COATING OF NZVI PARTICLES WITH MODIFIED STARCH:

COLLODIAL STABILITY AND NITRATE REDUCTION STUDIES

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Mary Francis Pate

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The Supervisory Committee certifies that this ***disquisition*** complies with North Dakota State University's regulations and meets the accepted standards for the degree of

MASTER OF SCIENCE

SUPERVISORY COMMITTEE:

Achintya Bezbaruah
Chair

Senay Simesk

Wei Lin

Shafiqur Rahman

Approved:

04/14/15
Date

Dinesh Katti
Department Chair

ABSTRACT

Nanoscale-zero valent iron (NZVI) is an effective groundwater remediation media because it can quickly reduce and absorb contaminants. However, NZVI quickly agglomerates in aqueous systems, reducing its remediation capacity. This work investigated coating NZVI with native and modified rice, wheat, maize, and tapioca starches to improve colloidal stability. Colloidal stability studies were conducted with native and commercially available starches; tapioca starch modified with 2-Octen-l-ylsuccinic anhydride (OSA) was the best. Four concentrations of OSA-tapioca starch were prepared (3, 15, 35, and 50% w/w). NZVI coated with 35% OSA-modified tapioca starch (concentration = 10 g L^{-1}) kept 66% of the coated particles suspended after 2 hours (compared to 4% of bare particles, $p = 0.000$). Bare NZVI reduced significantly more nitrate (20 mg L^{-1}) than coated NZVI ($p = 0.000$). Bare and coated NZVI provided the same nitrate reduction at 40 and 60 mg L^{-1} ($p = 0.939$ and $p = 0.815$, respectively).

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LIST OF ABBREVIATIONS

NH_4^+ .....Ammonium

$(NH_4)_2SO_4$ .....Ammonium Sulfate

APGC.....Amphiphilic Polysiloxane Graft Copolymer

AGU .....Anhydroglucose Unit

As (V) or As (III).....Arsenic

BOD .....Biochemical Oxygen Demand

CMC .....Carboxymethyl cellulose

COD .....Chemical Oxygen Demand

CNZVI.....Coated NZVI (35% OSA-modified tapioca starch)

DS .....Degree of Substitution

DI water .....Deionized water

DNAPL .....Dense Non-Aqueous Phase Liquid

DVLO.....Derjaguin-Landau-Verwey-Overbeek

D_20 .....Deuterium Oxide

$Cr_2O_7^{2-}$ .....Dichromate

DOC .....Dissolved Organic Carbon

EDS.....Energy Dispersive Spectroscopy

FTIR .....Fourier transform infrared

HPLC .....High-Performance Liquid Chromatography

HPSEC .....High-Performance Size-Exclusion Chromatograph

HA.....Humic Acid

HCl.....Hydrochloric Acid.

$FeSO_47H_20$ .....Iron (II) sulfate heptahydrate

LLS.....Laser Light Scattering

LiOH .....Lithium Hydroxide

MCL.....Maximum Contaminant Level

MLSS.....Mixed liquor suspended solids

NP.....Nanoparticles

NZVI .....Nanoscale zero-valent iron

NO_3^- .....Nitrate

NO_3-N.....Nitrate-nitrogen

N .....Nitrogen

NMR .....Nuclear Magnetic Resonance

OS .....Octenyl Succinic

OSA.....Octenyl Succinic Anhydride

PRB .....Permeable Reactive Barrier

P.....Phosphorous

PAA .....Poly(acrylic acid)

PMMA .....Poly(methyl methacrylate)

PSS .....Poly(styrenesulfonate)

Tween 20 .....Polyoxyethylene sorbitan monolaurate

PV3A .....Polyvinyl alchol-co-vinyl acetate-co-itamic acid

KBr.....Potassium Bromide

KOH .....Potassium Hydroxide

KNO_3 .....Potassium Nitrate

PTS .....Pump and Treat Systems

SEM.....Scanning Electron Microscopy

$NaBH_4$.....Sodium Borohydride

NaOH .....Sodium Hydroxide

Na_2SO_4 .....Sodium Sulfate

SOGC .....Soybean Oil based Graft Copolymer

ThOD.....Theoretical Oxygen Demand

TEM.....Transmission electron microscopy

TCE .....Trichloroethylene

XAFS .....X-ray absorption find structure

ZVI.....Zero-valent iron

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CHAPTER 1. LITERATURE REVIEW

1.1. Introduction

During the past two decades, zero-valent iron (ZVI) has been used to remediate contaminated. Studies have found millimetric ZVI is effective at degrading many chlorinated compounds from water[1]. ZVI has been used extensively in permeable reactive barriers (PRBs) as it is an effective and low-cost electron donor[2]. Research established that ZVI is able to degrade or remove a variety of contaminants by either reduction or adsorption[2]. Contaminants that can be treated by ZVI include: chlorinated organic compounds[2], nitroaromatic compounds[2] ,arsenic[2] , heavy metals[2] , nitrate[2] , dyes[2] , and phenol[2].

Many advances have been made to ZVI over the past fifteen years. Most notably is the development of nanoscale zero-valent iron (NZVI) particles. NZVI particles are able to quickly remediate contaminants because of their high reactive surface area[4] (25-54 m^2g^{-1} for NZVI [3-5] compared to 1-2 m^2g^{-1} for microscale ZVI[5, 6]) and fast reaction kinetics[7]. Much like ZVI particles, NZVI particles are capable of treating a wide range of organic and inorganic compounds through sorption and reduction[7], as shown in Figure 1-1. As a strong reducing agent NZVI is able to treat: chlorinated compounds[7-11], arsenic (As (V) and As (III))[12], heavy metals[13], anions (i.e. nitrate (NO_3^-) and dichromate ($Cr_2O_7^{2-}$)[13, 14], and pesticides[5, 13].

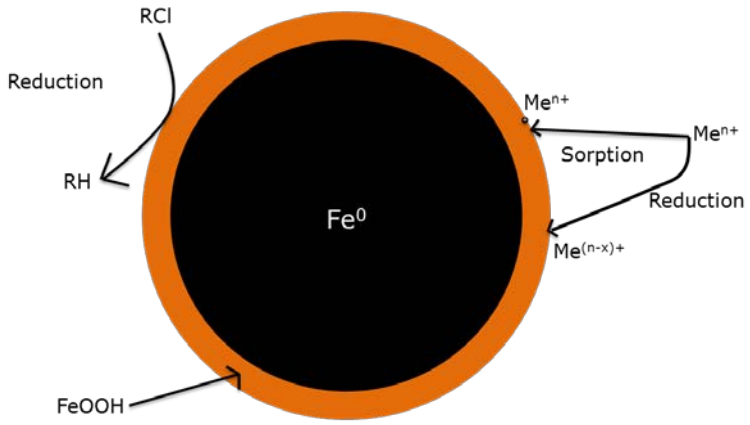

Figure 1-1. Schematic Model of Contaminant Reduction and/or Sorption using NZVI. Picture Developed from Tang et al.[7] and Li et al.[15].

While NZVI has many advantages, there are several physical properties that limit field applications. When injected into groundwater systems, NZVI particles tend to aggregate and settle[7, 8, 16], which reduces the effective surface area. Factors influencing magnetic nanoparticles (NPs) aggregation include particle size distribution, particle concentration, solution composition, surface chemistry, and magnetism of NPs[7]. In aquatic environments NP aggregation is controlled by particle-particle interactions[7, 8, 16]. Particle-particle interaction between NPs are traditionally described by Derjaguin-Landau-Verwey-Overbeek (DVLO) theory[7]. The DVLO theory describes colloidal stability by considering total interaction energy between particles[7, 17]. For NZVI, the total interaction energy is the sum of the van der Waals forces and electrical double layer interactions[7, 16]. Aggregation of NZVI occurs when attractive van der Waals and magnetic forces overpower repulsive forces[16]. To prevent aggregation, the repulsive forces between particles need to be improved, which is done by modifying the surface of NZVI[7, 8, 16].

1.2. Surface Modification of NZVI

Surface modification is used to improve the colloidal stability of NZVI particles[7, 8, 16, 18] by providing steric, electrostatic, or electrosteric stabilization[7, 8, 16]. Bare NZVI has a neutral or slightly positive surface potential[9], which causes NZVI to be attracted to

negatively charged surfaces common to aquifers. To overcome this attraction, electrostatic stabilization can be achieved by increasing the negative charge on the surface of NZVI[9, 16]. Commonly, electrostatic stabilization is achieved by coating NZVI particles with a polyelectrolyte polymer[7, 19, 20]. This method is very sensitive to ionic strength, water composition, and pH[18], which makes it difficult to use in uncontrolled groundwater system. Steric stabilization occurs when colloids, such as NZVI, are prevented from approaching at close distances[16]; maintaining a distance between particles keeps the attractive forces from overpowering repulsive forces. Electrosteric stabilization is a combination of electrostatic and steric stabilization[16] and is commonly used for surface modification.

To achieve steric or electrosteric stabilization, polymers are grafted to the surface of NZVI[7, 8, 18, 20]. Polymers are grafted onto the surface of NZVI by covalent bonds or physical adsorption[21]. Two methods of grafting have been effective for surface modification of NZVI; these methods are pre- and post- grafting[20]. To prepare pre-grafted particles, NZVI is synthesized in a polymer solution[20]. This method of synthesis influences the size, surface charge, surface chemistry, and polymer-iron interactions of NZVI[10, 20]. Surface modification by post-grafting is achieved by mixing bare NZVI particles with a polymer solution[20]; this allows the polymer to adsorb to the surface of NZVI. Polymers selected for coating have functional groups that improve complexion and bonding onto the surface of NZVI[7, 8]. Table 1-1 lists polymers used for coating NZVI.

The literature review presented in Table 1-1 highlights several important properties required to successfully coat NZVI. First, several studies emphasize the importance of having polymers with hydrophobic and/or hydrophilic components[8, 10, 12, 20-22]. Hydrophilic blocks are extremely important for obtaining steric stability of particles. These blocks prevent NZVI particles from coming into close contact with each other (see Figure 1-1a), thus providing steric stability[8, 9, 12, 21]. In particular, polymers with higher molecular weights

will further increase steric stability[23, 31]. Polymers with higher molecular weight increase the absorbed layer's thickness[23], which increases the steric repulsion between particles.

Hydrophobic components are attracted to oil interfaces, such as dense non-aqueous phase liquid (DNAPL), which improves NZVI's ability to target specific contaminants[3, 8, 21, 22]. The hydrophobic block anchors NZVI to the oil/water interface (shown in Figure 1-1b)[21], which improves contact between NZVI's surface and contaminants. It is ideal if the hydrophobic components have a low polarity, as this prevents water from oxidizing the iron surface , while still allowing contaminants to pass through the polymer[8, 21]. A polymer with both hydrophobic and hydrophilic groups, called an amphiphilic polymer, is ideal because it improves the colloidal stability and contaminant targeting abilities of NZVI particles.

Table 1-1. Polymers for Coating NZVI

Coating	Grafting Time	Characteristics	Citation
Polyvinyl alchol-co-vinyl acetate-co-itamic acid (PV3A)	Post Synthesis	Contains –OH, –CO–, and –COOH groups. Alters NZVI surface to have a negative charge at pH ≥ 4.5, thus improving electrostatic repulsion[9]. PV3A's large molecules also improve NZVI's steric stability[9]. Mobile in sand columns[19].	[9, 19]
Poly(methyl methacrylate) (PMMA)	Pre-Synthesis	Hydrophobic chains are attracted to oil phase, creating a strong affinity for NAPL contaminants. The hydrophobic chains also create a low polarity region, which prevents water from reaching NZVI surface.	[22]
Poly(styrenesulfonate) (PSS)	Pre & Post Synthesis	Creates a negative charge layer around NZVI[20]. Decreases the number of particles forming critical sized aggregates, thus improving suspension[23].	[20, 23]
Poly(acrylic acid) (PAA)	Post Synthesis	Contains carboxylic acid (–COOH) groups for anchoring. Prevents aggregation of NZVI by creating a highly negative surface charge [15]at dosages less than 50% (w/w)[19]. Mobile in porous media[24].	[3, 19, 24]
Triblock Copolymer	Post Synthesis	PMMA group anchors polymer to NZVI surface. Hydrophobic blocks provide strong affinity to NAPL. Hydrophilic PSS groups provide electrosteric stabilization between particles.	[21]
Amphiphilic Polysiloxane Graft Copolymer (APGC)	Post Synthesis	Uses pendant carboxylic acids to anchor polymer to NZVI surface. The polysiloxane backbone allows contaminants to permeate to surface of NZVI. Water-soluble PEG grafts provide colloidal stability.	[8]
Soybean Oil based Graft Copolymer (SOGC)	Post Synthesis	Natural polymer that is biodegradable. Keeps approximately 90% of particles suspended for up to 2 hours. Complex synthesis process.	[25]

Continued on next page

Table 1-1. Polymers for Coating NZVI (Continued)

Coating	**Grafting Time**	**Characteristics**	**Citation**
Polyoxyethylene sorbitan monolaurate (Tween 20)	Post Synthesis	Non-ionic surfactant. Hydrophilic block provides steric stability[12]. Mobile in sand packed column[12]. Particles are sterically stable[26].	12, 26
Carboxymethyl cellulose (CMC)	Pre & Post Synthesis	Binds to NZVI surface through carboxylate groups[20]. Best colloidal stability occurs when CMC is grafted pre-synthesis [20]. Mobile in silty clay/sand/gravel field aquifer[27].	20, 27
Guar Gum	Pre and Post Synthesis	High molecular weight polysaccharide with little to no charge[18]. Complex to NZVI surface through hydroxyl groups pre-synthesis[10]. Provides steric stability at coating concentrations over 0.5 g/L[18]. Mobile in quartz sand[28].	10, 18, 28
Water Soluble Starch	Pre-synthesis	Hydroxyl groups complex ferric ions to molecular matrix[29]. Improves steric stability of particles [26, 29].Mobile in soil[30].	26, 29, 30

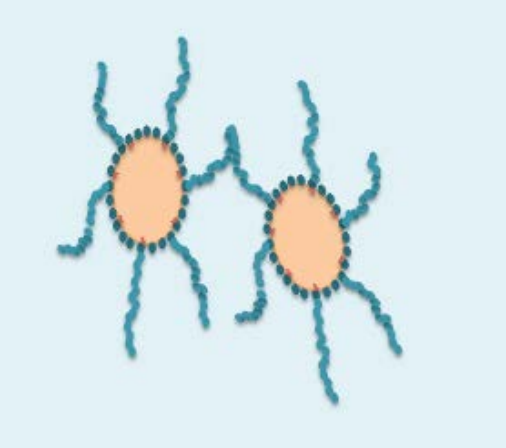

Figure 1-2. Surface Modification Schematic
Modified NZVI in Water. Picture Developed from Krajangpan et al. [8], Phenrat et al.[23], and Saleh et al. [21].

A polymer's ability to securely anchor onto the surface of NZVI is dependent upon its anchoring blocks. Cirtiu et al.[20] reported the use of amide and sulfonates for anchoring blocks. Both functional groups anchor to NZVI's surface through H-bond interactions[20]. Hydroxyl groups, such as in starch molecules, are able to complex to iron surfaces[26, 29]. In alkaline solutions, hydrophilic carboxylates have a strong affinity for anchoring organic molecules to an iron oxide surface[9, 19]. Several studies have successfully shown polymers with hydrophilic groups, such as esters and carboxyls[32], will strongly bind to the surface of NZVI[8, 21, 32, 33].

Carboxyl groups can bind to the surface of NZVI in three different complexation modes. The modes are: monodentate chelating, bidenate chelating, and bidentate bridging[20, 33], which are shown in Figure 1-2 and determined by Fourier transform infrared (FTIR) spectroscopy[20, 33]. Dissociation of a polymer's carboxylic acid groups can occur once the polymer is absorbed to NZVI's surface[9, 19, 20]. This causes a negative charge around NZVI particles, which is demonstrated by negative ζ-potentials[9, 19, 20]. Literature suggests a ζ-potential of at least ± 30 mV is needed to maintain colloidal stability[9]. Negative surface charges are ideal because they prevent NZVI aggregation and precipitation onto porous media[9, 19, 20, 26], along with improving aquifer mobility[19, 27, 31].

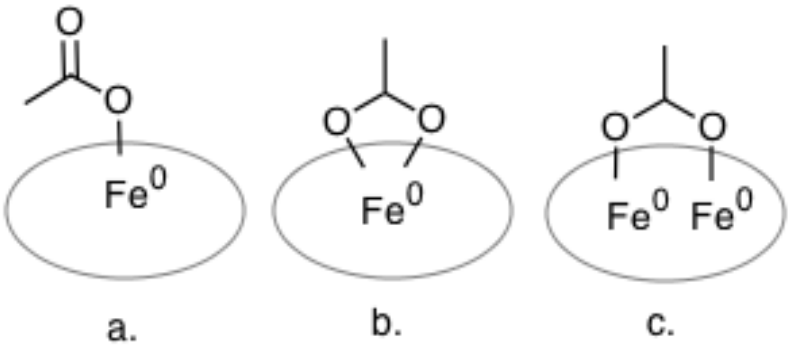

Figure 1-3. Modes of Iron-Carboxyl Complexation
a. Monodentate Chelating, b. Bidentate Chelating, and c. Bidentate Bridging. Modified from Cirtiu et al. [20].

The polymers presented in Table 1-1 are effective at improving NZVI's colloidal stability. However, production and environment concerns limit the use of some of these polymers. Several of the polymers have only been synthesized and/or coated in small batches and scale up to field use could be difficult[9, 23]. The cost of commercial polymers prohibits large-scale applications of several polymers[18]. Difficult synthesis and coating processes also limit the field applications[9, 19]. Some of the polymers are not biodegradable, which prohibits their use for groundwater application[8]. These issues present a gap in the literature and the need for a cheap, green, easily producible polymer for coating NZVI.

1.3. Biopolymers for Coating NZVI

In order develop a cost effective, green polymer for coating NZVI, the principles of green chemistry should be closely considered. Specifically, the polymer should be made from a renewable source, be non-toxic, and biodegradable[34]. Renewable sources, especially those from agriculture areas, are ideal because they produce fewer greenhouse gases, require less energy, and supplement local production economies[35]. Biopolymers are an ideal candidate for coating NZVI because they have a low cost, are produced from an annually renewable source, and biodegradable under the right conditions[36].

Biopolymers are used extensively in the food and medical industries for encapsulation and delivery systems. Polysaccharides are widely used in the food industry as stabilizers because of their ability to induce steric or electrostatic interactions between particles[37]. This property has resulted in the production of a wide range of food-grade polysaccharides biopolymers that are used as emulsion stabiliziers[38, 39]. Taking stride from the food industry, several studies have investigated the potential of using polysaccharides to coat NZVI.

Natural gums, such as xanthan and guar gum, have improved the colloidal stability of NZVI. Both gums have high molecular weights[18, 40], which increases the thickness of the layer absorbed onto NZVI[23]. Xanthan gum forms a gel network in solution, which results in high viscosity at low shear rates and low viscosity at high shear rates[16]. The carboxyl groups in gel network adsorb to the surface of NZVI, effectively reducing the NP's settling velocity[16]. Comba et al.[16] found higher concentration (6 g L^{-1}) xanthan solutions stabilized NZVI for a period of ten days[16]. Xanthan coated NZVI particles are highly mobile in porous media because it can easily flow near pore walls where high shear rates are predominate[40].

Guar gum, a non-ionic polysaccharide, is able to attach to NZVI's surface through hydroxyl groups[10, 18]. Since guar gum is a neutral polymer, it is only able to provide steric stability[10]. Tiraferri et al.[18] found coating NZVI with guar gum prevented agglomeration, even at high ionic strengths. Another study found guar gum solutions of 0.05% weight kept NZVI suspended for over 48 hours[10]. Guar gum coating also significantly enhances particle mobility in packed sand columns over a range of ionic strengths[28].

In addition to natural gums, several studies have used CMC to coat NZVI particles. CMC is a water soluble, anionic, polyelectrolyte containing both carboxylate and hydroxyl groups[20, 33]. Cirtiu et al.[20] found NZVI particles synthesized in the presence of CMC had superior stability over a wide range of ionic strength compared to particles grafted with CMC post synthesis[20]. NZVI particles synthesized in the presence of 0.2% (w/w) CMC and found

CMC-stabilized particles remained stable for over 9 hours[10, 33]. Sedimentation studies found increasing the molecular weight of CMC does not improve stability, indicating CMC stabilizes NZVI through electrostatic stabilization[10].

Column transport studies indicate CMC coated NZVI particles deposit on porous media at lower pore volumes [31, 33, 41]. Raychoudhury et al. [41] found CMC coated NZVI particles are retained on silica surfaces at intermediate groundwater velocities (0.455 cm min^{-1}). However, the particles began to detach after 5 pore volumes, resulting in a non-steady state effluent of iron[41]. Higher effluent concentrations occur when high pore velocities increase the drag forces acting on attached particles, causing them to detach from the media, which results in higher effluent concentrations[31]. He et at[27] performed a field study with CMC coated NZVI particles. CMC coated NZVI traveled up to 10 feet down-gradient of the injection point, creating a reactive barrier to treat chlorinated compounds[27]. The CMC coated NZVI also boosted the microbial activity, which further improved the anaerobic dechlorination process[27]. Overall, CMC is effective at stabilizing and transporting NZVI particles.

These examples illustrate the potential of biopolymers for coating NZVI. However, most of the work in this area is focused on the polysaccharide biopolymers presented here. Further research is needed to evaluate other biopolymer polysaccharides.

1.4. Starch for Coating NZVI

Starch is found in almost all green plants, along with a variety of plant tissues and organs, making it one of Earth's most abundant carbohydrates[42]. It is a branched, hydrophilic polymer containing approximately 20% amylose, along with an extensive number of hydroxyl groups[29, 42]. Native and modified starches are used extensively in the food industry as emulsifiers and stabilizers[38]. Its abundance, biodegradability, and renewability make it an ideal biopolymer for coating NZVI particles. The extensive number of hydroxyl groups present in the amylose help facilitate surface complexation to metal

surfaces[43]. Additionally, amylose is easily dispersed in water, which eliminates the use of organic solvents[43]. To date, several studies have used water-soluble starch to improve the colloidal stability of NPs.

He et al.[29] first synthesized NZVI particles in the presence of a water-soluble starch. Their work was inspired by Raveendran's use of water-soluble starch as a protecting agent for silver NPs[43]. Transmission electron microscopy (TEM) images revealed discrete and well-dispersed particles occurred when NZVI is synthesized in the presence of starch; particles synthesized without starch quickly aggregated into dense flocs[29]. The starch stabilized NPs remained suspended over 24 hours, while the non-stabilized NPs quickly settled[29]. The improved colloidal stability occurred because the hydroxyl groups bind to the surface of ferric ions before reduction[29, 43, 44]. Once reduced, the Fe^0 particles remained dispersed in the starch matrix through steric stabilization since starch is a neutral molecule[29, 43].

Starch stabilized NZVI particles were tested to see if immobilization and reduction of pertechnetate (ReO_4^-) is possible in soil and groundwater. Kinetic studies found the reduction rate of ReO_4^- by starch-stabilized NZVI particles was pseudo-first order[30]. Pseudo-first order reaction rates were also confirmed for trichloroethylene (TCE) degradation by starch stabilized NZVI particles[29]. *In situ* reductive immobilization of ReO_4^- was tested by passing starch-stabilized NZVI and bare NZVI particles (both concentrations at 560 mg/L) through a column of ReO_4^- laden loess[30]. Effluent iron concentrations indicated starch-stabilized NZVI is mobile in the loess bed[30]. Starch-stabilized NZVI particles reduced the effluent ReO_4^- concentrations by 57% compared to bare NZVI particles[30]. The increased contaminant reduction likely occurred because the particles remained discrete and moved throughout the column, thus increasing the available surface area and contact time.

In addition to pre-synthesis studies, a couple studies have focused on the stability of post-synthesis starch-stabilized NZVI particles. Pristine NZVI was coated with potato starch at seven different concentrations (0, 0.1, 0.2, 0.3, 0.4, 0.5, and 0.6 5 % w/w)[45]; NZVI

particles coated with 0.4% w/w potato starch had the best stability[45]. Sedimentation studies over one hour found nearly all of the starch-stabilized particles remained suspended[26, 45]. The ζ-potential for these particles was approximately -10 mV, indicating the potato starch provided some electrosteric stabilization[26, 45]. Particle stability was further improved with the addition of 2 mg L^{-1} of humic acid (HA)[45]. HA improved stability by decreasing the ζ-potential to approximately -15 mV, which increased the electrosteric repulsion effect[45].

Several studies have evaluated starch-stabilized magnetite NPs. Two studies synthesized magnetite NPs in a water-soluble starch solution of varying concentrations (0-0.5 % w/w)[44, 46]. Another study prepared magnetite NPs in the presence of hydrolyzed potato starch (0-0.13 % w/w)[47]. It was found magnetite NPs will rapidly flocculate and settle if the starch concentration is below 0.02% weight[46]. All studies concluded starch provides steric stabilization to magnetite NPs[44, 46, 47].

