, Dissertation Co-Advisor   Date
Professor and Chair of Department of Civil and Environmental Engineering, NJIT

_____

Dr. Tanapon Phenrat, Dissertation Co-Advisor   Date
Post Doctoral Researcher, Department of Civil and Environmental Engineering, CMU

_____

Dr. Sima Bagheri, Committee Member   Date
Professor of Department of Civil and Environmental Engineering, NJIT

_____

Dr. Robert Dresnack, Committee Member   Date
Professor of Department of Civil and Environmental Engineering, NJIT

_____

Dr. Hsin-Neng Hsieh, Committee Member   Date
Professor of Department of Civil and Environmental Engineering, NJIT

BIOGRAPHICAL SKETCH

Author: Ashish Dhananjay Borgaonkar

Degree: Doctor of Philosophy

Date: May 2011

Undergraduate and Graduate Education:

- Doctor of Philosophy in Environmental Engineering,
  New Jersey Institute of Technology, Newark, NJ 2011

- Master of Science in Environmental and Waste Management,
  Stony Brook University, Stony Brook, NY, 2005

- Bachelor of Engineering in Environmental Engineering,
  Shivaji University, Kolhapur, India, 2003

Major: Environmental Engineering

Publications:

A.D. Borgaonkar, T. Phenrat, T.F. Marhaba, Removal Efficiency of Engineered TiO_2 Nanoparticles from Water Using Cationic Surfactant-Modified Magnetite Nanoparticles, (2011) Journal of Water Research, In preparation, (2011)

A.D. Borgaonkar, T. Phenrat, T.F. Marhaba, Removal Efficiency of Engineered TiO_2 Nanoparticles from Water by Coagulation with Alum and Ferric Chloride, Journal of Water Research, In preparation, (2011)

T.F. Marhaba, A.D. Borgaonkar, K. Punburananon, Principal component regression model applied to dimensionally reduced spectral fluorescent signature for the determination of organic character and THM formation potential of source water, Journal of Hazardous Materials, 169 (1-3), (2009) 998-1004.

Presentations:

Enhancing Removal Efficiency of Engineered Nanoparticles From Water Using Cationic Surfactant-Modified Magnetite Nanoparticles:
Dana Knox Student Research Showcase (**Silver Medal**, NJIT, April 06, 2011)
The American Water Works Association (AWWA) Water Quality Technology Conference 2011, (Phoenix, AZ, Nov 2011, Abstract Submitted)

Removal of Engineered Nanoparticles from Water by Coagulation: *The American Water Works Association (AWWA) Water Quality Technology Conference 2010* (Nanoparticles: Treatment and Removal, Savannah, Georgia, Nov 14-18, 2010)

Evaluating Alternatives for the Removal of Engineered Nanoparticles from Water: E2 – Water Quality Workshop (Steven's Institute of Technology, Hoboken, NJ; September 29th 2009)

Spectral Fluorescent Signatures Post-Processing by Principal Component Analysis Model for Determination of Organic Character and THM Formation Potential: *The American Water Works Association (AWWA) Water Quality Technology Conference 2008* (Organic Compound Analysis: DBPs, VOCs, SOCs, and NOM, Cincinnati, Ohio, Nov 16-20, 2008)

Principal Component Analysis Model for Predicting Organic Character of Water Using Spectral Fluorescent Signature: *The 235th American Chemical Society (ACS) National Meeting* (Technical Program, Division: Environmental Chemistry, Section: Advances in Drinking Water Disinfection and Disinfection Byproduct Management, Format: Poster; New Orleans, Louisiana; April 06-10, 2008)

Characterization of THMs Precursors by Fractionation of Natural Organic Matter and UV Absorption: *The 235th American Chemical Society (ACS) National Meeting* (Technical Program, Division: Environmental Chemistry, Section: Advances in Drinking Water Disinfection and Disinfection Byproduct Management, Format: Poster; New Orleans, Louisiana; April 06-10, 2008)

Chapter on Monitoring Disinfectants: Contributed to this chapter, published in the *Handbook of Water Quality and Purity*, Willy Publication, 2009

Review Chapter on Biology Topic (Afternoon Session in Other/General Engineering) of Fundamentals of Engineering (FE/EIT) Examination: Contributed to this chapter, published in *Barron's FE Review Manual, second edition*, 2008

The Potential Advantages of Applying Operations Research Techniques to Optimize Waste Management in New Jersey: *The 1st Global Cleaner Production – International Conference and Exhibition* (Nasar City, Cairo, Egypt; Sept. 18-20, 2006)

Towards the Development of Sustainable Landfill:
The 1st Global Cleaner Production – International Conference and Exhibition (Nasar City, Cairo, Egypt; Sept. 18-20, 2006)
The Twenty-Second International Conference on Solid Waste Technology and Management (Philadelphia, PA; March 18-21, 2007)

A Rapid Approach to Characterize Natural Organic Matter in Water: 2007 Meadowlands Symposium II (Lyndhurst, NJ; May 15-17, 2007)

Vakratunda Mahakaya Surya Koti Samaprabha
Nirvighnam Kurumeydeva Sarva Karyeshu Sarvada

Meaning: O Lord Ganesha, of curved trunk, large body, and with the brilliance of a million suns, please remove all the hurdles in all our endeavors.

"Aum *bhūr bhuvaḥ svaḥ*
tát savitúr váreṇyaṃ
bhárgo devásya dhīmahi
dhíyo yó naḥ pracodáyāt"

Meaning: "We meditate on the glory of that Being who has produced this universe; may He enlighten our minds." – Swami Vivekananda

Dedication:

To my dear parents, Mr. Dhananjay Borgaonkar and Mrs. Nayana Borgaonkar
& My lovely sister Aditi

"For their support, encouragement, and unconditional love"

"Karmanye Vadhikaraste, Ma phaleshou kada chana,
Ma Karma Phala Hetur Bhurmatey Sangostva Akarmani"

A verse from the *Bhagavad Gita* meaning: You have a right to perform your prescribed action, but you are not entitled to the fruits of your action. Never consider yourself the cause of the results your activities, and never be associated to not doing your duty.

"Learn from yesterday, live for today, hope for tomorrow. The important thing is not to stop questioning. Intellectual growth should commence at life and cease only at death."
                                                – Albert Einstein (1879 – 1955)

ACKNOWLEDGMENT

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

FIGURE   **Page**

LIST OF ABBREVATIONS

TiO_2	Titanium Dioxide (Nanoparticles)
SWNT	Single Walled Carbon Nanotubes
MWNT	Multi-Walled Carbon Nanotubes
Ti	Titanium
UV	Ultraviolet
$FeCl_3$	Ferric Chloride as Coagulant
$Al_2(SO4)_3$	Alum as Coagulant
NOM	Natural Organic Matter (mg/L)
pH	Negative Logarithm (Base 10) of the Hydrogen Ion Concentration. Measure of Acidity or Alkalinity of an Aqueous Solution
UF	Ultra Filtration
RV	Reverse Osmosis
EDL	Electrical Double Layer
INC	Initial Nanoparticle Concentration (mg/L)
AR	Agitation Rate (Slow Mixing, rpm)
CD	Coagulant Dose (Alum or Ferric Chloride, mg/L)
IEP	Isoelectric Point
ZP	Zeta Potential (mV)
pH_{IEP}	pH Corresponding to Isoepectric Point
AHD	Average Hydrodynamic Diameter (nm)
DLVO	Derjaguin-Landau-Verwey-Overbeek Theory

NaCl	Sodium Chloride, Salt
Na+	Sodium Ion
Cl^-	Chlorine Ion
IS	Ionic Strength
DLS	Dynamic Light Scattering
KCl	Potassium Chloride, Salt
$MgCl_2$	Magnesium Chloride, Salt
$CaCl_2$	Calcium Chloride, Salt
nC_{60} OR C_{60}	Fullerene Nanoparticles
CdTe	Cadmium Telluride Nanoparticles
ZnO	Zinc Oxide
MGD	Million Gallons per Day
RNIP	Reactive Nanoscale Iron Particles
pH_{ZEP}	pH Corresponding to Zero Point Charge.
A_{123}	Hamaker Constants for Unretarded Interaction Between a Nanoparticle and Silica Collector in Water
A_{121}	Hamaker Constant for Unretarded Interaction Between Nanoparticles in Water.
Al_2O_3	Aluminum Oxide Nanoparticles
Au	Gold Nanoparticles
Fe_2O_3	Iron oxide Nanoparticles
nZVI	Zerovalent Iron Nanoparticles
SiO_2	Silica Nanoparticles
HSIP	Hsinchu Science-Based Industrial Park

PACI	Polyaluminum Chloride
EPA	Environmental Protection Agency
NCER	National Center for Environmental Research
CMP	Chemical Mechanical Polishing
CTAB	Cetyltrimethylammonium Bromide
UV-Vis	Ultraviolet-Visible (Spectroscopy)
ACS	American Chemical Society
DI	Deionized (Water)
DTAB	Dodecyltrimethylammonium Bromide
TOC	Total Organic Carbon
ST	Settling Time (min)
MD	Magnetite+CTAB Dose (mg/L)
MS	Microsoft, Inc.
SAS	Statistical Analysis Software
Mgte	Magnetite Nanoparticles

CHAPTER 1

INTRODUCTION

1.1   Purpose of Study

Nanomaterials, by definition, have at least one dimension 100 nm or less. Manufactured nanoparticles are important building blocks for the evolution of nanotechnology in industries and commercial products. Various engineered nanoparticles including metal oxide nanoparticles, carbon nanotubes, fullerene cages, Fe^0 nanoparticles, and quantum dots, currently find their use in sunscreen, tires, cosmetics, textile, biomedical, and environmental applications [1-9]. In New Jersey, several pharmaceutical industries use engineered nanoparticles in many products. Over 700 products containing engineered nanomaterials and nanotechnology have been commercially introduced into the market leading to an estimated amount of nanoparticles already in production by 2011 in millions of tons [2, 10, 11]. Engineered nanoparticles are used in pharmaceuticals, medical devices, environmental remediation, commercial products, and several industrial processes [1, 12]. The already multi-billion-dollar nanomaterials industry is expected to have a total impact of 1.5 trillion dollars on the world economy [2, 10, 11]. The production, use, and disposal of nanomaterials/products containing nanomaterials will undoubtedly introduce engineered nanoparticles to various media of the biosphere, and especially to water bodies [1, 6, 13, 14].

Although various kinds of nanoparticles have been used in industrial processes and commercial products, the nanoparticles used in massive quantity with the potential to be released to the environment in large quantities are: titanium dioxide (TiO_2) nanoparticles, silica nanoparticles, silver nanoparticles, single walled carbon nanotubes

(SWNTs) and multi-walled carbon nanotubes (MWNTs). In a state like NJ, which is rich in pharmaceutical companies and products thereof, TiO_2 nanoparticles are of utmost importance. Titanium (Ti) also occurs naturally in soils and as highly purified TiO_2 in many commercial products including: cosmetics, sunscreens, and hundreds of personal care products for their ultraviolet (UV) reflecting capability [14]. They are also used in paints and pigments, air-fuel ratio controllers in automobiles, and for demilitarization of chemical and biological warfare agents [14]. Considering all this, TiO_2 was the choice for nanoparticles to be studied for determining removal efficiency in this research.

Engineered nanoparticles may enter aquatic systems via several routes including, direct discharge, run off, wastewater effluents, atmospheric deposition, and other processes, including simple processes like washing of clothes (from <1 to 45% emitted during single washing cycle) [2, 6]. All these releases of engineered nanoparticles will eventually find their way to source water and drinking water treatment plants [2]. Drinking water therefore is likely to be a high potential route for nanoparticle exposure.

Nanoparticles in water and wastewater or drinking water source can have profound effects on both public health and the performance of conventional water treatment unit. Although the risk of nanoparticles to human heath and ecosystem is largely unknown [1, 12], several recent studies report the possibly undesirable effects to organisms [15, 16], plants [17], aquatic life [2, 13, 18], humans [2, 9, 19-23], and organisms analogous to human organs [22, 24]. In addition, Nanoparticles can adversely affect the performance of advanced wastewater and water treatment units such as: ultra-filtration (UF) and reverse-osmosis (RO) through membrane fouling [25, 26] and can potentially produce adverse impact on microbes in the activated sludge related processes

[27-29]. There has been evidence that nanoparticles escape sewage treatment facilities through biomass in the activated sludge process utilized as fertilizer or even directly to water bodies [30]. Raw sewage may contain from 100 to nearly 3000 µg Ti/L [14]. Ti larger than 0.7 µm was removed well by wastewater treatment plant (WWTP) processes, however, <0.7 µm size fraction of Ti escaped into effluent and was found in concentrations ranging from <5 to 15 µg/L [14]. Engineered TiO_2 was also found accumulated in settled solids, adsorbed onto activated sludge, in sewage, bio-solids, and liquid effluents at concentrations between 1 and 6 µg Ti/mg [14]. It is predicted that engineered TiO_2 nanoparticles can be found in sewage treatment effluents (up to 4 µg/L), sludge treated soil (up to 89 µg/kg), and surface waters (up to 21 ng/L) indicating that they may pose risk to aquatic organisms [13]. Thus, it is advantageous to achieve removal of nanoparticles at a pre-treatment process such as coagulation/flocculation and sedimentation in water or sewage treatment plants.

Even with the importance of removing nanoparticles from water as discussed above, few studies regarding the removal of nanoparticles using coagulation/sedimentation are available in the literature [18, 26, 27, 31-45]. Although the removal of micron-sized colloidal particles by coagulation/flocculation is relatively well understood, the study on removal of nanoparticles is very limited. Even the ones published on the removal of nanoparticles using coagulation do not provide the thorough analysis for the optimization of coagulation/flocculation for maximizing removal efficiency [26, 45].

For several reasons mentioned above, the removal of nanoparticles in wastewater and drinking water treatment processes is a very important step towards the protection of

environment and public health as well as maintaining water treatment units. It is essential to understand how effectively and at what conditions, a conventional pre-treatment process such as coagulation/flocculation can remove these potentially toxic engineered nanoparticles. This understanding will be useful for the optimization of coagulation/flocculation for the removal of engineered nanoparticles for the protection of the environment and public health in the State.

1.2 Specific Objectives

The overall objective is to evaluate the performance of conventional coagulation/flocculation and proposed cationic surfactant-modified nanoparticles for the removal of TiO_2 engineered nanoparticles in water at various operational conditions. The specific objectives are as follows:

1. To evaluate the performance of conventional coagulants including Ferric Chloride ($FeCl_{3)}$ and Alum ($Al_2(SO_4)_3$) for the removal of engineered nanoparticles (TiO_2).

2. To determine the conditions of coagulation/flocculation (coagulant dosages, pH, etc.) to maximize the removal of engineered nanoparticles (TiO_2).

3. To determine the effect of natural organic matter (NOM) on the removal by conventional coagulants.

4. To study the use of magnetic seeding aggregation using cationic surfactant-modified magnetite nanoparticles for the rapid removal of engineered nanoparticles (TiO_2) from water.

5. To determine the conditions of using cationic surfactant-modified magnetite nanoparticles (dose and pH) that maximize the removal of engineered nanoparticles (TiO_2) from water.

6. To determine the effect of natural organic matter on the removal using cationic surfactant-modified magnetite nanoparticles.

7. To compare conventional coagulation and magnetic seeding aggregation for removal of engineered nanoparticles (TiO_2) in water.

CHAPTER 2

BACKGROUND THEORY AND SURVEY OF LITERATURE

2.1 Use of Engineered Nanoparticles and Potential Impact to Public Health

Manufactured nanoparticles are important building blocks for the evolution of nanotechnology in industries and commercial products. Various engineered nanoparticles including titanium nanoparticles, carbon nanotubes, fullerene cages, silica nanoparticles, and quantum dots, currently find their use in sunscreen, tires, cosmetics, lubricants, and biomedical application, respectively [1]. The production, use, and disposal of nanomaterials/products containing nanomaterials will undoubtedly introduce engineered nanoparticles to various media of the biosphere [1]. Nanoparticles used in the products might be bare or surface functionalized by polymers or surfactants. Once bare nanoparticles are released into the environment, they might interact with natural macromolecules such as natural organic matters (NOM). The surface functionalization and the interaction with NOM can enhance the extent of migration of these nanoparticles in the environment [46]. Most of these commercial nanoparticles may find their way to aqueous environment.

A lot of literature is available on different possible ways nanomaterials can enhance existing technology, but only few of them address the possible health effects. Use of nanoparticles although advantageous in many ways, presents possible dangers, both environmentally and medically. Also, there is a good chance nanoparticle products may produce unintended consequences that are not yet known. Most of these challenges are due to the high surface to volume ratio, which can make the particles very reactive or catalytic [47]. Nanoparticles are known to be able to enter the human body and exhibit

some toxicity, such as a cytotoxicity response, and an inflammatory response [23, 45, 48]. In addition, many nanoparticles have the ability to pass through and cause damage to the cell membrane, although, the extent of interaction between nanoparticles and biological systems is relatively unknown [15, 16, 49]. Researchers have discovered that silver nanoparticles used in socks to reduce foot odor are being released in the wash with possible negative consequences [50]. A study at the University of Rochester found that when rats breathed in nanoparticles, the particles settled in the brain and lungs, which led to significant increases in biomarkers for inflammation and stress response [51].

For all these reasons, it is important that engineered nanoparticles do not escape treatment processes.

2.2   Removal of Engineered Nanoparticles During Water Treatment

Natural nanoparticles are already present in abundance in all source waters, e.g., 10^{13} particles per liter, with a diameter ≤ 10 nm, are estimated to be present in freshwater sources [52, 53]. The potential exposure to nanoparticles through drinking water is subject to efficacy of water treatment processes, which generally include rapid mixing, coagulation, flocculation, sedimentation, followed by filtration, and disinfection (Figure 2.1).
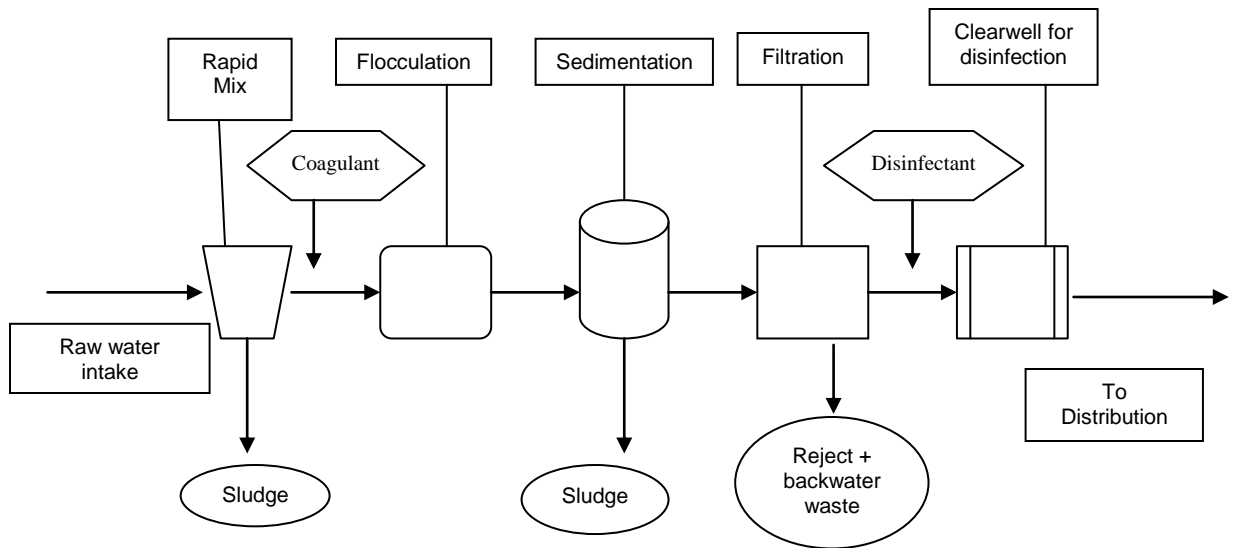
Figure 2.1 Schematic of conventional water treatment process train.

Removal of engineered nanoparticles during water treatment is governed by their sizes, surface properties, solution chemistry, and number concentrations [45, 54-56]. Nanoparticles can adversely affect the performance of advanced wastewater and water treatment units across New Jersey that use techniques such as ultra-filtration (UF) and reverse-osmosis (RO) through membrane fouling [25, 26] and can potentially produce adverse impact on microbes in the activated sludge related processes [27, 28]. Thus, the removal of nanoparticles has to be done at a pre-treatment process such as coagulation and sedimentation to protect both the subsequent treatment processes and public health. Also, free nanoparticles in the environment have a natural tendency to agglomerate to form bigger particles and thus leave the nano-regime [2, 29, 32, 45]. Making use of this natural aggregating ability of nanoparticles, it should therefore be possible as well as advantageous to attempt to remove nanoparticles during coagulation and flocculation process.

Only a few studies regarding the removal of nanoparticles using coagulation/sedimentation are available in the literature and will be discussed below. None of the understanding regarding the impact of polymeric/ surfactant surface modification and interaction with NOM on the removal of engineered nanoparticles via coagulation/flocculation is available. Thus, the understanding of factors affecting the removal of nanoparticles from water is still very limited. Fate of nanoparticles in water can be inferred based on decades of research on collides in water [42, 57]. Here is a review of some factors, which effect the removal of micron-sized colloidal particles by coagulation/flocculation because they are likely to influence the removal of engineered nanoparticles as well.

2.3 Factors Affecting the Removal of Colloids (Nanoparticles) by Coagulation / Flocculation

Colloidal (both nano- and micro-) particles can remain dispersed in the aqueous phase for very long time if their colloidal interactions are not favorable for aggregation, which consequentially results in removal of particles from aqueous phase through sedimentation [58-60]. Major colloidal forces affecting the colloidal stability of particles involve Electrical Double Layer (EDL) repulsion/attraction, Van der Waals attraction, and steric repulsion [58, 60, 61]. For particles with charges on the surface, EDL repulsion/attraction can play an important role. If two particles with opposite charges collide to one another, EDL attraction can promote aggregation [58]. In contrast, if two particles of the same charges collide to one another, EDL repulsion prohibits aggregation [58]. Van der Waals attraction is mostly attractive and promotes aggregation [58]. If the colloidal particles are coated with macromolecules such as polymers, polyelectrolytes, or natural

macromolecules (E.g., natural organic matter (NOM)), steric repulsion can prohibit aggregation and enhance colloidal stability of particles in aqueous phase [46, 61, 62].

Unless nanoparticles are aggregated by some means, there average size falls well below the practical lower limit (about 1000 nm) and therefore undergo very slow sedimentation [3, 63]. In fact, this sedimentation in such cases is so slow that the effect can be easily overcome by mixing tendencies induced in solution by diffusion and convection [3]. Coagulation/flocculation can destabilize colloidal particles by four mechanisms: double-layer compression, charge neutralization, enmeshment in a precipitate, and inter-particle bridging [64]. Different coagulants provide different degree of destabilization for the removal of colloidal particles. Economically and environmentally, effective coagulation should require the minimum use of coagulants and generate the smallest amount of sludge possible [65]. Coagulant doses, besides controlling the amount of sludge generated, influence the major colloidal removal mechanisms. At low coagulant doses, the major destabilization mechanism is charge neutralization through the adsorption of dissolved metal species or metal hydroxide precipitates. In contrast, at high coagulant doses, sweep coagulation (also called sweep-floc theory, states that coagulants added exceed the solubility product and form a precipitate, which settles by gravity in a reasonable time sweeping down everything in its path including colloidal particles) typically dominates the particle removal [64].