In addition to sedimentation analysis, both studies completed extensive characterizations of the magnetite NPs. X-ray absorption fine structure (XAFS) analysis found synthesizing magnetite NPs in the presence of starch does not affect the valences of iron atoms[44]. TEM images show well-defined, fully dispersed stable magnetite NPs when synthesized in the presence of starch[46, 47]. Monitoring mean diameter and particle size distribution with laser light scattering (LLS) found the NP size decreased with increased starch concentrations[44]. ζ-potential analysis found the starch-stabilized particles had a virtually neutral charge in the pH range of 2-9 and gradually decreased to a ζ value of -16 mV at pH equal to 11[46]. Arsenate removal studies found starch-stabilized magnetite NPs were more effective then CMC-stabilized magnetite NPs at reducing arsenate[46]; this is because the highly negative surface charge of CMC-stabilized NPs inhibits arsenate absorption[46].

Despite the demonstrated success of starch-stabilized NPs, a few complications have been documented. Starch can serve as a bridging agent, which results in the formation of starch-stabilized NZVI flocs after sitting for several days[29, 46]. However, the flocs are easily dispersed using sonication, indicating only loose bonds were formed between starch particles[29]. The tendency to form loose flocs after sitting for a few days indicates starch-stabilized NZVI particles need to be prepared directly before use. Kinetic studies found removal efficiencies are impacted by the thickness of starch coating[46, 47]. This is because a denser layer of starch increased the mass transfer resistance and surface accessibility[46, 47].

Although there are problems with stabilizing NZVI with starch, it still is a promising candidate for coating NPs. The pre-synthesis studies were likely conducted using unmodified starches, evidenced by near neutral ζ-potentials. Studies in the food industry show unmodified food starches lacks properties required for successful emulsification[48]. Attaching hydrophobic groups to the repeating glucose units creates amphiphilic starch molecules[39] that are effective stabilizers[48]. Native starch can also be modified to contain ester groups[49], which can help bond molecules to NZVI's surface[8, 21, 32, 33]. Additionally, the functional groups added to native starch during modification can provide a negative surface charge to provide electrostatic stabilization[44]. Coating NZVI particles with modified starches may help to improve the long-term colloidal stability because of the increased stabilization from electrostatic forces. Furthermore, the amphiphilic nature of modified starch may help to increase contaminant-targeting ability of NZVI particles.

The objective of this work is to: 1) evaluate the colloidal stability of post-synthesis modified NZVI with native and commercial starches, 2) develop a modified starch to coat NZVI with, 3) determine effects of starch modification on colloidal stability, and 4) assess reduction of nitrate by bare NZVI and coated NZVI particles.

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CHAPTER 2. MODIFICATION OF TAPIOCA STARCH FOR IMPROVING THE COLLODIAL STABILITY OF NANOSCALE ZERO-VALENT IRON PARTICLES

2.1. Introduction

Nanoscale zero-valent iron (NZVI) particles are increasingly becoming popular for groundwater remediation[1-6]. Compared to ZVI particles, NZVI particles are able to quickly treat contaminant plumes because of their high surface area to volume ratio, rapid kinetics, and high reactivity[1,3,6,7]. Unfortunately, NZVI particles quickly agglomerate and settle in aqueous environments, which reduces the available surface area for reduction/adsorption to occur[1,3,4, 6, 8]. Agglomeration occurs because attractive van deer Waal and magnetic forces overpower repulsive forces[9]. Surface modification is used to improve NZVI's colloidal stability by enhancing repulsive forces between particles. Repulsive forces can be increased by coating particles with polymers to provide steric, electrostatic, and electrosteric stabilization[9].

Polysaccharides are promising biopolymers for coating NZVI particles because of their ability to induce colloidal stability. One of Earth's most abundant polysaccharides is starch, which is found in all green plants and many plant tissues[10]. Starch is a branched, hydrophilic polymer composed of amylose/amylopectin and an extensive number of hydroxyl groups[10, 11]. The hydroxyl groups are ideal because they have a strong affinity for iron surfaces[3,12,13,14,15], which enables them to bind starch to the surface of NZVI. It is also a renewable source and can be harvested from a variety of crops including: potato, maize, wheat, rye, peas, rice, and tapioca[16].

In its native form, starch has limited use in the food industry because of its physical properties. Physical shortcomings of native starch include: insolubility[17, 18], cohesive texture[17, 19], low resistance to shear and high temperatures[20], and tendency to retrograde

during storage[17, 20]. To overcome these problems, native starch is modified to improve its functional groups[21]. Native starches are typically modified to by chemical cross-linking and substitution[19, 20]. Cross-linking introduces additional covalent bonds to the starch molecules, which stabilizes and strengthens the molecule[20]. Substitution adds substituents to the starch backbone[18]. A starch molecule with substituents has a weaker granular structure[20], which helps to improve their solubility and ability to act as an emulsion stabilizer[18, 21]. Modified starches are commonly used in the food, pharmaceutical, and personal care industries[21].

Several studies have evaluated the colloidal stability of nanoparticles (NPs) coated with modified starches. He et al.[11] synthesized discrete and well-dispersed NZVI particles in the presence of a water-soluble starch. These particles remained suspended for over 24 hours and improved the degradation of TCE compared to bare particles[11]. Despite improved colloidal stability, starch-stabilized NZVI particles formed flocs after a few days[11]. Dong et al.[22] coated NZVI with potato starch and found approximately 90% of the particles remained suspended after 1 hour. Liang et al.[23] reported coating magnetite nanoparticles with hydrolyzed potato starch improved colloidal stability by 27% compared to bare particles. Another study used starch stabilized NZVI particles to immobilize and reduce pertechnetate (ReO_4^-) in soil and groundwater[24]. Starch-stabilized NZVI particles reduced the effluent ReO_4^- concentrations by 57% compared to bare NZVI particles[24]. The increased contaminant reduction likely occurred because the particles remained discrete and moved throughout the column, thus increasing the available surface area and contact time. Two studies synthesized magnetite NPs in a water-soluble starch solution of varying concentrations (0-0.5% w/w)[23, 25]. Another study prepared magnetite NPs in the presence of hydrolyzed potato starch (0-0.13 % w/w)[26]. It was found magnetite NPs will rapidly flocculate and settle if the starch concentration is below 0.02% weight[23]. All of the studies on magnetite NPS concluded starch provides steric stabilization[23, 25, 26].

Octenyl succinic anhydride (OSA) starch is a promising modified starch for coating NZVI particles. The reaction of OSA with starch is commonly used throughout the food industry[17, 18, 21]. OSA starches are amphiphilic and function as emulsion stabilizers[21]. Applications for OSA starch are found in the food, pharmaceuticals, and personal care industries[17]. Starch is modified with OSA by suspending starch granules in water and mixing them with OSA under alkaline conditions[21]; the modification follows a standard esterification reaction[27]. The alkaline conditions enhance the nucleophilicity of the hydroxyl groups and causes the starch granules to swell[28]. Swollen starch granules are ideal because they allow diffusion of OSA molecules into the starch granules, thus providing increased contact between the starch and OSA molecules[18]. Once the reaction is complete, an OSA starch contains carboxyl and ester groups[29], which are reported to bind strongly to the surface of NZVI[3, 12, 15, 30].

The amphiphilic structure of OSA starch is ideal for coating NZVI particles because they contain both hydrophobic and hydrophilic blocks. Hydrophobic blocks are attracted to oil interfaces, such as such as dense non-aqueous phase liquid (DNAPL), which improves NZVI's ability to target specific contaminants[2, 3, 12, 31]. Meanwhile, hydrophilic blocks will prevent NZVI particles from approaching at close distants[6, 32]. Carboxyl and ester anchoring groups are ideal for coating NZVI particles because they have an affinity to bind with the surfaces of iron oxides[16,33]. Additionally, starches have high molecular weights, which improves colloidal stability by increasing steric repulsions[6].

The goal of this work is to identify a modified starch for coating NZVI that can easily be applied in the field. Field application is ideal because it limits storage time, which can result in oxidation and reduced efficiencies[1]. Specific objectives are: 1) evaluate the colloidal stability of NZVI coated with native and commercially available commercial starches, 2) identify a modified starch to coat NZVI with, 3) modify a native starch using the OSA reaction and characterize the modified starch, 4) evaluate colloidal stability of NZVI particles

coated with modified starch, and 5) characterize modified starch stabilized NZVI. See Figure 2-1 for the experimental plan.

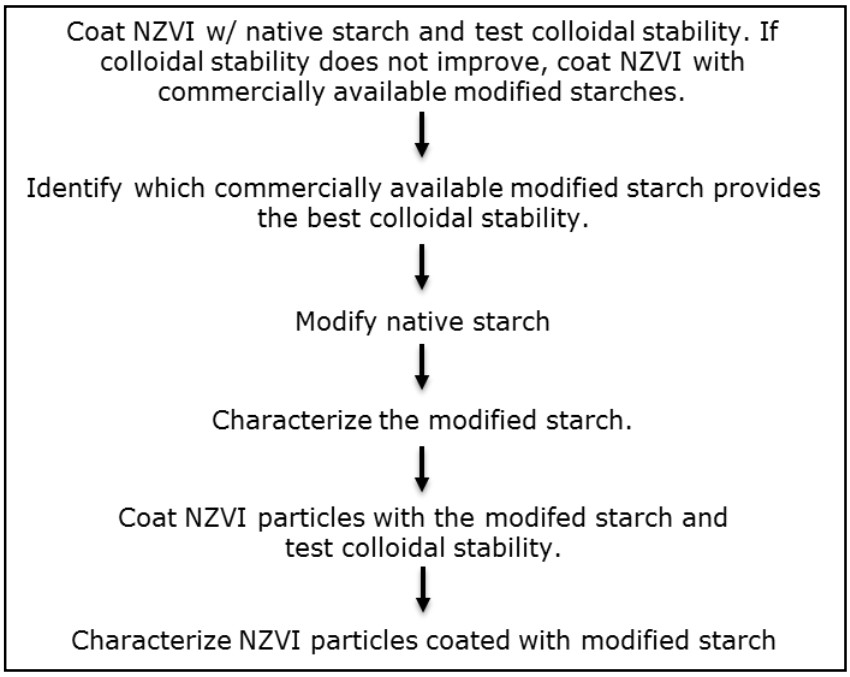


Figure 2-1. Experimental Plan for Evaluating Starch for Coating NZVI Particles

2.2. Materials and Methods

2.2.1. Materials

Iron (II) sulfate heptahydrate ($FeSO_47H_20$, Aldrich Chemical), sodium borohydride ($NaBH_4$, ACS grade, Alfa Aesar), methanol (95+%, BDH), sodium hydroxide (NaOH) (ACS grade, BDH), 2-Octen-l-ylsuccinic anhydride (OSA) (Dixie Chemical Company), hydrochloric acid (HCl, EMD Millipore), deuterium oxide (D_20, Sigma-Aldrich), sodium sulfate (Na_2SO_4, Sigma-Aldrich), potassium hydroxide (KOH, Sigma-Aldrich), urea (Sigma-Aldrich), and nitrogen (N_2, Praxair) were used as obtained.

Four different starches were selected for the initial screening. Starches were selected based on their region availability to groundwater problems. To address groundwater contamination in North America and Europe, wheat and maize starches were selected. In both areas, the majority of starches are produced from wheat and maize crops[34]. Rice starch was selected because rice is a primary Asian crop and would be readily available to

coat NZVI for treating groundwater in this region[10]. Lastly, tapioca starch was selected because it is cultivated in most equatorial regions, making it an ideal polymer for groundwater problems in South Asia and Africa[35]. Native and commercial grade rice, wheat, and maize starches were obtained from Sigma-Aldrich. Ingredion Company supplied native and commercial tapioca starches. Commercial grade starches were only used in the screening process.

2.2.2. NZVI Synthesis

NZVI was synthesized by borohydride reduction of ferrous iron in $FeSO_4 7H_20$ according to the Liu et al. method [3,36,37]. After reduction, the ZVI was washed with ethanol to remove excess $NaBH_4$. The ZVI was dried in a nitrogen vacuum oven over night. Dried ZVI was ground using a ceramic mortar and pestle to produce NPs. NZVI particles were stored in a nitrogen environment. Figure 2-2 shows the synthesis process.

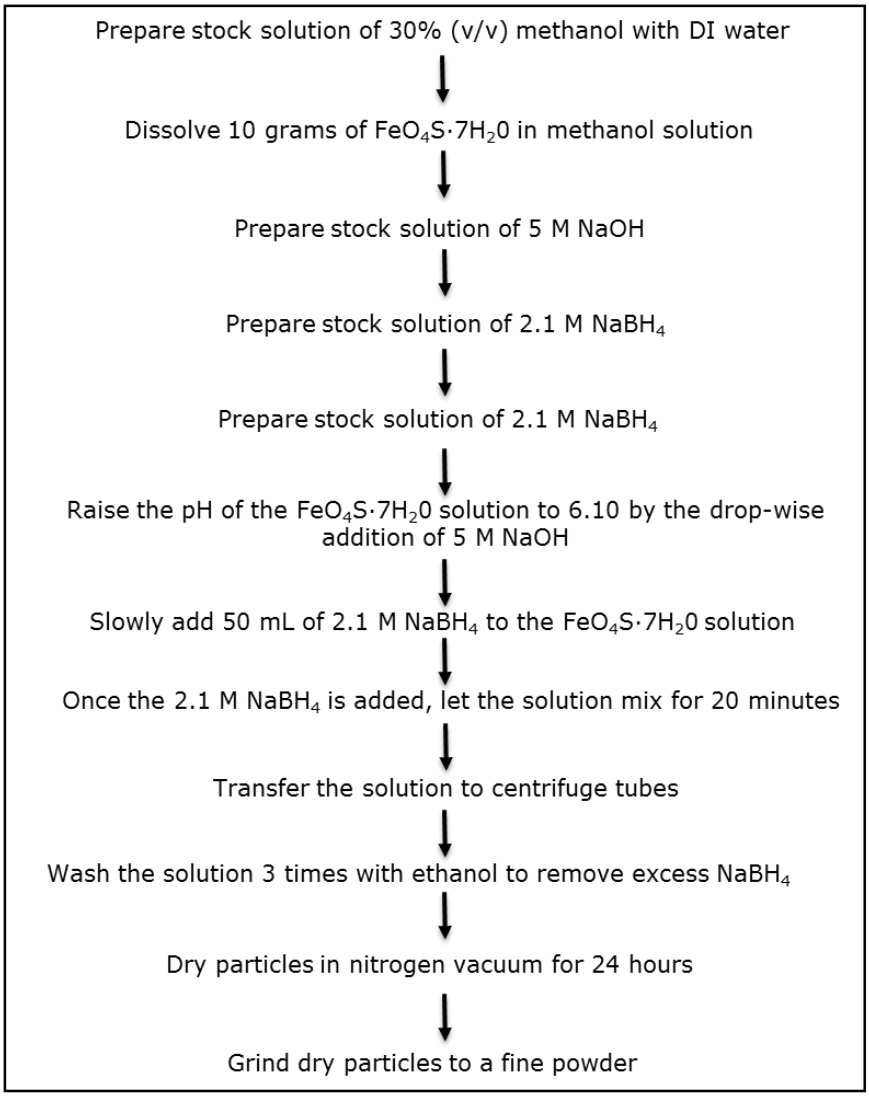


Figure 2-2. Flow Chart for Synthesizing NZVI

2.2.3. Surface Modification of NZVI with Starch

Native and commercial starches listed in the material section were tested to see if they improved colloidal stability of NZVI. To coat NZVI, various concentrations (1 g L^{-1}, 5 g L^{-1}, and 10 g L^{-1}) of each starch were prepared in deoxygenated deionized (DI) water. Starch solutions were brought to boil, cooled to 50°C, and stirred overnight (with heat) to produce a gelatinous solution. See Figure 2-3 for the starch preparation flow chart. Following starch preparation, NZVI particles (60 mg) were combined with 20 mL of starch (for each concentration) in 20 mL glass vials[3]. Nitrogen was blown into the head space and

the mixtures were sonicated for 30 minutes to prevent agglomeration of NZVI particles[3]. Immediately following sonication, the reactors were placed in a custom end-over-end shaker (28 rpm) and rotated for 72 hours[3]. After 72 hours, the particles were centrifuged and washed three times with deoxygenated-DI water to remove excess starch. Fresh deoxygenated-DI water (20 mL) was added to each vial after washing. After washing, the particles were sonicated for 15 minutes to break up any existing aggregations. Next, colloidal stability of the particles was monitored using UV spectrophotometry[3]. Sedimentation behavior of NZVI particles was interpreted from the change of light intensity at the wavelength of 508 nm over using a Hach DR 5000 UV spectrophotometer[3]. The 508 nm wavelength selected for UV-vis sedimentation studies is part of a standard protocol used by NZVI researchers throughout the world[38]. This particular wavelength is near the maximum absorptive intensity of ferrous iron complexes as established by spectroscopy[39], allowing researches to determine how much iron is suspended in a sample. See Figure 2-4 for the coating flow chart.

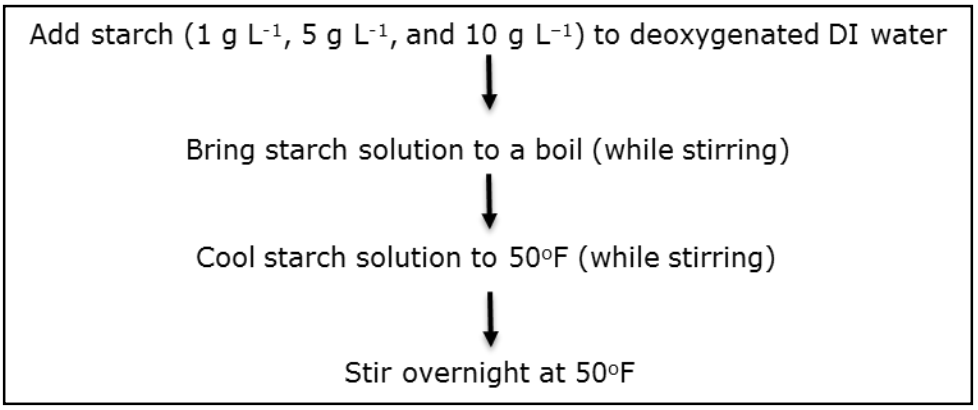


Figure 2-3. Flow Chart for Preparing Starch Solutions

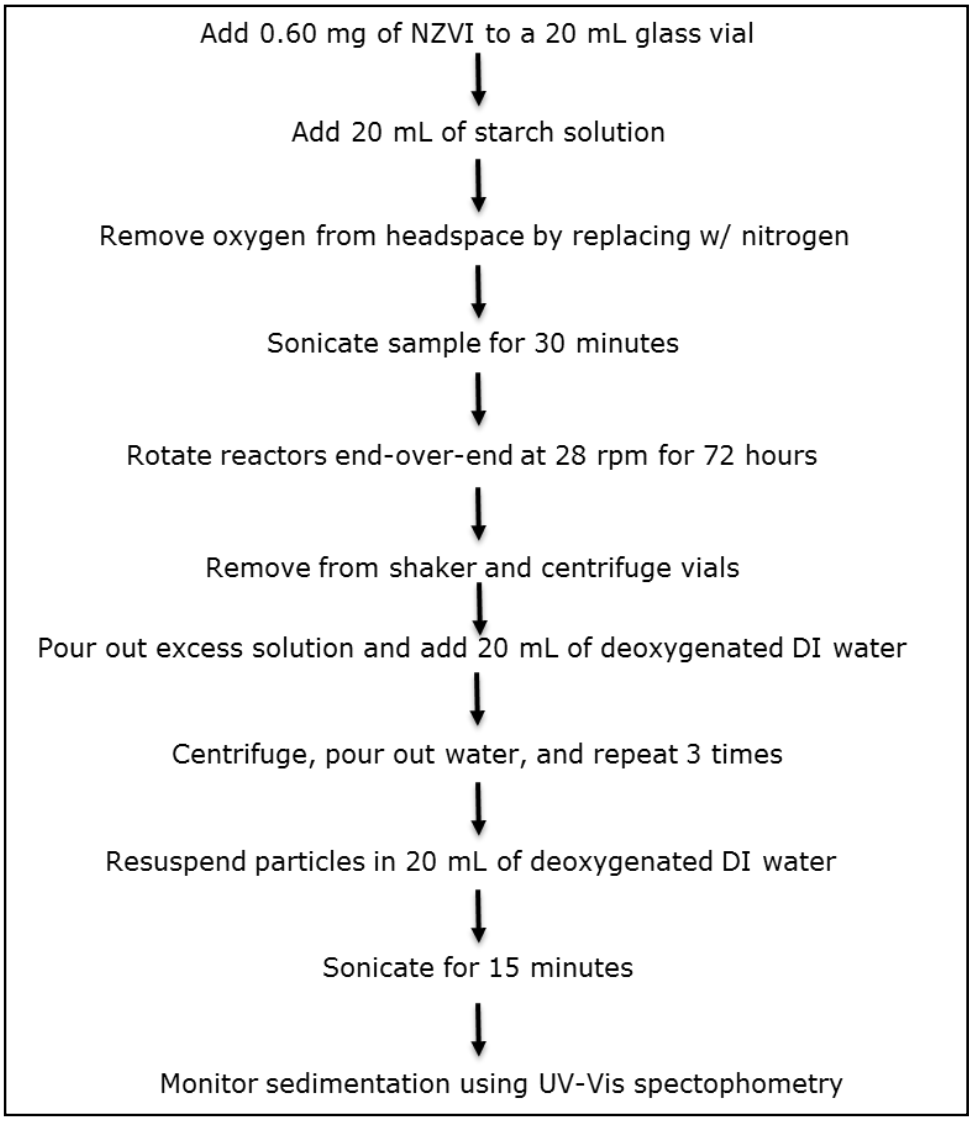


Figure 2-4. Flow Chart for Coating NZVI Particles with Starch

2.2.4. Screening of Native and Commercial Starches for Coating NZVI

Colloidal stability of NZVI particles coated with native starch (see Table 2-1 for starch types) was monitored using UV-vis spectrophotometric analysis. To monitor sedimentation, 2 mL of particles coated with native starch was pipetted into a glass cuvette immediately after sonicating for 15 minutes and placed into the UV spectrophotometer[3]. The sedimentation behavior of coated NZVI particles was interpreted from the change of light intensity at the wavelength of 508 nm over one hour[3]. A concentration of 3 g L^{-1} of bare

NZVI in deoxygenated water was evaluated as a control. Figure 2-5 was used to determine if the native starch improves colloidal stability and should be further characterized. A particle colloidal stability of 50% to match literature reports of at least 50% when NZVI is coated with starch and other biopolymers. Dong et al.[22] reported 90% colloidal stability of starch coated NZVI particles after 1 hour and Cirtiu et al.[40] reported 50% colloidal stability of CMC stabilized particles after 1 hour.

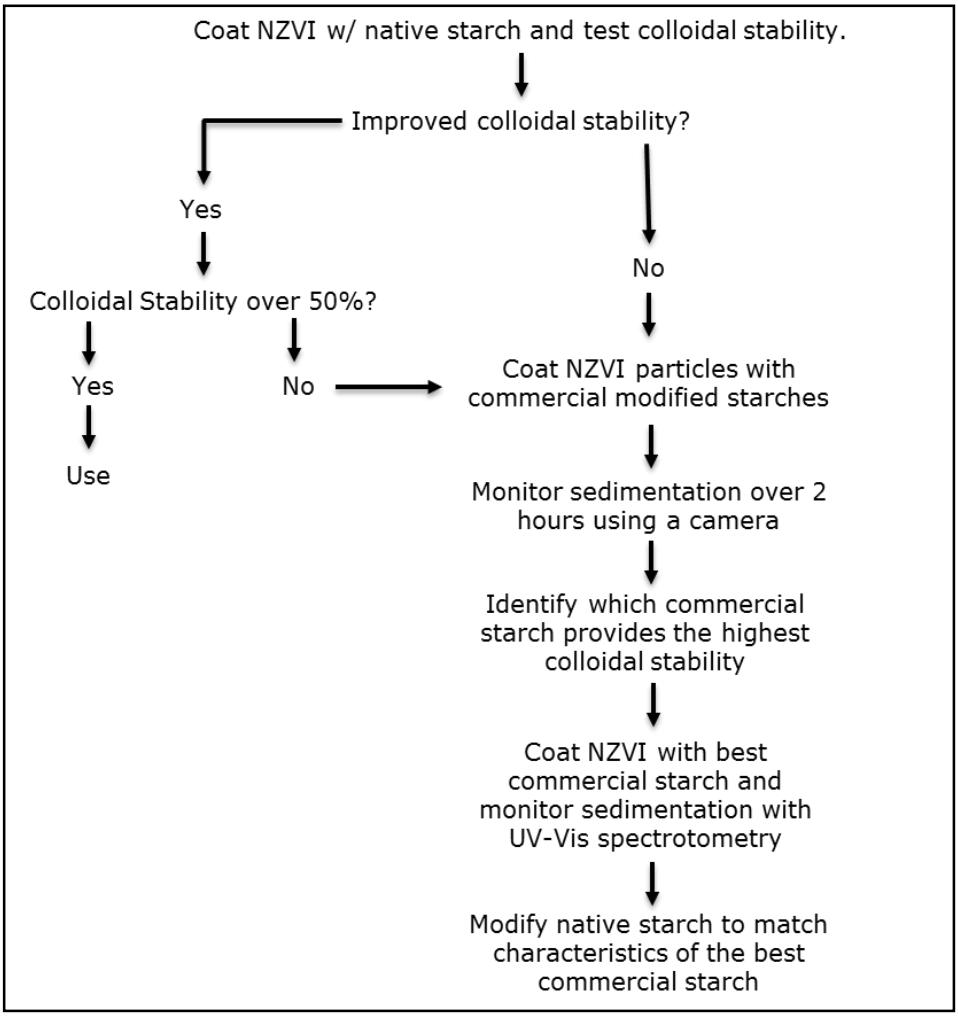


Figure 2-5. Flow Chart for Evaluating Native and Commercial Tapioca Starch

Visual sedimentation studies were conducted for NZVI particles coated with commercial starch (see Table 2-2 for starches). Sedimentation was assessed over two hours using a high-resolution camera. These studies started immediately after sonicating the

samples for 15 minutes and the samples were undisturbed over 2 hours. OSA modified tapioca starch was identified as the best starch for coating NZVI.

Table 2-1. Native Starches used to Coat NZVI to Test for Improved Colloidal Stability

Starch	Coating Concentration	Source
Native Maize	10 g/L	Sigma Aldrich
	5 g/L	
	1 g/L	
Native Wheat	10 g/L	Sigma Aldrich
	5 g/L	
	1 g/L	
Native Tapioca	10 g/L	Sigma Aldrich
	5 g/L	
	1 g/L	
Native Rice	10 g/L	Sigma Aldrich
	5 g/L	
	1 g/L	

Table 2-2. Commercial Starches used to Coat NZVI for Improved Colloidal Stability

Starch	Coating Concentration	Source
Modified Tapioca Starch 1	10 g/L	Sigma Aldrich
	5 g/L	
	1 g/L	
Modified Tapioca Starch 2	10 g/L	Sigma Aldrich
	5 g/L	
	1 g/L	
Modified Tapioca Starch 3	10 g/L	Sigma Aldrich
	5 g/L	
	1 g/L	
Modified Corn Starch 1	10 g/L	Sigma Aldrich
	5 g/L	
	1 g/L	
Modified Corn Starch 2	10 g/L	Sigma Aldrich
	5 g/L	
	1 g/L	
Modified Corn Starch 3	10 g/L	Sigma Aldrich
	5 g/L	
	1 g/L	
Non-waxy Modified Starch	10 g/L	Sigma Aldrich
	5 g/L	
	1 g/L	
Acetylated Wheat Starch	10 g/L	Sigma Aldrich
	5 g/L	
	1 g/L	
Modified Rice Starch	10 g/L	Sigma Aldrich
	5 g/L	
	1 g/L	

2.2.5. Preparation of OSA Modified Tapioca Starch

Native tapioca starch was modified with octenyl succinic anhydride (OSA) to create an amphiphilic starch. OSA modification was performed as described by Bai et al.[21] and Han et al.[41]. Starch (100 g) was dispersed in 224 mL DI water by stirring. The pH of the slurry (at approximately 25°C) was adjusted to 8.5-9.0 by dropwise addition of 1 M NaOH. While maintaining the pH of the solution, OSA (concentrations of 3, 15, 35, and 50% w/w starch) was slowly added to the solution using a burette. Following the addition of OSA, the mixture was stirred for 6 hours with a constant pH of 8.5. At high OSA concentrations (greater than 15%), Na_2SO_4 was added to prevent the starch granules from swelling (5, 13.6, and 20% w/w starch for 15, 35, and 50% OSA, respectively). Once the reaction was complete, the

slurry was neutralized to pH 7 with 1 M HCL. The modified starch was centrifuged at 2500 rpm for 15 minutes three times with DI water and once with acetone. Once washed, the modified starch was dried for 24 hours at 40°C. Starch modification is shown in Figure 2-6. The starches produced by this modification are listed in Table 2-3.

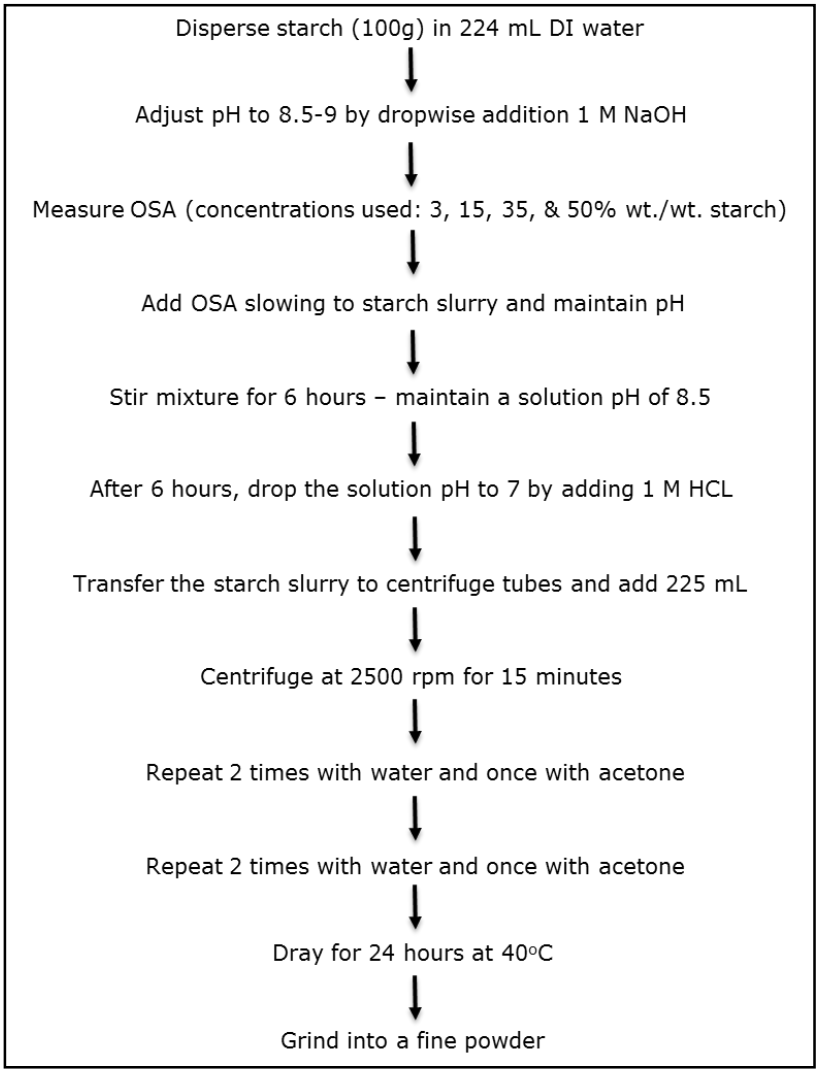


Figure 2-6. Flow Diagram for Modifying Tapioca Starch with OSA

Table 2-3. Modified OSA Tapioca Starches used to Coat NZVI to Test for Improved Colloidal Stability

Starch	Coating Concentration	Source	Reference
3% OSA	10 g/L	Native Starch from Sigma Aldrich	Modification procedure from Bai et al.[21] and Han et al.[41]
	5 g/L		
	1 g/L		
15% OSA	10 g/L	Sigma Aldrich	Modification procedure from Bai et al.[21] and Han et al.[41]
	5 g/L		
	1 g/L		
35% OSA	10 g/L	Sigma Aldrich	Modification procedure from Bai et al.[21] and Han et al.[41]
	5 g/L		
	1 g/L		
50% OSA	10 g/L	Sigma Aldrich	Modification procedure from Bai et al.[21] and Han et al.[41]
	5 g/L		
	1 g/L		

2.2.6. Characterization of OSA Modified Tapioca Starch

FTIR was used to confirm the substitution of carbonyl groups of OSA on the starch molecule. A FTIR spectrometer (FTIR, Nicolet 8700 Thermo Scientific) was used to obtain IR spectrum of native and OSA modified starches. Approximately 1.5 grams of sample was ground with potassium bromide (KBr) and pressed into a pellet disc. The samples were scanned over the wavelength range from 400 to 4000 cm^{-1}. Sample spectra were subtracted from background spectra. FTIR was obtained for native, commercial, and modified starches. Figure 2-7 shows the FTIR analysis process.

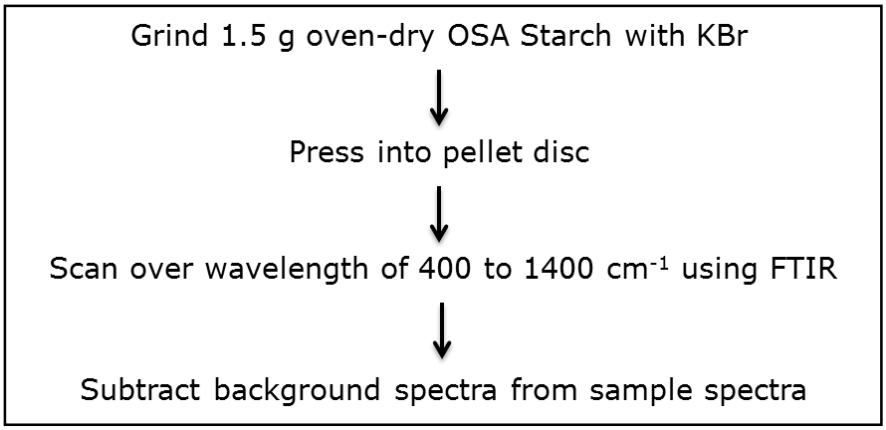


Figure 2-7. Flow Chart for FTIR Characterization of OSA Modified Tapioca Starch

Nuclear magnetic resonance (NMR) was used to confirm the presences of OSA methyl protons and to determine the degree of substitution (DS). DS is a measures of the number hydroxyl groups attached to each glucose unit compromising a starch molecule[28]. The increased number of hydroxyl groups indicates more OS molecules (containing esters and carbonyls) were substituted onto the starch molecule during modification[28]. The starch samples were purged with D_2O three times; samples were lyophilized between each purge. Next, the samples were dissolved in D_2O (0.6 mL) a final time at 80°C for 1 hour and placed in NMR tubes (8 inch, 5 mm, thing wall). 1H spectra were obtained using a Bruker (Billerica, MA, USA) Ascend 400 MHz NMR. The analysis was conducted at 25°C for 64 scans with a delay time of 1 second. Figure 2-8 shows the NMR analysis process. DS was calculated according to the methods of Shih et al.[42]. The internal standard was the equatorial proton of the anhydroglucose unit (AGU) of starch (5.2-5.4 ppm). Extent of OSA substitution was determined by the integration of the methyl protons of the OSA (0.8-0.9 ppm). DS was calculated with Equation 2-1[42].

$$\mathrm{DS} = \frac{A_{0.8-0.9}}{3 * A_{5.2-5.4}} \qquad (2\text{-}1)$$

Where:

$A_{0.8\text{-}0.9}$ = Methyl protons of OSA

$A_{5.2\text{-}5.4}$ = Equatorial portion of the AGU of starch

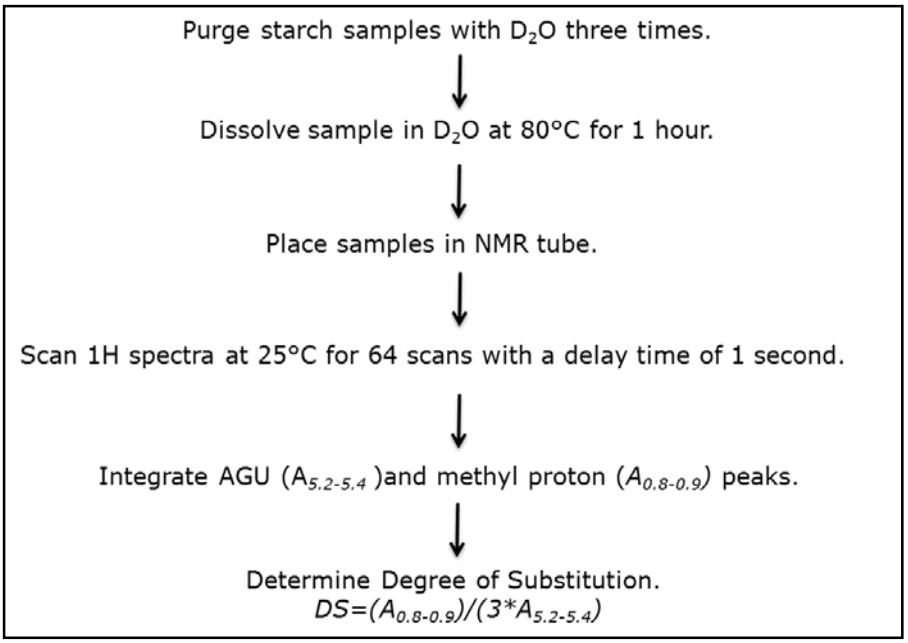


Figure 2-8. Flow Chart for NMR Characterization of OSA Modified Tapioca Starch

Molecular weight and amylose/amylopectin content were determined by high-performance size-exclusion chromatography (HPSEC). The starch was dissolved in 5 mL of 1M KOH and 6M Urea (9:1) for 90 minutes (temperature = 100°C) with intermittent vortexing[43]. 1 mL of the starch solution was neutralized (pH ≈ 7) with 1M HCl; volume of HCl used for each sample was used to calculate final concentration of starch. The samples were filtered through a 0.45µm nylon syringe filter into a glass vial[43, 44]. An Agilent 1200 high-performance liquid chromatography (HPLC) system was used to analyze the samples at the following conditions: effluent: 0.1 μ m filtered HPLC grade water, flow rate: 0.5 ml/min, and column and refractive index detector temperature: 30°C. The columns were Waters Ultra-Hydrogel guard column with Waters Ultra-hydrogel 1000 and linear columns in

sequence. Figure 2-9 shows the molecular weight and amylose/amylopectin analysis process.

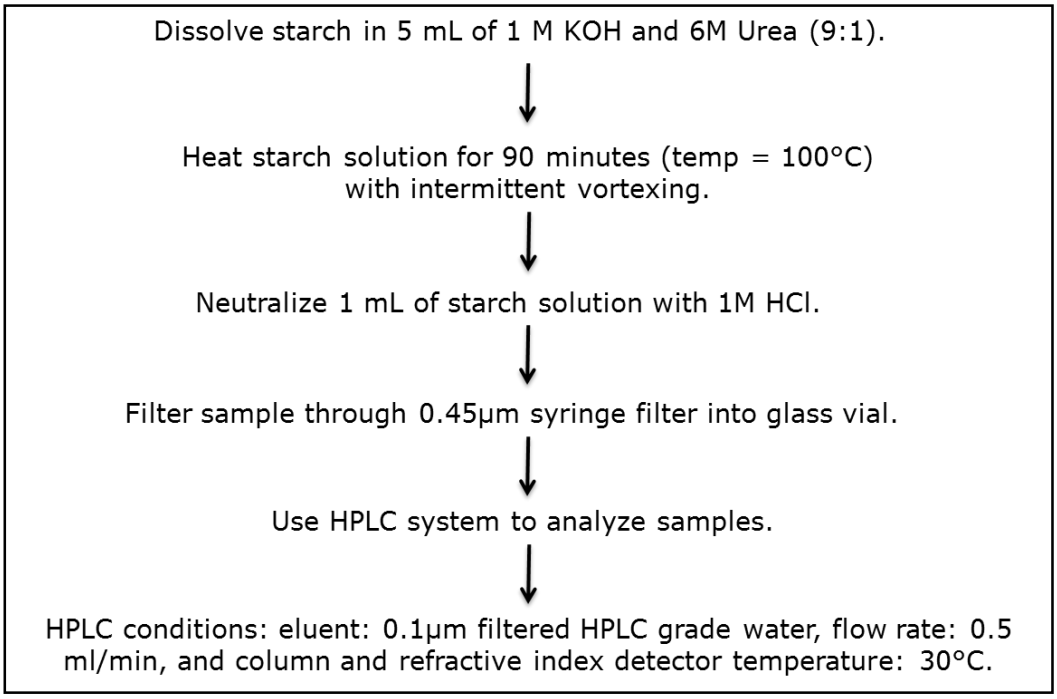


Figure 2-9. Flow Chart for HPLC Characterization of OSA Modified Tapioca Starch

Peaks in the refractive index sign chromatogram produced from the HPLC were integrated to determine amylopectin and amylose content[43, 44]. Agilent Chemstation Software (version B.04.03) was used for integration and data processing of refractive index signals. The molar mass of starch was determined using multi angle light scattering (MALS) detection using a light scattering detector and Astra software version 6.0.5 from Wyatt Technologies (Santa Barbara, CA). A dn/dc of 0.146 was used to determine starch molar mass. Average weight averaged molar mass (Mw) of starch was calculated using a Debye model (fit degree = 1) and results were fitted to a 2nd order polynomial model[45,46]. FTIR, NMR, molecular weight and amylose/amylopectin content analyses were conducted by NDSU's Plant Science Department.

2.2.7. Colloidal Stability Studies

The colloidal stability of coated NZVI was evaluated by measuring the sedimentation rates of suspended particles. Particles were coated as described in Section 2.2.3. Native tapioca starch and 3, 15, 35, and 50% OSA modified tapioca starch were used for coating. Colloidal stability was monitored for 2 hours using UV-Vis spectrophotometry as described in Section 2.2.3.

2.2.8. Characterization of NZVI and Coated NZVI Particles

Bare NZVI particles were characterized previously by Krajangpan et al.[3]. Particle size distribution was determined using transmission electron microscopy (TEM, JEOL JEM-100CX II, JEOL USA, Inc., Peabody, Massachusetts)[3]. Surface morphology and elemental composition of bare NZVI were determined using scanning electron microscopy (SEM) along with energy dispersive spectroscopy (EDS) (SEM/EDS, JEOL JSM-6300, JEOL USA, Inc., Peabody, Massachusetts)[3].

NZVI particles were coated with 35% OSA-modified tapioca starch as described in Section 2.2.3. Once coated and washed, the samples were dried in a nitrogen environment for 24 hours. Dried samples were sprinkled onto carbon tabs attached to aluminum mounts. Images were obtained with SEM (JEOL JSM-7600F, JEOL USA, Inc., Peabody, Massachusetts). EDS information was acquired using an UltraDry silicon drift X-ray detector and NSS-212e NORAN System 7 X-ray Microanalysis System (Thermo Fisher Scientific, Madison, Wisconsin).

2.2.9. Quality Control and Statistical Analysis

Colloidal stability experiments were conducted in triplicate. Average values and standard deviations are reported. One-way ANOVA analysis was used to compare sedimentation data for statistical significance for colloidal stability experiments. Tukey's pairwise comparison was used after the one-way ANOVA to identify which groups among the samples tested are significantly different. Statistical analysis for the sedimentation studies

were conducted in Minitab 17. Starch characterization experiments were performed in duplicates and analyzed with ANOVA with LSD using SAS software.

2.3. Results and Discussion

2.3.1. Screening of Native and Commercial Starches for Coating NZVI

As a preliminary screening step, NZVI particles were coated with native starches at three concentrations (1, 5, and 10 g L^{-1}) and sedimentation was monitored using UV-vis spectrophotometry. This screening was completed to determine if native starches would provide significant particle stabilization. One-way ANOVAs were performed for each individual native starch and P-values are listed in Table 2-4. Data for native starch, including sedimentation curves, hypothesis statement, and ANOVA tables, can be found in Appendix A-Sections A.1-2.

Table 2-4. One-way ANOVA for Native Starches

Native Starch (all concentrations)	**p-value**	**Significantly improves colloidal stability compared to bare NZVI**
Maize	0.001	Yes
Tapioca	0.098	No
Rice	0.295	No
Wheat	0.570	No

Coating NZVI with native tapioca, rice, and wheat starch did not improve particle stability. These result are expected because many native starches lack emulsification properties[17] and anchoring groups[16, 33]. Modifying starch to contain carboxyl[33] and ester[16] groups will help bind the starch molecules to the surface of NZVI particles[3, 12, 15, 30].

The sedimentation curves for native maize starch are shown in Figure 2-10. There is a significant difference ($p = 0.001$) in mean particle stability between bare NZVI and the NZVI particles coated with native starch. Native maize starch only significantly improved particle stability at a coating concentration of 10 g L^{-1} (see Tukey's Pairwise Comparision in

Appendix A.2). Approximately 45% of particles coated with 10 g L^{-1} maize starch remained suspended after one hour of monitoring, as shown in Figure 2-10, while only 6% of bare NZVI particles were suspended. Coating NZVI particles with native maize starch increased the colloidal stability of the particles by 39%, which is below the colloidal stability goal set in Section 2.2.4.

While native maize starch improved the colloidal stability of NZVI, it did not improve colloidal stability as much other starches and biopolymers have. Cirtiu et al.[40] reported approximately 50% of NZVI particles remained suspended after 1 hour when coated with CMC. Others have reported extended colloidal stability (up to 48 hours) when the particles were coated with guar gum[47, 48]. Water-soluble starch has been reported to stabilize iron NPs for up to 24 hours[15, 23]. Dong et al.[49] reported approximately 95% of NZVI particles coated with potato starch remain suspended after 1 hour. Since other starches have achieved better colloidal stability, native maize starch is not the best candidate for coating NZVI. However, since native maize starch did improve colloidal stability of the particles, it still has potential for use as a coating/emulsifying agent.

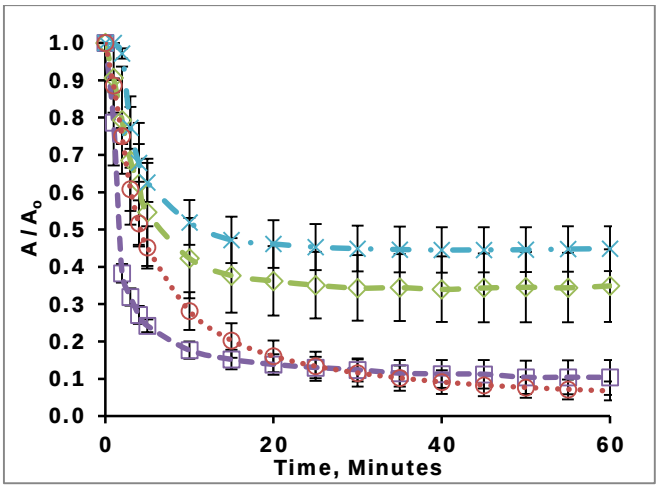


Figure 2-10. Sedimentation Behavior for NZVI Particles Coated Native Maize Starch ···○··· Bare NZVI, -□- CNZVI (Starch Concentration = 1 g L^{-1}), -◇- CNZVI (Starch Concentration = 5 g L^{-1}), and -·-X-·-CNZVI (Starch Concentration = 10 g L^{-1}).

2.3.2. Screening of Commercial Starches for Coating NZVI

Since the native starches were not able to improve colloidal stability by 50%, commercial starches were investigated as a surface modifier. Commercial starches were investigated because they are modified starches to improve their emulsion properties[28]. Though coating NZVI particles with native maize starch significantly improved colloidal stability as compared to bare NZVI (45% of particles remained suspended after 1 hour), modified starches were selected to represent each starch tested in Section 2.3.1. Modified starches have improved emulsification properties and these properties would likely improve NZVI's colloidal stability when coated with each type of starch[17]. A 2-hour visual sedimentation study found OSA-modified tapioca starch provided the best colloidal stability. Pictures from the visual sedimentation study are found in Appendix A-Section A.3. A sedimentation study was conducted using UV-Vis spectrophotometry on three commercially available OSA-modified tapioca starches (commercial grade) and the data set is presented in Appendix A-Section A.4-5.

2.3.3. Characterization of OSA-Modified Tapioca Starch

2.3.3.1. FTIR

FTIR was used as an initial screening tool to confirm the esterification reaction occurred between starch hydroxyl groups and OSA. OSA modification is confirmed by the presence of adsorption bands around 1720 and 1570 cm^{-1}. The band around 1720 cm^{-1} corresponds to C=O stretching vibration caused by the formation of an ester group and the peak at 1570 cm^{-1} represents the asymmetric stretching vibration of carboxyl groups[18,28,29]. FTIR analysis was conducted in NDSU's Plant Science Department.

2.3.3.2. H-NMR

H-NMR was used to quantify the chemical modification of the OSA starches and to determine the DS[17, 18, 21]. Since OSA starches are amphiphilic, they tend to form aggregates in aqueous media[18], which inhibits water solubility. Poor solubility can significantly reduce

NMR signals, which can result in an estimated DS[18]. To overcome solubility issues, the samples were prepared and scanned in D_20, which partially dissolves starch samples[18, 42]. D_20 was used as starch is relatively insoluble in H_20.

OSA modification is confirmed by the addition of signals between 0.7-3.0 ppm[21] and changes in signals around 5.50[17, 21]. Figure 2-11 shows the H-NMR spectra for native, modified tapioca starch 1, and 3, 15, 35, and 50% OSA-modified starches. Peaks between 0.7-3.0 ppm of Figure 2-11 (b, c, d, e, and f) match literature reports for OSA substitution[17, 18, 21, 42]. Figure 2-12 shows the peak assignments and molecular structure of OSA modified starch.

The broad peaks in Figure 2-11 (c, d, e, and f) located between 0.8-0.9 ppm are from the methyl protons of the Octenyl Succinate (OS) group. Peaks located between 5.2-5.4 ppm represent the AGU protein of the starch[42]. These peaks were integrated using Bruker Topspin v3.2 software and the DS for each starch was determined with Equation 2-1 (results are shown in Table 2-5). The integral values for the methyl proton and AGU peaks, along with additional H-NMR spectra, are presented in Appendix A-Section A.8. NMR analysis was conducted by NDSU's Plant Science Department.