Several physicochemical parameters including coagulant type, pH, type and concentration of target colloidal particles (initial nanoparticle concentration (INC)), and agitation rate (AR) determine the coagulant doses (CD) required for the removal of colloidal particles. For example, according to the double layer compression mechanism,

the higher the valence of the counter-ion, the greater the coagulant's destabilizing effect will be and the lower the dose required [64].

According to the charge neutralization mechanism, pH plays an important role on the removal of colloids by coagulation because pH determines whether the interaction between colloids and floc formed will be attractive or repulsive [64]. In addition, pH also affects the rate at which and the amount of floc formed, which directly affects the removal of colloids by enmeshment in a precipitate [60].

Hydrodynamic diameter and surface charge are very important properties that influence the stability of nanoparticle dispersions. Nanoparticles in aqueous solution undergo surface ionization followed by adsorption by anions and cations resulting in surface charge and an electric potential that will be developed between surface of the particle and surrounding dispersion medium [66-68]. Zeta potential is a good representation of surface charge. Isoelectric point (IEP) is a point where zeta potential (ZP) equals zero [69, 70], and the corresponding pH is denoted by pH_{IEP}. Surface charge of TiO_2 nanoparticles is a function of solution pH [66]. Changes in values of solution pH bring about major changes in surface charge.

Condition 1. $pH = pH_{IEP} =>$ zero surface charge and zero zeta potential [66-68, 71].

Condition 2. $pH < pH_{IEP} =>$ positive surface charge and positive zeta potential [66-68, 71].

Condition 3. $pH > pH_{IEP} =>$ negative surface charge and negative zeta potential [66-68, 71].

As discussed above, the average diameter of dispersion represented by dispersion hydrodynamic diameter, is one of the important factors that influence the settling of nanoparticles and other colloids. Higher diameter particles undergo faster settling. For effective coagulation, it is important that big flocs are formed at very quick rate immediately following the addition of coagulant. Average hydrodynamic diameter (AHD) is dependent of rate of agglomeration of nanoparticles in solution. Classical Derjaguin-Landau-Verwey-Overbeek (DLVO) theory estimates the aggregation of nanoparticles by the sum of attractive forces (Van der Waals forces) and repulsive forces (electrostatic, interactions between nanoparticles surrounded by electrical double layer) [66, 72, 73]. Increase in zeta potential can enhance the electrostatic repulsive force, suppress the agglomeration, and in turn reduce the hydrodynamic size of dispersion [66, 72, 73]. Suttiponparnit et. al., [66] studied the effect of solution ionic strength and pH on zeta potential and hydrodynamic diameter of TiO_2 dispersion. Findings of their study are summarized in Figure 2.2 below [66]. An electrolyte such as NaCl that is inert to TiO_2 dispersion (no specific adsorption of Na^+ or Cl^- by TiO_2 nanoparticles) has no effect on IEP irrespective of the ionic strength (IS) of the solution obtained by varying NaCl concentration [66, 69, 74]. However at any pH value different from pH_{IEP}, increase in IS compresses the electrical double layer causing reduction in zeta potential of dispersion according to reported values [31, 34, 66, 75] as well as predictions of classical colloidal theory [66, 76]. Therefore it is essential to find out a value of pH or a range at which particles in suspension will carry favorable surface charge (varies as per situation, type of coagulant, and other factors, but a minor negative charge is preferred in most cases)

leading to aggregation between particles and with coagulant. From Figure 2.2, it is likely that a pH range of 6-8 will be useful to optimize removal of TiO_2 nanoparticles.
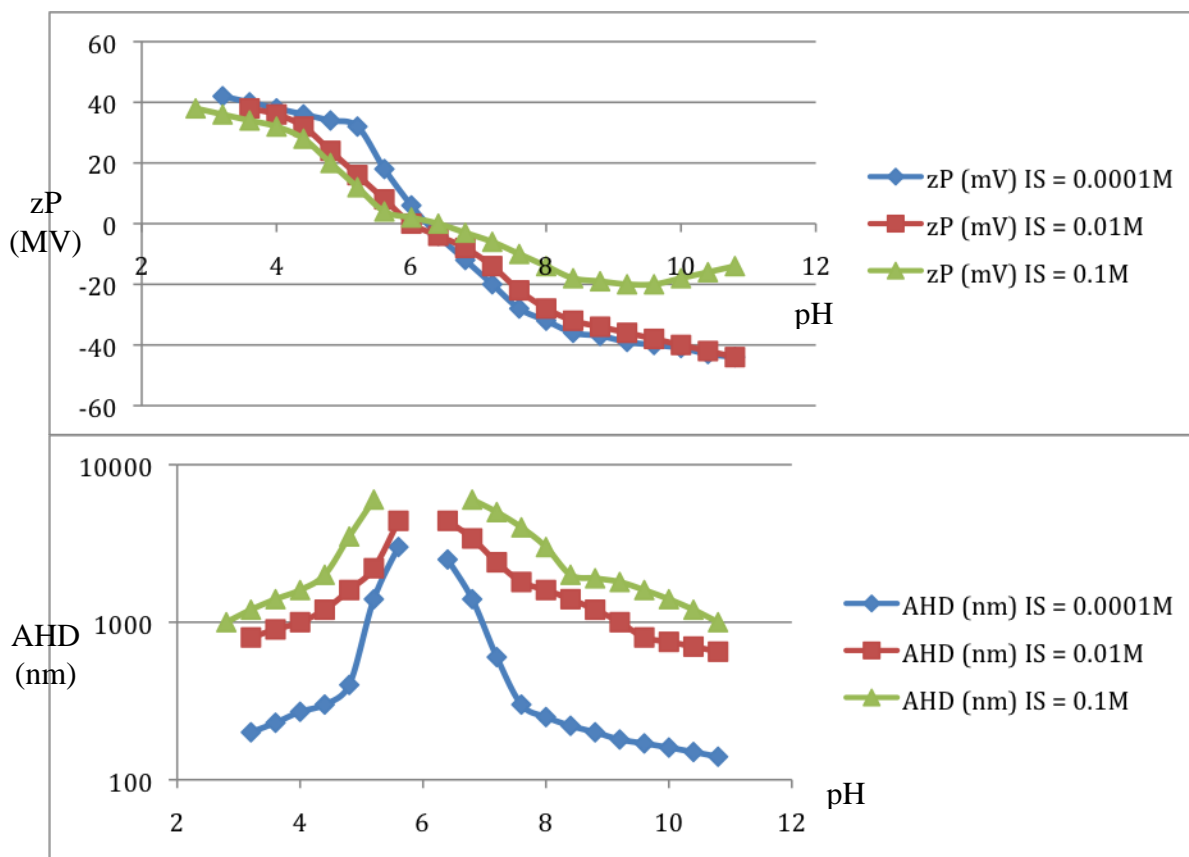
Figure 2.2   Influence of solution ionic strength (IS) and pH on TiO2 dispersion properties: a. zeta potential, b. hydrodynamic diameter ([66].

The agitation speed (rate of slow mixing) also substantially influences the removal of colloids because it controls the collision rate between colloids and floc. In addition, the agitation rate affects the charge stabilization mechanism. A recent study [77] reported that the short-lived, positively charged, poorly soluble aluminum hydroxide sols formed during the first seconds after coagulant addition play the most important role on particle destabilization by neutralizing negative charge of the particles. Aged aluminum hydroxide flocs (aged for few minutes) are less effective for removing colloidal particles

or reducing their surface charge. These results emphasize the importance of mixing and assuring rapid particle-sol interactions when destabilization is the primary goal of the coagulation process [77].

The presence of environmental constitutes such as salt concentration or NOM may also affect the nanoparticle removal efficiency. Xie et al. [78] found that NOM caused disaggregation of nanoparticles (C_{60}) leading to significant changes in particle size and morphology. Westerhoff et al. [42] carried out series of laboratory experiments to study the impact of salt concentration and salt type on removal efficiency of nanoparticles using coagulation (jar test) followed by filtration with 0.45 μm filter membrane, zeta potential, and aggregate size. In all their experiments, highest % removal of engineered nanoparticles of any type was 95% [42]. In general, an increase in salt concentration in the solution increases the average diameter of aggregates formed for all types of nanoparticles. It also decreases the zeta potential of the particles. A summary of the results of their experiments is presented in Table 2.1.

Table 2.1 Summary of Effect of Salt Type and Salt Concentration on Removal Efficiency (Using Coagulation, Flocculation, and Filtration), Zeta Potential, and Average Aggregate Particle Size [42]

Type of nanoparticle	Salt used	Salt concentration (mM)	Removal efficiency (%)	Zeta potential (mV)	Average diameter of aggregates by DLS (nm)
TiO$_2$	----	0	90	-22	550
	KCl	20	N/A	-12	800+
	KCl	100	N/A	-4	1000+
	MgCl$_2$	100	95	+2	1200+
Silica	----	0	40 (no filtration)[a]	-25	700
	KCl	40	N/A	-25	700
	KCl	100	N/A	-10	1000+
	MgCl$_2$	100	50 (no filtration)[a]	-6	1300+
Fullerene (nC$_{60}$)	----	0	0	N/A	N/A
	NaCl	10	40		
	NaCl	100	95		
CdTe quantum dot	----	0	0	-32	8
	KCl	100	N/A	-20	8
	CaCl$_2$	0.5	N/A	-26	800+
	MgCl$_2$	1	N/A	-24	3000+
ZnO	----	0	5 (no filtration)[a]	24	300
	KCl	20	N/A	14	800+
	KCl	100	N/A	8	900+
	MgCl$_2$	100	30 (no filtration)[a]	8	1100+

[a] – Removal efficiency after sedimentation only. Filtration would have improved the efficiency.

N/A – Not available

Settling of micron or larger size particles can usually be explained using the DLVO theory. The DLVO theory combines the double-layer repulsion with van der Walls attraction [35, 79, 80]. However, the traditional DLVO theory was derived using the Derjaguin approximation that makes two important assumptions: 1) characteristic thickness of the EDL is smaller than radius of curvature of the particle, and 2) the distance between particle and the surface must be less than the size of the particle [3, 35, 79, 80]. These assumptions although valid for most colloidal suspensions, do not hold for nanoparticles due to their very small size. Therefore the traditional DLVO theory may not completely explain settling of nanoparticle solution until and unless aggregates of significantly higher size (roughly 5000 nm or higher) are formed. However, the extent to which nanoparticles behave like conventional suspended particles is high [2, 13, 18, 38, 41, 66, 81]. Hence their behavior in water may largely be explained using classic flocculation models, such as Smoluchowski [82] rectilinear collision models for spheres [3, 83].

The rate of nanoparticle attachment r_{ij} can be described as follows:

$$r_{ij} = \alpha \beta_{ij} n_i n_j$$

Where,

r_{ij} = Rate of attachment between i and j nanoparticles (collisions/L^3.T);

α = Collision efficiency factor (attachments per collision, range 0 – 1);

β_{ij} = Overall collision frequency between i and j particle;

n_i = Concentration of i nanoparticles, (number of particles/L^3);

n_j = Concentration of j nanoparticles, (number of particles/L^3);

Brownian motion (microscale or perikinetic flocculation), fluid shear due to gentle mixing of water (macroscale or orthokinetic flocculation), and differential sedimentation are the three mechanisms by which collisions between suspended nanoparticles in water can occur [33, 84].

The collision frequency function β_{ij} is therefore contributed by all the flocculation mechanisms [3, 33, 85]:

$$\beta_{ij} = \beta_M + \beta_\mu + \beta_{DS}$$

$$\beta_M = \frac{1}{6} G(d_i + d_j)^3$$

$$\beta_\mu = \frac{2kT}{3\mu}(\frac{1}{d_i} + \frac{1}{d_j})(d_i + d_j)$$

$$\beta_{DS} = \frac{\pi(\rho_p - \rho_w)g}{72\mu}(d_i + d_j)2\left|d_i - d_j\right|$$

Where,

β_M = Macroscale collision frequency;

β_μ = Microscale collision frequency;

β_{DS} = Differential settling collision frequency;

$G = \sqrt{\varepsilon / \upsilon}$ = Average velocity gradient;

ε = Local rate of energy dissipation, L^2/T^3;

υ = Kinematic viscosity, L^2/T

d_i = Particle diameter of i nanoparticles;

d_j = Particle diameter of j nanoparticles;

k = Boltzmann's constant, (1.3807e23 J/K);

T = Absolute temperature, K;

μ = Absolute viscosity of water at temperature T, Ns/m^2

ρp = Density of nanoparticles, M/L^3;

ρw = Density of water, M/L^3;

Figure 2.3 and Table 2.2 briefly explain mechanisms of aggregation of nanoparticles.
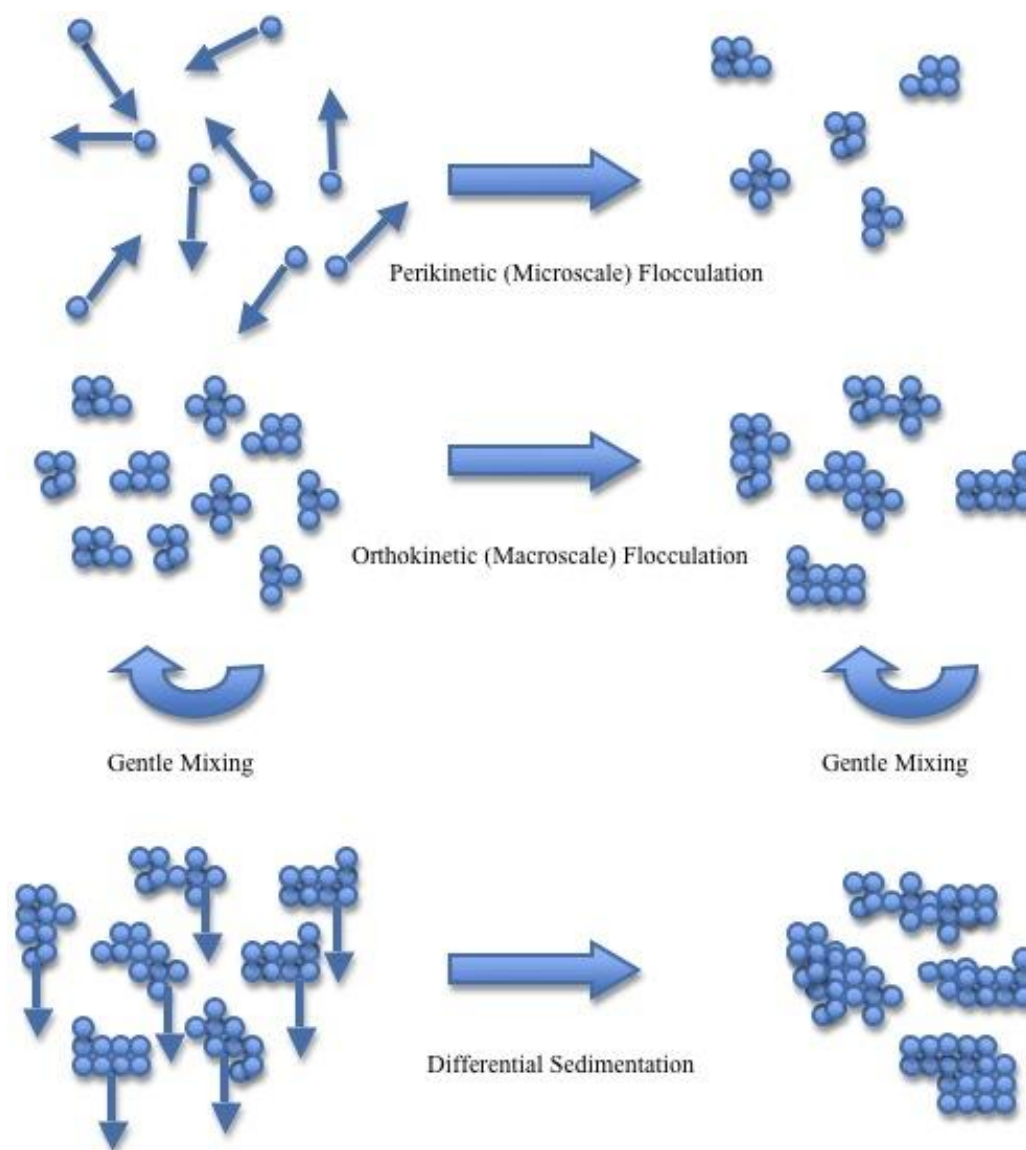
Figure 2.3 Aggregation mechanisms of nanoparticles in water [3].

Table 2.2 Description of Aggregation Mechanisms of Nanoparticles in Water [3]

Mechanism	Average particle size	Description
Perikinetic (Microscale) Flocculation	1 nm – 100 nm	Brownian motion leading to random collisions of nanoparticles between themselves and with fluid molecules.
Orthokinetic (Macroscale) Flocculation	> 1 μm	Gentle mixing causes velocity gradient, which in tern leads to more and more collisions and aggregation of nanoparticles. At the same time, these micro-flocs break down due to uneven shearing forces. After a period of continued mixing, the rate of floc formation and break up becomes equal causing steady-state aggregate size distribution.
Differential Sedimentation	> 500 μm	Now the nanoparticles' aggregates are large enough to settle under gravitational forces. Different aggregates reach different settling velocities respective to their size. This causes further collisions and aggregation resulting in differential sedimentation.

The temperature of water can have a significant effect on most of the treatment processes, including mainly – coagulation and flocculation [60, 86, 87]. In general, as the temperature decreases so do the rate of floc formation and removal efficiency [60]. This effect is highest in dilute solutions. The solubility of many coagulants, rate of hydrolysis and metal hydroxide precipitation, and the rate of hydrolysis product dissolution or re-equilibration all decrease with decreasing temperature [60]. Also at lower temperatures, poly-nuclear species tend to persist for a longer period of time [60]. In a turbulent flow field, temperature affects the distribution of kinetic energy over the scale of fluid motion [86, 87]. Finally, temperature also affects the size distribution of flocs [88, 89]. It is believed that the effect of temperature on the performance of coagulation and flocculation is related more to physical factors rather than chemical kinetic factors [88, 89]. Despite

all this, temperature adjustment is not usually practiced at water treatment plants; mainly because it is energy consuming and costly to increase the temperature of water flowing in at a high rate (usually 5 MGD or more) and even more so to maintain the high temperature. Effect of temperature on removal efficiency is not studied in this research.

2.4   Removal of Nanoparticles from Water by Coagulation and Flocculation

Analogies between natural and engineered nanoparticles provide good understanding that the stability of engineered nanoparticles in natural waters as well as treatment processes is a function of their size, number concentration, surface properties including surface charge, concentration, and ability to interact with other constituents in water through electrostatic double layer (EDL) compression due to ionic strength, ion complexation, or complexation by NOM [42]. Table 2.3 lists the characteristic properties (typical size, nature of net surface charge at neutral pH, iso-electric point (IEP), Hamaker constants, and typical applications) of some popularly used nanoparticles. These properties are very important to predict the stability and behavior of nanoparticles in suspension with and without presence of external agents such as: coagulants and NOM. Nanoparticles exhibiting similar or close to similar properties are likely to respond to similar treatment methods. Although in this research, conventional coagulation and flocculation and magnetic seeding aggregation are studied only on TiO_2 nanoparticles only; results of this research may be applied to many other types of nanoparticles, mainly: metal, metal oxide nanoparticles, and multi-walled nanotubes (MWNTs). Some nanoparticles such as silica and quantum dots may not return same degree of success for the methods investigated in this research due to differences in IEP and other properties.

Metal oxide nanoparticles in particular have direct analogies to natural nanoparticles and colloids [42] including the natural tendency to aggregate in solution [21]. Many nanoparticles, especially reactive nanoscale iron particles (RNIP) having strong magnetic properties can form aggregates in as little as 10 minutes (60 mg/L RNIP, average radius = 20 nm) [32]. It is also observed that nanoparticles settle more slowly in aqueous solution than bigger particles of the same material [3].

Table 2.3 Some Popular Nanoparticles and Their Key Properties [42, 90]

Type of nanoparticles	Typical size (nm)	Net surface charge at pH = 7	IEP (pH$_{zpc}$)	Hamaker Constant		Typical Applications	Refns
				A$_{123}$ (10^{-20} J)	A$_{121}$ (10^{-20} J)		
Aluminum oxide (Al$_2$O$_3$)	60 - 158 nm	Negative, positive, or neutral	5.3-7.9	1.9	5.3	Dentistry electrical insulation filters	[91-95]
MWNTs	d = 9 -70 nm L = 1-2 µm	Negative	4.7-6.4	N/A	1-20	Batteries, electronics, orthopedic, implants, plastics, sensors	[96-98]
SWNTs	d = 0.7-1.1 nm L = 80-200 nm	Negative	2.2	N/A	1-20		[97, 99, 100]
fullerenes (C$_{60}$)	168 - 725 nm	Negative	0.45-2.3	N/A	0.67	Cosmetics, tires, batteries tennis rackets	[100-102, 103{Chen, 2006 #300]}
Gold (Au)	2 - 6 nm	Usually negative	4.9-5.5	3.2	27	Catalysts electronics medical applications	[97, 104, 105]
Quantum dots	45 - 100 nm	Usually negative	< 2	N/A	N/A	Medical imaging photovoltaics security inks solar cells therapeutics	[97, 106, 107]
Iron oxide (Fe$_2$O$_3$)	10 nm – 100+ nm	Negative	6-8	2.1	5.4		[108, 109]
Zerovalent iron (nZVI)	106 nm	Positive, negative, or neutral	8.1			Water, sediment, soil remediation	[97, 110]

Table 2.3 Some Popular Nanoparticles and Their Key Properties [42, 90] (Continued)

				A_{123}	A_{121}		
Silica (SiO$_2$)	57 nm	Negative	2-2.1	0.77	0.85	Electrical insulators electronics sensors thin films	[95, 100, 111, 112]
Titanium dioxide (TiO$_2$)	4 - 230 nm	Negative	3.6-6.7	1.4	6	Coatings cosmetics paints solar cells sunscreens	[95, 97, 100, 113, 114]
Titanium dioxide - rutile (TiO$_2$)				4.5			[94]
Titanium dioxide - anatase (TiO$_2$)					0.35		[115]
Zinc oxide (ZnO)	10 nm – 100+ nm	Positive, negative, or neutral		0.58	1.89	N/A	[116]

Typical sizes refer only to corresponding references listed. Full range of sizes of these nanoparticles may contain sizes other than reported in Table 2.3

N/A – Not reported in the reference used.

pH_{ZEP} – pH corresponding to zero point charge.

A_{123} - Hamaker constants for unretarded interaction between a nanoparticle and silica collector in water.

A_{121} - Hamaker constant for unretarded interaction between nanoparticles in water.

Although the removal of micron-sized colloidal particles by coagulation/flocculation is relatively well understood, the study on removal of nanoparticles is very limited. Very few studies on the removal of nanoparticles using coagulation are recently published [26, 45] and neither of them provides the thorough understanding for the optimization of coagulation/flocculation for maximizing removal efficiency. Zhang et al. [45] studied the removal of metal nanoparticles using alum coagulation and found that at an alum dosage of 20 mg/L, 20-80% of nanoparticles were removed. Zhang et al. [45] concluded that the natural aggregating tendency of nanoparticles and the presence of electrolytes in water play a critical role in their removal during the treatment process. Chang et al. [26, 41] studied the removal of micro- and nanoparticles in wastewater from Hsinchu Science-Based Industrial Park (HSIP) using polyaluminum chloride (PAC) as coagulants followed by sedimentation. This coagulation/sedimentation process removed 88-94% turbidity (suspended solids and micro-sized particles) from the wastewater influence. However, this pre-treated wastewater still had nanoparticles with the high potential to foul the UF and RO membranes. Prolonged PAC contact did improve removal efficiency, but it made the process time consuming and impractical [41]. Chang et al. [26] suggested an alternative for the pre-treatment using 24-h thermal treatment at 65 ℃ to induce nanoparticle aggregation. This thermal treatment removed up to 98.5% turbidity. However, the issue regarding the cost associated with the intensive energy required and relatively long treatment time may make this optional pre-treatment impractical. Table 2.4 summarizes the works by Zhang et al. [45] and Chang et al. [26, 41].

Table 2.4 Summary of Recent Studies on Removal of Nanoparticles Using Coagulation

Study	Findings
Zhang et al. [45] – The removal of metal nanoparticles using alum coagulation	At alum dosage of 20 mg/L, 20-80% of nanoparticles were removed. The natural aggregating tendency of nanoparticles and the presence of electrolytes in water play a critical role in their removal during the treatment process.
Chang et al. [26] – The removal of micro- and nanoparticles in wastewater from Hsinchu Science-Based Industrial Park (HSIP) using polyaluminum chloride (PACI) as coagulants followed by sedimentation.	The pre-treated wastewater still had nanoparticles with the high potential to foul the UF and RO membranes.

It should be noted that none of the understanding regarding the impact interaction with NOM on the removal of engineered nanoparticles via coagulation/flocculation is available. Thus, the understanding of factors affecting the removal of nanoparticles is still very limited. Also, bare nanoparticles, once released to the surface or groundwater, can interact with NOM. The adsorbed synthetic or natural macromolecules or surfactants can substantially decrease the removal of nanoparticles by coagulation/flocculation because of the additional electrosteric stabilization provided by the macromolecules [46]. However, the understanding of the effect of surface modification of nanoparticles on the removal efficiency using coagulation/flocculation is not available.

2.5 Removal of Nanoparticles from Water by Magnetic Seeding Aggregation (MSA)

Another approach for the removal of nanoparticles from water is magnetic seeding aggregation. Magnetic seeding is a particle separation technique aimed primarily at separating nonmagnetic or weakly magnetic particles from suspension [117]. The concept involves seeding of strongly magnetic particles, such as magnetite, into a suspension of weakly magnetic target particles of interest. The seeded particles then combine with target particles and the resulting seed-target particle agglomerates can now be removed by sedimentation or filtration in the presence of an applied magnetic field [117]. The key to successfully apply magnetic seeding is to maximize the amount of target particles removed in the least possible time. Although the feasibility and efficacy of magnetic seeding as a particle separation technique has been known for a few decades, its mechanism is not very well understood [117]. Magnetic seeding has been successfully applied in a variety of environmental, biomedical, and chemical application [117-127]. The use of magnetic nanoparticles (magnetites) is even more wide spread with Environmental Protection Agency's (EPA) National Center for Environmental Research (NCER) is funding a variety research institutes and small businesses to develop innovative techniques involving application of magnetites and other nanoparticles for a variety of environmental problems such as: remediation [128], detection of microorganisms [129], and many other. Although, coagulation has been the focus of many experimental and theoretical studies of magnetic seeding, applying this technique to water treatment can be a little tricky as several parameters influence its overall effectiveness [127, 130-133].

Tsouris and Scott [133] studied the flocculation of paramagnetic particles under the influence of a strong magnetic field. They reported that the effect of such important process parameters as particle size, susceptibility of particles, strength of magnetic field, and zeta potential on flocculation rate, as well as on the initial size distribution of the particles is worth considering [133]. Chin et al. [44] proposed a technique for the rapid removal of silica nanoparticles in chemical mechanical polishing (CMP) wastewater from semiconductor industry using magnetite nanoparticles in magnetic seeding aggregation. This approach requires pH adjustment to around pH 6 where silica nanoparticles and magnetite nanoparticles are highly oppositely charged to induce aggregation between silica nanoparticles and magnetite nanoparticles. The applied magnetic field can be used to separate silica nanoparticles, which attach to magnetite nanoparticles from water. This method is more rapid and less energy intensive than the thermal treatment mentioned prior [26]. However, this approach can be material intensive because the method to reuse the magnetite nanoparticles is still not available [44]. It is unlikely that magnetite nanoparticles can be reused because the aggregation happens by EDL attraction coupled with van der Waals attraction under primary minimum energy well. Thus, the aggregation is predicted to be irreversible [58].

2.6 Proposed Approach for the Removal of Nanoparticles Using Recoverable / Reusable Surfactant-Modified Magnetic Nanoparticles

Coagulation and flocculation requires the use of coagulants and generates sludge, which needs to be properly managed as solid waste or hazardous waste afterwards [60, 84]. Inherent disadvantage with coagulation and flocculation or any other chemical treatment process is that most of them are additive processes [134]. These chemicals are not only

expensive, but in most cases impractical or impossible to reuse [134]. Therefore, the major cost of the coagulation/flocculation is associated with the cost of coagulants, sludge treatment, and pre-conditioning of water to be treated. The magnetic seeding aggregation technique studied by Chin et al. [44] has potential to be the better approach for the removal of engineered nanoparticles if the magnetite nanoparticles could be reused.

The use of cationic surfactants (such as cetyltrimethylammonium bromide (CTAB)) for the modification of magnetite nanoparticles might offer a promising opportunity for the improvement of magnetic seeding aggregation technique. At natural pH range, magnetite nanoparticles are negatively charged. Cationic surfactants can adsorb onto the surface of magnetite nanoparticles and impart the absolute positive charge onto the surface of magnetite nanoparticles (Figure 2.4). These surfactant-modified magnetite nanoparticles can be used to remove TiO_2 engineered nanoparticles that are normally negatively charged in the natural pH range. Negatively charged engineered nanoparticles in water will attach to the positively charged surfactant-modified magnetite nanoparticles. Then, applied magnetic field can be used to remove surfactant-modified magnetite nanoparticles together with attached engineered nanoparticles out of water. Adding an organic solvent such as cyclohexane to concentrated solution of surfactant-modified magnetite nanoparticles together with attached engineered nanoparticles can achieve the reuse of magnetite nanoparticles. The cationic surfactants will be desorbed from the surface of magnetite nanoparticles by the formation of reverse micelle or partitioning into the organic solvent [135] because CTAB has a higher affinity for organic solvent than magnetites. Then, the negatively charged

nanoparticles will detach from the surface of bare, negatively charged magnetite nanoparticles due to EDL repulsion (Figure 2.4).
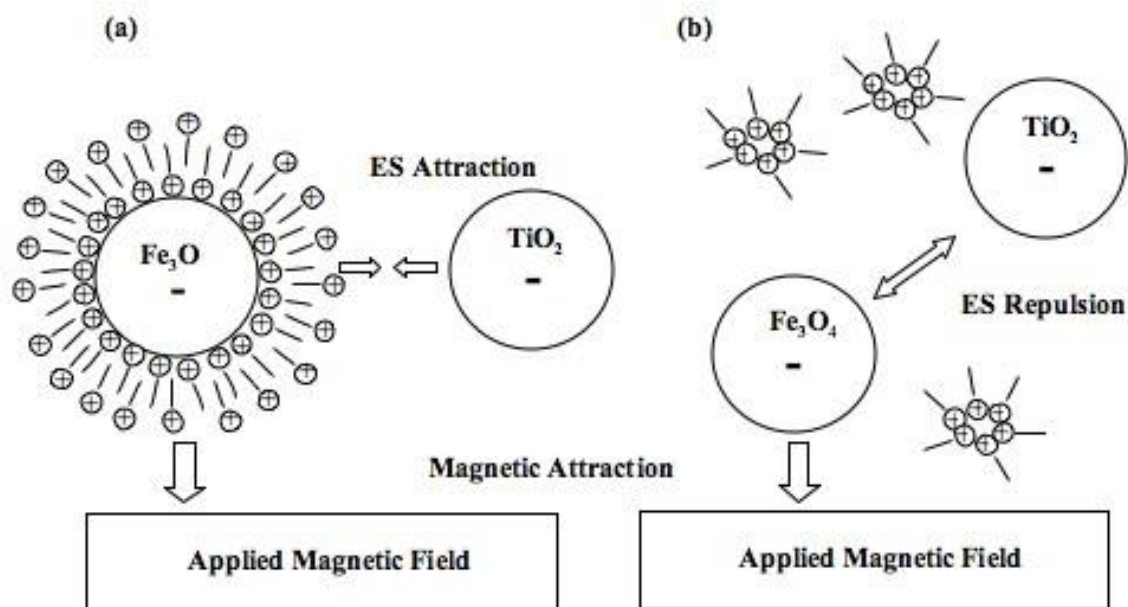
Figure 2.4 (a) The conceptual model for the removal of engineered nanoparticles (TiO_2 in this case) from water using CTAB-modified magnetite nanoparticles and applied magnetic field. (b) The conceptual model for the reuse/recovering of magnetite nanoparticles and separation of engineered nanoparticles using organic solvent and applied magnetic field. The desorption of CTAB from magnetite nanoparticles in (b) is due to reverse micelle formation/and partitioning into the organic solvent.

Again, magnetite nanoparticles can be recovered from the organic solvents using applied magnetic field. Then, these bare magnetite nanoparticles can be re-modified by cationic surfactants and reused for the removal of engineered nanoparticles.

CHAPTER 3

MATERIALS, METHODS AND OPTIMIZATION MODEL

3.1 Materials

3.1.1 TiO$_2$ Engineered Nanoparticles

Titanium oxide (TiO$_2$, purity: 99%, appearance: transparent, white liquid) nanoparticles were purchased from Nanostructured and Amorphous Materials Inc (Los Alamos, NM). The average size of TiO$_2$ nanoparticles is 5 nm and pH between 6 and 8.

Characterization of nanoparticles is necessary to establish the understanding and control of removal efficiency using each of the methods to be studied. A variety of different techniques, drawn mainly from material science, are available for nanoparticle characterization. (UV-Vis) spectroscopy is used to quantify nanoparticles in this research. A variety of different types of nanoparticles, especially TiO$_2$, are commonly quantified using UV-Vis spectroscopy [24, 32, 36, 39, 107, 113, 136-145]. UV-Vis spectroscopy is the method of choice for quantifying TiO$_2$ nanoparticles in this research. TiO$_2$ does not always have a specific absorbance. Therefore as suggested in most of the published literature, a range of wavelengths between 200 and 300 nm (using quartz cuvette) was tested. In most cases, a peak was observed between 250 and 270 nm. In cases where there was no distinct peak, a wavelength of high absorbance (high sensitivity) and high signal to noise ratio (>4) was selected. For quantification of TiO$_2$ nanoparticles, 260 nm was the most commonly used wavelength in this research. Humic acid was used to study the effect of NOM on removal of TiO$_2$ nanoparticles. Absorbance of NOM (humic acid) was recorded at the selected wavelength to use as background for accurate quantification of

TiO$_2$ nanoparticles in presence of NOM. However NOM values recorded post-sedimentation when coagulant dose of 20 mg/L or higher was used were <0.05 mg/L in most cases indicating that there will be little or no effect on nanoparticle quantification. Also humic acid does not produce a distinct peak at the selected wavelength of 260 nm for UV-Vis analysis.

3.1.2 Coagulants

The coagulants used in this study are FeCl$_3$ and Al$_2$(SO4)$_3$. The stock solutions of FeCl$_3$ and Al$_2$(SO4)$_3$ were prepared from ACS grade Ferric chloride (anhydrous) and Aluminum sulfate octadecahydrate, respectively, in DI water at the concentration of 3 g/L. To prevent aging effects, fresh stock solutions were prepared for each sequence of experiments and stored in a refrigerator at 4°C.

3.1.3 Surfactant-modified Magnetite Nanoparticles

Magnetite nanoparticles (Fe3O4, 98%+, purity: 98+%, specific surface area: >=40 m2/g, color: black, morphology: spherical, true density: 4.8-5.1 g/cm3, typical magnetic properties: saturation magnetization Ms: 63 emu/g, remanent magnetization Mr: 0.3 emu/g, coercivity: 17 Oe) were purchased from Nanostructured and Amorphous Materials Inc (Los Alamos, NM). The average diameter of magnetite nanoparticles is 28 nm (range 20-30 nm).

Aqueous dispersions (3g/L) of bare magnetite nanoparticles was prepared in a 1 mM NaHCO3 solution (pH = 7.4). Cetyltrimethylammonium bromide (CTAB) is very frequently used as cationic surfactant capable of being extracted using an organic solvent (by reverse micelle formation) in many biomedical applications.

Dodecyltrimethylammonium bromide (DTAB) is the other popular surfactant. The difference between CTAB, DTAB and other cationic surfactant is the length of carbon backbone, which does not affect the removal, but might affect the regeneration. The need for this study is only the cationic group for electrostatic attraction between surface modified magnetite and target nanoparticles. In this research, CTAB is used to study its effectiveness as the cationic surfactant for the modification of magnetite nanoparticles. The surface modification was conducted by physisorption of various doses (0.05 to 2g/L) of CTAB to 1 g/L magnetite nanoparticles. Two-day equilibration was allowed for the modification. The adsorbed mass of CTAB on magnetite nanoparticles was determined using TOC. The excess (un-adsorbed) CTAB was not removed from the dispersion and CTAB modified magnetite with the excess CTAB were used in the study on removal of nanoparticles from water. Two criteria that govern the selection of optimum CTAB dose are charge conversion, and ability to desorb in organic solvents. The optimum dose must be high enough to convert negatively charged magnetite nanoparticles to positively charged. At the same time, the dose must also allow desorption of CTAB, when CTAB-modified magnetite nanoparticles are soaked with organic solvents. Once the optimization of CTAB-modified magnetite nanoparticles is done, the study of its performance on removing engineered nanoparticles from water can be conducted. The optimum dose of CTAB for the modification was determined to be 50 mg/L for 1 g/L magnetite. Post-treatment magnetites were quantified using UV-Vis spectroscopy at 450 nm using plastic cuvette. CTAB + cyclohexane absorbance was measured at same wavelength and was used as background to correct the concentration of magnetite nanoparticles.

3.2   Methods

3.2.1 Sample Preparation

Aqueous dispersion of bare TiO_2 nanoparticles were prepared by mixing powder of nanoparticles in DI water at a concentration of 25 g/L. This solution was sonicated for 30 minutes using ultrasonic probe to break possible aggregates formed.

To evaluate the effect of natural organic matters on the removal efficiency, humic acid was used to modify nanoparticles at 50 mg/L humic acid and 3 g/L bare nanoparticles. Total Organic Carbon (TOC) analyzer (UV/Persulphate oxidation with a Phoenix 8000 TOC analyzer, Tekmar Dohrmann, Cincinnati, OH using Standard Methods 5310) was used to quantify humic acid left in the solution post sedimentation. In addition, one set of jar tests were conducted on solution prepared in a sample from Passaic river collected near Harrison, NJ, instead of the DI water used for all other samples. The TOC of this sample was found to be 3.9 mg/L.

The stock dispersions of bare and surface modified nanoparticles was diluted to the particle concentration of interest in the synthetic solution for the coagulation and magnetic seeding aggregation studies.

3.2.2 Coagulation

Coagulation studies were conducted using Phipps and Bird Inc., jar tester with 6 glass beakers. The coagulation studies in this research were designed to evaluate the effect of coagulant dose, solution chemistry (pH), and settling time on the removal of engineered nanoparticles. Five different pH values including pH 4, 6, 7, 8, and 9 were

evaluated. The ionic strength of sample was adjusted to 50 mM Na^+. The pH and ionic strength of synthetic solution containing engineered nanoparticles were adjusted before coagulation. The rapid mixing at 300 rpm was maintained for 1 minute followed by slow mixing (agitation) of 50 rpm for 8.5 minute for all jar tests except while studying the effect of agitation rate. To study the effect of change in agitation rate (slow mixing), 0 (only rapid mixing), 20, 50, and 100 rpm rates were used. The doses of coagulants (same for both alum and ferric chloride) used in this study are 0 (as a control), 20, 50, 200, 500, and 750 mg/L, while the doses of engineered nanoparticles in sample were 25, 50 and 100 mg/L. The effect of settling time on the removal efficiency was evaluated by comparing the engineered nanoparticles removed form the water at different settling time 10, 30, and 60 minutes. Table 3.1 lists the different parameters considered with the range of their variation. The coagulation studies were conducted for bare, and humic-modified nanoparticles. The jar tests were done in duplicate for each condition. All graphs are generated using values of percent removal of nanoparticles averaged over at least 12 jar tests. At least 72 jar tests were done to cover variation of coagulant dose, settling time, and initial nanoparticle concentration for each value of pH and agitation rate. For example at pH = 4 (agitation rate = 50 rpm), 6 values of coagulant dose (0, 20, 50, 200, 500, and 750 mg/L), multiplied by 3 values of settling time (10, 30, and 60 min), multiplied by 3 values of initial nanoparticle concentration (25, 50, and 100 mg/L), multiplied by 2 for duplication gives 108 jar tests. With 5 values of pH (4, 6, 7, 8, and 9) and 4 values of agitation rate (0, 20, 50, and 100), 972 jar tests were performed to understand the effect of design parameters on removal efficiency using conventional

coagulation alone. Most of this set up was repeated for magnetic seeding aggregation studies.

Table 3.1 Design Parameters and Their Variation

Parameter	Variation
Initial nanoparticle concentration (INC)	25, 50, 100 (all in mg/L)
pH	4, 6, 7, 8, and 9
Agitation rate (slow mixing) (AR)	0, 20, 50, and 100, (all in rpm)
Coagulant dosage (CD)	0 (as control), 20, 50, 200, 500, and 750 (all in mg/L)
Settling time (ST)	10, 30, and 60 (all in minutes)
Humic acid	50 mg/L in 3 g/L nanoparticles

3.2.3 Magnetite Nanoparticles Coated with Cationic Surfactant (CTAB)

The removal efficiency of nanoparticles by cationic surfactant-modified magnetite nanoparticles is studied by rapid mixing different doses of modified magnetite nanoparticles (1, 5, 10, 25, and 100 mg/L) with water contaminated with TiO_2 engineered nanoparticles for 1 min, followed by slow mixing (50 rpm for all jar tests except when studying the effect of agitation rate) for 8.5 minutes. Then, the external magnetic field was applied to remove magnetite nanoparticles together with adsorbed engineered nanoparticles from the solution. External magnetic field was applied using either two rectangular enclosed ceramic magnets (maximum pull of 75 lb each), or a single ultra-high-pull encased neodymium-iron-boron round magnet (maximum pull 300 lb). All magnets were purchased from McMaster-Carr Inc. Rectangular magnets are of of 4.5" * 1.25" * 1.25" size and round magnet is 4.9" diameter and 0.5" thick. Maximum flux density applied was 2.35 kG (at the bottom of collection flask).

The effect of solution chemistry (pH), concentration of engineered nanoparticles, and type of surface coating on the removal of engineered nanoparticles was evaluated as mentioned in the coagulation study. The reusability of magnetite nanoparticles was evaluated by washing cationic surfactant-modified magnetite nanoparticles with organic solvents and recovering the magnetite particles using applied magnetic field.

3.2.4 Nanoparticle Quantification

In this research, nanoparticle quantification was carried out using UV-Vis spectroscopy (double beam Varian Inc. DMS 300 UV/Visible spectrophotometer, Palo Alto, CA). A separate calibration curve for each stock solution of nanoparticles was constructed as a function of nanoparticle concentrations in dispersion and absorbance at the pre-selected wavelength range of interest (200-300nm) using quartz cuvette. A specific wavelength was then selected based on peak location in most cases and high absorbance and high signal to noise ratio (>4) in few cases. 260 nm was the most commonly used frequency for TiO_2 quantification. Magnetites were quantified at 450 nm using plastic cuvette. The response factor obtained from this calibration curve was used to convert the absorbance measured in the synthetic solution after treatment to nanoparticle concentrations, and the removal efficiency was calculated. Background correction was made by measuring absorbance of NOM and/or CTAB + cyclohexane at same wavelength used to quantify respective nanoparticles.

3.3   Optimization Analysis

Objective function: Maximize $R = F (pH, CD, MD, ST, CT, INC, AR)$

Where,
RE –   Removal Efficiency, %
pH –   pH of the solution (4, 6, 7, 8, and 9),
CD –   Coagulant Dosage (0, 20, 50, 200, 500, and 750 mg/L)
MD –   Magnetite+CTAB Dosage (1, 5, 10, 25, 50, and 100 mg/L)
ST –   Settling Time (10, 30, and 60 min)
INC –   Nanoparticle concentration (25, 50, and 100 mg/L)
AR –   Agitation rate (0, 20, 50, and 100 rpm)

Series of jar tests produced data matrices covering pre-selected ranges of design parameters. Correlation analysis was done between removal efficiency and each of the parameter to determine the strength of function. For each dataset, highest value of removal efficiency was identified. This optimum removal was selected to be between this value as upper limit and 10% lower value as lower limit, e.g. if maximum removal were identified to be 85% then optimum removal range would be 75% - 85% (85% upper limit and 75% lower limit). Using the concept of confidence intervals, optimum ranges for each of the 4 independent variables were determined at 95% confidence level. All statistical analysis was performed using MS excel, Minitab 16 (Minitab Inc.), and Statistical Analysis Software (SAS 9.1). The results of experimental design and analysis are discussed below.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Removal Using Conventional Coagulation and Flocculation

Series of jar tests were conducted to cover the variation of design parameter values. For all the sets of jar tests aimed and covering the variation of coagulant dosage – single jar was added no coagulant as control. Following Figures 4.1a and 4.1b show typical matrices for nanoparticle removal efficiency using alum and ferric chloride. Both these matrices are for initial nanoparticle concentration of 100 mg/L.
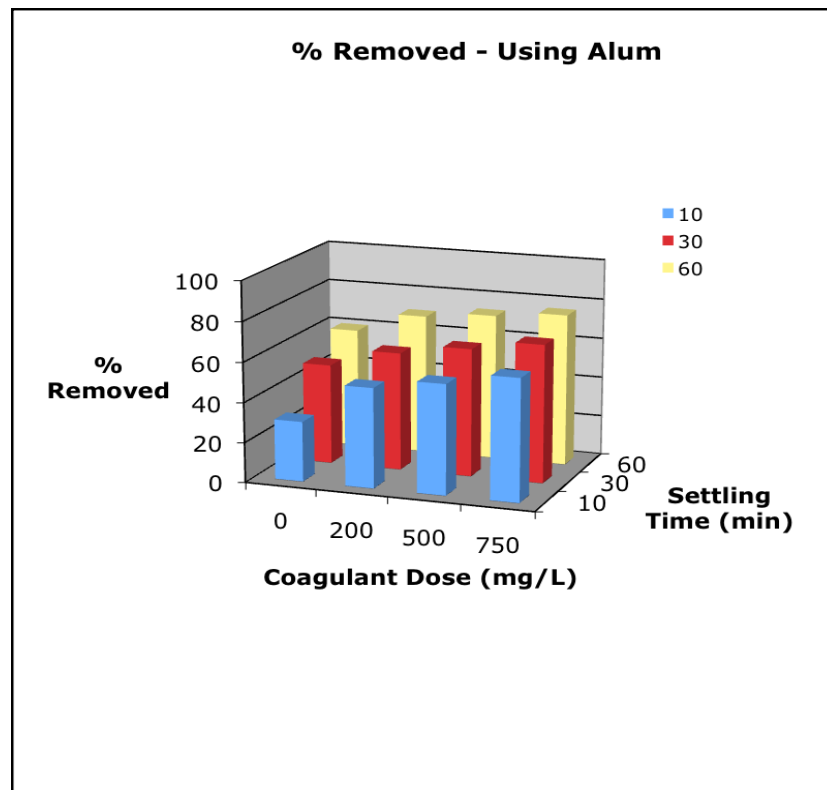
Figure 4.1a Typical data matrix for removal using alum.
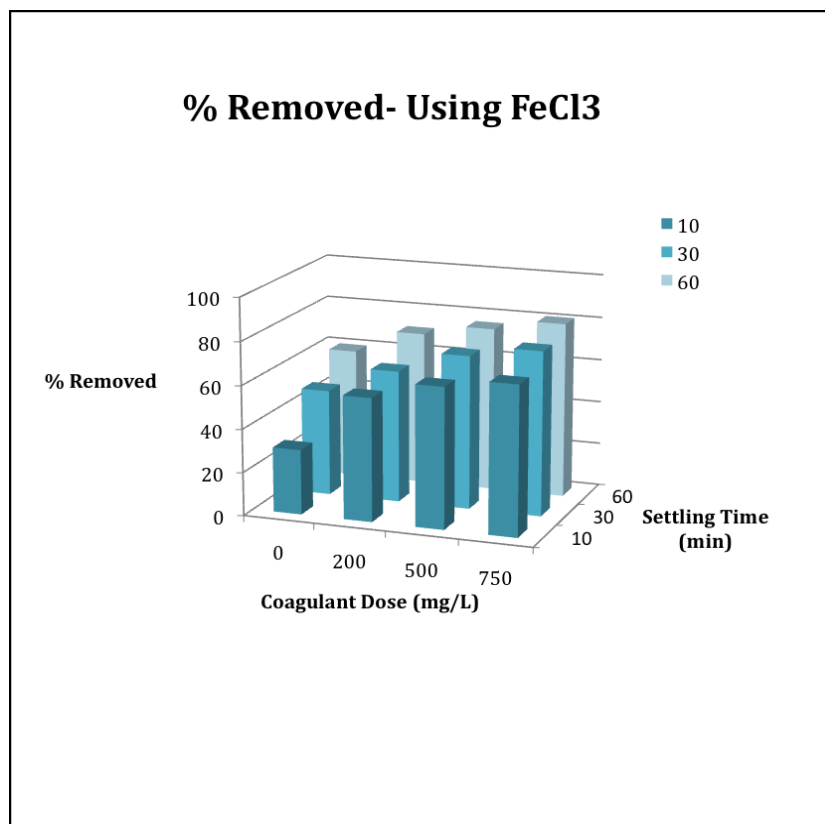
Figure 4.1b Typical data matrix for removal using FeCl3.