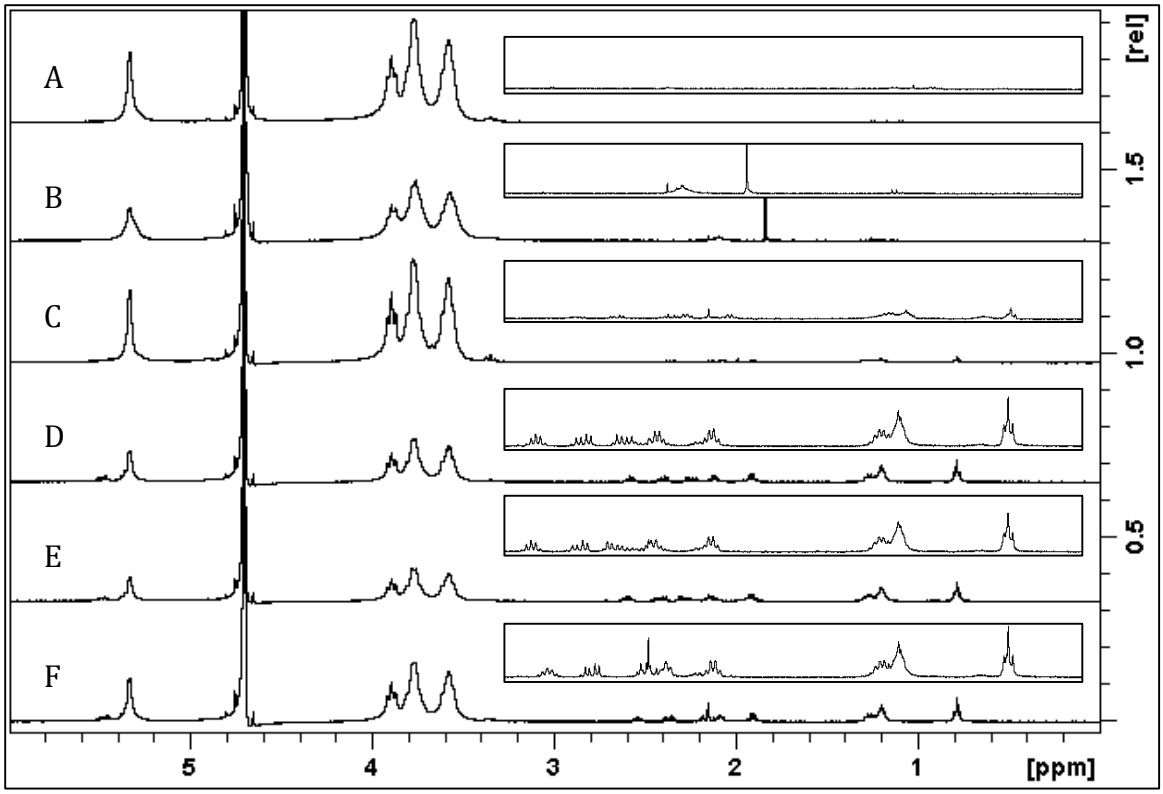


Figure 2-11. NMR Spectra of OSA Tapioca Starch Samples. a. Native, b. Modified Tapioca Starch 1, c. 3% OSA, d. 15% OSA, e. 35% OSA, and f. 50% OSA. Inserts: Spectra Expansion of 0.5-2.7ppm.

The DS for 15% OSA starch in this research is twice reported values, which could be attributed to differences the addition rate of OSA, solution pH, and reaction time. Bai et al.[21] reported the solution's pH dropped rapidly and was difficult to maintain at OSA concentrations at or above 15%. As DS decreases when the solution pH drops below 8.5[28], it is possible the reduced amount of OS substituted in Bai's study was because of the rapid pH drop during OSA addition. Song et al.[28] used a reaction time of 4 hours, while the current study allowed the reaction to continue for 6 hours. The higher DS reported here compared to Song et al.[28] is possibly because of the extended contact time between OSA and starch molecules.

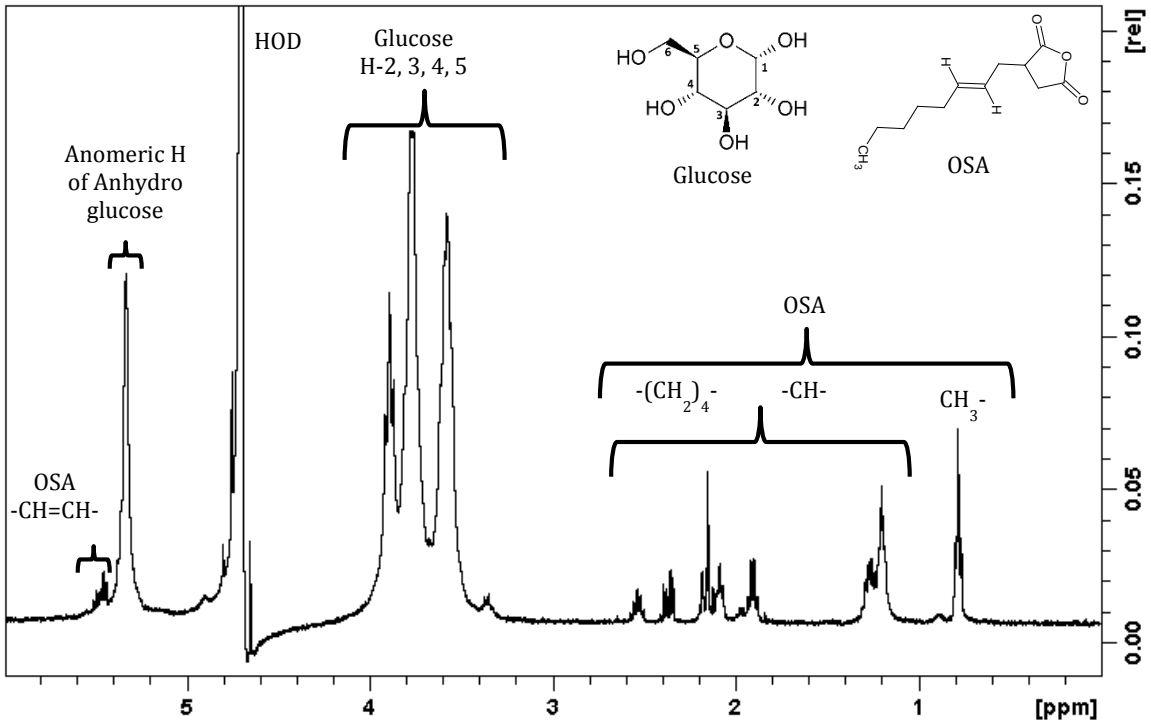


Figure 2-12. NMR of OSA Modified Starch

Table 2-5. Degree of Substitution

Tapioca Starch	Degree of Substitution	Reported DS Values
Commercially Modified	0.019	NA*
3% OSA	0.018	0.016-0.017[28, 42, 50]
15% OSA	0.110	0.045-0.051[21, 28]
35% OSA	0.126	NA*
50% OSA	0.093	0.088[21]

*NA = Not Available

Higher DS values on starches modified with increased OSA concentrations match literature reports[21, 28, 29]. Bai et al. has reported DS = 0.11[29] and 0.088[21] for 25 and 50% OSA starch, respectively, which mirror the results presented in Table 2-5. DS likely decreases at 50% OSA because the solution's pH was difficult to maintain and the starch granules swelled, despite the addition of Na_2SO_4[21]. Swelling starch granules made the solution difficult to stir, which limits the number of starch molecules contacting OSA. The results presented here and by Bai et al.[21, 29] suggest there is a critical OSA concentration for optimizing DS.

2.3.3.3. Molecular Weight

Analysis of molecular weight was conducted on native tapioca starch, commercial tapioca starch, and the four OSA tapioca starches. Molecular weight data for and statistical results presented in Appendix A-Sections A.9-10, respectively. The mean percentages of amylose/amylopectin vary significantly between each sample (ANOVA, $p=0.000$). The mean molecular weights of amylose/amylopectin in each starch did not vary significantly between samples (ANOVA, $p=0.631$). Differences in percentage amylose/amylopectin in each sample may impact the colloidal stability because of the differences in molecular weight. Molecular weight and amylose/amylopectin content analyses were conducted by NDSU's Plant Science Department.

2.3.4. Colloidal Stability of OSA-Modified Tapioca Starch

NZVI was coated with OSA-modified tapioca starch at three concentrations (1, 5, and 10 g L^{-1}) and sedimentation was monitored using UV-vis spectrophotometry. The concentration of NZVI was 3 g L^{-1}. Sedimentation curves were prepared for each concentration and one-way ANOVAs were performed for each concentration. Data for OSA-modified starch, including sedimentation curves and ANOVA tables, can be found in Appendix A-Sections A.11-12.

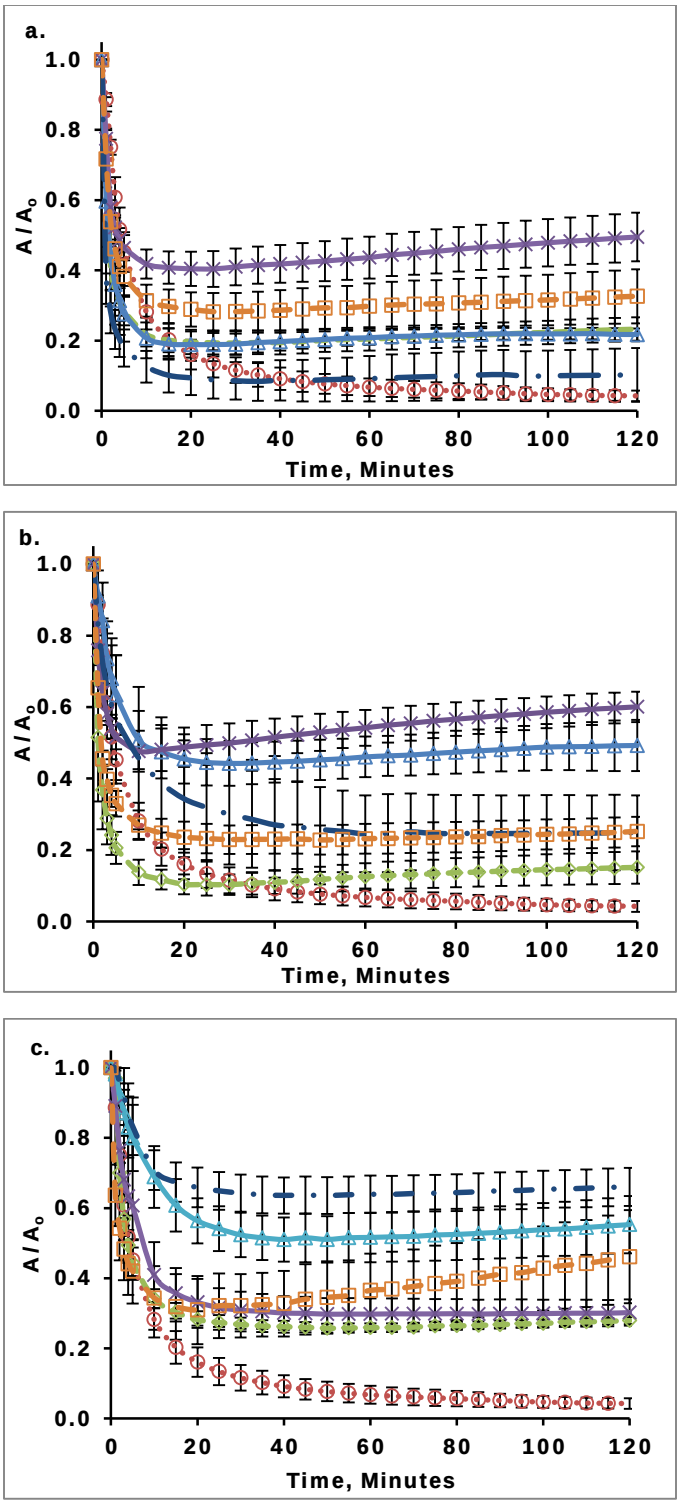


Figure 2-13. Sedimentation Curves for NZVI Coated with OSA-Modified Tapioca Starch a. Coating Concentration = 1 g L^{-1}, b. Coating Concentration = 5 g L^{-1}, and c. Coating Concentration = 10 g L^{-1}. ···○··· Bare NZVI, -◇- Native Tapioca Starch, –Δ– 3% OSA Tapioca Starch, –X– 15% OSA Tapioca Starch, - · - 35% OSA Tapioca Starch, and -□- 50% OSA Tapioca Starch.

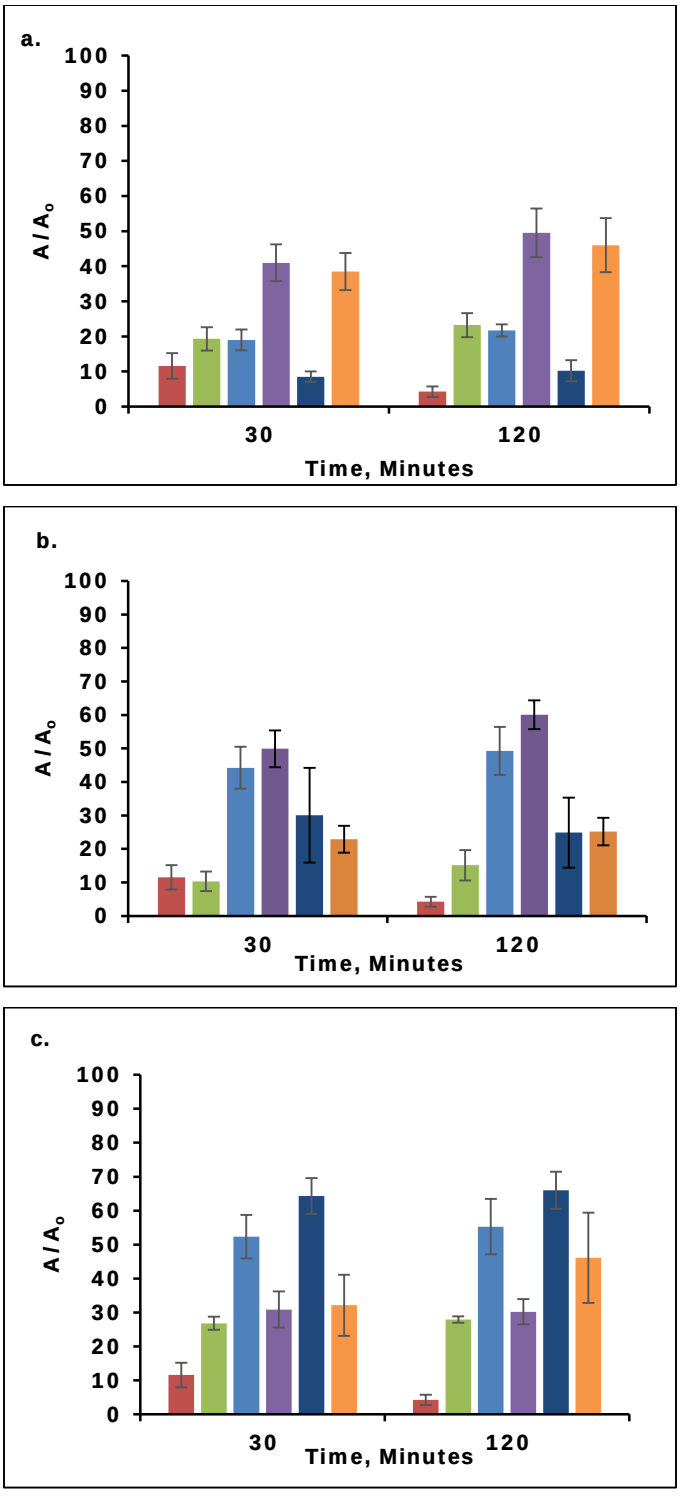


Figure 2-14. Colloidal Stability (%) for NZVI Coated with OSA-Modified Tapioca Starch a. Coating Concentration = 1 g L^{-1}, b. Coating Concentration = 5 g L^{-1}, and c. Coating Concentration = 10 g L^{-1}.▪Bare NZVI, ▪Native Tapioca Starch,▪3% OSA Tapioca Starch, ▪ 15% OSA Tapioca Starch, ▪ 35% OSA Tapioca Starch, and ▪ 50% OSA Tapioca Starch.

Figure 2-13 shows the sedimentation curves for NZVI coated with native tapioca starch and various types of OSA-modified tapioca starch. The sedimentation curves indicate that OSA-modified tapioca can significantly improve sediment behavior of coated NZVI. The increase in colloidal stability is caused by the oxidation of NZVI. Oxidation will release oxygen gas, which cause the particles to suspend. One-way ANOVA analysis for each concentration found the OSA-modified starch significantly improves NZVI's colloidal stability ($p = 0.000$ for all three concentrations). Statistical analyses are presented in Appendix A-Section A.12. Coating NZVI with either native tapioca starch or OSA modified tapioca starch improves the particle stability compared to bare NZVI, as shown in Table 2-6 and Figure 2-14. Compared to NZVI particles coated with native tapioca starch, OSA-modified tapioca improved colloidal stability at higher concentrations (5 g L^{-1} and 10 g L^{-1}). At a coating concentration of 1 g L^{-1}, coating NZVI particles with OSA-modified tapioca starch only improved colloidal stability for the OSA modifications of 15 and 50%, as shown in Table 2-6 and Figure 2-14. The decrease in colloidal stability for 3 and 35% OSA, shown in Table 2-6 and Figure 2-14, maybe related to bridging between starch molecules, which caused the particles to floc and settle. Bridging between starch molecules at low coating concentrations was reported by Liang et al.[23], He at el.[11], and Dong et al.[22]

At a coating concentration of 10 g L^{-1}, 35% OSA-modified tapioca starch provided the highest colloidal stability (Figure 2-13c). The remaining studies presented in this work used NZVI particles coated with 35% OSA-modified tapioca starch (concentration = 10 g L^{-1}); these particles will be referred to as coated NZVI (CNZVI). 35% OSA-modified tapioca starch had the highest DS (as discussed in Section 2.3.3). DS is a measures of the number hydroxyl groups attached to each glucose unit compromising a starch molecule[28]. The increased number of hydroxyl groups indicates more OS molecules (containing esters and carbonyls) were substituted onto the starch molecule during modification. As esters,

carbonyls, and hydroxyls are effective at anchoring onto iron surfaces, the improved steric stability is likely related to more anchoring groups.

Table 2-6. Colloidal Stability of Bare NZVI and NZVI Coated with Native and OSA Tapioca Starch

Treatment	% of NZVI Particles Suspended	% Improved Colloidal Stability (compared to bare NZVI)	% Improved Colloidal Stability (compared to native tapioca starch)
Bare NZVI	4.2	NA	
1 g L^{-1}			
Native Tapioca Starch	23.2	19.0	NA
3% OSA	21.7	17.5	-1.4
15% OSA	49.5	45.2	26.3
35% OSA	10.1	6.0	-13.0
50% OS	32.6	41.7	22.8
5 g L^{-1}			
Native Tapioca Starch	15.1	10.9	NA
3% OSA	49.2	45.0	34.1
15% OSA	60.7	55.8	44.9
35% OSA	24.7	20.6	9.7
50% OS	25.2	21.0	10.1
10 g L^{-1}			
Native Tapioca Starch	27.9	23.6	NA
3% OSA	55.3	51.0	27.4
15% OSA	30.2	25.9	2.3
35% OSA	66.0	61.8	38.1
50% OS	46.1	41.9	18.2

The colloidal stability of NZVI particles also increased as the starch concentration increase (Figure 2-13 a, b, and c). Increased colloidal stability with higher coating concentrations has been reported by others[3, 23, 47]. However, at lower concentrations, the starch molecules can act as bridging agents and promote flocculation instead of improving colloidal stability[11, 23]. The tendency of starch to flocculate at low concentrations may be related to the decrease in colloidal stability, as demonstrated in the sedimentation studies in Figure 2-13 a & b.

Several sets of sedimentation studies had large standard deviations, as shown in Appendix A-Section A.11. The large standard deviations could be attributed to non-uniform

OSA modification. Non-uniform starch modification arises because the modification reaction is performed under heterogeneous conditions[18]. This can result in the uneven distribution of substituent groups along the starch backbone[18, 29]. The largest standard deviations were seen when NZVI particles were coated with 50% OSA-modified tapioca starch. Since the OSA reaction is difficult to control at high OSA concentrations, the non-uniform modification may be related to the drop in solution pH and grain swelling, which limits contact between OSA and starch molecules.

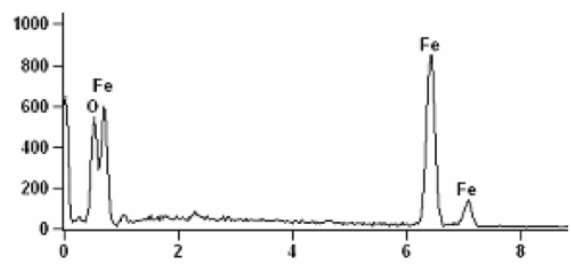
2.3.5. Characterization of NZVI and Coated NZVI Particles

Bare NZVI particles were black in color (see Figure 2-15c) and had a particle size of 10 to 90 nm (average diameter ~ 35 nm)[3]. SEM/EDS spectra (see Figure 2-15 a) show the particles are composed of ~84% iron and ~16% oxygen[3]. The oxygen is present in the oxide shell seen in Figure 2-15 c. The oxide shell is possibly made of amorphous FeOOH and protects the NPs from rapid oxidation[3]. Krajanpan et al. [3] reporte the specific surface area of NZIV particles as 25 $m^2 g^{-1}$.

Four different points were used to obtain SEM/EDS data for CNZVI; the point analysis is presented in Appendix A-Section A.13. Figure 2-15b shows the EDS spectra of freshly prepared CNZVI show the presence of sodium, carbon, and oxygen in addition to iron; other spectra and EDS data are presented in Appendix A-Section A.13. The average elemental composition of the particles is 7.665% carbon, 25.063% oxygen, 65.868% iron, 0.22% silicon, and 0.875% sodium. CNZVI particles have approximately 9% more oxygen, 8% more carbon, and 18% less iron than bare NZVI particles. The increase in oxygen and carbon is likely attributed to the ester and carbonyl groups from the OSA-modified starch. Sodium (from controlling the pH with NaOH) is likely present because of side reactions that occurred during modification[18, 21, 28]. The percentage of sodium is very low, which indicates side reactions were probably not dominant. Further, Na might be present in the NZVI as $FeSO_4$ was reduced with $NaBH_4$ during the NP synthesis process.

SEM images of CNZVI (Figure 2-15 e and f) show discrete particles surrounded by a starch coating (white layer around black particles). CNZVI particles range in size from 47.5-325 nm (see Figure 2-15 c) with an average particle size of 118.6 nm; 200 particles were measured to determine the average particle size. Some of the particles have agglomerated into chains (Figure 2-15 e). Individual particles are still visible in the chains, which is in contrast to SEM images of bare NZVI[51,52]. Xiao et al. [53] reported similar characteristics with potato-starch coated NZVI particles. An enlarged imaged (Figure 2-15 f), shows the agglomeration is mostly comprised of small chains, with a few large clusters (see arrows). Larger agglomerations may have occurred while the samples were dried for imaging due to the magnetic forces between particles. The CNZVI/starch matrix also appears to be relatively porous (Figure 2-15 f), which should help maintain NZVI's large surface area. Since the individual particles in each chain are well defined by a starch coating, it is likely the starch served as a bridging agent between particles. Starch has been reported to act as a bridging agent by Liang et al.[23], He et al.[11], and Dong et al.[22].

a.



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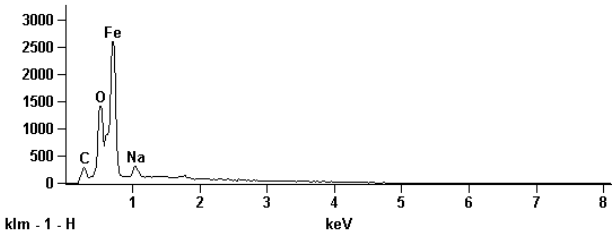

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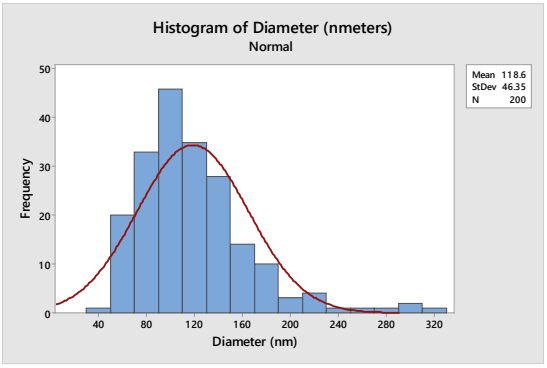

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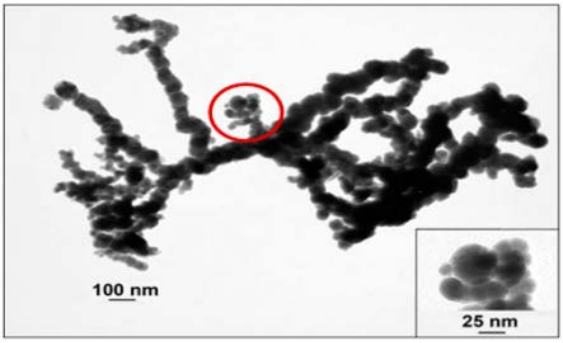

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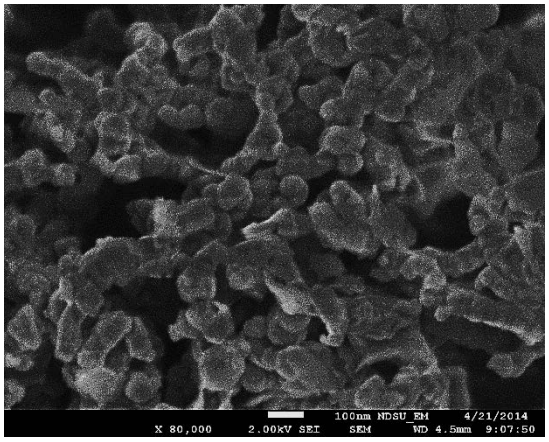

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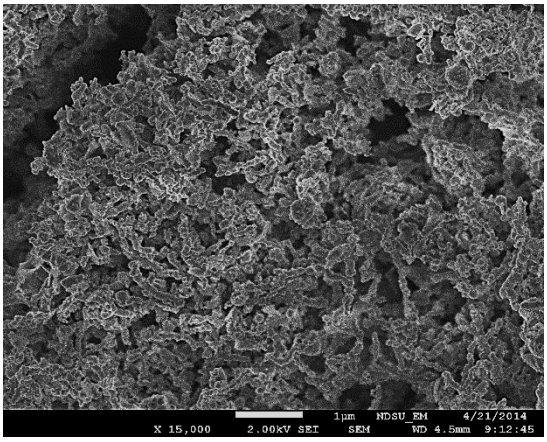

Figure 2-15. CNZVI Characterization
a. EDS Spectra of Freshly Prepared NZVI (image from Krajangpan et al.[3]), b. EDX Spectra of Freshly Prepared CNZVI,
c. Histogram of CNZVI Particle Size d. TEM Images of NZVI (image from Krajangpan et al.[3]), e. Scanning Electron Micrograph of CNZVI, and f. Scanning Electron Micrograph of CNZVI/Starch Matrix.

2.4. Conclusion

NZVI was coated with many different starches throughout this study to measure differences in colloidal stability. The first coating study investigated the potential for using native starches to coat NZVI particles. Native maize, rice, wheat, and tapioca starches were coated to NZVI particles. Statistical analysis for that coating NZVI with native rice, wheat, and tapioca starches does not significantly improve colloidal stability ($p = 0.295$, 0.57, and = 0.098, respectively). These native starches were not able to provide steric stability because they lack functional properties, such as anchoring groups. Coating NZVI with native maize starch significantly improved colloidal stability at a coating concentration of 10 g L^{-1}. NZVI particles coated with native maize starch had a colloidal stability of 45% after 1 hour, while bare NZVI particles only had a colloidal stability of 6% (a 39% increase). Though the native maize coating improved colloidal stability, others have reported higher colloidal when NPs are coated with starch. Since others have reported higher colloidal stability, a study was conducted to determine if modified starches would provide better colloidal stability. Starches are commonly modified to improve their functionality[19, 20,21]. A visual sedimentation study with commercial starches found NZVI particles coated with OSA-modified tapioca starch had the highest colloidal stability.

After establishing OSA-modified tapioca starch provided the highest colloidal stability, native tapioca starch was modified in the lab. Native tapioca starch was modified with four concentrations (3, 15, 35, and 50% of OSA weight per starch weight). NMR characterization of the modified tapioca starch confirmed the OSA modification by addition of signals between 0.7-3.0 ppm and changes in signals around 5.50 ppm[17, 21]. Calculations determined that 35% OSA-modified tapioca starch had highest DS (DS = 0.126). The DS is a measure of the number of the number of OSA groups attached to the starch molecule. The more OSA groups attached to the starch molecule indicates that there are more ester, carbonyl, and hydroxyl which are reported to bind strongly to the surface of NZVI[3, 12, 15, 30].

NZVI particles were coated with the four OSA-modified tapioca starches at three coating concentrations (1 g L^{-1}, 5 g L^{-1}, and 10 g L^{-1}). Coating NZVI with the OSA modified tapioca starch significantly improved colloidal stability compared to bare NZVI particles at three coating concentrations ($p = 0.000$ for all concentrations). NZVI particles coated with 35%-OSA-modified tapioca starch at a coating concentration of 10 g L^{-1} had the highest colloidal stability. Particles coated with this starch had a colloidal stability of 66% after 2-hours, while only 4% of bare NZVI particles were still suspended. The 35% OSA-modified tapioca starch also improved colloidal stability 38% compared to NZVI coated with native tapioca starch.

SEM images show discrete particles surrounded by a starch coating. The coated particles have an average particle size of 118.6 nm, while bare NZVI particles have an particle diameter of 35 nm[3]. SEM/EDX spectra show the coated particles are composed of 7.665% carbon, 25.063% oxygen, 65.868% iron, 0.22% silicon, and 0.875% sodium. Sodium (from controlling the pH with NaOH) is likely present because of side reactions that occurred during modification[18, 21, 28].

Overall, this study found that starch works well for coating NZVI particles. Native starches are not the best candidate for coating because they lack emulsification properties. Modified starches were found to be an effective agent to coat NZVI. In particular, OSA-modified tapioca starch was able to provide significant improvements in colloidal stability. Additional work is needed to determine how the starch coating impacts the reaction efficiency of NZVI.

2.5. Work Cited

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CHAPTER 3. EFFECT OF USING OSA-MODIFIED STARCH TO STABILIZE NZVI PARTICLES ON NITRATE REDUCTION

3.1. Introduction

An incredible number of sources contribute to groundwater nitrate (NO_3^-) contamination, including fertilizers, septic systems, and industrial atmospheric pollution[1,2,3]. Shallow groundwater systems are particularly at risk for NO_3^- contamination because the substance easily leaches through soil[3]. The health effects of elevated nitrate-nitrogen (NO_3-N) levels in groundwater are especially worrisome[1, 2, 4]. Exposure to this containment has been implicated in cancers, such as non-Hodgkins lymphoma, and neonatal disease, including blue baby syndrome[5, 6]. To protect human health, the U.S. Environmental Protection Agency (USEPA) set the maximum contaminant level (MCL) for nitrate at 10 mg L^{-1} (as N) [6]. Several studies have suggested that nanoscale zero-valent iron (NZVI) is an especially promising remediation tool. Many researchers even believe it can overcome the limitations of methods currently employed in groundwater remediation, such as the costs associated with reverse osmosis[7 8].

NZVI is able to quickly reduce nitrate concentrations within hours because of its large surface area (25-54 m^2g^{-1} for NZVI[9-11] compared to microscale 1 m^2g^{-1} for ZVI[11, 12]) and fast reaction kinetics[13]. Hwang et al.[14] was able reduce 100 mg L^{-1} of nitrate to zero within 2 hours of contact with bare NZVI (1250 mg L^{-1}) particles. Kassaee et al.[15] reported a 34% reduction in nitrate concentration (initial concentration of 30 mg L^{-1}) over 48 hours with an NZVI concentration of 2,666 mg L^{-1}. Ryu et al.[16] reduced 1000 mg L^{-1} of nitrate to zero within 1 minute of contact with bare NZVI (10 g L^{-1}). An et al.[17] reported 100% removal of nitrate (initial concentration 50 mg L^{-1}) within 4 days of contact with bare NZVI (0.7 mg L^{-1}). Zhang et al.[18] reported a 62.3% reduction in nitrate concentration (initial concentration of 50 mg L^{-1}) with bare NZVI at a concentration of .2 g L^{-1} in 2 hours. Bezbaruah et al.[10]

reduced 100 mg L^{-1}, 60 mg L^{-1}, and 20 mg L^{-1} of nitrate to 27 mg L^{-1} (73% reduction), 26 mg L^{-1} (57% reduction), and 10 mg L^{-1} (50% reduction), respectively; the NZVI concentration was 2 g L^{-1}).

$$NO_3^- + 4Fe^0 + 10H^+ \rightarrow 4Fe^{2+} + NH_4^+ + 3H_20 \quad (3\text{-}1)$$

Nitrite is also reported as an intermediate product when nitrate is reduced by NZVI [8,9], as shown in Equation 3-2.

$$Fe^0 + N0_3^- + 2H^+ \rightarrow Fe^{2+} + H_20 + NO_2^- \quad (3\text{-}2)$$

$$3Fe^0 + 2N0_2^- + 8H^+ \rightarrow 3Fe^{2+} + 4H_20 + N_{2(g)} \quad (3\text{-}3)$$

The main nitrate reduction reaction equation is shown in Equation 3-1[14-19] and the intermediate reaction equation is shown in Equation 3-2[9] and Equation 3-3[18]. Several studies report these reactions following either first order kinetics[10, 20] or pseudo first order kinetics[14, 16, 19, 21-23]. Hwang et al.[14] established nitrate was completely removed by pseudo first-order kinetics within 2 hours and ammonium (NH_4^+) was the main by-product. Experimental results found the ammonium concentration increased until nitrate reduction stopped[14]. The ammonium , generated by the nitrate reduction, was stripped to the gas phase at high pH conditions (pH ≥ 11)[14]; causing a decline in the aqueous solution's total nitrogen (TN)[14]. Similar results were reported by An et al.[17], Zhang et al.[18], and Tang et al.[24]. Hwang et al.[14] experiment also monitored the system for nitrogen gas and found that nitrogen gas was not produced during nitrate reduction. However, other studies have reported that nitrogen gas could be an end product[20, 25].

Other studies have evaluated how experimental conditions, such as storage time and pH, impact NZVI's reduction ability. Studies monitoring the impact of pH on nitrate removal

found NZVI's reduction ability is best when the nitrate solution starts at a neutral pH[10, 14, 16-18, 26]. As expected from Equation 3-1, many studies solution pH increases as the reaction was completed[14, 15, 27 21].

While NZVI is highly effective at removing nitrate, as demonstrated above, physical properties of NZVI can result in decreased removal efficiencies. When injected into groundwater systems, NZVI particles will quickly agglomerate and settle[13, 28, 29], which reduces the effective surface area and removal efficiency. NZVI particles can be coated with polymers to improve particle colloidal stability[13, 28, 29]. Other studies that have coated NZVI with starch have reported improved removal efficiency. He et[30] reported NZVI coated with starch removed 98% of Trichloroethylene (TCE) in 3 hours, while bare NZVI particles removed 78%. He et al.[31] reported 100% removal of TCE within 1 hour with NZVI particles stabilized with carboxymethyl cellulose (CMC), compared to 40% removal using bare NZVI. Krajangpan et al.[29] reported NZVI particles coated with Amphiphilic Polysiloxange Graft Copolymer (APGC) removed 89% of TCE in 12 hours, while bare NZVI removed 81%.

Since NZVI has proven to be effective at reducing nitrate concentrations in batch studies, there is potential for field application. This study was conducted to compare nitrate reduction by bare NZVI and CNZVI to see if the starch coated particles negatively impact, maintain, or improve removal efficiencies. Specific goals are: 1) evaluate nitrate reduction using bare NZVI and CNZVI particles and 2) characterize spent CNZVI particles. The experimental plan is shown in Figure 3-1.

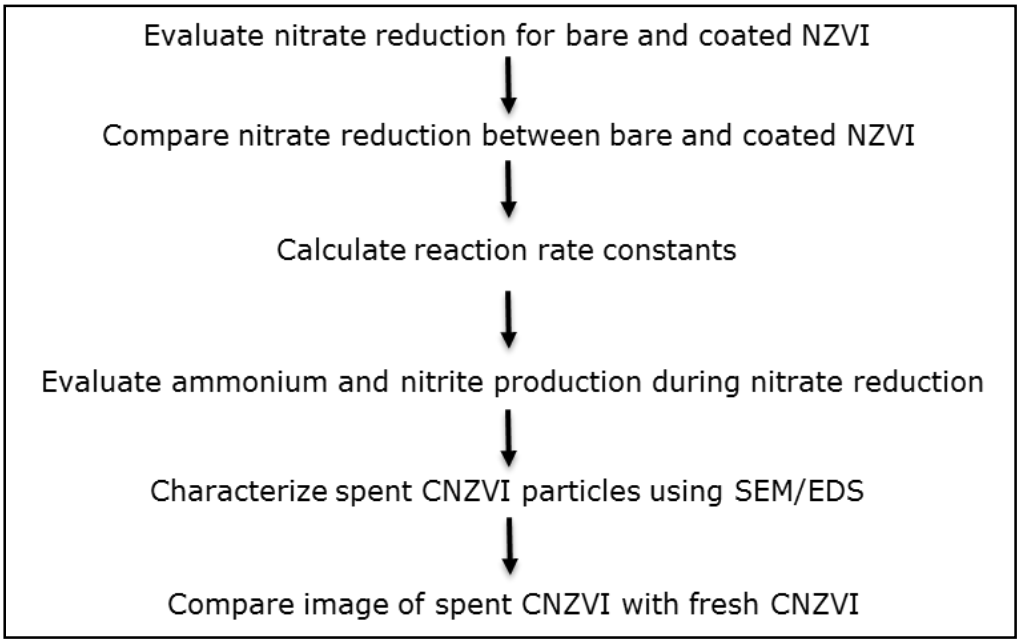


Figure 3-1. Flow Chart for Evaluating the Impact of Starch Coating on NZVI

3.2. Materials and Methods

3.2.1. Materials

$FeSO_4 7H_20$ (Aldrich Chemical), $NaBH_4$ (ACS grade, Alfa Aesar), methanol (95+%, BDH), NaOH (ACS grade, BDH), 2-Octen-l-ylsuccinic anhydride (OSA) (Dixie Chemical Company), HCL (EMD Millipore), native tapioca starch (Ingredion Company), potassium nitrate (KNO_3, Mallinckrodt Chemicals), ammonium sulfate ($(NH_4)_2SO_4$, J.T. Baker), and N_2 gas (Praxair) were used as obtained. Silica sand was purchased from Petco.

3.2.2. NZVI Synthesis

NZVI was synthesized by borohydride reduction of ferrous ion in $FeSO_4 7H_20$ according to the Liu et al. method[10,32]. The synthesis procedure is described in Section 2.2.2.

3.2.3. Coating NZVI

NZVI was coated with 35% OSA tapioca starch. To coat NZVI, a 10 g L^{-1} solution of 35% tapioca starch was prepared. NZVI particles were coated at a concentration of 1 g L^{-1}. All steps were completed as described in Section 2.2.3.

3.2.4. KNO_3 Preparation

A nitrate stock solution was prepared following Standard Method 4500 NO_3^- -D Nitrate Electrode Method[33]. The nitrate stock solution (100 mg L^{-1}) was prepared by drying 0.7218 grams of KNO_3 for 24 hours (oven temperature = 105°C). The dried KNO_3 was dissolved in 1 L of deoxygenated-DI water. Fresh stock solutions were prepared for each experiment. Diluted solutions (20, 40, and 60 mg L^{-1}) were prepared from the stock solution for reduction experiments. The dilutions were prepared in deoxygenated DI water. Deoxygenation was done by bubbling the DI water with pure N_2-gas for 2 hours.

3.2.5. Nitrate Reduction

Commercial grade polyethylene terephthalate bottles (225 mL) were used as anaerobic reactors for nitrate reduction batch studies. Reduction studies were conducted at initial concentrations of 20, 40, and 60 mg L^{-1} NO_3^--N without pH adjustment (See Appendix B.1 for initial pH values). Bare NZVI (1 g L^{-1}) or CNZVI (1 g L^{-1}) were added into 225 mL of NO_3^--N solution, oxygen was removed from the headspace, and the reactors were sealed with a rubber stopper to create an anaerobic environment. Controls with only 35% OSA tapioca starch (10 g L^{-1}) in the NO_3^--N solution or blanks (only NO_3^--N solution) were used. The reactors were rotated in an end-over-end at 28 rpm in a custom made shaker[10]. Aliquots were withdrawn from the sacrificial reactors at predetermined intervals (30, 60, 120, 240, 360, and 720 minutes). NZVI was filter from the solution using a vacuum filter and 0.2 µm filter; this filter was selected because it retains NZVI[11, 17, 26]. All experiments were conducted in triplicate. See Figure 3-2 for experiment flow chart. An NZVI concentration of 1 g L^{-1} was selected because 950 mg (based on the stoichiometric

calculations) of iron is needed to reduce 60 mg L^{-1} of nitrate. Using the smallest amount of iron necessary is ideal for treatment because it reduces the amount of raw material needed and waste material (oxidized iron particles) produced. The kinetics of nitrate reduction were evaluated using zero-, first-, and second order reactions.

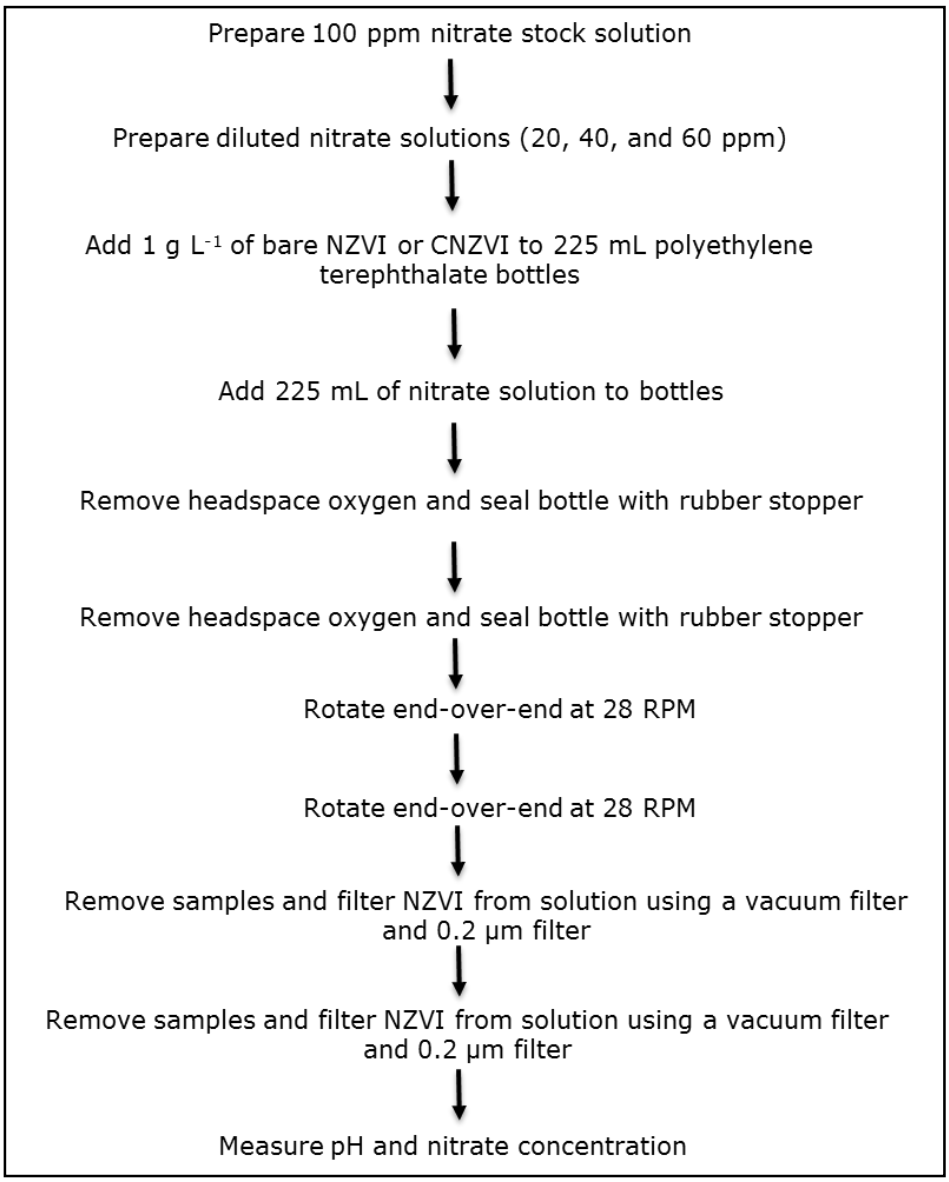


Figure 3-2. Flow Chart for Nitrate Reduction Experiment

3.2.6. Analytical Methods

Immediately after filtering, each sample was tested for pH and NO_3^--N concentration. pH was measured using an Orion Triode Combination pH/ATC Probe (purchased from VWR). NO_3^--N was measured using a double junction nitrate electrode (purchased from VWR) and Standard Method 4500 NO_3^- -D Nitrate Electrode Method[33] was followed.

A mass balance analysis was conducted for bare NZVI and CNZVI samples used in the 20 mg L^{-1} reduction studies. These samples were tested for nitrite (NO_2^--N), ammonium (NH_4^+-N), and nitrate (NO_3^--N). Samples were tested at 0, 1, 2, 6, and 12 hours. Samples were tested using an AutoAnalyzer 3. Nitrate/Nitrite were tested using AutoAnalyzer method no. G-139-95, Rev. 5 with a cadmium column. The stock solution for nitrite and nitrate was nitrate standard (20 mg L^{-1} as N). Nitrite samples were analyzed as nitrate and converted to NO_2^--N. Ammonium was tested using AutoAnalyzer method no. 145-95, Rev. 4. The stock solution for ammonium was ammonium standard (1000 mg L^{-1} as N). Ammonium samples were analyzed as nitrate and converted to NH_4^+-N. Table 3-2 shows the parameters of the AutoAnalyzer. AutoAnalyzer analysis was performed by NDSU Soil Testing Lab.

Table 3-1. AutoAnalyzer Settings

Machine Part	**Setting**
Nitrate / Nitrite	
Colorimeter	520 nm
Heating Bath	5.37 ml/37°C
Orn/wht (0.23)	Color
Orn/wht (0.23)	Di water
Orn/wht (0.23)	sample
Red/red (0.80)	NH_4Cl
Blk/blk (0.32)	air
Grn/grn (2.00)	water
Ammonium	
Colorimeter	630 nm
Heating Bath	5.37 ml/37°C
Orn/wht (0.23)	Hypochlorite
Orn/wht (0.23)	Phenol
Orn/wht (0.23)	Sample
Red/red (0.80)	EDTA
Blk/blk (0.32)	Air
Grn/grn (2.00)	Water

The nitrate reduction data was tested to see if it was a zero, first, or section order reaction. Equation 3-4 was used to determine mass balance for NO_3^--N reduction.

$$C_{TN} = C_{NO_3} + C_{NH_4} + C_{NO_2} \quad (3\text{-}4)$$

Where:

C_{NO3} = Concentration of NO_3^- (mg L^{-1})

C_{NH4} = Concentration of NH_4^+ (mg L^{-1})

C_{NO2} = Concentration of NO_2^- (mg L^{-1})

C_{TN} = Sum of CNO_3 + CNH_4 + CNO_2 (mg L^{-1})

3.2.6. Quality Control and Statistical Analysis

Nitrate treatability experiments were conducted in triplicate. Average values and standard deviations are reported. One-way ANOVA analysis was used to compare nitrate reduction data obtained from CNZVI and bare NZVI. Statistical analysis was conducted in Minitab 17.

3.3. Results and Discussion

3.3.1. Nitrate Reduction

Nitrate reduction experiments were conducted to see how coating the particles impacts treatment efficiency of NZVI. During the 12-hour study, bare NZVI reduced the NO_3^- -N (Figure 3-3) from 20, 40, and 60 mg L^{-1} to 0.19 mg L^{-1} (99% reduction), 8 mg L^{-1} (70% reduction), and 35.4 mg L^{-1} (57% reduction), respectively. CNZVI reduced NO_3^--N concentrations from 20, 40, and 60 mg L^{-1} to 5.81 mg L^{-1} (71% reduction), 11.68 mg L^{-1} (69% reduction), and 28.39 mg L^{-1} (54% reduction), respectively (see Figure 3-3). The high reduction percentages observed during the 20 mg L^{-1} is likely related to the excess amount of NZVI in the system. There is excess NZVI in the reactor during the 20 mg L^{-1} because the experiment provided just enough NZVI to reduce 60 mg L^{-1}. Complete NO_3^--N reduction

data is available in Appendix B-Section B.1, pH data is located in Appendix B-Section B.1, and ANOVA results are in Appendix B-Section B.2.

As shown in Figure 3-3, bare NZVI reduced significantly ($p = 0.000$) more nitrate than CNZVI at a nitrate concentration of 20 mg L^{-1} (bare NZVI reduced 28% more nitrate than CNZVI). There was not a significant difference between the amount of nitrate reduced by bare NZVI and CNZVI at 40 mg L^{-1} and 60 mg L^{-1} ($p = 0.939$ and $p = 0.815$, respectively). Kinetic studies found both NZVI and CNZVI reduce nitrate by a second order reaction [$-dC/dt = k_{SA}\rho_A C = k_{obs}[C]^2$, where kSA is the surface normalized reaction rate constant (L $m^{-2}h^{-1}$), ρ_A is the iron surface area concentration (m^2 L^{-1}), t is time (hours), and C is nitrate concentration], as shown in Table 3-2. Surface normalized reaction constants for nitrate reduction ranged from 0.003 to 0.02 L $m^{-2}h^{-1}$ and .007 to .003 L $m^{-2}h^{-1}$ for bare NZVI and CNZVI, respectively. A second order reaction, instead of a first order/pseudo first order reaction commonly reported, was likely observed because NZVI was not in excess in the system. A pseudo first order reaction will occur when one of the components is available in excess in the system, causing the concentration of the excess to remain constant. Though the actual mass of NZVI remained constant throughout the experiment, the reactive surface area declined as the particles were oxidized. Oxidized particles are not effective reducing agents, the reduction capacity declines, showing that the reaction is dependent on both nitrate concentration and NZVI. Kinetic graphs are presented in Appendix B-Section B.3.