It can be observed that the settling of nanoparticles is very slow without addition of any coagulant to the solution. Even with such a high initial concentration of nanoparticles in the solution (100 mg/L) only about 50% are removed after 60 minutes of settling. TiO_2 carry a minor negative surface charge in aqueous solutions [3]. It can be reasoned that although they show some natural tendency to aggregate and settle, the minor charge (-5 mV to -20 mV zeta potential near neutral pH [3]) causes EDL repulsion that in turn prohibits aggregation. Furthermore, gentle stirring and prolonged settling times are not good enough to promote aggregation and hence majority of the nanoparticles in the solution do not leave their nano-regime. In such cases, Van der Waals attractive forces are easily overcome by mixing tendencies induced in solution by

diffusion and convection [3]. Addition of coagulant will increase the chances of floc formation increasing the settling.

Looking at Figures 4.1a and 4.1b, it is clear that coagulant dose, coagulant type, and settling time all affect the removal efficiency. It is very important to understand this effect not only for optimization of coagulation for removal of nanoparticles, but also for understanding of removal mechanism. In addition, pH, agitation rate, initial nanoparticle concentration, and presence of NOM also have various effects on removal efficiency. All these factors are discussed below.

4.1.1 Effect of Addition of Coagulant and Coagulant Dosage on Removal Efficiency

To study the effectiveness of conventional coagulation on removal of nanoparticles, alum and ferric chloride were used as choice of coagulants with concentrations ranging between 0 and 750 mg/L. Figure 4.2 is a graph that shows the variation of removal efficiency for increasing dosage of alum and ferric chloride. All other design parameters were kept constant – initial nanoparticle concentration at 50 mg/L, settling time of 30 min, and agitation rate at 50 rpm.
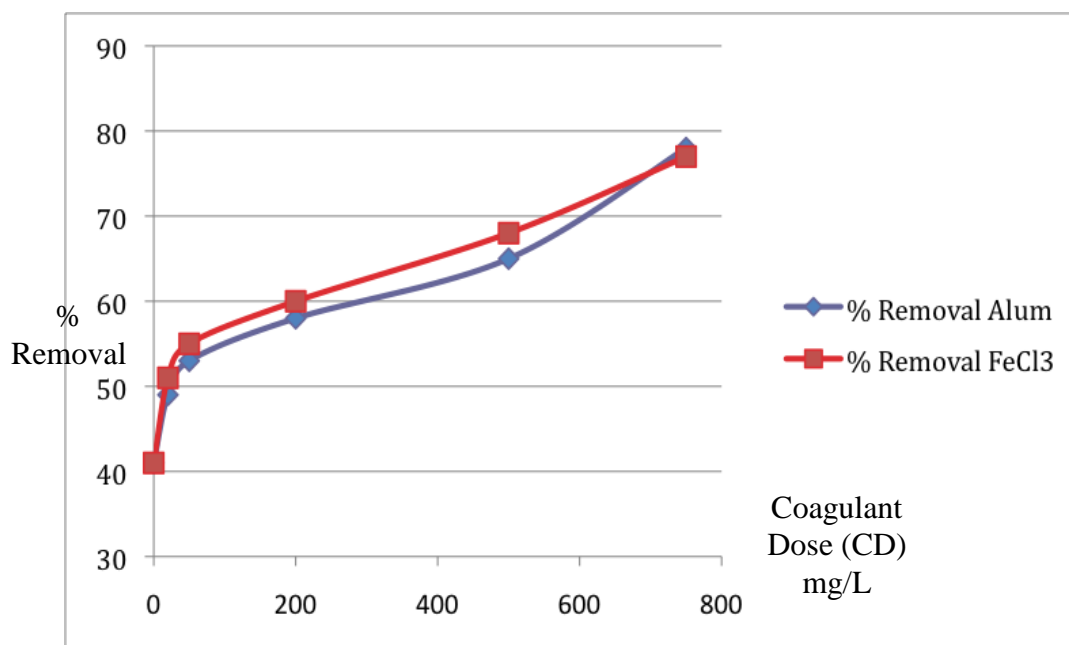
INC = 50 mg/L, ST = 30 min, pH = 7, AR = 50 /min

Figure 4.2 Effect of coagulant dosage.

It can be observed that the there is a rapid increase in removal efficiency as soon as coagulant is added − even at lower coagulant concentrations. The slope of graph changes significantly at coagulant concentration of about 80 mg/L for both alum and ferric chloride. Coagulants destabilize colloidal particles by four mechanisms: double-layer compression, charge neutralization, enmeshment in a precipitate, and inter-particle bridging [60, 64]. Different mechanisms dominate in different situations depending on the nature of turbidity and solution chemistry. TiO_2 particles are reported to have net negative surface charge at neutral pH [3]. Addition of coagulant to the solution causes rapid floc formation due to EDL attraction and leads to increased settling and removal of nanoparticles. This can be seen in the initial rapid slope of the graph.

In conventional coagulation targeted at removing turbidity, adding more and more coagulant results in reverse charge formation and decrease in the removal efficiency. This is governed by Debye screening theory based on electrostatic repulsion. Increase in

coagulant concentration has great effect on charge screening. However, the case of removal of TiO_2 in water does not seem to agree with Debye screening theory. There is definitely a drop in the rate of increase of removal efficiency beyond 80 mg/L concentration of coagulant (both alum and ferric chloride), but the removal efficiency does not decrease for any higher concentration of coagulant relative to subsequent lower concentration. This clearly hints at sweep coagulation in which the removal is mainly due to enmeshment in precipitate. Higher the precipitate better is the removal efficiency. In conclusion, it can be reasoned that removal of nanoparticles using conventional coagulation is governed by charge neutralization for lower concentrations of coagulants and then by sweep coagulation at higher concentrations.

4.1.2 Effect of Presence of NOM on Removal Efficiency

Engineered nanoparticles are often coated to enhance their functionality. Bare nanoparticles are attracted towards a variety of entities present in water and wastewater and get coater, most commonly be adsorption. Colloidal particles that are coated with macromolecules such as polymers, polyelectrolytes, or natural macromolecules (e.g., NOM are more difficult to remove using coagulation because steric repulsion can prohibit aggregation and enhance colloidal stability of particles in aqueous phase [46, 61, 62]. In this research the effect of presence of NOM in water is studied based on how it affects the relationship between coagulant dosage and removal efficiency. Figure 4.3a shows the graph of removal efficiency against the coagulant dosage in the presence of NOM in the form of humic acid. Figure 4.3b shows the graph of removal efficiency against the coagulant dosage in the presence of NOM in the form of Passaic river sample

with pre-treatment TOC = 3.9 mg/L and post-treatment TOC <0.05 mg/L for a coagulant

dose >= 20 mg/L.
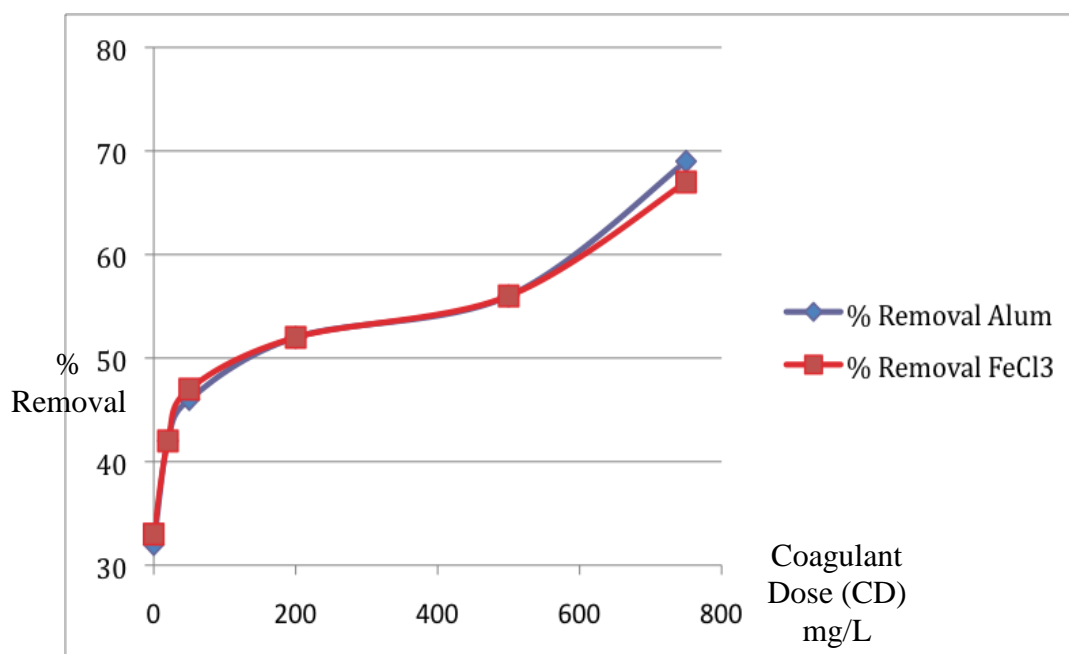
INC = 50 mg/L, ST = 30 min, pH = 7, AR = 50 /min

Figure 4.3a Effect of coagulant dosage with NOM present (humic acid).
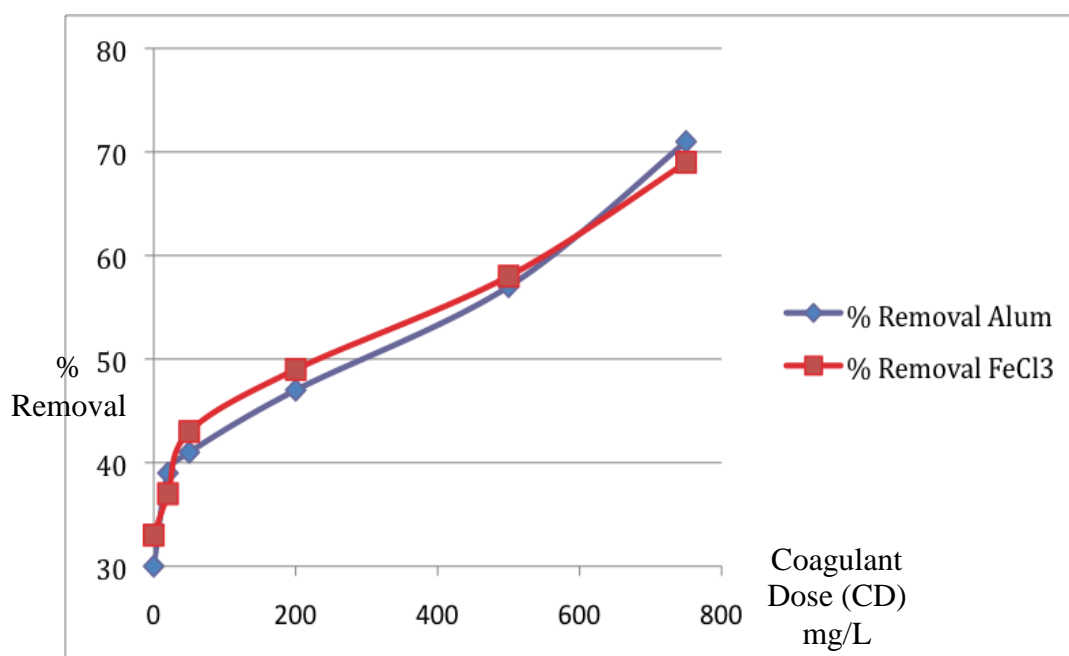
INC = 50 mg/L, ST = 30 min, pH = 7, AR = 50 /min

Figure 4.3b Effect of coagulant dosage with NOM present (Passaic river sample).

Comparing Figures 4.2, 4.3a, and 4.3b it can be seen that although the graphs follow somewhat similar curves, there is 10-20% decrease in removal efficiency in the presence of NOM. The difference in removal efficiencies with or without NOM is much higher at lower concentrations of coagulant and gradually reduces at higher concentrations.

NOM easily adsorbs onto bare nanoparticles [46, 61, 62]. These adsorbed NOM cause electrosteric repulsion that prohibits attachment of nanoparticles to floc. This is further supported by the fact the difference in removal efficiencies with and without NOM is higher at lower concentrations of coagulant, where charge neutralization is dominating removal mechanism. At higher concentrations of coagulant, the difference in removal efficiencies gradually reduces because the sweep coagulation slowly becomes the dominating removal mechanism and NOM adsorption onto nanoparticles has little effect on removal efficiency.

4.1.3 Effect of Initial Nanoparticle Concentration on Removal Efficiency

Initial nanoparticle concentration has a direct relationship with removal efficiency. As can be seen in Figure 4.4, higher the initial concentration better is the removal efficiency. Although the graph in Figure 4.4 is produced at a high coagulant dosage of 250 mg/L, additional tests showed that the relationship is similar at low coagulant concentrations as well.
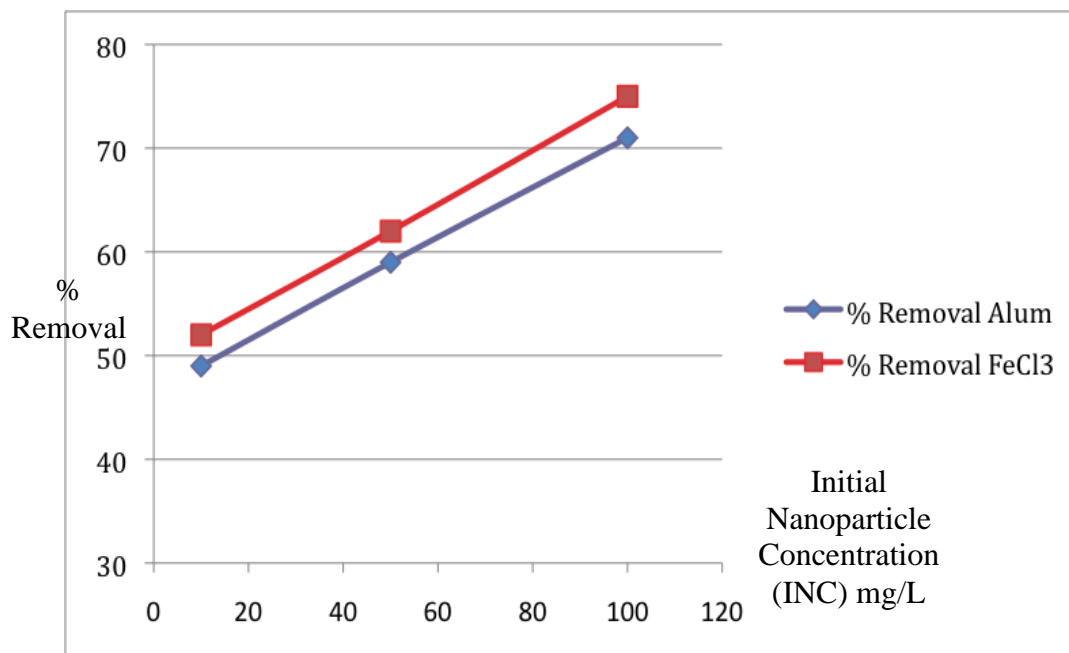
pH = 7, CD = 250 mg/L, ST = 30 min, AR = 50 /min

Figure 4.4 Effect of initial nanoparticle concentration on removal efficiency.

Since coagulation is a second order phenomenon, it is dependent on the number of collisions per unit time. Higher INC has higher chances of inter-particle collisions, which in turn will cause faster floc formation. At sufficient concentrations, nanoparticles can often spontaneously to form clusters even in the absence of destabilizing agents [31, 60]. If the nanoparticle concentration is increased further then average hydrodynamic size of the dispersion is also expected to increase due to the fact that frequency of particle collision is a strong function of particle number concentration [33, 66, 146]. However, high initial nanoparticle concentration will also mean high effluent concentration. Although the % removal efficiency is high at high initial nanoparticle concentration, the number concentration left in effluent will be higher than that found in cases of low initial nanoparticle concentrations.

4.1.4 Effect of pH on Removal Efficiency

As discussed in the background theory (Section 2.2), pH plays a significant role in removal of turbidity (also nanoparticles) using coagulation and flocculation. Figures 4.5a and 4.5b show the variation of removal efficiency with respect to changes in pH with all other parameters kept at a constant value (Difference between the 2 graphs is coagulant dosage, first one is plotted at CD = 250 mg/L and second one is at CD = 50 mg/L).
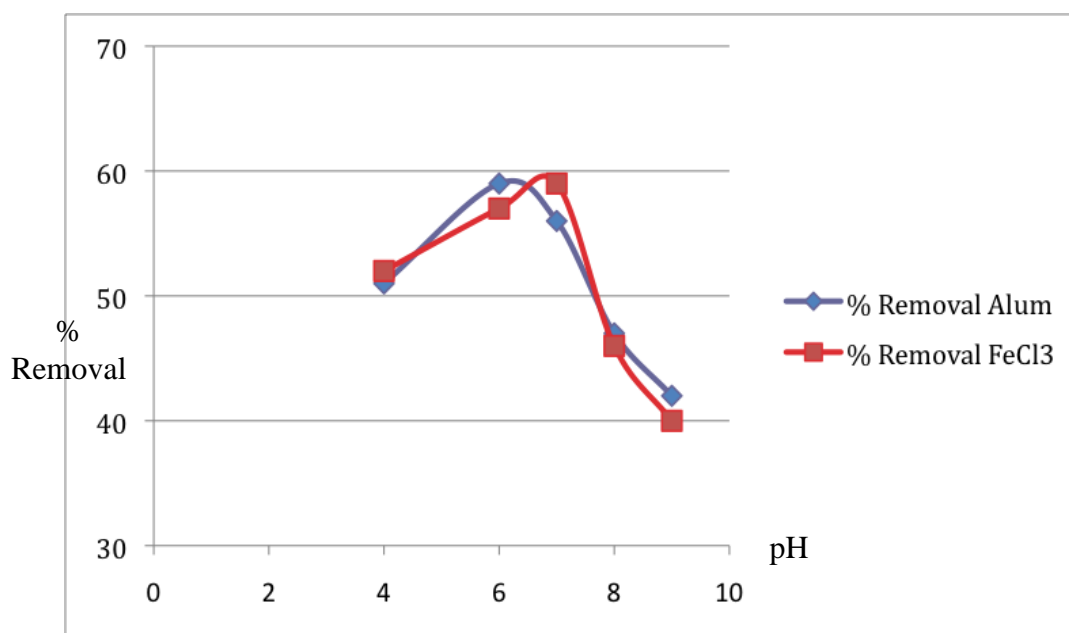
INC = 50 mg/L, CD = 250 mg/L, ST = 30 min, AR = 50 /min

Figure 4.5a Effect of pH (CD = 250 mg/L).
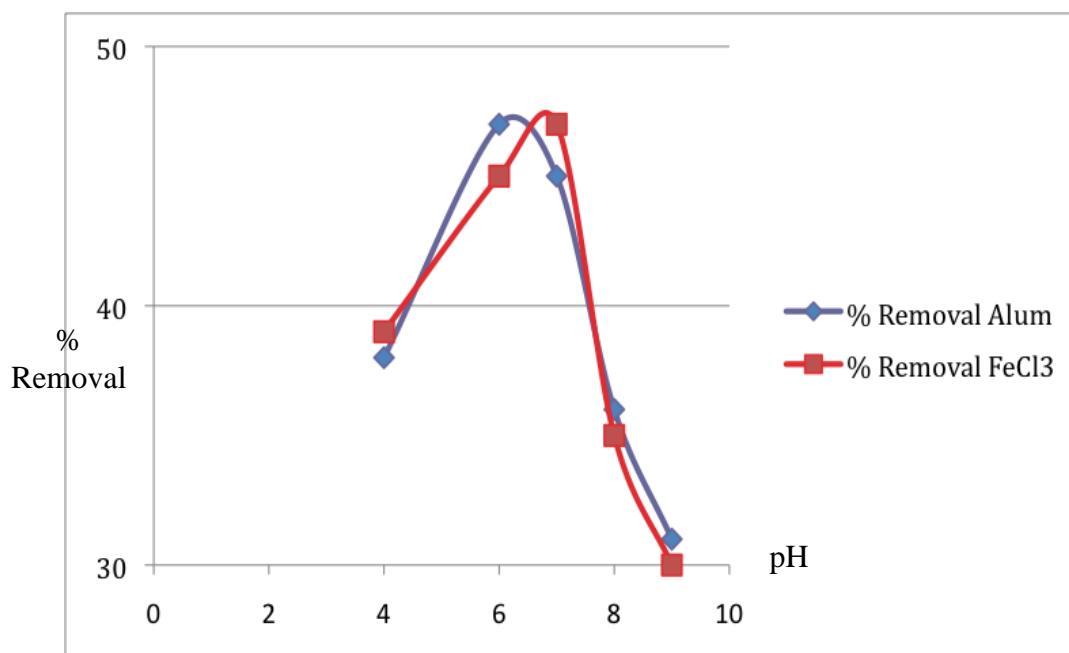
INC = 50 mg/L, CD = 50 mg/L, pH = 7, AR = 50 /min

Figure 4.5b Effect of pH (CD = 50 mg/L).

Upon carefully observing the above two graphs, it can be seen that variation in pH of solution causes significant variation in removal efficiency at both low and high concentration of coagulant. For both alum and ferric chloride, removal efficiency drops considerably at acidic as well as basic conditions, with optimum removal achieved near neutral pH. This observed effect of pH is really interesting and can be explained as follows. At low values of coagulant concentration, charge neutralization is predominant mechanism of removal. Nature of interactions (favorable (attractive) or unfavorable (repulsive)) between the colloids and floc formed are highly pH dependent [64]. Therefore, changes in pH values cause reduction in removal efficiency. At high concentrations of coagulants, sweep coagulation is the predominant removal mechanism. For effective sweep coagulation, it is necessary to achieve rapid floc formation in the solution. These flocs will then be trapped by settling precipitate, causing them also to

settle. Since pH also affects the rate at which flocs are formed and the total amount of flocs formed [60], it directly affects removal efficiency.

Changes in solution pH change the particle surface charge and affect the hydrodynamic size of dispersion [66, 72, 73]. Removal efficiency is highest near IEP due to significant agglomeration of nanoparticles [66]. From the graphs it can be seen that for TiO_2, IEP is approximately 6.2, which is consistent with those reported in other studies [34, 66, 147, 148]. At values of pH that are considerably different (<5 or >8) from IEP for TiO_2 (approximately 6.2), the absolute zeta potential value increases and hydrodynamic size decreases resulting in decrease in removal efficiency and this observation is also in agreement with published literature [66].

4.1.5 Effect of Settling Time on Removal Efficiency

Figure 4.6 shows the relationship between settling time and removal efficiency. It can be observed that longer settling time produces higher removal of nanoparticles with all other factors being constant. 60 minutes of settling provides 70%+ removal of nanoparticles at neutral pH and 250 mg/L coagulant dosage. Settling time is a function of floc formation kinetics and sedimentation kinetics [60, 149]. Particle settling velocity (representation of rate at which particles settle), which is a function of floc size and floc density is the most important parameter for determination of optimum settling time [60, 149].
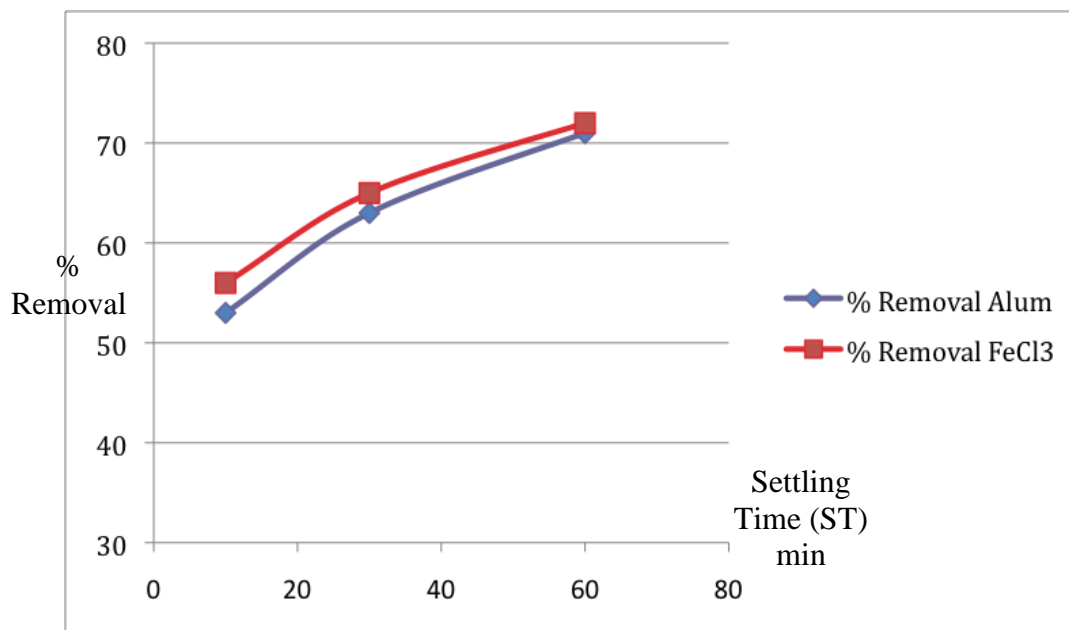
INC = 50 mg/L, CD = 250 mg/L, pH = 7, AR = 50 /min

Figure 4.6 Effect of settling time on removal efficiency.

4.1.6 Effect of Agitation Rate on Removal Efficiency

Stability of colloidal particles in solution is highly dependant on rate of collisions. Generally, higher the chances of collision, better is floc formation and hence settling. This is initiated by gentle mixing of the solution in coagulation tank. However if the mixing rate is too high then the collision energy will cause breakage of flocs as opposed to attachment of particles onto flocs [60, 77, 149]. It is therefore very important to maintain optimum agitation rate before flocs are allowed to settle. Figure 4.7 shows the variation of removal efficiency against the agitation rate. Initially, removal efficiency steadily increases with increase in agitation rate. This is due to increase in number of collisions leading to rapid floc formation. At an agitation rate of about 50 rpm, peak removal efficiency is observed. Any increase in agitation rate beyond the value of 50 rpm causes rapid collisions that lead to breaking of flocs and decrease in removal efficiency.
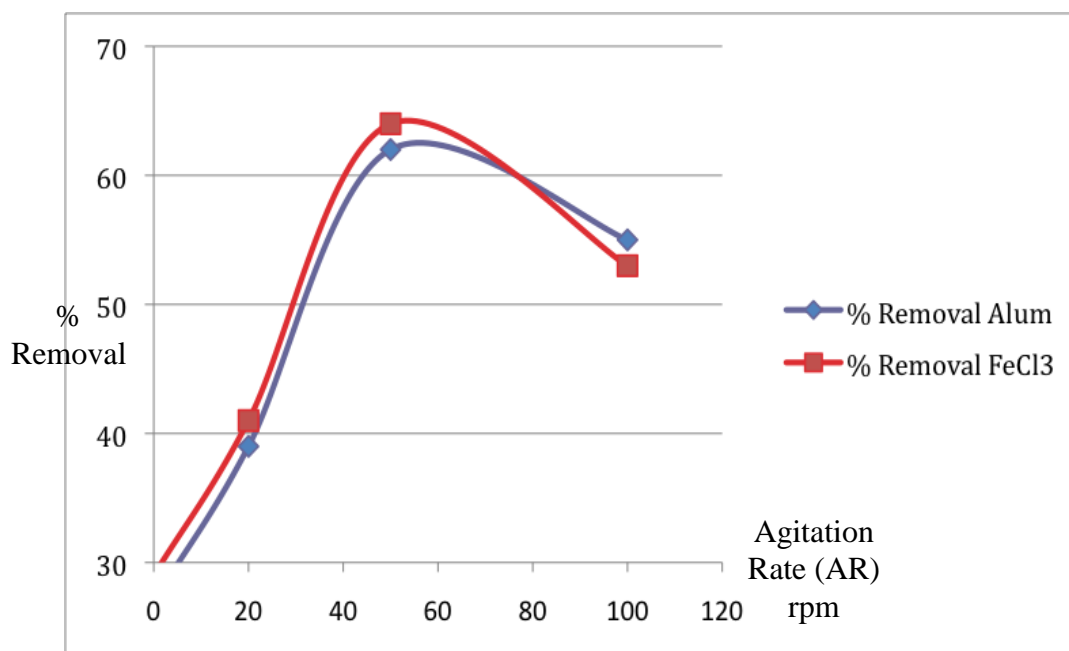
INC = 50 mg/L, ST = 30 min, pH = 7, CD = 250 mg/L

Figure 4.7 Effect of agitation rate on removal efficiency.

4.1.7 Alum v/s Ferric Chloride

Statistically, there is little difference between removal efficiencies using alum and ferric chloride as coagulants. In fact, the effect of design parameters (pH, agitation rate, settling time, and presence of NOM) is remarkably similar for both the coagulants. It can be reasoned that titanium nanoparticles have no special affinity towards either of the coagulant as compared to other. Also referring to the Figures 4.1a, 4.1b, and 4.2, it can be seen that lower concentrations of coagulants is not good enough to remove nanoparticles from water. At high coagulant concentrations, sweep coagulation is the dominating removal mechanism and therefore both coagulants produce similar performance in removing nanoparticles.

4.1.8 Optimum Operating Conditions

Objective function of the model was to optimize design parameters to maximize removal efficiency of nanoparticles. Correlation analysis indicated that removal efficiency is a strong function of coagulant dose, and a function of settling time and pH of the solution. However, pH and coagulant dosage were highly correlated and only one of them could be present in objective function at a time. The nature of dataset obtained from experimental results was such that highest number of observations was available for variation of coagulant dosage and settling time. Variation of pH and agitation rate was covered using relatively less number of data points. Therefore the optimum ranges of pH and agitation rate were fixed first. It was done by observing the graphs and by applying confidence interval principle. Afterwards all the data points within this optimum range for pH and agitation rate were used to calculate optimum ranges for coagulant dose and settling time. This was also done by observing the graphs for the same parameters, and by applying concept of confidence interval.

If the graphs of variation of removal efficiency against the variation of parameter value are observed carefully, it can be see that for coagulant dose and settling time – higher is better. In simple words, addition of more coagulant, and using longer settling times will lead to better removal. However, this will also increase the cost significantly and render the method impractical. Therefore arbitrary cost constrains were placed to determine optimum operating range without letting the chemical cost exceed $1.5 per 1000 gallons of water treated. Since contribution of coagulant dose and settling time to overall cost is higher than the cost to control pH and agitation rate, their values are

affected when cost constrains are considered with ranges for pH and agitation rate remaining the same.

The effect of presence of NOM was determined in terms of coagulant dosage required with and without NOM in solution. To calculate optimum coagulant dosage when NOM was present in the solution, cost constrains were raised to $1.65 per 1000 gallons of water treated to allow similar level of removal as in the absence of NOM. Removal efficiency is more or less directly proportional to initial concentration and INC is not a control parameter in practice, but a target parameter. Therefore, no optimum range was calculated for INC. Table 4.1 shows the optimum ranges of all the design parameters for both alum and ferric chloride coagulant, with and without presence of NOM. Based on experimental results presented in section 4.1, 60-80% removal efficiency can be expected if the conditions in table 4.1 are maintained.

Table 4.1 Optimum Operating Conditions for Maximum % Removal of Nanoparticles Using Conventional Coagulation and Flocculation

Parameter	Optimum range (with cost constrains) for Alum	Optimum range (with cost constrains) for FeCl$_3$
pH	6 – 7.5 (6 – 7.5)	6 – 7.5 (6 – 7.5)
Agitation Rate (slow mixing)	45-55 (45-55)	40-55 (40-55)
Coagulant Dose	750 mg/L (150 mg/L)	750 mg/L (130 mg/L)
Coagulant Dose (with NOM)	750 mg/L (200 mg/L)	750 mg/L (210 mg/L)
Settling Time	60 min (30 min)	60 min (30 min)

4.2 Removal of Nanoparticles Using Magnetic Seeding Aggregation

Optimum operating ranges of design parameters, obtained during experiments with conventional coagulation and flocculation, were used as basis to reduce the number of jar tests for removal using magnetite nanoparticles. Additional jar tests were performed to study the effect of pH, settling time, initial nanoparticle concentration, and agitation rate, and NOM.

Figures 4.8a, 4.8b, 4.8c, and 4.8d shows four data matrices: 1) removal using alum as coagulant, 2) removal using ferric chloride as coagulant, 3) removal using bare magnetites, and 4) removal using magnetites surface modified with CTAB.
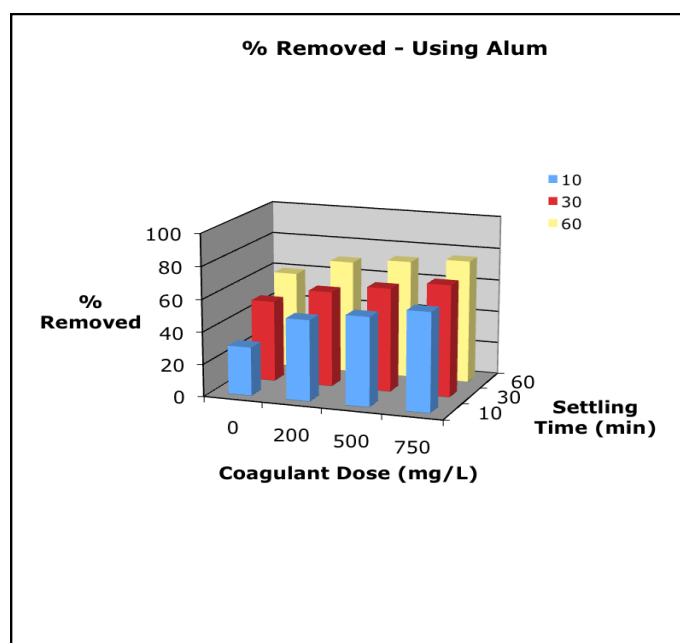
Figure 4.8a Data matrices for comparison of removal using conventional coagulation/flocculation method, and using magnetites – removal using alum as coagulant.
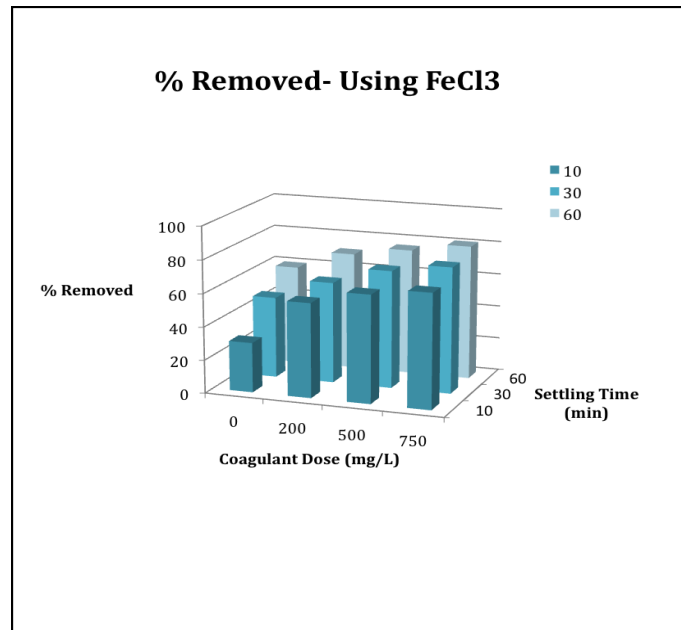
Figure 4.8b Data matrices for comparison of removal using conventional coagulation/flocculation method, and using magnetites – removal using ferric chloride as coagulant.
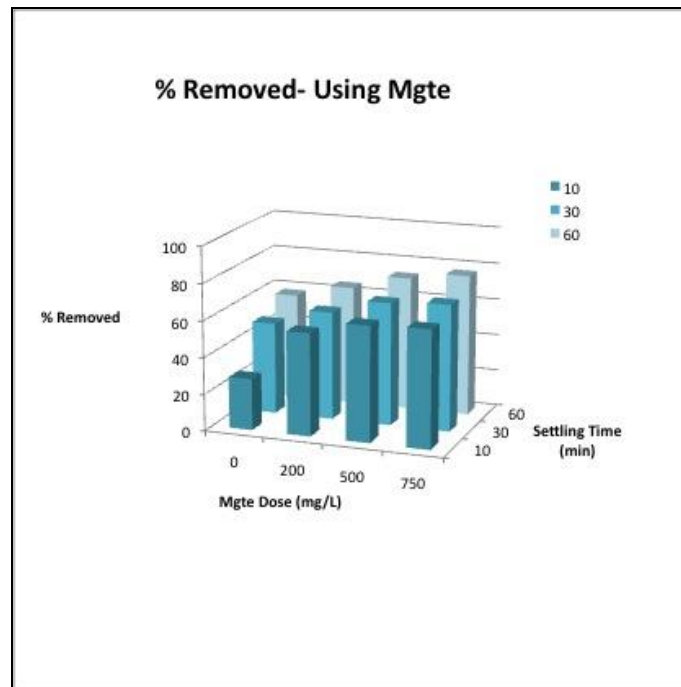
Figure 4.8c Data matrices for comparison of removal using conventional coagulation/flocculation method, and using magnetites – removal using bare magnetites.
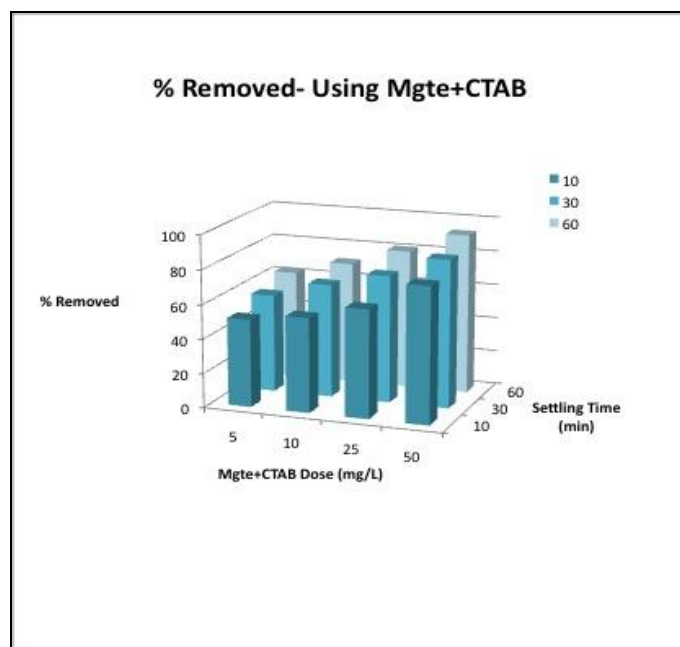
Figure 4.8d Data matrices for comparison of removal using conventional coagulation/flocculation method, and using magnetites – removal using magnetites surface coated with CTAB.

It should be noted that for Figure 4.8, conventional coagulant and bare magnetite concentrations vary between 0 and 750 mg/L, whereas surface coated magnetite concentration varies only between 5 and 50 mg/L. It can be seen that magnetites are much more efficient in removing TiO_2 nanoparticles from water. Bare magnetites carry weakly negative charge in solution at neutral pH [3]. They are no more effective than any of the conventional coagulants. However, magnetites surface modified with CTAB carry a distinct positive charge and are able to remove TiO_2 nanoparticles with relative ease. Moreover, surface modified magnetic nanoparticles can be recovered with addition of organic solvent under application of magnetic field, making it a very useful technique.

4.2.1 Effect of Dose of Surface Coated Magnetites

To study the relationship between magnetite dosage and removal efficiency, concentration of magnetites was varied between 1 and 100 mg/L. Figure 4.9 is a graph that shows the variation of removal efficiency for increasing dosage magnetites. All other design parameters were kept constant – initial nanoparticle concentration at 100 mg/L, settling time of 30 min, and agitation rate at 50 rpm.
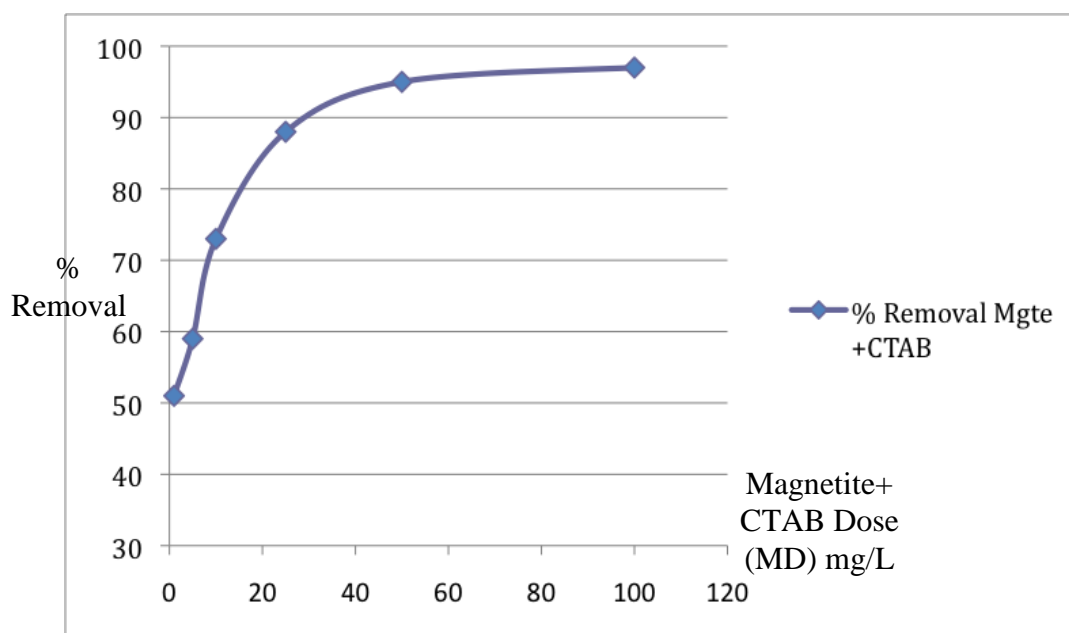
INC = 100 mg/L, ST = 30 min, pH = 7, AR = 50 /min

Figure 4.9 Effect of concentration of surface coated magnetites.

From Figure 4.9, it can be seen that removal efficiency is a strong function of dosage of magnetites. 80%+ nanoparticles are removed at 25 mg/L magnetite dosage. Addition of more magnetites to solution does increase removal efficiency, but at a very slow rate. No negative charge formation (and hence reduction in removal efficiency due to repulsion) is observed at magnetite concentration as high as 100 mg/L. Also, from the nature of the graph it can be reasoned that the dominating removal mechanism is charge neutralization throughout the applied range of magnetite concentration.