Table 3-2. Second-Order Rate Constants for Nitrate Reduction

Sample	K_{obs}(L h^{-1})	K_{sa} (L $m^{-2}h^{-1}$)	R^2
20 Bare	0.5075	0.0203	0.9967
20 Coated	0.1842	0.007368	0.9287
40 Bare	0.1857	0.007428	0.9729
40 Coated	0.1834	0.007336	0.979
60 Bare	0.1066	0.004264	0.9688
60 Coated	0.0825	0.0033	0.9134

While these results show the surface modifier does not negatively impact the particles reaction efficiency, several studies report increased removal efficiencies for starch

stabilized NZVI[30, 34-36]. Zhang et al.[36] also reported increased arsenate removal using starch stabilized magnetite NPs. Liang et al.[35] reported improved arsenic removal in starch coated NZVI particles compared to bare particles. An et al.[37] found starch stabilized magnetite NPs removed 5 times for arsenic than their bare counterparts. This study also found arsenic removal is related to the starch coating concentration, indicating there is an optimal concentration to achieve coating and removal efficiencies[37]. It is thought that the presence of starch on the NPs results in the formation of additional adsorbing sites[36], which increases the amount of arsenate removed from the system. He et al.[30] also increased TCE removal with starch stabilized NZVI. Comparing the results reported here with the literature, there is a lot of potential for using NZVI stabilized with OSA-modified tapioca starch in the industry. It may be possible to improve the nitrate reduction of CNZVI particles by adjusting the concentration starch is coated to the particles. There is also a lot of promise for the application of these particles into arsenic remediation.

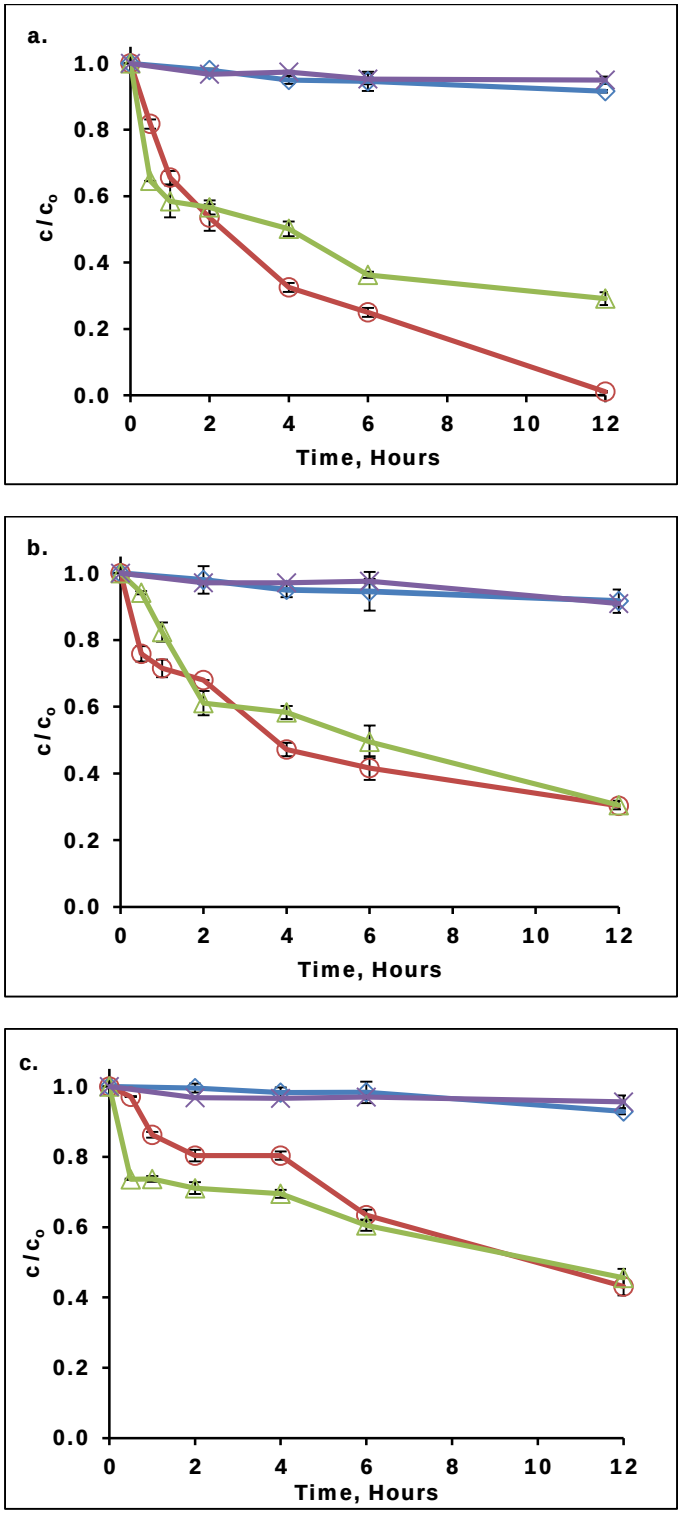


Figure 3-3. Nitrate Reduction by CNZVI and Bare NZVI
a). Initial NO_3^--N Concentration = 20 mg L^{-1}. b). Initial NO_3^--N Concentration = 40 mg L^{-1}. c). Initial NO_3^--N Concentration = 60 mg L^{-1}. Vertical Bars are ± Standard Error. -○- Bare NZVI, -Δ- CNZVI, -X- OSA Starch, and -◇- Blank.

3.3.2. Mass Balance

Since ammonium is generated when NZVI reduces NO_3^--N (see Equation 3-1), samples treated with CNZVI and bare NZVI were analyzed for nitrogen species. Mass balances for both types of NZVI are shown in Figure 3-4. For bare NZVI, the ammonium generation is comparable to literature results[14, 22]. Hwang et al. [14] reported ammonium stripping in their reduction experiments; ammonium stripping was evident by a declining mass balance and the solution pH (above 11). In this study, the ammonium concentration continued to increase throughout the study and the pH remained below 10.20, indicating ammonium stripping did not occur (see Figure 3-4). The concentration of nitrogen species decreased to 75% of the initial concentration of nitrogen species over 12 hours when bare NZVI was used (see Figure 3-4). CNZVI removed significantly less nitrate from the study ($\alpha = 0.05$, $p = 0.018$, see Figure 3-4), as reported in Section 3.3.1.

The nitrogen mass balance, for reduction of nitrate using bare NZVI (see Figure 3-4 a, purple line), shows how balance of nitrogen species in the reactor changes over through the experiment. This line initially declines during the first hour, then increases between hours 1 and 2. The initial decline is related to the decrease in nitrogen species as nitrate is quickly reduced. Hwang et al. [14] reported the same nitrogen mass balance scenario. It is possible the decline in the mass balance over time is related to the generation of nitrogen gas (see Equation 3.3), which has been a reported end product of the NZVI mediated reaction[20, 25]. The mass balance for CNZVI is shown in Figure 3-4 b.

Compared to bare NZVI, nitrite and ammonium production were significantly lower when CNZVI was present (one-way ANOVA, $p = 0.05$, $p=0.044$ and $p = 0.001$, respectively). The samples contained 60% ammonium when nitrate was reduced by CNZVI, while the samples contained 75% ammonium when reduced by bare NZVI (a 15% decline in ammonium generation). This is line with the significantly lower amount of NO_3^--N reduced

by CNZVI during the experiment. It is unlikely ammonium stripping occurred as the pH remained below 10.20 (see Figure 3-4).

Mass balance data is in Appendix B-Section B.4, one-ANOVA data is in Appendix B-Section B.5, and pH data is in Appendix B-Section B.1.

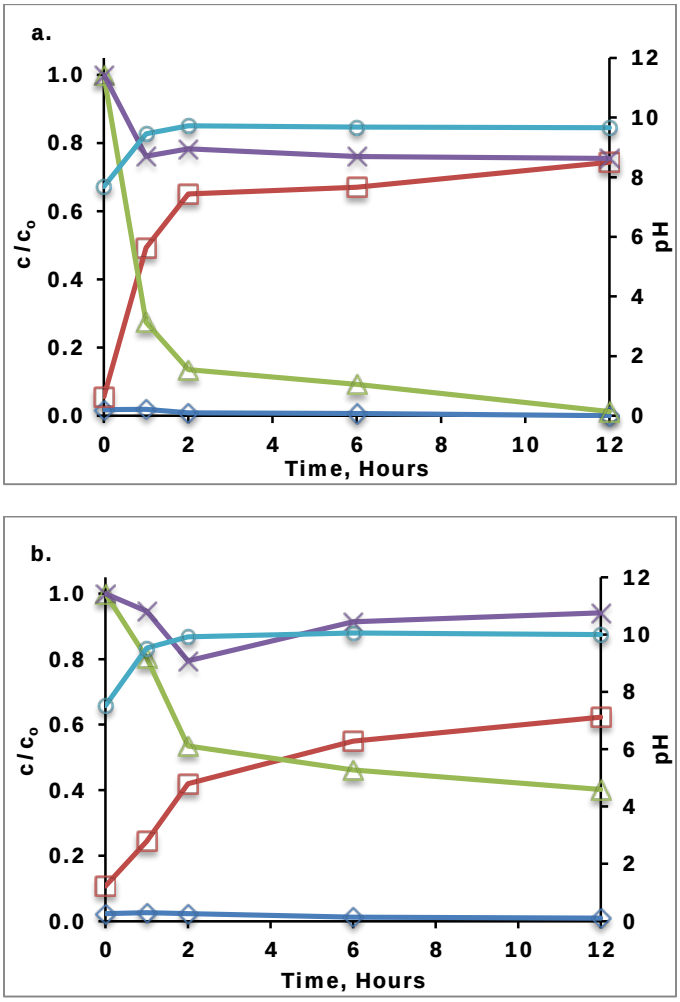


Figure 3-4: Nitrogen Mass Balances when Nitrate Solution (C_o = 20 mg L^{-1}) was Treated with a.) Bare NZVI and b.) CNZVI. -□- Ammonium, -◇- Nitrite, -Δ- Nitrate, and -X- Nitrogen Balance (Aqueous Phase), -o- pH

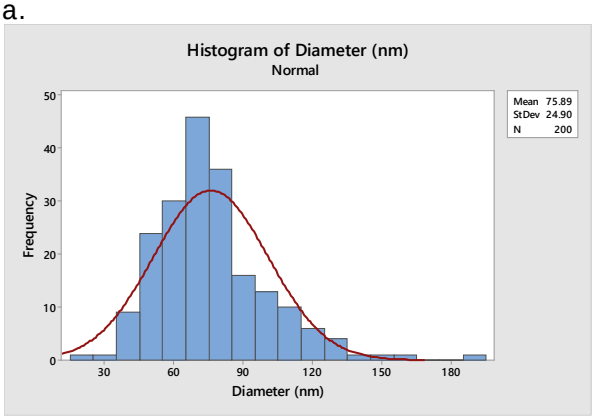
3.3.3. CNZVI Characterization

3.3.3.1. SEM/EDS Comparison

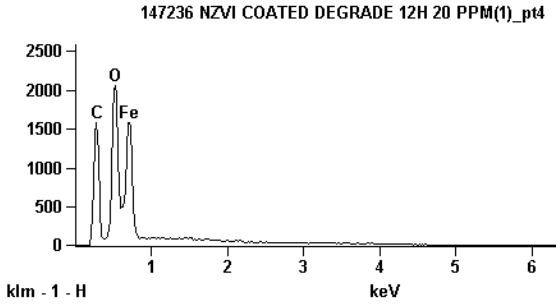
Spent CNZVI particles were characterized with SEM/EDS to compare with fresh CNZVI. Four different points were used to obtain SEM/EDS data for spent CNZVI. The surface morphology of spent CZNVI and fresh CNZVI were examined (see Figure 3-5 c and d, respectively). Spent CNZVI particles appear to be irregularly shaped and have rougher surfaces. The average particle size of spent CNZVI (75.89 nm, n=200, see Figure 3-5 a) is lower than fresh CNZVI (118.6 nm), indicating the starch layer may have degraded. Since the particles are still larger than bare NZVI (ave. diameter ~ 35nm, see Section 2.3.5), it can be assumed a starch layer is still present on the particles, which prevented the particles from aggregating. SEM images of CNZVI particles have flake like structures, which could be free starch molecules (from the starch detaching from NZVI) or iron oxide plates. Ryu et al. [16] reported the presence of iron oxide plates after reacting nitrate with NZVI.

Figure 3-5 a shows the EDS spectra of spent CNZVI. EDS analysis of spent CNZVI found the sample contained 31.66% carbon, 31.93% oxygen, 0.85% silicon, and 35.56% iron (see Figure 3-5 b). Analysis of fresh CNZVI found the samples 7.665% carbon, 25.063% oxygen, 65.868% iron, 0.22% silicon, and 0.875% sodium. The decrease (24%) in carbon content is likely from the starch detaching from the surface of NZVI. Free starch molecules in the reactors would be lost from the system when the sample was vacuum filtered. The 7% increase in oxygen content, compared to the fresh CNZVI, discussed in Section 2.3.5, is likely caused by the oxidation of particles during nitrate reduction. Additional EDS spectra and particle distribution data are located in Appendix B-Section B.6.

a.



b.



c.

d.

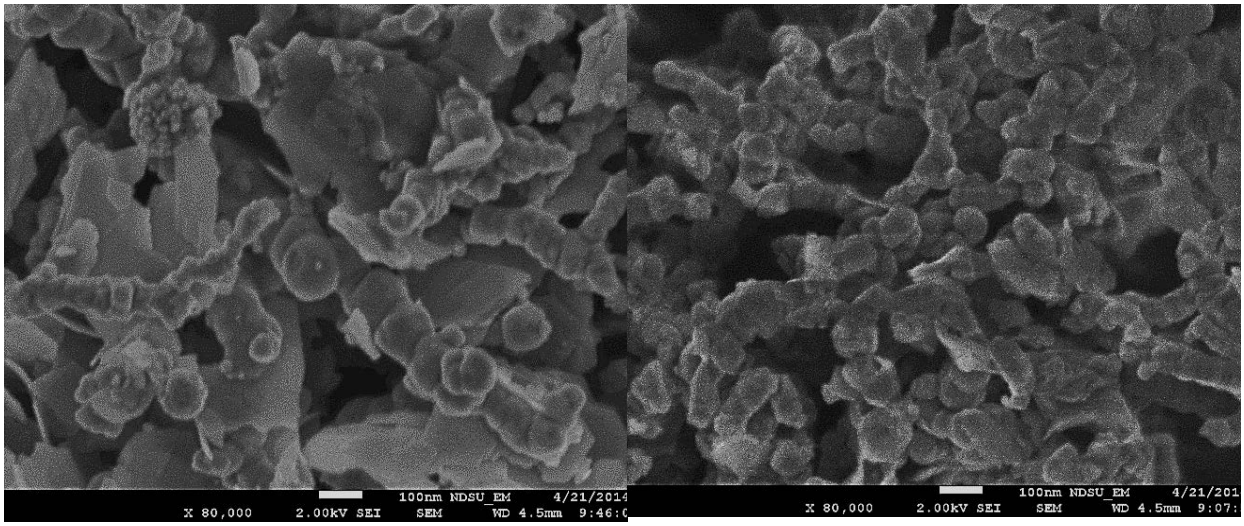


Figure 3-5. Spent CNZVI Characterization
a. Particle Size Distribution, b. EDS Spectra of Spent CNZVI, c. Scanning Electron Micrograph of Spent CNZVI and d. Scanning Electron Micrograph of Fresh CNZVI

3.4. Conclusion

Nitrate reduction studies were conducted to determine if coating NZVI with 35% OSA tapioca starch (coating concentration 10 g L^{-1}) decreased removal efficiencies compared to bare NZVI. NO_3^--N was degraded from three different initial concentrations (20, 40, and 60 mg L^{-1}). There was a significant difference in nitrate reduction between bare and coated particles when the nitrate concentration was 20 mg L^{-1} ($p = 0.000$). At this concentration, bare NZVI was able to reduce 99% of the nitrate, while CNZVI reduced 71%. However, there was not a significant difference in nitrate reduction between the two particle types at

nitrate concentrations of 40 and 60 mg L^{-1} ($p = 0.939$ and $p = 0.815$, respectively). Bare NZVI reduced the 40 mg L^{-1} solution by 70% and the 60 mg L^{-1} solution by 57%, while CNZVI reduced 69% and 54%, respectively. More nitrate was reduced at the lower concentrations because there was more NZVI in the system than necessary to reduce nitrate. Less nitrate was reduced in the 60 mg L^{-1} system because there was just enough NZVI in the system. This was done to limit the amount of NZVI used and to see if significant degradation could occur while minimizing the amount of material needed.

The nitrate reduction followed a second order reaction, which was likely observed because NZVI was not in excess in the reactor system. Since NZVI was not in excess in the system, there was a decline in reactive surface area as some of the particles were oxidized, which decreases the amount of nitrate that can be reduced. Mass balance analysis found that both nitrite and ammonium are produced when nitrate is reduced by NZVI. The samples reduced by bare NZVI had significantly more nitrite and ammonium present ($p = 0.044$ and $p = 0.001$, respectively) than those reduced with CNZVI. This occurred because more nitrate was reduced by bare NZVI than CNZVI.

The spent CNZVI particles appear to be irregularly shaped and had rougher surfaces than fresh CNZVI particles. The average particle diameter of spent CNZVI decreased to approximately 75 nm, while fresh CNZVI had an average particle diameter of 119 nm. However, the spent particles were still larger than bare NZVI (average particle diameter is approximately 35 nm), indicating there is still a starch layer present on the coated particles.

This study shows there is a large potential for coating NZVI, and other NPs, with OSA-modified tapioca starch. In particular, NZVI particles coated with this starch may be particularly well suited for removing contaminants by sorption. Several studies have found that coating NZVI and magnetite NPs with starch drastically improves arsenic sorption compared to bare NZVI[30, 34-36]. Further investigations should be conducted to evaluate if

coating NZVI with OSA-modified tapioca starch will have improved removal of contaminants that are removed by sorption mechanisms.

3.5. Work Cited

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CHAPTER 4. CONCLUSION

4.1. Introduction

NZVI is a power groundwater remediation tool. It's highly reactive surface area (25-54 m^2g^{-1} [1-3]) and fast kinetics[4] allow it to treat a wide range of organic, inorganic, and heavy metal contaminants[1]. Unfortunately, NZVI will quickly agglomerate and settle in an aqueous systems[2,4,5,6], reducing the particle's available surface area. In order to prevent aggregation, the surface of NZVI particles is modified with polymers to provide steric and/or electrosteric stability[2,7] .

Many of the polymers used to coat NZVI particles have limited environmental applications because of issues related to cost and biodegradability[2,7,8,9]. To improve the applicability of NZVI particles, researchers have focused on biopolymers for coating NZVI particles. Biopolymers, such as xanthan gum, guar gum, and CMC, are effective at improving the colloidal stability of NZVI particles[7,10,11,12,13,14,15,16,17]. However, very few studies have focused on starch as a biopolymer for coating magnetic NPs[18,19,20,21,22] . Since there are few studies using starch as a coating agent, this work focused on assessing the potential of starch to coat NZVI particles.

4.2. Evaluation of Starch for Coating NZVI

Initial sedimentation experiments were conducted by coating NZVI particles with four native starches (maize, tapioca, rice, and wheat). It was found that native rice, wheat, and tapioca starches did not significantly improve the colloidal stability of NZVI ($p = 0.295$, 0.57, and = 0.098, respectively). This was expected as native starches lack emulsification properties[23] and anchoring groups[24,25], which prohibited the starches from achieving high colloidal stability. However, native maize starch was able to keep 45% of particles suspended after 1 hour (only 6% of bare NZVI particles were suspended after 1 hour).

Though native maize starch improved colloidal stability, several other studies reported coating NZVI with starch or other biopolymers kept at least 50% of the particles suspend[8, 11, 18, 21, 7, 22]. As other others have reported better colloidal stability, a visual sedimentation study was conducted using commercially available modified starches.

Starches are commonly modified to overcome physical shortcomings, such as lacking emulsification properties[23]. The screening study evaluated modified version of the four native starches (maize, wheat, rice, and tapioca). It found NZVI particles coated with OSA-modified tapioca starch had the highest colloidal stability. Following the visual study, native tapioca starch was modified with four concentrations of OSA (3%, 15%, 35%, and 50% w/w). The OSA-modified tapioca starches were characterized using FTIR, H-NMR, and HPLC. H-NMR data was used to figure out the DS for each OSA-modified tapioca starch. NMR characterization of the modified tapioca starch confirmed the OSA modification by addition of signals between 0.7-3.0 ppm and changes in signals around 5.50 ppm[23, 26]. Calculations determined that 35% OSA-modified tapioca starch had highest degree of substation (DS) (DS = 0.126). The DS is a measure of the number of the number of OSA groups attached to the starch molecule, indicating more ester, carbonyl, and hydroxyl groups were present.

NZVI particles were coated with the four starches at three concentrations (1, 5, and 10 g L^{-1}) and sedimentation was monitored using UV-vis spectrophotometry. It was found the colloidal stability of NZVI improved when coated with all four starches at the three coating concentrations ($p = 0.000$ for all concentrations). Visual inspection of the sedimentation curves and statistical analysis (Tukey's Pairwise Comparisons) found that NZVI particles coated with coated with 35% OSA-modified tapioca starch (10 g L^{-1}) had the highest colloidal stability. Particles coated with this OSA-modified tapioca starch had a colloidal stability of 66%, 23% of particles coated with native tapioca starch were suspended, and while only 4% of bare NZVI particles were still suspended after 2 hours (OSA-modified tapioca starch improved colloidal stability by 38%). This starch modification

has the highest DS of the four modified starches. A high DS indicates more OS molecules were substituted per glucose molecule, which translates to more ester and carbonyl anchoring groups.

SEM analysis found CNZVI particles were larger (average particle diameter = 118 nm) than bare NZVI (average particle diameter = 35 nm), which is due to the starch coating. CNZVI particles also appeared to create a porous matrix instead of agglomerating like bare NZVI. EDS analysis showed an increase in carbon and oxygen, which is related to the starch coating.

4.3. Nitrate Reduction Studies

Nitrate degradation experiments were conducted to determine how the starch coating impacted the reduction capacity of the particles. NO_3^--N was degraded from three different initial concentrations (20, 40, and 60 mg L^{-1}). There was a significant difference in nitrate reduction between bare (99% of nitrate reduced) and coated particles (71% of nitrate reduced) when the nitrate concentration was 20 mg L^{-1} ($p = 0.000$). At higher concentrations, there was not a significant difference between nitrate removed by bare NZVI and CNZVI ($p = 0.939$ and $p = 0.815$, respectively). Bare NZVI reduced the 40 mg L^{-1} solution by 70% and the 60 mg L^{-1} solution by 57%, while CNZVI reduced 69% and 54%, respectively. Nitrate reduction followed a second order reaction. A mass balance analysis found both nitrite and ammonium are produced during this reaction. Nitrate degradation by bare NZVI produced significantly more nitrite and ammonium present ($p = 0.044$ and $p = 0.001$, respectively) than the nitrate samples reduced with CNZVI. This occurred because more nitrate was reduced by bare NZVI than CNZVI.

SEM analysis found the spent CNZVI particles to be irregularly shaped and had rougher surfaces than fresh CNZVI particles. The average particle diameter also decreased from 118 nm (fresh CNZVI) to 75 nn (spent CNZVI). However, the spent particles were still

larger than bare NZVI (average particle diameter = 35 nm), indicating the starch coating is still present.

4.4. Conclusion

The colloidal stability of NZVI is significantly improved when coated with OSA-modified tapioca starch. To the best of my knowledge, this study reports the first use of OSA-modified tapioca starch as a surface modifier for NPs. Coating NZVI particles with OSA-modified tapioca starch potentially has widespread scientific and industrial potential.

The carboxylic and ester anchoring groups on the starch backbone will anchor to a wide range of inorganic/metal NPs. Coating other types of NPs with OSA-modified tapioca starch would increase the number of industrial applications. Other industries that could benefit from this surface modifier are drug delivery, electronic/optoelectronic, photocatalytics, tissue engineering, and antimicrobial applications. Expanding the application of tapioca starch will increase the demand for the starch, which will benefit agricultural industries. An increased demand for tapioca starch could stimulate economies in the developing countries where tapioca is cultivated.

In groundwater remediation, the coated particles may improve *in situ* groundwater remediation because the particle's physical features. The physical features of the coated particles may be ideal for creating an iron treatment wall by injection. Injecting iron treatment walls will reduce the cost and time of constructing traditional PRBs, which will hopefully improve the usability of iron PRBs. The biodegradability of OSA modified tapioca starch is also ideal for injecting into groundwater systems (see Appendix C). Additionally, a review of the literature suggests the NZVI coated with OSA-modified tapioca starch may improve arsenic removal. This is because several studies have reported increased arsenic removal from NZVI and magnetite NPs coated with starch [18,27,28,29] . It is thought that starch coating increases the number of sorption sites on each particle, which results in more arsenic being absorbed onto the particle and removed from the system[29].

Although OSA-modified tapioca starch improved colloidal stability and is able to degrade nitrate, further work is needed to understand how it can be utilized in groundwater rememdiation. In particular, experiments should be conducted to evaluate how NZVI coated with OSA-modified tapioca starch behaves for removing contaminants by sorption. Other studies should be conducted to determine the transportation characteristics of the CNZVI particles. Studies in this area should monitor: particle mobility in other types of soil (i.e. soils predominant in different agriculture regions), long-term porosity of the iron wall, particle mobility in heavy rains, and treatment efficiencies.

This study evaluated the potential for using starch as a coating agent for NZVI particles. Starch is an ideal candidate for coating NZVI particles because it is a cost-effective, biopolymer that is easily produced from a renewable source. These are extremely important characteristics because they are underrepresented in literature about surface modification of NZVI. Overall, it was found coating NZVI particles with starch improves the colloidal stability, while not impacting the particles reduction efficiencies.

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APPENDIX A. SUPPORTING DATA FOR CHAPTER 2

A.1. Food Starch Screening

Table A.1. Bare NZVI Sedimentation Data

Bare NZVI											
Sample A			Sample B			Sample C			Ave. A/A_o	Std. Dev.	Std. Error
Time (min)	Abs (A)	A/A_o	Time (min)	Abs (A)	A/A_o	Time (min)	Abs (A)	A/A_o			
0	2.97	1.00	0	2.69	1.00	0	4.61	1.00	1.00	0.00	0.00
1	2.59	0.87	1	2.33	0.86	1	4.26	0.92	0.89	0.03	0.02
2	2.27	0.76	2	2.10	0.78	2	3.27	0.71	0.75	0.04	0.02
3	2.00	0.67	3	1.77	0.66	3	2.27	0.49	0.61	0.10	0.06
4	1.80	0.60	4	1.48	0.55	4	1.83	0.40	0.52	0.11	0.06
5	1.62	0.54	5	1.25	0.46	5	1.61	0.35	0.45	0.10	0.06
10	1.13	0.38	10	0.67	0.25	10	0.99	0.22	0.28	0.09	0.05
15	0.88	0.30	15	0.43	0.16	15	0.70	0.15	0.20	0.08	0.05
20	0.73	0.25	20	0.31	0.12	20	0.55	0.12	0.16	0.07	0.04
25	0.63	0.21	25	0.24	0.09	25	0.46	0.10	0.13	0.07	0.04
30	0.56	0.19	30	0.20	0.07	30	0.39	0.08	0.12	0.06	0.04
35	0.50	0.17	35	0.17	0.06	35	0.34	0.07	0.10	0.06	0.03
40	0.46	0.15	40	0.15	0.06	40	0.29	0.06	0.09	0.05	0.03
45	0.42	0.14	45	0.13	0.05	45	0.26	0.06	0.08	0.05	0.03
50	0.39	0.13	50	0.12	0.05	50	0.24	0.05	0.08	0.05	0.03
55	0.37	0.12	55	0.11	0.04	55	0.22	0.05	0.07	0.05	0.03
60	0.35	0.12	60	0.11	0.04	60	0.20	0.04	0.07	0.04	0.03

Table A.2. Maize Starch Sedimentation Data (1 g L^{-1})

Maize Starch 1 g L^{-1}											
Sample A			Sample B			Sample C			Ave. A/A_o	Std. Dev.	Std. Error
Time (min)	Abs (A)	A/A_o	Time (min)	Abs (A)	A/A_o	Time (min)	Abs (A)	A/A_o			
0	3.77	1.00	0	3.77	1.00	0	3.77	1.00	1.00	0.00	0.00
1	3.77	1.00	1	2.29	0.61	1	2.83	0.75	0.79	0.20	0.11
2	1.34	0.36	2	1.36	0.36	2	1.63	0.43	0.38	0.04	0.02
3	1.14	0.30	3	1.10	0.29	3	1.38	0.37	0.32	0.04	0.02
4	0.95	0.25	4	0.92	0.24	4	1.20	0.32	0.27	0.04	0.02
5	0.89	0.24	5	0.81	0.22	5	1.04	0.28	0.24	0.03	0.02
10	0.58	0.15	10	0.58	0.15	10	0.84	0.22	0.18	0.04	0.02
15	0.47	0.12	15	0.48	0.13	15	0.77	0.20	0.15	0.05	0.03
20	0.40	0.11	20	0.44	0.12	20	0.73	0.19	0.14	0.05	0.03
25	0.35	0.09	25	0.42	0.11	25	0.70	0.19	0.13	0.05	0.03
30	0.32	0.08	30	0.39	0.10	30	0.70	0.18	0.12	0.05	0.03
35	0.29	0.08	35	0.30	0.08	35	0.70	0.19	0.11	0.06	0.04
40	0.28	0.07	40	0.30	0.08	40	0.71	0.19	0.11	0.06	0.04
45	0.27	0.07	45	0.29	0.08	45	0.71	0.19	0.11	0.07	0.04
50	0.17	0.05	50	0.28	0.07	50	0.72	0.19	0.10	0.08	0.04
55	0.17	0.05	55	0.28	0.07	55	0.73	0.19	0.10	0.08	0.05
60	0.17	0.04	60	0.27	0.07	60	0.74	0.20	0.10	0.08	0.05

Table A.3. Maize Starch Sedimentation Data (5 g L^{-1})

Maize Starch 5 g L^{-1}											
Sample A			Sample B			Sample C			Ave. A/A_o	Std. Dev.	Std. Error
Time (min)	Abs (A)	A/A_o	Time (min)	Abs (A)	A/A_o	Time (min)	Abs (A)	A/A_o			
0	3.77	1.00	0	3.77	1.00	0	3.77	1.00	1.00	0.00	0.00
1	2.71	0.72	1	3.77	1.00	1	3.77	1.00	0.91	0.16	0.09
2	1.95	0.52	2	3.77	1.00	2	3.25	0.86	0.79	0.25	0.14
3	1.54	0.41	3	3.77	1.00	3	2.44	0.65	0.69	0.30	0.17
4	1.36	0.36	4	3.48	0.92	4	2.20	0.58	0.62	0.28	0.16
5	1.15	0.31	5	3.03	0.80	5	2.00	0.53	0.55	0.25	0.14
10	0.89	0.24	10	2.30	0.61	10	1.60	0.42	0.42	0.19	0.11
15	0.75	0.20	15	2.05	0.54	15	1.46	0.39	0.38	0.17	0.10
20	0.73	0.19	20	1.93	0.51	20	1.44	0.38	0.36	0.16	0.09
25	0.70	0.19	25	1.86	0.49	25	1.41	0.37	0.35	0.15	0.09
30	0.68	0.18	30	1.81	0.48	30	1.40	0.37	0.34	0.15	0.09
35	0.67	0.18	35	1.83	0.48	35	1.40	0.37	0.34	0.16	0.09
40	0.66	0.17	40	1.79	0.47	40	1.40	0.37	0.34	0.15	0.09
45	0.65	0.17	45	1.84	0.49	45	1.40	0.37	0.34	0.16	0.09
50	0.64	0.17	50	1.85	0.49	50	1.42	0.38	0.35	0.16	0.09
55	0.63	0.17	55	1.82	0.48	55	1.45	0.39	0.34	0.16	0.09
60	0.62	0.17	60	1.87	0.50	60	1.46	0.39	0.35	0.17	0.10

Table A.4. Maize Starch Sedimentation Data (10 g L^{-1})

Maize Starch 10 g L^{-1}											
Sample A			Sample B			Sample C			Ave. A/A_o	Std. Dev.	Std. Error
Time (min)	Abs (A)	A/A_o	Time (min)	Abs (A)	A/A_o	Time (min)	Abs (A)	A/A_o			
0	3.76	1.00	0	3.77	1.00	0	3.77	1.00	1.00	0.00	0.00
1	3.76	1.00	1	3.77	1.00	1	3.77	1.00	1.00	0.00	0.00
2	3.61	0.96	2	3.61	0.96	2	3.77	1.00	0.97	0.02	0.01
3	2.99	0.79	3	2.51	0.67	3	3.23	0.86	0.77	0.10	0.06
4	2.73	0.72	4	2.18	0.58	4	2.77	0.73	0.68	0.09	0.05
5	2.56	0.68	5	1.97	0.52	5	2.55	0.68	0.63	0.09	0.05
10	2.24	0.60	10	1.51	0.40	10	2.11	0.56	0.52	0.10	0.06
15	2.12	0.56	15	1.33	0.35	15	1.88	0.50	0.47	0.11	0.06
20	2.08	0.55	20	1.28	0.34	20	1.85	0.49	0.46	0.11	0.06
25	2.06	0.55	25	1.27	0.34	25	1.79	0.48	0.45	0.11	0.06
30	2.05	0.54	30	1.26	0.33	30	1.76	0.47	0.45	0.11	0.06
35	2.04	0.54	35	1.26	0.33	35	1.75	0.46	0.45	0.11	0.06
40	2.04	0.54	40	1.26	0.33	40	1.73	0.46	0.45	0.11	0.06
45	2.05	0.54	45	1.26	0.34	45	1.72	0.46	0.45	0.11	0.06
50	2.05	0.54	50	1.27	0.34	50	1.72	0.46	0.45	0.10	0.06
55	2.07	0.55	55	1.28	0.34	55	1.71	0.45	0.45	0.11	0.06
60	2.07	0.55	60	1.30	0.34	60	1.70	0.45	0.45	0.10	0.06

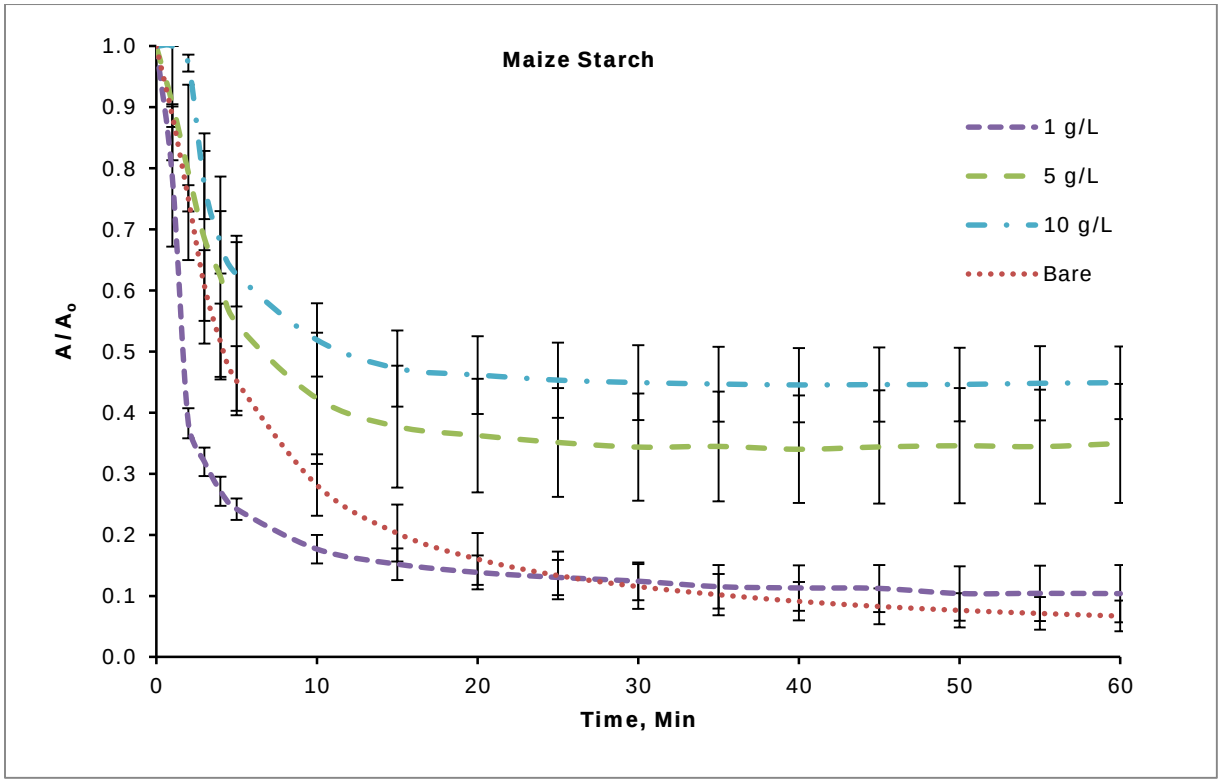


Figure A.1. Maize Starch Sedimentation Curves

Table A.5. Wheat Starch Sedimentation Data (1 g L^{-1})

Wheat Starch 1 g L^{-1}											
Sample A			Sample B			Sample C			Ave. A/A_o	Std. Dev.	Std. Error
Time (min)	Abs (A)	A/A_o	Time (min)	Abs (A)	A/A_o	Time (min)	Abs (A)	A/A_o			
0	3.77	1.00	0	3.77	1.00	0	3.78	1.00	1.00	0.00	0.00
1	2.43	0.64	1	3.77	1.00	1	1.82	0.48	0.71	0.27	0.15
2	1.80	0.48	2	3.77	1.00	2	1.58	0.42	0.63	0.32	0.18
3	1.56	0.41	3	3.49	0.93	3	1.41	0.37	0.57	0.31	0.18
4	1.47	0.39	4	2.81	0.75	4	1.30	0.34	0.49	0.22	0.13
5	1.38	0.37	5	2.35	0.62	5	1.24	0.33	0.44	0.16	0.09
10	1.07	0.28	10	1.45	0.39	10	0.96	0.25	0.31	0.07	0.04
15	0.90	0.24	15	1.14	0.30	15	0.81	0.22	0.25	0.05	0.03
20	0.75	0.20	20	0.97	0.26	20	0.71	0.19	0.22	0.04	0.02
25	0.67	0.18	25	0.91	0.24	25	0.64	0.17	0.20	0.04	0.02
30	0.63	0.17	30	0.85	0.23	30	0.56	0.15	0.18	0.04	0.02
35	0.58	0.15	35	0.82	0.22	35	0.53	0.14	0.17	0.04	0.02
40	0.53	0.14	40	0.79	0.21	40	0.49	0.13	0.16	0.04	0.02
45	0.50	0.13	45	0.76	0.20	45	0.46	0.12	0.15	0.04	0.03
50	0.48	0.13	50	0.74	0.20	50	0.44	0.12	0.15	0.04	0.03
55	0.46	0.12	55	0.74	0.20	55	0.44	0.12	0.14	0.04	0.03
60	0.45	0.12	60	0.73	0.19	60	0.42	0.11	0.14	0.04	0.03

Table A.6. Wheat Starch Sedimentation Data (5 g L^{-1})

Wheat Starch 5 g L^{-1}											
Sample A			Sample B			Sample C			Ave. A/A_o	Std. Dev.	Std. Error
Time (min)	Abs (A)	A/A_o	Time (min)	Abs (A)	A/A_o	Time (min)	Abs (A)	A/A_o			
0	3.79	1.00	0	3.29	1.00	0	3.75	1.00	1.00	0.00	0.00
1	2.29	0.60	1	2.70	0.82	1	3.06	0.82	0.75	0.12	0.07
2	1.79	0.47	2	2.18	0.66	2	2.54	0.68	0.60	0.11	0.07
3	1.61	0.43	3	1.86	0.57	3	2.17	0.58	0.52	0.08	0.05
4	1.48	0.39	4	1.71	0.52	4	1.89	0.50	0.47	0.07	0.04
5	1.38	0.36	5	1.57	0.48	5	1.67	0.45	0.43	0.06	0.03
10	1.05	0.28	10	1.15	0.35	10	1.10	0.29	0.31	0.04	0.02
15	0.88	0.23	15	0.95	0.29	15	0.81	0.22	0.25	0.04	0.02
20	0.78	0.21	20	0.83	0.25	20	0.71	0.19	0.22	0.03	0.02
25	0.68	0.18	25	0.74	0.22	25	0.65	0.17	0.19	0.03	0.02
30	0.62	0.16	30	0.66	0.20	30	0.60	0.16	0.17	0.02	0.01
35	0.58	0.15	35	0.64	0.19	35	0.56	0.15	0.17	0.02	0.01
40	0.54	0.14	40	0.61	0.18	40	0.55	0.15	0.16	0.02	0.01
45	0.51	0.13	45	0.58	0.18	45	0.54	0.14	0.15	0.02	0.01
50	0.49	0.13	50	0.57	0.17	50	0.52	0.14	0.15	0.02	0.01
55	0.47	0.12	55	0.56	0.17	55	0.52	0.14	0.14	0.02	0.01
60	0.45	0.12	60	0.55	0.17	60	0.51	0.14	0.14	0.02	0.01

Table A.7. Wheat Starch Sedimentation Data (10 g L^{-1})

Wheat Starch 10 g L^{-1}											
Sample A			Sample B			Sample C			Ave. A/A_o	Std. Dev.	Std. Error
Time (min)	Abs (A)	A/A_o	Time (min)	Abs (A)	A/A_o	Time (min)	Abs (A)	A/A_o			
0	2.51	1.00	0	3.79	1.00	0	3.79	1.00	1.00	0.00	0.00
1	2.23	0.89	1	3.79	1.00	1	3.79	1.00	0.96	0.06	0.04
2	1.61	0.64	2	3.79	1.00	2	3.79	1.00	0.88	0.21	0.12
3	1.30	0.52	3	3.60	0.95	3	3.79	1.00	0.82	0.26	0.15
4	1.14	0.45	4	2.99	0.79	4	3.14	0.83	0.69	0.21	0.12
5	1.03	0.41	5	2.71	0.71	5	2.78	0.73	0.62	0.18	0.11
10	0.73	0.29	10	1.98	0.52	10	1.73	0.46	0.42	0.12	0.07
15	0.57	0.23	15	1.58	0.42	15	1.32	0.35	0.33	0.10	0.06
20	0.48	0.19	20	1.36	0.36	20	1.13	0.30	0.28	0.08	0.05
25	0.43	0.17	25	1.19	0.31	25	1.02	0.27	0.25	0.07	0.04
30	0.40	0.16	30	1.09	0.29	30	0.94	0.25	0.23	0.07	0.04
35	0.37	0.15	35	1.04	0.27	35	0.88	0.23	0.22	0.06	0.04
40	0.35	0.14	40	0.97	0.26	40	0.84	0.22	0.20	0.06	0.04
45	0.34	0.13	45	0.93	0.25	45	0.79	0.21	0.20	0.06	0.03
50	0.33	0.13	50	0.89	0.24	50	0.77	0.20	0.19	0.05	0.03
55	0.33	0.13	55	0.89	0.23	55	0.74	0.20	0.19	0.05	0.03
60	0.32	0.13	60	0.83	0.22	60	0.70	0.18	0.18	0.05	0.03

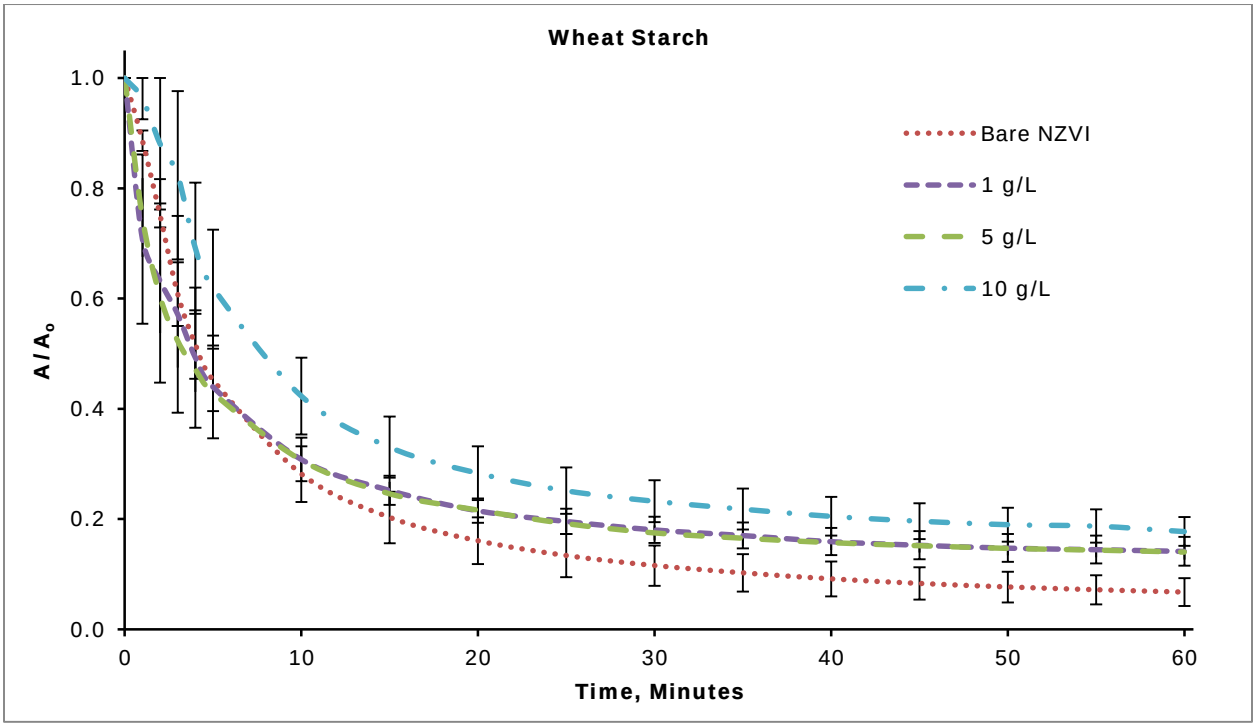


Figure A.2. Wheat Starch Sedimentation Curves

Table A.8. Tapioca Starch Sedimentation Data (1 g L^{-1})

Tapioca Starch 1 g L^{-1}											
Sample A			Sample B			Sample C			Ave. A/A_o	Std. Dev.	Std. Error
Time (min)	Abs (A)	A/A_o	Time (min)	Abs (A)	A/A_o	Time (min)	Abs (A)	A/A_o			
0	3.28	1.00	0	3.76	1.00	0	3.38	1.00	1.00	0.00	0.00
1	2.14	0.65	1	3.54	0.94	1	2.98	0.88	0.82	0.15	0.09
2	1.61	0.49	2	2.37	0.63	2	2.70	0.80	0.64	0.15	0.09
3	1.40	0.43	3	1.98	0.53	3	2.37	0.70	0.55	0.14	0.08
4	1.27	0.39	4	1.68	0.45	4	2.08	0.62	0.48	0.12	0.07
5	1.14	0.35	5	1.47	0.39	5	1.88	0.56	0.43	0.11	0.06
10	0.87	0.27	10	1.01	0.27	10	1.30	0.39	0.31	0.07	0.04
15	0.69	0.21	15	0.76	0.20	15	1.06	0.31	0.24	0.06	0.04
20	0.67	0.20	20	0.71	0.19	20	0.94	0.28	0.22	0.05	0.03
25	0.63	0.19	25	0.66	0.18	25	0.86	0.25	0.21	0.04	0.02
30	0.61	0.19	30	0.63	0.17	30	0.82	0.24	0.20	0.04	0.02
35	0.59	0.18	35	0.62	0.16	35	0.77	0.23	0.19	0.03	0.02
40	0.59	0.18	40	0.61	0.16	40	0.73	0.22	0.19	0.03	0.02
45	0.58	0.18	45	0.61	0.16	45	0.72	0.21	0.18	0.03	0.01
50	0.58	0.18	50	0.62	0.16	50	0.71	0.21	0.18	0.02	0.01
55	0.58	0.18	55	0.62	0.17	55	0.72	0.21	0.19	0.02	0.01
60	0.58	0.18	60	0.62	0.16	60	0.72	0.21	0.18	0.03	0.01

Table A.9. Tapioca Starch Sedimentation Data (5 g L^{-1})

Tapioca Starch 5 g L^{-1}											
Sample A			Sample B			Sample C			Ave. A/A_o	Std. Dev.	Std. Error
Time (min)	Abs (A)	A/A_o	Time (min)	Abs (A)	A/A_o	Time (min)	Abs (A)	A/A_o			
0	3.77	1.00	0	3.77	1.00	0	3.78	1.00	1.00	0.00	0.00
1	3.77	1.00	1	3.77	1.00	1	3.78	1.00	1.00	0.00	0.00
2	2.35	0.62	2	2.95	0.78	2	3.78	1.00	0.80	0.19	0.11
3	1.90	0.50	3	2.21	0.59	3	2.71	0.72	0.60	0.11	0.06
4	1.72	0.46	4	1.77	0.47	4	2.24	0.59	0.51	0.08	0.04
5	1.60	0.42	5	1.58	0.42	5	1.98	0.52	0.46	0.06	0.03
10	1.01	0.27	10	1.06	0.28	10	1.48	0.39	0.31	0.07	0.04
15	0.87	0.23	15	0.87	0.23	15	1.29	0.34	0.27	0.06	0.04
20	0.77	0.20	20	0.81	0.22	20	1.21	0.32	0.25	0.06	0.04
25	0.67	0.18	25	0.77	0.20	25	1.21	0.32	0.23	0.08	0.04
30	0.64	0.17	30	0.75	0.20	30	1.17	0.31	0.23	0.08	0.04
35	0.60	0.16	35	0.74	0.19	35	1.17	0.31	0.22	0.08	0.05
40	0.59	0.16	40	0.73	0.19	40	1.17	0.31	0.22	0.08	0.05
45	0.57	0.15	45	0.73	0.19	45	1.17	0.31	0.22	0.08	0.05
50	0.56	0.15	50	0.74	0.20	50	1.18	0.31	0.22	0.08	0.05
55	0.56	0.15	55	0.74	0.20	55	1.19	0.32	0.22	0.09	0.05
60	0.55	0.15	60	0.75	0.20	60	1.19	0.31	0.22	0.09	0.05