4.2.2 Effect of the Presence of NOM on Removal Efficiency Using Surface Coated Magnetites

As discussed in earlier sections (2.2 and 4.1.2), NOM and other entities in water easily

coat engineered nanoparticles [46, 61, 62]. Figure 4.10a shows the effect of presence of

NOM in solution in form of humic acid by means of change in removal efficiency for

same range of magnetite dosage. Figure 4.10b shows the effect of presence of NOM in

solution in form of TOC = 3.9 mg/L from Passaic river sample by means of change in

removal efficiency for same range of magnetite dosage.
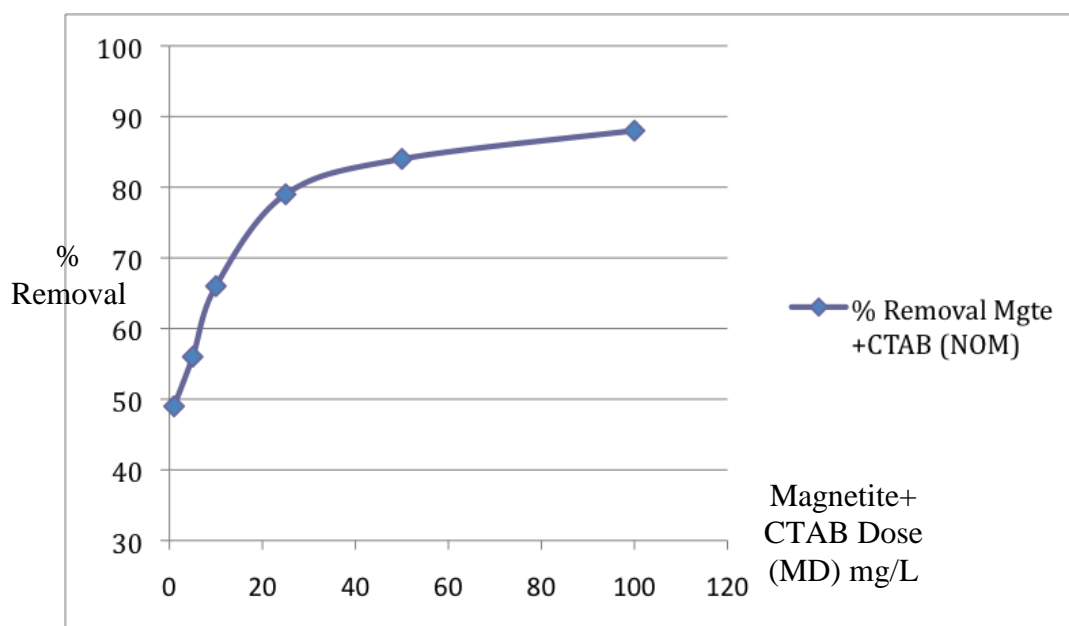
INC = 100 mg/L, ST = 30 min, pH = 7, AR = 50 /min

Figure 4.10a Effect of concentration of surface coated magnetites with NOM present (humic acid).
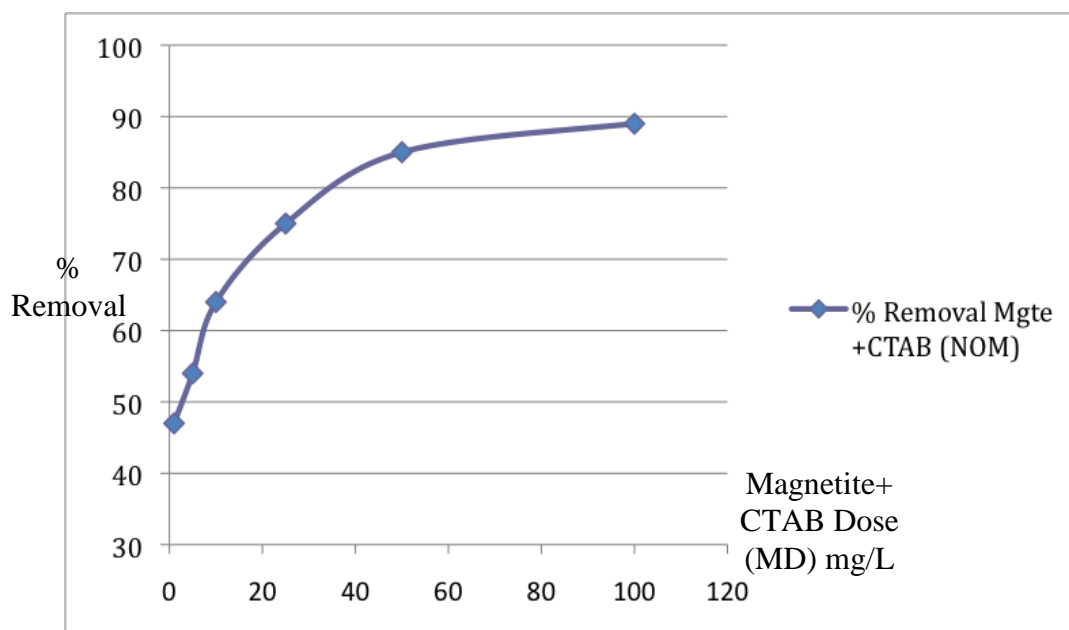
INC = 100 mg/L, ST = 30 min, pH = 7, AR = 50 /min

Figure 4.10b Effect of concentration of surface coated magnetites with NOM present (Passaic river sample)

Comparing Figures 4.9, 4.10a, and 4.10b it can be seen that there is a definite reduction (5-15%) in removal efficiency in the presence of NOM. The effect is very similar to that in case of conventional coagulants. Therefore, the reduction in removal efficiency can be explained by NOM adsorption onto bare nanoparticles causing decrease in chances of attachment onto flocs [46, 61, 62].

4.2.3 Effect of Initial Nanoparticle Concentration on Removal Efficiency Using Surface Coated Magnetites

Like in case of conventional coagulation, initial nanoparticle concentration has a direct relationship with removal efficiency. As can be seen in Figure 4.11, higher the initial concentration better is the removal efficiency.
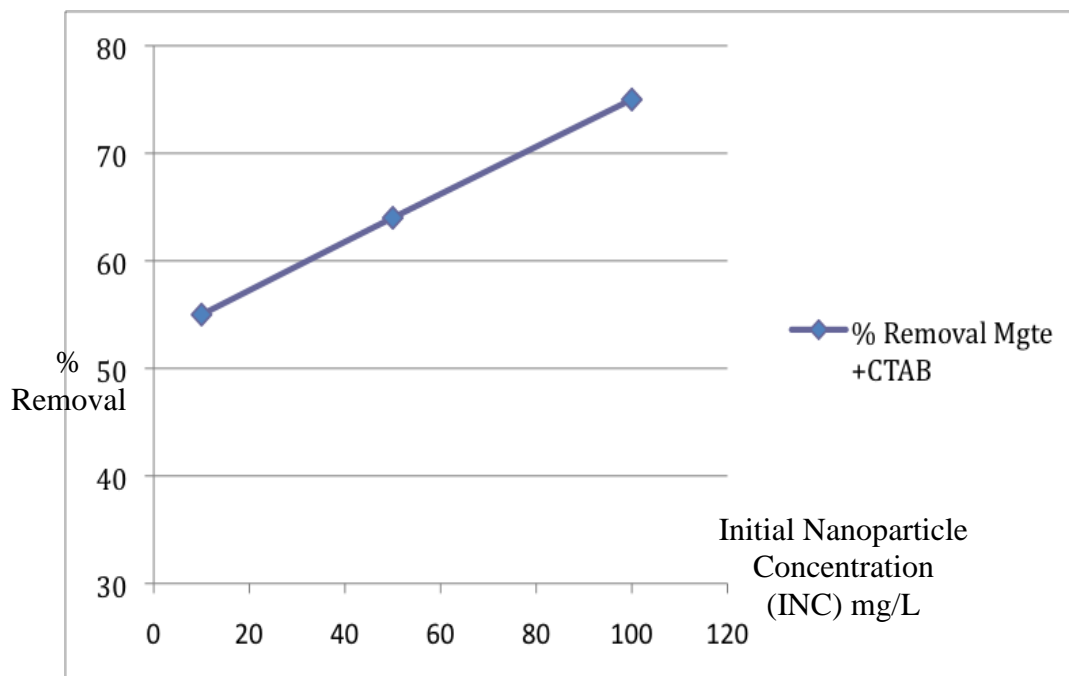
pH = 7, MD = 25 mg/L, ST = 30 min, AR = 50 /min

Figure 4.11 Effect of initial nanoparticle concentration on removal by surface coated magnetites.

Similar to in case of conventional coagulation, this effect can be explained by the fact that average hydrodynamic size of dispersion is higher at high particle concentration due to high frequency of particle collision [33, 66, 146].

4.2.4 Effect of pH on Removal Efficiency Using Surface Coated Magnetites

Figure 4.12a shows the variation of removal efficiency with respect to changes in pH with all other parameters kept at a constant value for samples treated with surface coated magnetites and ferric chloride coagulant. Figure 4.12b shows the variation of removal efficiency with respect to changes in pH with all other parameters kept at a constant value for samples treated only with surface coated magnetites.
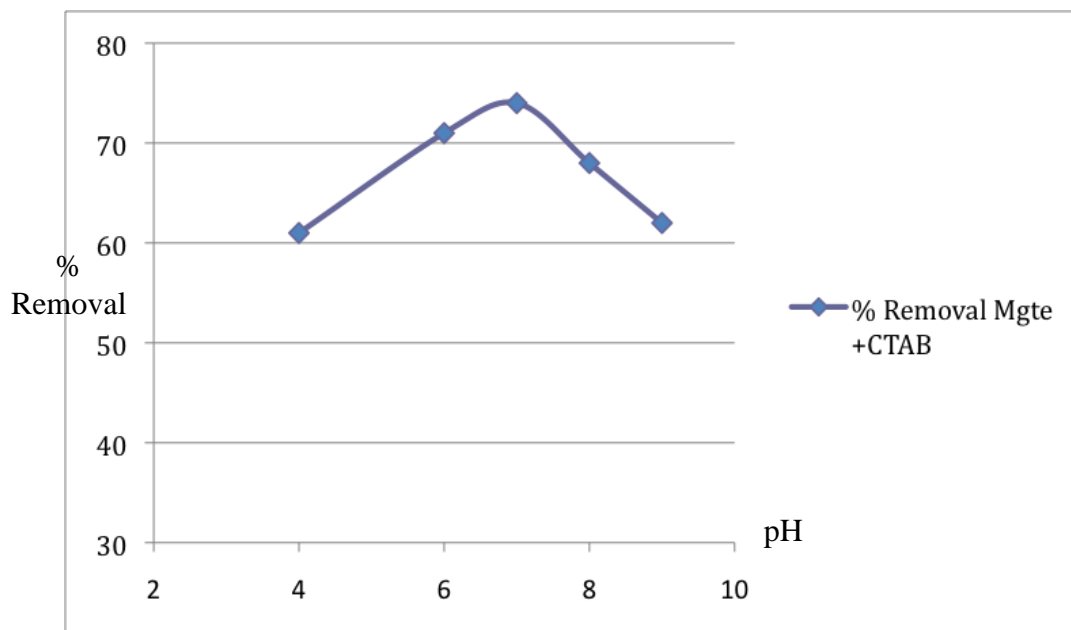
INC = 50 mg/L, CD = 25 mg/L, MD = 25 mg/L, ST = 30 min, AR = 50 /min

Figure 4.12a Effect of pH on removal by surface coated magnetites and ferric chloride.
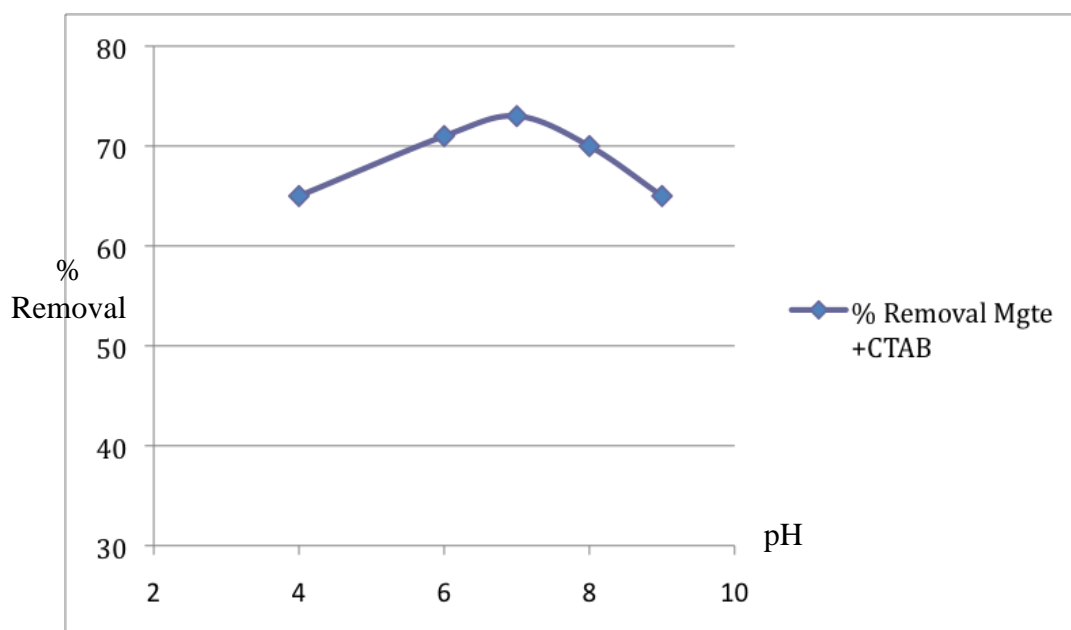
INC = 50 mg/L, MD = 25 mg/L, ST = 30 min, AR = 50 /min

Figure 4.12b Effect of pH on removal by surface coated magnetites.

The effect of pH on removal efficiency of TiO_2 nanoparticles using surface coated magnetites is similar to that observed in case of conventional coagulants. Removal efficiency decreases at both low and high values of pH with peak efficiency observed between pH of 6.5 and 7.5. This effect is highly similar for samples treated with surface coated magnetites and ferric chloride. However for samples treated with surface coated magnetites alone, the effect of pH is very low. Removal efficiency varies only by 5% within a pH range of 4 – 6.

As mentioned before, charge neutralization is dominating mechanism in removal of nanoparticles by surface coated magnetites. As pH influences the particle interactions (attractive or repulsive) by altering the net particle surface charge, changes in pH values reduce the removal efficiency [64].

4.2.5 Effect of Settling Time on Removal Efficiency by Surface Coated Magnetites

Figure 4.13a shows the variation in removal efficiency relative to settling time for removal of nanoparticles with surface coated magnetites and ferric chloride. Figure 4.13b shows the variation in removal efficiency relative to settling time for removal of nanoparticles with surface coated magnetites only. As was in case of conventional coagulation, longer settling times produce higher removal efficiency (80%+ at 60 min of settling). Removal efficiency is therefore a direct function of settling time.
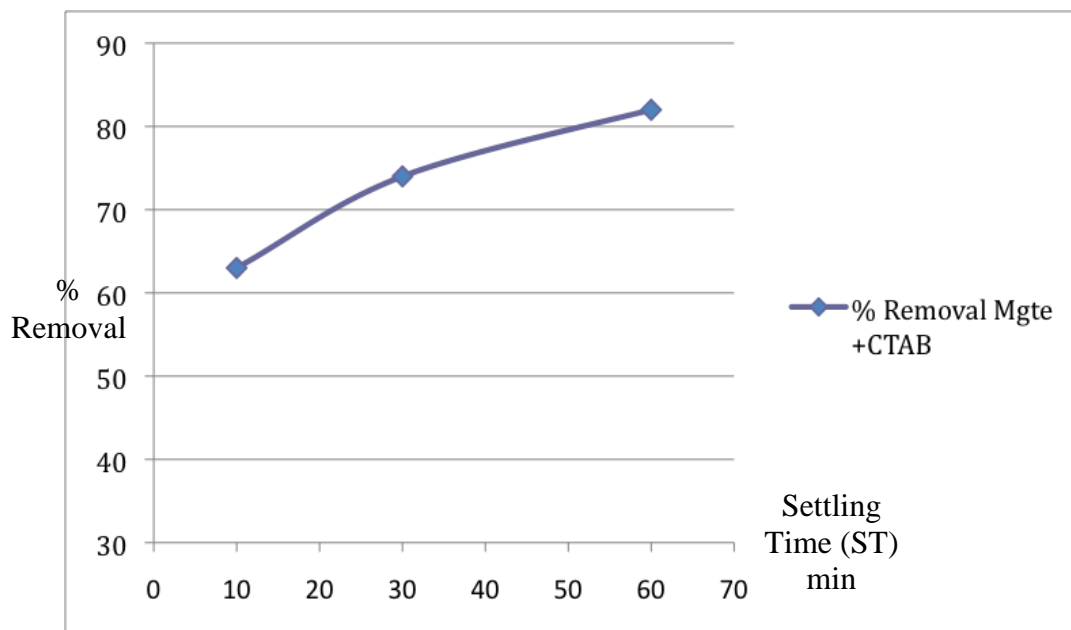
INC = 100 mg/L, CD = 25 mg/L, MD = 25 mg/L, pH = 7, AR = 50 /min

Figure 4.13a Effect of Settling Time on removal by surface coated magnetites and ferric chloride.
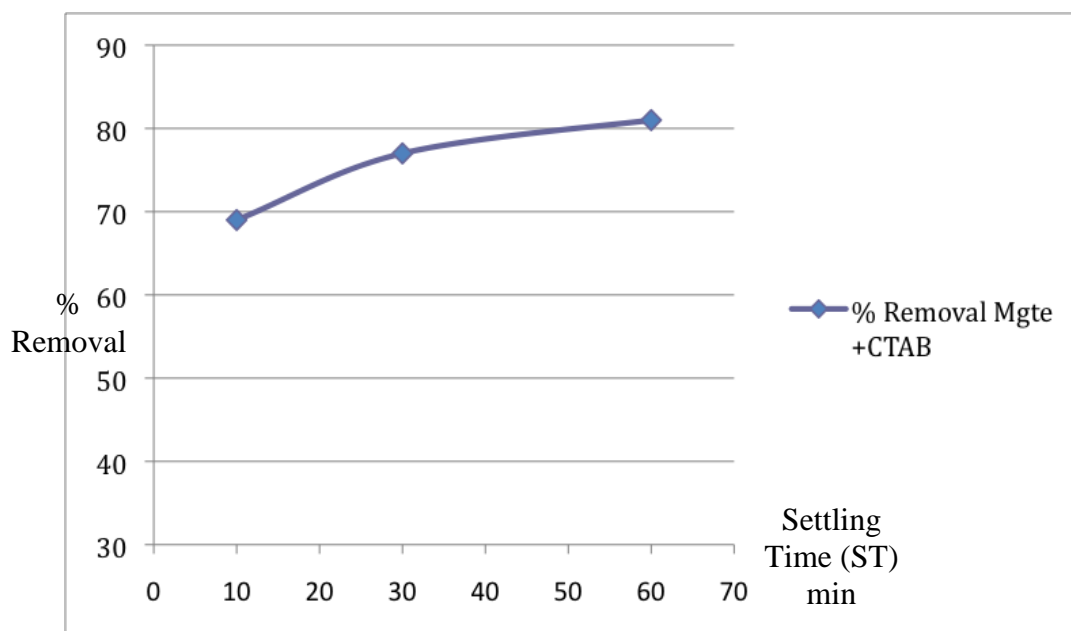
INC = 100 mg/L, MD = 25 mg/L, pH = 7, AR = 50 /min

Figure 4.13b Effect of Settling Time on removal by surface coated magnetites.

Major difference between the removal efficiency curves with or without ferric chloride is that higher removal efficiency is observed at low values of settling time. This is mainly because the magnetic seeding aggregation uses applied magnetic field to pull down magnetite-CTAB-nanoparticles aggregates and does not depend on gravity as in case of conventional coagulation. This observation also indicates that majority of the aggregate formation takes place within 30 min of mixing of magnetite to solution.

4.2.6 Effect of Agitation Rate on Removal Efficiency by Surface Coated Magnetites

As discussed before (2.2 and 4.1.6), frequency and rate of collisions largely influence the removal efficiency as long as they are not high enough to cause breaking of flocs [60, 77, 149]. Figure 4.14a shows the changes in removal efficiency with agitation rate for removal of nanoparticles using surface coated magnetites and ferric chloride. Figure 4.14b shows the changes in removal efficiency with agitation rate for removal of nanoparticles using surface coated magnetites only. Initially, removal efficiency steadily increases with increase in agitation rate. This is due to increase in number of collisions leading to rapid floc formation. At a range of agitation rate 45 -60 rpm, peak removal efficiency is observed. Any increase in agitation rate beyond the value of 60 rpm causes severe increase in frequency of collisions that lead to breaking of flocs and decrease in removal efficiency.

Although the shapes of curves for effect of agitation rate on removal efficiency with or without ferric chloride are little different, the overall effect is still the same with optimum agitation rate between 45 and 60 rpm.
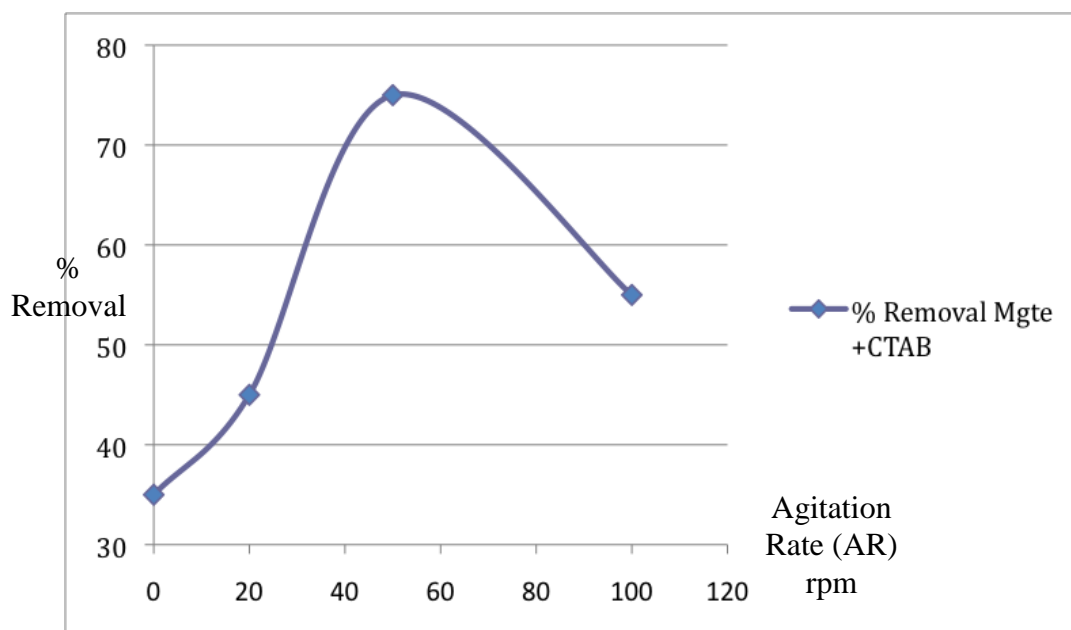
INC = 100 mg/L, ST = 30 min, pH = 7, CD = 25 mg/L, MD = 25 mg/L

Figure 4.14a Effect of Agitation Rate on removal by surface coated magnetites and ferric chloride.
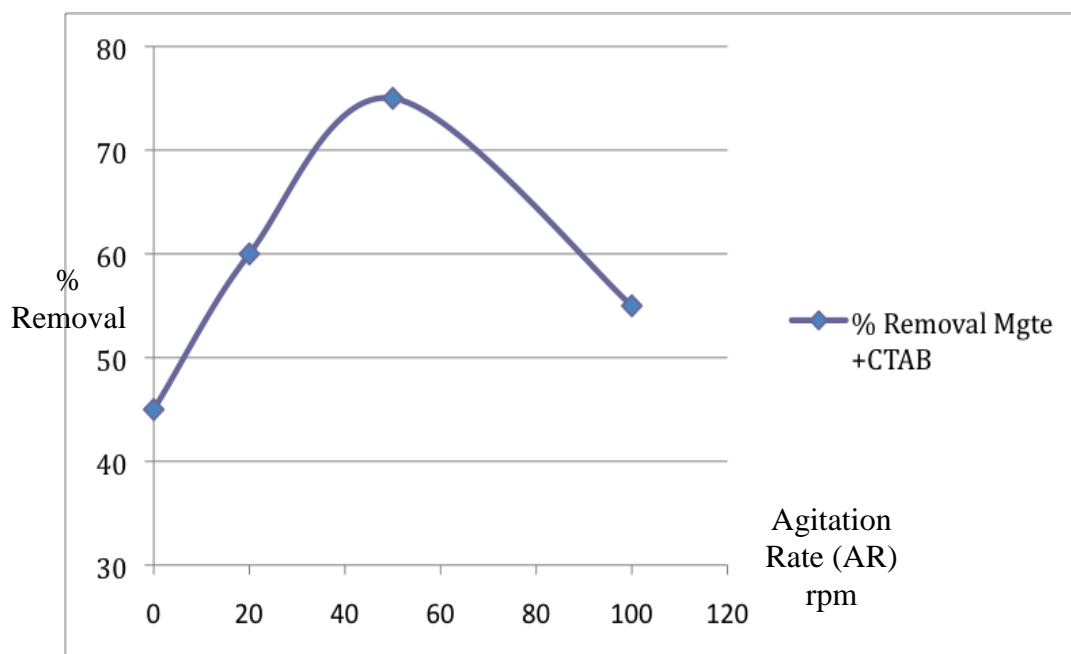
INC = 100 mg/L, ST = 30 min, pH = 7, MD = 25 mg/L

Figure 4.14b Effect of Agitation Rate on removal by surface coated magnetites.

4.2.7 Optimum Operating Conditions for Removal by Surface Coated Magnetites

As in case of conventional coagulation, objective function of the model was to optimize design parameters to maximize removal efficiency of nanoparticles. Removal efficiency is strong function of dosage of surface coated magnetites and a function of settling time. Agitation rate, INC, NOM, and pH also influence the removal efficiency. Table 4.2 shows the optimum ranges of all the design parameters for removal using surface coated magnetites. From the experimental results, expected removal efficiency will be in the range of 80-95% if the following conditions are maintained.

Table 4.2 Optimum Operating Conditions for Maximum % Removal of Nanoparticles Using Surface Coated Magnetites

Parameter	Optimum range
pH	6 – 7.5
Agitation Rate (slow mixing)	45 – 60 rpm
CTAB-Magnetite Dose	25 mg/L
CTAB-Magnetite Dose (with NOM)	35 mg/L
Settling Time	30 – 40 min

4.3   Comparison of Conventional Coagulation and Magnetic Seeding Aggregation for Removal of TiO$_2$ Nanoparticles from Water

From results and discussion presented in section 4.1 it can be seen that conventional coagulation alone is not adequate to efficiently remove engineered nanoparticles from water. At normal ranges of coagulant dosage for water treatment operations (10-30 mg/L), only 40-50% of total engineered nanoparticles in water are removed. This removal percentage is only marginally higher than the removal of 35-45% attained simply by prolonged settling without addition of any chemicals. A very high dose of

either alum or ferric chloride (>500 mg/L) is needed if a 70%+ removal was to be achieved.

A typical mid-size water treatment facility spends less than a dollar on coagulation and flocculation per 1000 gallons of water treated [150]. This includes cost of chemicals used, labor, operation and maintenance, and sludge collection, transportation and disposal. If the coagulant dose is increased from the typical value of 10-30 mg/L to more than 500 mg/L then the chemical cost alone would increase more than 20-30 times the usual amount. Increase in coagulant dose to such high numbers will also increase the amount of sludge resulting from chemical precipitation and the cost associated with it. Most water treatment facilities are not even equipped to handle such a high volume of sludge. Even wastewater treatment facilities use such high dosage only in worst-case scenarios to control sludge disposal costs. The handling and disposal of the sludge has always been one of the greatest difficulties faced by water treatment plants that use chemical treatment. Sludge is produced in great volume from most chemical precipitation operations in water and wastewater treatment, and often reaching 0.5 percent of the volume of wastewater treated when alum is used [60, 84, 134, 150]. The hazardous waste issue associated with sludge may increase the cost 10-20 fold [60, 84, 134, 150], mainly because handling, management, transportation, and disposal (e.g. landfill tipping fees) for hazardous waste costs much higher [134] than non-hazardous waste. The estimated cost of treatment with such a high dosage of coagulants and volume of sludge generated could rise above $15 per 1000 gallons of water treated. Clearly, use of conventional coagulation alone is not only very expensive, but also impractical to remove engineered nanoparticles from water.

Figure 4.15 presents direct comparison of removal efficiencies using magnetite and conventional coagulants.
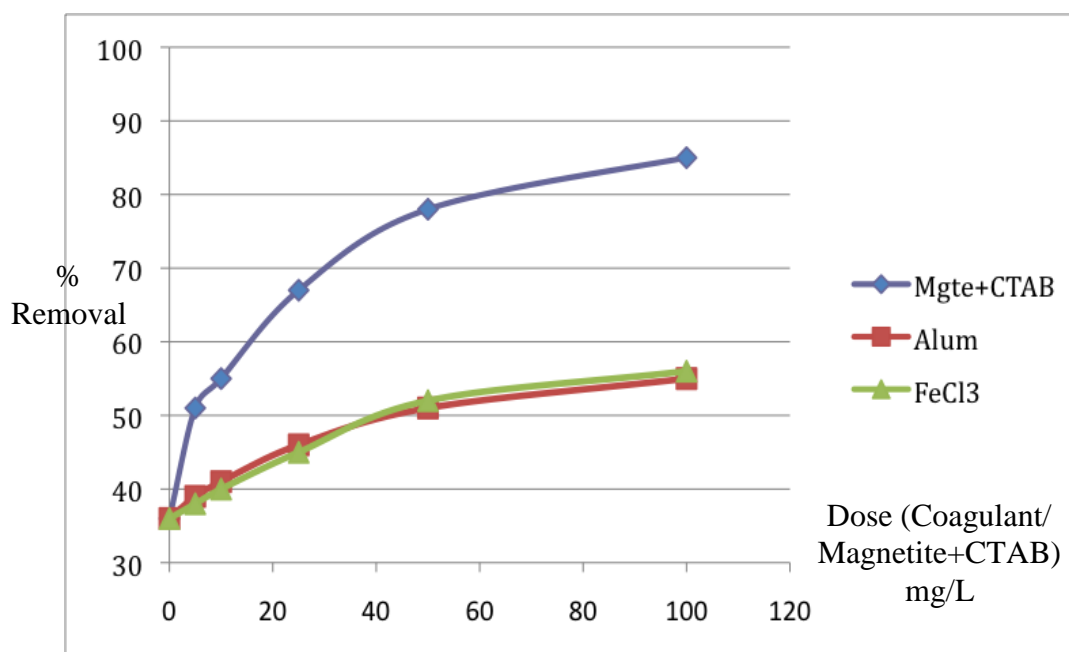
INC = 50 mg/L, ST = 30 min, pH = 7, AR = 50 rpm

Figure 4.15 Comparison of removal efficiencies using conventional coagulants (alum and ferric chloride) and surface coated magnetites.

From Figure 4.15, and from results and discussion presented in section 4.2 it can be concluded that magnetic seeding aggregation is a very viable method for removal of engineered nanoparticles from water. A removal efficiency of 85%+ was observed at surface coated magnetite dosage as low as 25 mg/L for samples with initial nanoparticle concentration of 100 mg/L. This is much lower than dosage of conventional coagulant (750 mg/L) required to achieve similar levels of removal efficiencies. Use of surface coated magnetites not only reduces the chemical cost, but also generates much less sludge. In fact, with 50 – 70% (as high as 90% in few cases) recycling of magnetites on average, as achieved in this research, total sludge generated in this method would be less than 10% of chemicals added. Use of magnetic seeding aggregation will also help to keep

the treatment cost at less than a dollar per 1000 gallons of water treated. Clearly, using magnetite-seeding aggregation to aid water treatment process to remove engineered nanoparticles from water is a green solution.

Introduction of magnetic seeding aggregation into an existing water treatment facility will require some infrastructure changes. Most importantly, a mechanism to apply magnetic field and collect CTAB-magnetite + nanoparticles aggregates needs to be installed. Many of the incineration facilities are equipped with heavy-duty magnets to collect metals from bottom ash. Such a system may be used to collect CTAB-magnetite + nanoparticles aggregates with some modifications. To install a completely new system to perform the above task may cost anywhere between $50,000 and $100,000 for a typical conventional water treatment plant of 100 MGD capacity [150]. This additional cost can be subsidized by money saved on coagulant dosage, sludge collection, transportation, and treatment/disposal, and by efficient recycling of magnetites within 2 years for a 100 MGD capacity conventional water treatment plant.

In addition to being a green technique and cost savings, magnetic seeding aggregation also has some other advantages and a few disadvantages over the conventional coagulation and flocculation. A summary of comparison of magnetic seeding aggregation and conventional coagulation for removal TiO_2 nanoparticles is presented in Table 4.3 below.

Table 4.3 Comparison of Conventional Coagulation and Magnetic Seeding Aggregation for Removal of TiO$_2$ Nanoparticles from Water

Parameter	Conventional Coagulation	Magnetic Seeding Aggregation
Removal Efficiency (RE)	RE is poor at normal dosage used for water treatment. Significantly high dosage is required to reach satisfactory levels of RE.	RE > 80% with as low as 25 mg/L dose of magnetites. Even better RE if the INC is high.
Dosage	In general, better removal is achieved as the dosage amount is increased. 50 mg/L or lower dose has little effect on increasing removal from natural aggregating tendencies. About 50% nanoparticles may still escape conventional coagulation treatment, unless very high coagulant dose (>200 mg/L) is applied.	As the dose of magnetites increases, so does the RE. Magnetites work particularly well if the INC is high. In comparison the magnetite dose required falls within range of normal coagulant dosage used for water treatment. If applied before conventional coagulation, this method can reduce the amount of nanoparticles that reach filtration and further units to less than 10%.
Effect of pH	pH has profound effect on removal using conventional coagulation both at high and low dose of coagulant, irrespective of the coagulant used (alum or ferric chloride). Near neutral pH is best to achieve maximum RE. This means that for most common scenarios, pre-conditioning for pH will not be required.	Solution pH affects the RE in this method too. The effect is more if magnetites are used in combination with ferric chloride. Even if water is treated only with magnetite-CTAB, pH still causes up to 10% variation in removal efficiency. Maximum removal is achieved at near neutral pH, which is the case for most common scenarios; hence little or no pre-conditioning for pH is required.
Effect of Presence of NOM	NOM adsorbs onto nanoparticles easily to reduce their attachment with coagulant. This reduces the RE by 10-25% at different dosages of coagulants.	NOM reduces the RE in this case as well. However the reduction is 5-10% less than that observed in case of conventional coagulation at similar levels of coagulant dose.
Effect of Agitation Rate (AR in rpm)	Too slow or too fast mixing causes reduction in RE. Maximum removal is observed at about 50 rpm for both alum and ferric chloride.	Agitation rate affects the RE in this case as well. Maximum removal is observed between 45 and 60 rpm mixing rate. The effect of AR on removal using magnetites is very similar to that of conventional coagulation.

Table 4.3 Comparison of Conventional Coagulation and Magnetic Seeding Aggregation for Removal of TiO$_2$ Nanoparticles from Water (Continued)

Effect of Settling Time (ST in min)	Prolonged settling times give better RE. However STs in excess of 60 min are not practical. High coagulant dose is therefore necessary to remove at least 70% nanoparticles at 30 min of settling. The relationship between ST and RE is somewhat liner within the range of 10-30 min.	This method uses applied magnetic field to collect magnetite-CTAB + nanoparticles aggregates. The effect of ST is therefore less. Most of the aggregates are formed within 30 min of mixing of chemicals and therefore prolonged settling is not necessary to achieve high RE.
Effect of Initial Nanoparticle Concentration (INC in mg/L)	INC has direct relationship with RE. Higher the INC, easier they are to remove from water. Removal of INC of 100 mg/L showed 10-25% higher RE than removal of INC of 50 mg/L.	Relationship of INC and RE in this case is very similar to that of conventional coagulation. Higher values of INC were removed much more efficiently (15%-25% higher RE) than lower INC values.
Recovery and Reuse (%)	N/A	50%-70% magnetites were recovered and reused successfully by using organic solvent to break the magnetite-CTAB + nanoparticles bond.
Sludge generation (% by volume)	Amount of sludge generated can be up to 50% of added coagulant; hence aiming to achieve good RE means significant volumes of sludge generated that will require handling, transportation and disposal. In some cases, changes to existing infrastructure may be required to manage such high volume of sludge.	Majority of the volume of sludge generated comes from volume of coagulant added at high dosages. Since much lower dose of magnetites is required as compared to conventional coagulation, sludge volume is not a major issue in this case. Also, recycling and reuse of magnetites will further reduce sludge volumes.
Cost ($)	High dosage, high sludge volumes everything will lead to high cost of operation. Hazardous waste issue related to sludge handling might increase the cost further by 10-20 fold.	Low dosage of magnetites, their recycling and reuse, and good management practices can keep the cost of treatment to a minimum. The goal is to achieve nanoparticle removal with very little or no additional cost to existing water treatment facility.

CHAPTER 5

CONCLUSION AND SIGNIFICANCE OF RESEARCH

5.1   Conclusion

Nanotechnology offers an innovative method for the removal of undesired engineered nanoparticles from water. Magnetic seeding aggregation using cationic surfactant modified magnetite nanoparticles significantly increases the efficiency of removal of TiO_2 from water. Cationic surfactant-modified magnetite nanoparticles offer a potential to rapidly remove engineered nanoparticles (normally negatively charged at the natural pH condition) from the water under the applied magnetic field. Although some infrastructure changes may be necessary to use the proposed method at water treatment facilities, cost savings from chemical usage and sludge handling will recover the capitol investment. The fact that these magnetite nanoparticles have potential to be reused for several times in the treatment process and also minimize secondary solid waste generated (i.e. little or no sludge produced as in the coagulation/flocculation process) makes this alternative approach economically and environmentally promising. The success rate of recovery and reuse of nanoparticles was less (50-70%) than expected (90% or higher) in this research. This is mainly because of loss of material while attempted recovery from individual jars. If the magnetic field was applied to large volume of water then higher % recovery is possible.

In summary, this research answers the critical question of whether the conventional coagulation/flocculation can be optimized to remove nanoparticles. Also, this research provides a viable alternative, surfactant-modified magnetic nanoparticle, in case that the conventional coagulation/flocculation is not applicable.

Key Observations

1. TiO_2 dispersion may remain stable for a very long time without coagulation.

2. Addition of coagulants increases removal efficiency, but very high dosage (750 mg/L) is required to reach 75%+ removal efficiency.

3. Removal efficiency is a strong function of coagulant dose and different removal mechanism dominate at low and high values of dosage.

4. Initial nanoparticle concentration, pH, settling time, and agitation rate all affect removal efficiency.

5. Magnetite aggregation seeding is very viable method for removal of nanoparticles from water.

6. Recovery and reuse of magnetites makes the method much more practical and cost efficient.

5.2   Suggested Future Work

The stability of nanoparticles in suspension is a complex phenomenon. This research has presented the effect of solution chemistry and presence of NOM on removal of TiO_2 nanoparticles from water. However, a typical wastewater or source water sample may contain variety of different constituents, which may interact with nanoparticles in water and affect their removal. It is important to understand the effect of these constituents as well as surface coating of nanoparticles on the removal efficiency using coagulation / flocculation and magnetic seeding aggregation.

Following are some areas worth looking into to expand the knowledge and understanding of the removal of nanoparticles.

1. Conduct similar studies using source water or wastewater for sample preparation rather than DI water.

2. Study the effect of surface modification of target nanoparticles on removal efficiency using coagulation / flocculation and magnetic seeding aggregation.

3. Study the effect of coagulant aids on removal efficiency using both the methods investigated in this study.

4. Optimize the amount of CTAB to be used for surface modification of magnetite nanoparticles.

5. Investigate the effectiveness of the methods studied in this research on the removal of different types of nanoparticles present in water individually and together.

6. Study the optimization of the magnetic field to achieve maximum recovery of magnetite nanoparticles.

7. Determine the life cycle cost analysis of the two methods studied in this research.

5.3   Significance of Research

The results of this project will enhance the science, technology and engineering, providing water and wastewater utilities guidelines for the performance of conventional coagulation/flocculation and cationic surfactant-modified nanoparticles for the removal of various engineered nanoparticles in water and wastewater at typical operational conditions. Understanding the optimization of conventional coagulation/flocculation and the application of cationic surfactant-modified magnetite nanoparticles to remove engineered nanoparticles in water can make water authorities ready to deal with nanoparticles as emerging contaminants. This result will provide a basis and understanding of the effect of different parameters on the removal of engineered nanoparticles. In addition, the results will benefit water utilities in managing and intercepting potentially harmful nanoparticles in process streams. The uniqueness and novelty of this research will make it of interest to a broad range of environmental researchers.

REFERENCES

1. M.R. Wiesner G.V. Lowry P. Alvarez D. Dionysiou P. Biswas, Assessing the risks of manufactured nanomaterials, Environ. Sci. Technol. 40 (2006) 4336-4345.

2. M. Ngo, A. S. Smiley-Jewell P. Aldous K. Pinkerton, E., Nanoscience and Nanotechnology: Environmental and Health Impacts - Nanomaterials and the Environment, ed., V.H. Grassian. John Wiley and Sons: Hoboken, NJ, (2008).

3. T. Zhang R. Surampalli K. Lai Z. Hu, Nanotechnologies for Water Environment Applications. Amer Society of Civil Engineers, (2009).

4. T. Phenrat Y. Liu R.D. Tilton G.V. Lowry, Adsorbed polyelectrolyte coatings decrease Feo nanoparticle reactivity with TCE in water: Conceptual model and mechanisms, Environmental Science and Technology 43 (2009) 1507-1514.

5. N. Saleh, Phenrat, T., Sirk, K., Dufour, B., Ok, J., Sarbu, T., Matyjaszewski, K., Tilton, R. D., Lowry, G. V., Adsorbed triblock copolymers deliver reactive iron nanoparticles to the oil/water interface, Nano Letters 5 (2005) 2489-2494.

6. L. Geranio M. Heuberger B. Nowack, The behavior of silver nanotextiles during washing, Environmental Science and Technology 43 (2009) 8113-8118.

7. A.K. Gupta M. Gupta, Synthesis and surface engineering of iron oxide nanoparticles for biomedical applications, Biomaterials 26 (2005) 3995-4021.

8. G. Sui W. Zhong X. Yang S. Zhao, Processing and material characteristics of a carbon-nanotube-reinforced natural rubber, Macromolecular Materials and Engineering 292 (2007) 1020-1026.

9. T.M. Barbara Karn, Wei-xian Zhang, Vicki Colvin, Paul Alivisatos, Nanotechnology and the Environment Applications and Implications ACS Symposium. ACS Publications, (2005).

10. A.M. Thayer, Firms find a new field of dreams, Chem. Eng. News 78 (2000) 36-38.

11. K.C. Hilary A. Godwin, Kenneth A. Bradley and Yoram Cohen, The University of California Center for the environmental implications of nanotechnology: Assessing nanomaterials for human health and ecotoxicological impact can be well aided by using high-throughput laboratory methods., Environmental Science and Technology 43 (2009) 6453-6457.

12. B. Nowack T. Bucheli, Occurrence, behavior, and effects of nanoparticles in the environment, Environ. Pollut. 150 (2007) 5-22.

13. F. Gottschalk T. Sonderer R.W. Scholz B. Nowack, Modeled environmental concentrations of engineered nanomaterials (TiO2, ZnO, Ag, CNT, fullerenes) for different regions, Environmental Science and Technology 43 (2009) 9216-9222.

14. M.A.W. Kiser, P. Benn, T. Wang, Y. Perez-Rivera, J. Hristovski, K., Titanium nanomaterial removal and release from wastewater treatment plants, Environmental Science and Technology 43 (2009) 6757-6763.

15. E. Oberdorster, Manufactured nanomaterials (fullerenes, C60) induce oxidative stress in the brain of juvenile largemouth bass, Environ. Health Perspect. 112 (2004) 1058-1062.

16. S. Pal Y.K. Tak J.M. Song, Does the antibacterial activity of silver nanoparticles depend on the shape of the nanoparticles? A study of the gram-negative bacterium Escherichia coli, Appl. Environ. Microbiol. 73 (2007) 1712-1720.

17. K. Hund-Rinke M. Simon, Ecotoxic effect of photocatalytic active nanoparticles TiO2 on algea and daphnids, Environ. Sci. Pollut. Res. Int. 13 (2006) 225-232.

18. E.M. Hotze T. Phenrat G.V. Lowry, Nanoparticle aggregation: Challenges to understanding transport and reactivity in the environment, Journal of Environmental Quality 39 (2010) 1909-1924.

19. K.N. Savolainen, H. Falck, G. Lindberg, H. Tuomi, T. Vippola, M., et al., Nanotechnologies, engineered nanomaterials and occupational health and safety - A review, Safety Science 48 (2010) 957-963.

20. P. Simeonova N. Opopol M. Luster, Nanotechnology--toxicological issues and environmental safety. Springer Verlag, (2007).

21. R. Hester R. Harrison, Nanotechnology: Consequences for human health and the environment. Royal Society of Chemistry, (2007).

22. T. Long N. Saleh R. Tilton G.V. Lowry B. Veronesi, Titanium Dioxide (P25) Produces Oxidative Stress in Immortalized Brain Microglia (BV2): Implication of Nanoparticle Neurotoxicity, Environ. Sci. Technol. 40 (2006) 4346-4352.

23. H.A. Jeng J. Swanson, Toxicity of metal oxide nanoparticles in mammalian cells, Journal of Environmental Science and Health - Part A Toxic/Hazardous Substances and Environmental Engineering 41 (2006) 2699-2711.

24. T. Phenrat T.C. Long G.V. Lowry B. Veronesi, Partial oxidation ("Aging") and surface modification decrease the toxicity of nanosized zerovalent Iron, Environmental Science and Technology 43 (2009) 195-200.

25. D.Y. Kwon S. Vigneswaran, Influence of particle size and surface charge on critical flux of crossflow microfiltration, Water Sci. Technol. 38 (1998) 481-488.

26. M.R. Chang D.J. Lee J.Y. Lai, Coagulation and filtration of nanoparticles in wastewater from Hsinchu Science-based Industrial Park (HSIP), Sep. Sci. Technol. 41 (2006) 1303-1311.

27. J.D. Fortner, Lyon, D.Y., Sayes, C.M., Boyd, A.M., Falkner, J.C., Hotze, E.M., Alemany, L.B., Tao, Y.J., Guo, W., Ausman, K.D., Colvin, V.L., Hughes, J.B., C60 in water: nanocrystal formation and microbial response, Environ. Sci. Technol. 39 (2005) 4307-4316.

28. P.K. Stoimenov R.L. Kilnger G.L. Marchin K.J. Klabunde, Metal oxide nanoparticles as bactericidal agents, Langmuir 18 (2002) 6679-6686.

29. Z. Li K. Greden P.J.J. Alvarez K.B. Gregory G.V. Lowry, Adsorbed polymer and NOM limits adhesion and toxicity of nano scale zerovalent iron to E. coli, Environmental Science and Technology 44 (2010) 3462-3467.

30. L. Limbach, Muler, E., K. Bereiter, R. Krebs, R. Stark, W. J., Galli, R., Removal of oxide nanoparticles in a model wastewater treatment plant: Influence of agglomeration and surfactants on clearing efficiency, Environmental Science and Technology 42 (2008) 5828-5833.

31. J. Brant H. Lecoanet M.R. Wiesner, Aggregation and deposition characteristics of fullerene nanoparticles in aqueous systems, Journal of Nanoparticle Research 7 (2005) 545-553.

32. T. Phenrat N. Saleh K. Sirk R.D. Tilton G.V. Lowry, Aggregation and sedimentation of aqueous nanoscale zerovalent iron dispersions, Environmental Science and Technology 41 (2007) 284-290.

33. C.R. O'Melia, Aquasols: The behavior of small particles in aquatic systems, Environmental Science and Technology 14 (1980) 1052-1060.

34. J. Jiang G. Oberdorster P. Biswas, Characterization of size, surface charge, and agglomeration state of nanoparticle dispersions for toxicological studies, Journal of Nanoparticle Research 11 (2009) 77-89.

35. T. Tadros, Colloid stability: The Role of Surface Forces - Part I. Colloids and Interface Science Series, Vol. 1. Wiley-VCH Verlag GmbH & Co. KGaA. Germany, (2007).

36. J. Brant H. Lecoanet M. Hotze M. Wiesner, Comparison of electrokinetic properties of colloidal fullerenes (n-C 60) formed using two procedures, Environmental Science and Technology 39 (2005) 6343-6351.

37. W. Den C. Huang, Electrocoagulation of silica nanoparticles in wafer polishing wastewater by a multichannel flow reactor: A kinetic study, Journal of Environmental Engineering 132 (2006) 1651-1658.

38. Y.K. Zhang, B. A. Chen, Y. Westerhoff, P. Capco, D. G. Crittenden, J. Fate, transport and toxicity of nanomaterials in drinking water. in 2007 NSTI Nanotechnology Conference and Trade Show - NSTI Nanotech 2007, Technical Proceedings. (2007).

39. N. Saleh, Kim, H. J., Phenrat, T., Matyjaszewski, K., Tilton, R. D., Lowry, G. V., Ionic strength and composition affect the mobility of surface-modified Fe0 nanoparticles in water-saturated sand columns, Environmental science & technology 42 (2008) 3349-3355.

40. N. Savage M.S. Diallo, Nanomaterials and water purification: Opportunities and challenges, Journal of Nanoparticle Research 7 (2005) 331-342.

41. M.R. Chang D.J. Lee J.Y. Lai, Nanoparticles in wastewater from a science-based industrial park-Coagulation using polyaluminum chloride, Journal of Environmental Management 85 (2007) 1009-1014.

42. P. Westerhoff Z. Yang J. Crittenden Y. Chen, Nanoscience and Nanotechnology: Environmental and Health Impacts - Properties of Commercial Nanoparticles that Affect Their Removal During Water Treatment, ed., V.H. Grassian. John Wiley and Sons: Hoboken, NJ, (2008).

43. T. Phenrat, Kim, H. J., Fagerlund, F., Illangasekare, T., Tilton, R. D., Lowry, G. V., Particle size distribution, concentration, and magnetic attraction affect transport of polymer-modified Fe0 nanoparticles in sand columns, Environmental Science and Technology 43 (2009) 5079-5085.

44. C.-J.M. Chin P.-W. Chen L.-J. Wang, Removal of nanoparticles from CMP wastewater by magnetic seeding aggregation, Chemosphere 63 (2006) 1809-1813.

45. Y. Zhang Y. Chen P. Westerhoff K. Hristovski J.C. Crittenden, Stability of commercial metal oxide nanoparticles in water, Water Research 42 (2008) 2204-2212.

46. D. Napper, Polymeric Stabilization of Colloidal Dispersions. Academic Press. New York, (1983).

47. J. Ying, Nanostructured materials. Academic Press, New York, (2001).

48. T.J.W. Brunner, P. Manser, P. Spohn, P. Grass, R. N. Limbach, L. K. A. Bruinink W.J. Stark, In vitro cytotoxicity of Oxide Nanoparticles: Comparison to Asbestos, Silica, and effects of particle solubility, Environ. Sci. Technol 44 (2006) 4373-4381.

49. C.L.B. Tran, D. Cullen, R. T. Searl, A. Jones, A. D. Donaldson, K., Inhalation of poorly soluble particles. II. Influence of particle surface area on inflammation and clearance, Inhalation Toxicology 12 (2000) 1113-1126.

50. N. Lubick, Silver socks have cloudy lining, Environmental science & technology 42 (2008) 3910.

51. A. Elder, Tiny Inhaled Particles Take Easy Route from Nose to Brain - URMC Press Room, (2007).

52. A. De Momi J.R. Lead, Size fractionation and characterisation of fresh water colloids and particles: Split-flow thin-cell and electron microscopy analyses, Environmental Science and Technology 40 (2006) 6738-6743.

53. J. Buffle H. Leeuwen, Environmental Particles. Volume 1. Boca Raton, FL: Lewis Publishers, (1992).

54. A.P. Black M.R. Vilaret, Effect of Particle Size on Turbidity Removal, AWWA-J 61 (1969) 209-214.

55. D.F. Lawler, Removing particles in water and wastewater, Environmental Science and Technology 20 (1986) 856-861.

56. M. Tagawa K. Gotoh M. Yokokura A. Syutoh S. Takechi, Influence of surface properties of particles on their adhesion and removal, Colloid & Polymer Science 267 (1989) 434-439.

57. P. Hiemenz R. Rajagopalan, Principles of colloid and surface chemistry. CRC Press, 1997.

58. D.F. Evans H. Wennerstrom, The Colloidal Domain; Where Physics, Chemistry, Biology, and Technology Meet. Wiley-VCH. New York, (1999).

59. T. Phenrat N. Saleh K. Sirk R. Tilton, D. G. Lowry, V., Aggregation and sedimentation of aqueous nanoscale zerovalent iron dispersions, Environ. Sci. Technol. 41 (2007) 284-290.

60. AWWA, Water Quality & Treatment: A Handbook on Drinking Water, ed., J. Edzwald. McGraw-Hill Education, (2010).

61. T. Phenrat, Saleh, N., Sirk, K., Kim, H.J., Tilton, R.D., Lowry, G.V., Stabilization of aqueous nanoscale zerovalent iron dispersions by anionic polyelectrolytes: Adsorbed anionic polyelectrolyte layer properties and their effect on aggregation and sedimentation, Journal of Nanoparticle Research 10 (2008) 795-814.

62. T. Phenrat, Song, J. E., Cisneros, C. M., Schoenfelder, D. P., Tilton, R. D., Lowry, G. V., Estimating attachment of nano- and submicrometer-particles coated with organic macromolecules in porous media: Development of an empirical model, Environmental Science and Technology 44 (2010) 4531-4538.

63. H. Hyung J.-H. Kim, Dispersion of C60 in natural water and removal by conventional drinking water treatment processes, Water Research 43 (2009) 2463-2470.

64. H.A. Aziz S. Alias F. Assari M.N. Adlan, The use of alum, ferric chloride, and ferrous sulphate as coagulants in removing suspended solids as coagulants in removing suspended solids, colour, and COD from semi-aerobic landfill leachate at controlled pH, Waste Manage. Res. 25 (2007) 556-565.

65. T. Phenrat T.F. Marhaba M. Rachakornkij, Leaching behaviors of arsenic from arsenic-iron hydroxide sludge during TCLP, Journal of Environmental Engineering 134 (2008) 671-682.

66. K.J. Suttiponparnit, J. Sahu, M. Suvachittanont, S. Charinpanitkul, T. Biswas, P., Role of Surface Area, Primary Particle Size, and Crystal Phase on Titanium Dioxide Nanoparticle Dispersion Properties, Nanoscale Research Letters 6 (2011) 1-8.

67. J.A. Davis R.O. James J.O. Leckie, Surface ionization and complexation at the oxide/water interface. I. Computation of electrical double layer properties in simple electrolytes, Journal of colloid and interface science 63 (1978) 480-499.

68. W. Stumm, Morgan, J.J., Aquatic Chemistry. Wiley-Interscience. New York, (1996).

69. M. Kosmulski, Surface Charging and Points of Zero Charge. CRC Press. Boca Raton, (2009).

70. I.D. Morrison, Ross, S., Colloidal Dispersions: Suspensions, Emulsions, and Foams. Wiley-Interscience. New York, (2002).

71. G.A. Parks, The isoelectric points of solid oxides, solid hydroxides, and aqueous hydroxo complex systems, Chemical Reviews 65 (1965) 177-198.

72. B.V. Derjaguin, Landau, L.D., Acta Physicochim URSS. Vol. 14, (1941).

73. E.J.W. Verwey, Overbeek, J.T.G., Theory of the Stability of Lyophobic Colloids. Elsevier. Amsterdam, (1948).

74. D.G. Grahame, The electrical double layer and the theory of electrocapillarity, Chemical Reviews 41 (1947) 441-501.

75. J. Widegren L. Bergstrom, Electrostatic stabilization of ultrafine titania in ethanol, Journal of the American Ceramic Society 85 (2002) 523-528.

76. R.J. Hunter, Zeta Potential in Colloid Science. Academic Press Inc., London, (1981).

77. I. Licsko, Realistic coagulation mechanisms in the use of aluminium and iron(III) salts, Water Sci. Technol. 36 (1997) 103-110.

78. B. Xie Z. Xu W. Guo Q. Li, Impact of natural organic matter on the physicochemical properties of aqueous C60 nanoparticles, Environmental Science and Technology 42 (2008) 2853-2859.

79. E. Verwey J. Overbeek, Theory of the stability of lyophobic colloids, Amesterdam: Elsevier, (1948).

80. E. Verwey, Theory of the Stability of Lyophobic Colloids, The Journal of Physical Chemistry 51 (1947) 631-636.

81. P. Biswas C.Y. Wu, Nanoparticles and the environment, Journal of the Air and Waste Management Association 55 (2005) 708-746.

82. M. Smoluchowski, Versuch einer mathematischen Theorie der Koagulationskinetik kolloider Lˆsungen, Z. phys. Chem 92 (1917) 129-168.

83. D.N. Thomas S.J. Judd N. Fawcett, Flocculation modelling: A review, Water Research 33 (1999) 1579-1592.

84. MWH, Water treatment principles and design, ed., J.T. Crittenden, RR Hand, DW Howe, KJ Tchobanoglous, G. J. Wiley, (2005).

85. B. Logan, Environmental transport processes. Wiley-Interscience, 1999.

86. A.T. Hanson J.L. Cleasby, Effects of temperature on turbulent flocculation. Fluid dynamics and chemistry, Journal / American Water Works Association 82 (1990) 56-73.

87. L.S. Kang J.L. Cleasby, Temperature effects on flocculation kinetics using Fe(III) coagulant, Journal of Environmental Engineering 121 (1995) 893-901.

88. J.K. Morris W.R. Knocke, Temperature effects on the use of metal-ion coagulants for water treatment, Journal / American Water Works Association 76 (1984) 74-79.

89. S. West W.R. Knocke. Effects of Low Temperature Conditions on the Use of Metal Ion Coagulants for the Removal of Soluble Organic Compounds from Surface Waters. 1984. Dallas, TX, USA: AWWA.

90. A.R. Petosa D.P. Jaisi I.R. Quevedo M. Elimelech N. Tufenkji, Aggregation and deposition of engineered nanomaterials in aquatic environments: Role of physicochemical interactions, Environmental Science and Technology 44 (2010) 6532-6549.

91. M. Das N. Saxena P.D. Dwivedi, Emerging trends of nanoparticles application in food technology: Safety paradigms, Nanotoxicology 3 (2009) 10-18.

92. S. Ghosh H. Mashayekhi B. Pan P. Bhowmik B. Xing, Colloidal behavior of aluminum oxide nanoparticles as affected by pH and natural organic matter, Langmuir 24 (2008) 12385-12391.

93. B.S. Necula I. Apachitei L.E. Fratila-Apachitei C. Teodosiu J. Duszczyk, Stability of nano-/microsized particles in deionized water and electroless nickel solutions, Journal of colloid and interface science 314 (2007) 514-522.

94. H.D. Ackler R.H. French Y.M. Chiang, Comparisons of Hamaker constants for ceramic systems with intervening vacuum or water: From force laws and physical properties, Journal of colloid and interface science 179 (1996) 460-469.

95. H.J. Butt B. Cappella M. Kappl, Force measurements with the atomic force microscope: Technique, interpretation and applications, Surface Science Reports 59 (2005) 1-152.

96. K.L. Chen B.A. Smith W.P. Ball D.H. Fairbrother, Assessing the colloidal properties of engineered nanoparticles in water: Case studies from fullerene C60 nanoparticles and carbon nanotubes, Environmental Chemistry 7 (2010) 10-27.

97. S.J. Klaine, Alvarez, P. J. J., Batley, G. E., Fernandes, T. F., Handy, R. D., Lyon, D. Y., Mahendra, S., McLaughlin, M. J., Lead, J. R., Nanomaterials in the environment: Behavior, fate, bioavailability, and effects, Environmental Toxicology and Chemistry 27 (2008) 1825-1851.

98. D. Lin, Liu, N., Yang, K., Zhu, L., Xu, Y., Xing, B., The effect of ionic strength and pH on the stability of tannic acid-facilitated carbon nanotube suspensions, Carbon 47 (2009) 2875-2882.

99. D.P. Jaisi N.B. Saleh R.E. Blake M. Elimelech, Transport of single-walled carbon nanotubes in porous media: Filtration mechanisms and reversibility, Environmental Science and Technology 42 (2008) 8317-8323.

100. H.F. Lecoanet M.R. Wiesner, Velocity effects on fullerene and oxide nanoparticle deposition in porous media, Environmental Science and Technology 38 (2004) 4377-4382.

101. D. Bouchard X. Ma C. Isaacson, Colloidal properties of aqueous fullerenes: Isoelectric points and aggregation kinetics of C60 and C60 derivatives, Environmental Science and Technology 43 (2009) 6597-6603.

102. X. Ma D. Bouchard, Formation of aqueous suspensions of fullerenes, Environmental Science and Technology 43 (2009) 330-336.

103. T. Xia, Kovochich, M., Brant, J., Hotze, M., Sempf, J., Oberley, T., Sioutas, C., Yeh, J. I., Wiesner, M. R., Nel, A. E., Comparison of the abilities of ambient and manufactured nanoparticles to induce cellular toxicity according to an oxidative stress paradigm, Nano Letters 6 (2006) 1794-1807.

104. I. Arnaud J.P. Abid C. Roussel H.H. Girault, Size-selective separation of gold nanoparticles using isoelectric focusing electrophoresis (IEF), Chemical Communications (2005) 787-788.

105. Y.I. Rabinovich N.V. Churaev, Results of numerical calculations of dispersion forces for solids, liquid interlayers, and films, Colloid journal of the USSR 52 (1990) 256-262.

106. I.R. Quevedo N. Tufenkji, Influence of solution chemistry on the deposition and detachment kinetics of a CdTe quantum dot examined using a quartz crystal microbalance, Environmental Science and Technology 43 (2009) 3176-3182.

107. Y. Zhang Y. Chen P. Westerhoff J.C. Crittenden, Stability and removal of water soluble CdTe quantum dots in water, Environmental Science and Technology 42 (2008) 321-325.

108. Y. Wang E. Forssberg R.J. Pugh, The influence of pH on the high gradient magnetic separation of < 10 Œºm particles of hematite and quartz, International Journal of Mineral Processing 36 (1992) 93-105.

109. R. Amal J.R. Coury J.A. Raper W.P. Walsh T.D. Waite, Structure and kinetics of aggregating colloidal haematite, Colloids and Surfaces 46 (1990) 1-19.

110. Y.P. Sun X.Q. Li W.X. Zhang H.P. Wang, A method for the preparation of stable dispersion of zero-valent iron nanoparticles, Colloids and Surfaces A: Physicochemical and Engineering Aspects 308 (2007) 60-66.

111. X. Song N. Jiang Y. Li D. Xu G. Qiu, Synthesis of CeO2-coated SiO2 nanoparticle and dispersion stability of its suspension, Materials Chemistry and Physics 110 (2008) 128-135.

112. S. Tabatabaei A. Shukohfar R. Aghababazadeh A. Mirhabibi, Experimental study of the synthesis and characterisation of silica nanoparticles via the sol-gel method, Journal of Physics: Conference Series 26 (2006) 371-374.

113. K.A.D. Guzman M.P. Finnegan J.F. Banfield, Influence of surface potential on aggregation and transport of titania nanoparticles, Environmental Science and Technology 40 (2006) 7688-7693.

114. N.H. Tkachenko Z.M. Yaremko C. Bellmann, Effect of 1-1-charged ions on aggregative stability and electrical surface properties of aqueous suspensions of titanium dioxide, Colloids and Surfaces A: Physicochemical and Engineering Aspects 279 (2006) 10-19.

115. A.I. G√≥mez-Merino F.J. Rubio-Hern√°ndez J.F. Vel√°zquez-Navarro F.J. Galindo-Rosales P. Fortes-Quesada, The Hamaker constant of anatase aqueous suspensions, Journal of colloid and interface science 316 (2007) 451-456.

116. L. Bergstrom, Hamaker constants of inorganic materials, Advances in Colloid and Interface Science 70 (1997) 125-169.

117. S. Relle S.B. Grant, One-step process for particle separation by magnetic seeding, Langmuir 14 (1998) 2316-2328.

118. P. Anand J.E. Etzel F.J. Friedlaender, Heavy Metals Removal by High Gradient Magnetic Separation, IEEE Transactions on Magnetics Mag-21 (1985) 2062-2064.

119. G. Bitton R. Mitchell C. De Latour E. Maxwell, Phosphate removal by magnetic filtration, Water Research 8 (1974) 107-109.

120. G. Bitton, Pancorbo, O., Gifford, G. E., Factors affecting the adsorption of polio virus to magnetite in water and wastewater, Water Res. 10 (1976) 978.

121. C. De Latour, Magnetic Separation in Water Pollution Control, IEEE Transactions on Magnetics Mag-9 (1973) 314-316.

122. C. De Latour, kolm, Henry, Magnetic Separation in Water Pollution Control - 2, IEEE Transactions on Magnetics Mag-11 (1975) 1570-1572.

123. K. Harding W. Baxter, Application of High Gradient Magnetic Separation to Ferric Hydroxide Filtration, IEEE Transactions on Magnetics Mag-17 (1981) 2795-2797.

124. P.A. Munro P. Dunnill M.D. Lilly, Magnetic Particles as Supports in Immobilised Enzyme Reactors, IEEE Transactions on Magnetics Mag-11 (1975) 1573-1575.

125. L. Nunez B.A. Buchholz G.F. Vandegrift, Waste remediation using in situ magnetically assisted chemical separation, Sep. Sci. Technol. 30 (1995) 1455-1471.

126. L. Petrakis P.F. Ahner, High Gradient Magnetic Separations in Water Effluents, IEEE Transactions on Magnetics Mag-14 (1978) 491-493.

127. J. Ugelstad, Berge, A., Ellingsen, J., Bjorgum, R., Schmid, R., Stenstad, P., Aune, O., Nilsen, T. N., Funderud, S., Nustad, K., Future Directions in Polymer Colloids, Nato ASI Series E: Applied Sciences-No. 138 (1987) 355.

128. M. Hull, Final Report: Magnetite Nanoparticles for Enhanced Environmental Remediation, EPA-NCER. (2007).
129. N. Hartman, Final Report: Engineered Magnetic Nanoparticles for Advanced Biosensor Signal Processing and Detection of Waterborne Pathogens, EPA-NCER. (2007).

130. M.R. Parker R.P.A.R. van Kleef H.W. Myron P. Wyder, Study of Particle Behaviour in High Field Magnetic Flocculation, IEEE Transactions on Magnetics Mag-18 (1982) 1647-1649.

131. R.A. Williams X. Jia, Simulation of magnetic flocculation behaviour of fine minerals, International Journal of Mineral Processing 32 (1991) 175-191.

132. S. Yiacoumi D.A. Rountree C. Tsouris, Mechanism of particle flocculation by magnetic seeding, Journal of colloid and interface science 184 (1996) 477-488.

133. C. Tsouris T.C. Scott, Flocculation of Paramagnetic Particles in a Magnetic Field, Journal of colloid and interface science 171 (1995) 319-330.

134. L. Metcalf H.P. Eddy G. Tchobanoglous, Wastewater engineering: treatment, disposal, reuse. McGraw-Hill New York, 1991.

135. S. Krishnakumar P. Somasundaran, Role of surfactant-adsorbent acidity and solvent polarity in adsorption-desorption of surfactants from nonaqueous media, Langmuir 10 (1994) 2786-2789.

136. T. Phenrat, Cihan, A., Kim, H. J., Mital, M., Illangasekare, T., Lowry, G. V., Transport and deposition of polymer-modified Fe0 nanoparticles in 2-D heterogeneous porous media: Effects of particle concentration, Fe 0 content, and coatings, Environmental Science and Technology 44 (2010) 9086-9093.

137. T. Phenrat, Mittal, M., Kim, H. J., Fagerlund, F., Illangasekare, T., Lowry, G. Effectiveness of nanoscale zerovalent iron (NZVI) to reduce contaminant mass emission from a NAPL source zone in an intermediate-scale aquifer system, San Francisco, CA, (2010).

138. I.G. Godinez C.J.G. Darnault, Aggregation and transport of nano-TiO2 in saturated porous media: Effects of pH, surfactants and flow velocity, Water Research 45 (2011) 839-851.

139. R.F. Domingos, Baalousha, M. A., Ju-Nam, Y., Reid, M. M., Tufenkji, N., Lead, J. R., Leppard, G. G., Wilkinson, K. J., Characterizing manufactured nanoparticles in the environment: Multimethod determination of particle sizes, Environmental Science and Technology 43 (2009) 7277-7284.

140. S. Torkzaban Y. Kim M. Mulvihill J. Wan T.K. Tokunaga, Transport and deposition of functionalized CdTe nanoparticles in saturated porous media, Journal of Contaminant Hydrology 118 (2010) 208-217.

141. T. Ben-Moshe I. Dror B. Berkowitz, Transport of metal oxide nanoparticles in saturated porous media, Chemosphere 81 (2010) 387-393.

142. S.R. Kanel D. Nepal B. Manning H. Choi, Transport of surface-modified iron nanoparticle in porous media and application to arsenic(III) remediation, Journal of Nanoparticle Research 9 (2007) 725-735.

143. R. Schneider, Wolpert, C., Guilloteau, H., Balan, L., Lambert, J., Merlin, C., The exposure of bacteria to CdTe-core quantum dots: The importance of surface chemistry on cytotoxicity, Nanotechnology 20 (2009).

144. J. Lee M. Cho J.D. Fortner J.B. Hughes J.H. Kim, Transformation of aggregated C60 in the aqueous phase by UV irradiation, Environmental Science and Technology 43 (2009) 4878-4883.

145. Y. Wang, Li, Y., Kim, H., Walker, S. L., Abriola, L. M., Pennell, K. D., Transport and retention of fullerene nanoparticles in natural soils, Journal of Environmental Quality 39 (2010) 1925-1933.

146. C.R. O'Melia, Aquatic Chemistry. American Chemical Society. Washington, DC, (1995).

147. M. Kosmulski, The significance of the difference in the point of zero charge between rutile and anatase, Advances in Colloid and Interface Science 99 (2002) 255-264.

148. M. Kosmulski, pH-dependent surface charging and points of zero charge. IV. Update and new approach, Journal of colloid and interface science 337 (2009) 439-448.

149. AWWA, Manual of Water Supply Practices - M37: Operational Control of Coagulation and Filtration Processes. Second ed., American Water Works Association. Denver, CO, (2000).

150. W.T. McGivney, Kawamura, S, Cost Estimating Manual for Water Treatment Facilities. John Wiley & Sons, (2008).