Table A.10. Tapioca Starch Sedimentation Data (10 g L^{-1})

Tapioca Starch 10 g L^{-1}											
Sample A			Sample B			Sample C			Ave. A/A_o	Std. Dev.	Std. Error
Time (min)	Abs (A)	A/A_o	Time (min)	Abs (A)	A/A_o	Time (min)	Abs (A)	A/A_o			
0	2.40	0	0.00	3.72	1.00	0	2.80	1.00	1.00	0.00	0.00
1	1.47	1	1.00	3.72	1.00	1	2.27	0.81	0.81	0.19	0.11
2	1.07	2	2.00	3.72	1.00	2	1.88	0.67	0.71	0.28	0.16
3	0.84	3	3.00	2.90	0.78	3	1.61	0.57	0.57	0.21	0.12
4	0.73	4	4.00	2.40	0.65	4	1.42	0.51	0.49	0.17	0.10
5	0.66	5	5.00	2.14	0.57	5	1.27	0.45	0.43	0.15	0.09
10	0.42	10	10.00	1.52	0.41	10	0.89	0.32	0.30	0.12	0.07
15	0.38	15	15.00	1.32	0.35	15	0.78	0.28	0.26	0.10	0.06
20	0.37	20	20.00	1.22	0.33	20	0.73	0.26	0.25	0.09	0.05
25	0.36	25	25.00	1.18	0.32	25	0.69	0.25	0.24	0.08	0.05
30	0.36	30	30.00	1.15	0.31	30	0.67	0.24	0.23	0.08	0.05
35	0.36	35	35.00	1.14	0.31	35	0.67	0.24	0.23	0.08	0.04
40	0.37	40	40.00	1.13	0.30	40	0.67	0.24	0.23	0.08	0.04
45	0.37	45	45.00	1.13	0.30	45	0.66	0.24	0.23	0.08	0.04
50	0.37	50	50.00	1.13	0.30	50	0.66	0.24	0.23	0.07	0.04
55	0.38	55	55.00	1.13	0.30	55	0.67	0.24	0.23	0.07	0.04
60	0.39	60	60.00	1.13	0.30	60	0.68	0.24	0.24	0.07	0.04

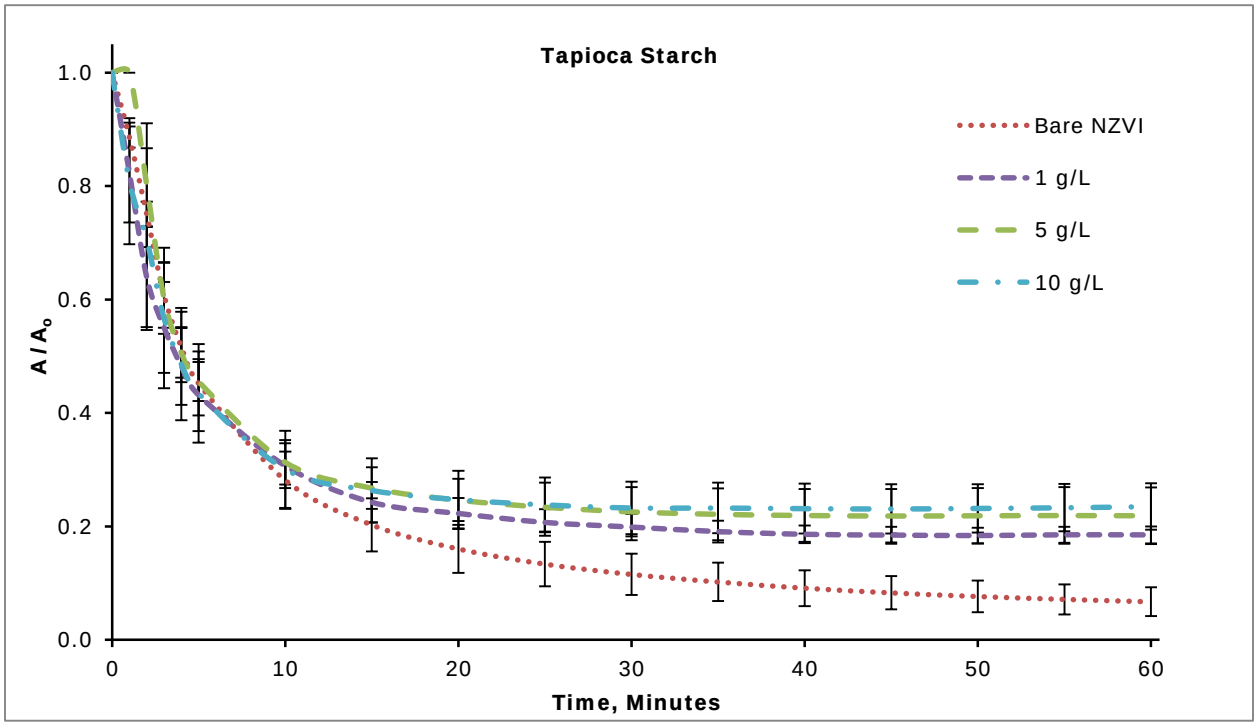


Figure A.3. Tapioca Starch Sedimentation Curves

Table A.11. Rice Starch Sedimentation Data (1 g L^{-1})

Rice Starch 1 g L^{-1}											
Sample A			Sample B			Sample C			Ave. A/A_o	Std. Dev.	Std. Error
Time (min)	Abs (A)	A/A_o	Time (min)	Abs (A)	A/A_o	Time (min)	Abs (A)	A/A_o			
0	3.76	1.00	0	3.76	1.00	0	3.76	1.00	1.00	0.00	0.00
1	0.98	0.26	1	1.00	0.26	1	0.97	0.26	0.26	0.00	0.00
2	0.81	0.22	2	0.82	0.22	2	0.97	0.26	0.23	0.02	0.01
3	0.66	0.18	3	0.67	0.18	3	0.80	0.21	0.19	0.02	0.01
4	0.61	0.16	4	0.56	0.15	4	0.67	0.18	0.16	0.01	0.01
5	0.54	0.14	5	0.50	0.13	5	0.58	0.15	0.14	0.01	0.01
10	0.38	0.10	10	0.31	0.08	10	0.37	0.10	0.09	0.01	0.01
15	0.29	0.08	15	0.26	0.07	15	0.31	0.08	0.08	0.01	0.00
20	0.28	0.07	20	0.25	0.07	20	0.29	0.08	0.07	0.00	0.00
25	0.29	0.08	25	0.25	0.07	25	0.30	0.08	0.07	0.01	0.00
30	0.32	0.09	30	0.27	0.07	30	0.31	0.08	0.08	0.01	0.00
35	0.35	0.09	35	0.28	0.08	35	0.31	0.08	0.08	0.01	0.00
40	0.39	0.10	40	0.29	0.08	40	0.31	0.08	0.09	0.01	0.01
45	0.41	0.11	45	0.29	0.08	45	0.32	0.08	0.09	0.02	0.01
50	0.42	0.11	50	0.30	0.08	50	0.32	0.09	0.09	0.02	0.01
55	0.43	0.11	55	0.30	0.08	55	0.33	0.09	0.09	0.02	0.01
60	0.43	0.12	60	0.31	0.08	60	0.33	0.09	0.10	0.02	0.01

Table A.12. Rice Starch Sedimentation Data (5 g L^{-1})

Tapioca Starch 5 g L^{-1}											
Sample A			Sample B			Sample C			Ave. A/A_o	Std. Dev.	Std. Error
Time (min)	Abs (A)	A/A_o	Time (min)	Abs (A)	A/A_o	Time (min)	Abs (A)	A/A_o			
0	3.76	1.00	0	3.76	1.00	0	3.76	1.00	1.00	0.00	0.00
1	1.29	0.34	1	1.45	0.38	1	2.66	0.71	0.48	0.20	0.11
2	1.31	0.35	2	1.56	0.42	2	1.83	0.49	0.42	0.07	0.04
3	1.18	0.31	3	1.35	0.36	3	1.60	0.43	0.37	0.06	0.03
4	1.06	0.28	4	1.25	0.33	4	1.42	0.38	0.33	0.05	0.03
5	0.96	0.26	5	1.16	0.31	5	1.30	0.35	0.30	0.05	0.03
10	0.75	0.20	10	0.91	0.24	10	1.01	0.27	0.24	0.03	0.02
15	0.62	0.17	15	0.69	0.18	15	0.83	0.22	0.19	0.03	0.02
20	0.57	0.15	20	0.64	0.17	20	0.76	0.20	0.17	0.03	0.01
25	0.54	0.14	25	0.60	0.16	25	0.69	0.18	0.16	0.02	0.01
30	0.53	0.14	30	0.60	0.16	30	0.66	0.17	0.16	0.02	0.01
35	0.52	0.14	35	0.57	0.15	35	0.64	0.17	0.15	0.02	0.01
40	0.51	0.14	40	0.56	0.15	40	0.64	0.17	0.15	0.02	0.01
45	0.50	0.13	45	0.56	0.15	45	0.63	0.17	0.15	0.02	0.01
50	0.50	0.13	50	0.55	0.15	50	0.63	0.17	0.15	0.02	0.01
55	0.50	0.13	55	0.55	0.15	55	0.63	0.17	0.15	0.02	0.01
60	0.50	0.13	60	0.55	0.15	60	0.62	0.16	0.15	0.02	0.01

Table A.13. Rice Starch Sedimentation Data (10 g L^{-1})

Rice Starch 10 g L^{-1}											
Sample A			Sample B			Sample C			Ave. A/A_o	Std. Dev.	Std. Error
Time (min)	Abs (A)	A/A_o	Time (min)	Abs (A)	A/A_o	Time (min)	Abs (A)	A/A_o			
0	3.76	1.00	0	3.76	1.00	0	3.76	1.00	1.00	0.00	0.00
1	1.29	0.34	1	1.61	0.43	1	1.47	0.39	0.39	0.04	0.02
2	1.09	0.29	2	1.32	0.35	2	1.25	0.33	0.32	0.03	0.02
3	1.02	0.27	3	1.11	0.29	3	1.12	0.30	0.29	0.01	0.01
4	0.93	0.25	4	1.01	0.27	4	1.04	0.28	0.26	0.01	0.01
5	0.86	0.23	5	0.93	0.25	5	0.97	0.26	0.24	0.01	0.01
10	0.66	0.18	10	0.68	0.18	10	0.73	0.19	0.18	0.01	0.01
15	0.52	0.14	15	0.52	0.14	15	0.63	0.17	0.15	0.02	0.01
20	0.48	0.13	20	0.44	0.12	20	0.61	0.16	0.14	0.02	0.01
25	0.47	0.13	25	0.41	0.11	25	0.59	0.16	0.13	0.02	0.01
30	0.46	0.12	30	0.40	0.11	30	0.59	0.16	0.13	0.03	0.01
35	0.46	0.12	35	0.40	0.11	35	0.58	0.16	0.13	0.03	0.01
40	0.46	0.12	40	0.39	0.10	40	0.59	0.16	0.13	0.03	0.01
45	0.46	0.12	45	0.39	0.10	45	0.59	0.16	0.13	0.03	0.02
50	0.47	0.12	50	0.39	0.10	50	0.60	0.16	0.13	0.03	0.02
55	0.47	0.13	55	0.40	0.11	55	0.60	0.16	0.13	0.03	0.02
60	0.47	0.13	60	0.40	0.11	60	0.60	0.16	0.13	0.03	0.02

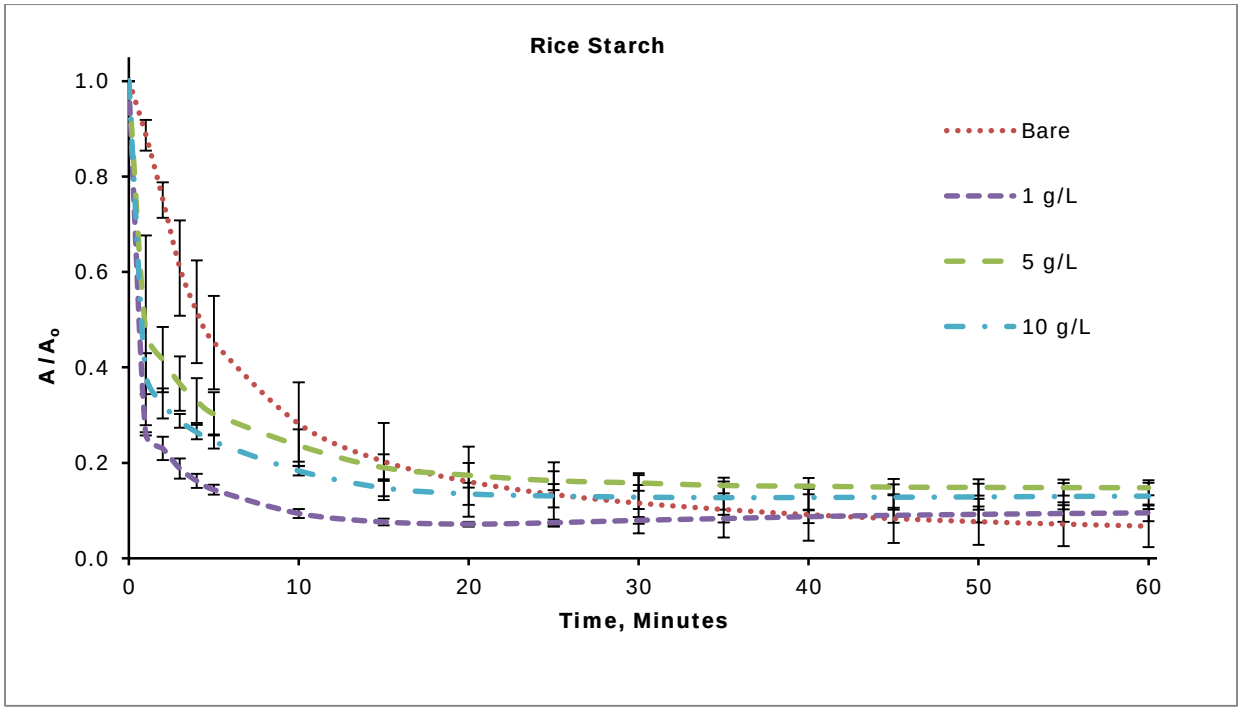


Figure A.4. Rice Starch Sedimentation Curves

A.2. One-Way ANOVA for Native Starches

Selection Reason:

One-way ANOVA is used to determine if there are significant differences between two or more independent groups. The independent groups in this study are: bare NZVI, NZVI coated with a native starch at 1 g L^{-1}, NZVI coated with a native starch at 5 g L^{-1}, and NZVI coated with a native starch at 10 g L^{-1}. One-way ANOVAs were performed for each native starch.

Hypothesis

H_o: There is not a significant difference between the mean particle stability of bare NZVI particles and NZVI coated at different concentrations ($x_0 = x_1 = x_2 = x_3$).

H_a: at least one mean particle stability is different.

where:

x_0 = bare NZVI

x_1 = coated NZVI (starch concentration = 1 g L^{-1})

x_2 = coated NZVI (starch concentration = 5 g L^{-1})

x_3 = coated NZVI (starch concentration = 10 g L^{-1})

Maize Starch

Table A.14. Data used for One-Way ANOVA Analysis of Native Maize Starch

Treatment	Sedimentation Data
Bare NZVI	Average C/C_o from Table A.1.i.a (All time periods)
NZVI coated w/ Native Maize Starch at a coating concentration of 1 g L^{-1}	Average C/C_o from Table A.1.i.b (All time periods)
NZVI coated w/ Native Maize Starch at a coating concentration of 5 g L^{-1}	Average C/C_o from Table A.1.i.c (All time periods)
NZVI coated w/ Native Maize Starch at a coating concentration of 10 g L^{-1}	Average C/C_o from Table A.1.i.d (All time periods)

Table A.15. Maize Starch One-Way ANOVA

Source	DF	Adj. SS	Adj. MS	F-Value	P-Value
Treatment*	3	1.205	0.40165	6.24	0.001
Error	64	4.120	0.06438		
Total	67	5.325			

*The four levels of treatment are presented in the hypothesis section above.

Tukey's test was used after the One-Way ANOVA. Tukey's test compares the means of the groups tested in the One-Way ANOVA and identifies which groups among the samples tested are significantly different.

Table A.16. Maize Starch Tukey Pairwise Comparison

Treatment	N	Mean	Std. Dev.	99.5% CI	Grouping**
0	17	0.3294	0.3127	(0.1524, 0.5063)	B, C
1	17	0.2573	0.2562	(0.0784, 0.4362)	C
2	17	0.4988	0.2214	(0.3199, 0.6777)	A, B
3	17	0.5932	0.2124	(0.4142, 0.7721)	A

** Means that do not share a letter are significantly different.

Wheat Starch

Table A.17. Data used for One-Way ANOVA Analysis of Native Wheat Starch

Treatment	Sedimentation Data
Bare NZVI	Average C/C_o from Table A.1.i.a (All time periods)
NZVI coated w/ Native Wheat Starch at a coating concentration of 1 g L^{-1}	Average C/C_o from Table A.1.i.e (All time periods)
NZVI coated w/ Native Wheat Starch at a coating concentration of 5 g L^{-1}	Average C/C_o from Table A.1.i.f (All time periods)
NZVI coated w/ Native Wheat Starch at a coating concentration of 10 g L^{-1}	Average C/C_o from Table A.1.i.g (All time periods)

Table A.18. Wheat Starch One-Way ANOVA

Source	DF	Adj. SS	Adj. MS	F-Value	P-Value
Treatment*	3	0.1616	0.05387	0.68	0.570
Error	64	5.1037	0.07975		
Total	67	5.2653			

*The four levels of treatment are presented in the hypothesis section above.

Tukey's test was used after the One-Way ANOVA. Tukey's test compares the means of the groups tested in the One-Way ANOVA and identifies which groups among the samples tested are significantly different.

Table A.19. Wheat Starch Tukey Pairwise Comparison

Treatment	N	Mean	Std. Dev.	99.5% CI	Grouping**
0	17	0.3294	0.3127	(0.1302, 0.5285)	A
1	17	0.3477	0.2530	(0.1485, 0.5468)	A
2	17	0.3420	0.2524	(0.1429, 0.5412)	A
3	17	0.4512	0.3058	(0.2521, 0.6504)	A

** Means that do not share a letter are significantly different.

Tapioca Starch

Table A.20. Data used for One-Way ANOVA Analysis of Native Tapioca Starch

Treatment	Sedimentation Data
Bare NZVI	Average C/C_o from Table A.1.i.a (All time periods)
NZVI coated w/ Native Tapioca Starch at a coating concentration of 1 g L^{-1}	Average C/C_o from Table A.1.i.h (All time periods)
NZVI coated w/ Native Tapioca Starch at a coating concentration of 5 g L^{-1}	Average C/C_o from Table A.1.i.i (All time periods)
NZVI coated w/ Native Tapioca Starch at a coating concentration of 10 g L^{-1}	Average C/C_o from Table A.1.i.j (All time periods)

Table A.21. Tapioca Starch Two-Way ANOVA

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Treatment*	3	0.3946	0.13154	2.18	0.098
Error	64	3.8540	0.06022		
Total	67	4.2486			

*The four levels of treatment are presented in the hypothesis section above.

Tukey's test was used after the One-Way ANOVA. Tukey's test compares the means of the groups tested in the One-Way ANOVA and identifies which groups among the samples tested are significantly different.

Table A.22. Tapioca Starch Tukey Pairwise Comparison

Treatment	N	Mean	Std. Dev.	99.5% CI	Grouping**
0	17	0.3294	0.3127	(0.1563, 0.5024)	A
1	17	0.3247	0.2394	(0.1517, 0.4978)	A
2	17	0.2740	0.2084	(0.1010, 0.4471)	A
3	17	0.4780	0.3127	(0.1563, 0.5024)	A

** Means that do not share a letter are significantly different.

Rice Starch

Table A.23. Data used for One-Way ANOVA Analysis of Native Rice Starch

Treatment	Sedimentation Data
Bare NZVI	Average C/C_o from Table A.1.i.a (All time periods)
NZVI coated w/ Native Rice Starch at a coating concentration of 1 g L^{-1}	Average C/C_o from Table A.1.i.j (All time periods)
NZVI coated w/ Native Rice Starch at a coating concentration of 5 g L^{-1}	Average C/C_o from Table A.1.i.k (All time periods)
NZVI coated w/ Native Rice Starch at a coating concentration of 10 g L^{-1}	Average C/C_o from Table A.1.i.l (All time periods)

Table A.24. Rice Starch One-Way ANOVA

Source	DF	Adj. SS	Adj. MS	F-Value	P-Value
Treatment*	3	0.2257	0.07522	1.26	0.295
Error	64	3.8139	0.05959		
Total	67	4.0396			

*The four levels of treatment are presented in the hypothesis section above.

Tukey's test was used after the One-Way ANOVA. Tukey's test compares the means of the groups tested in the One-Way ANOVA and identifies which groups among the samples tested are significantly different.

Table A.25. Rice Starch Tukey Pairwise Comparison

Treatment	N	Mean	Std. Dev.	99.5% CI	Grouping**
0	17	0.3294	0.3127	(0.1572, 0.5015)	A
1	17	0.1720	0.2210	(-0.0002, 0.3441)	A
2	17	0.2772	0.2148	(0.1051, 0.4494)	A
3	17	0.2358	0.2136	(0.0637, 0.4080)	A

** Means that do not share a letter are significantly different.

A.3. Visual Sedimentation Study

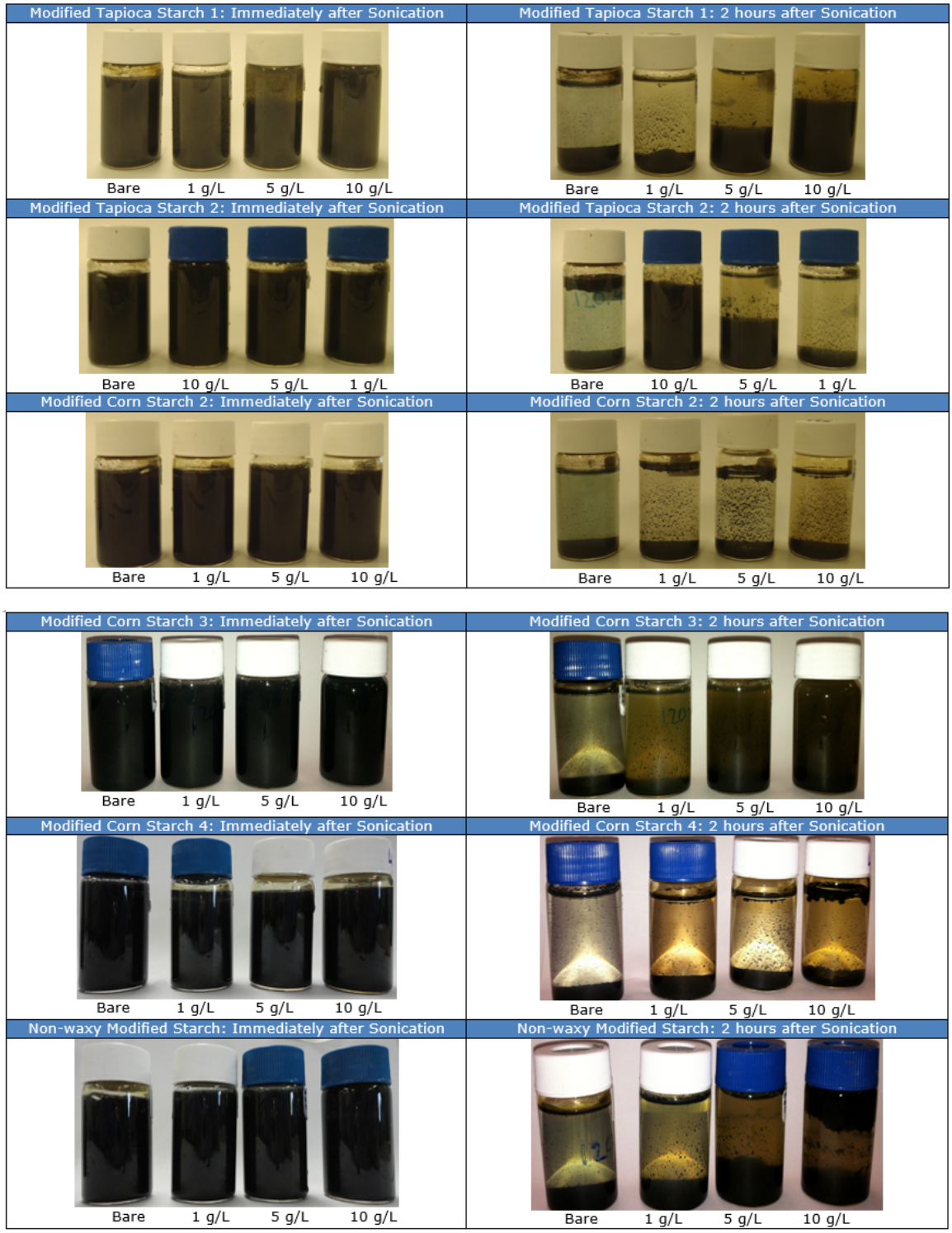


Figure A.5. Visual Sedimentation Study

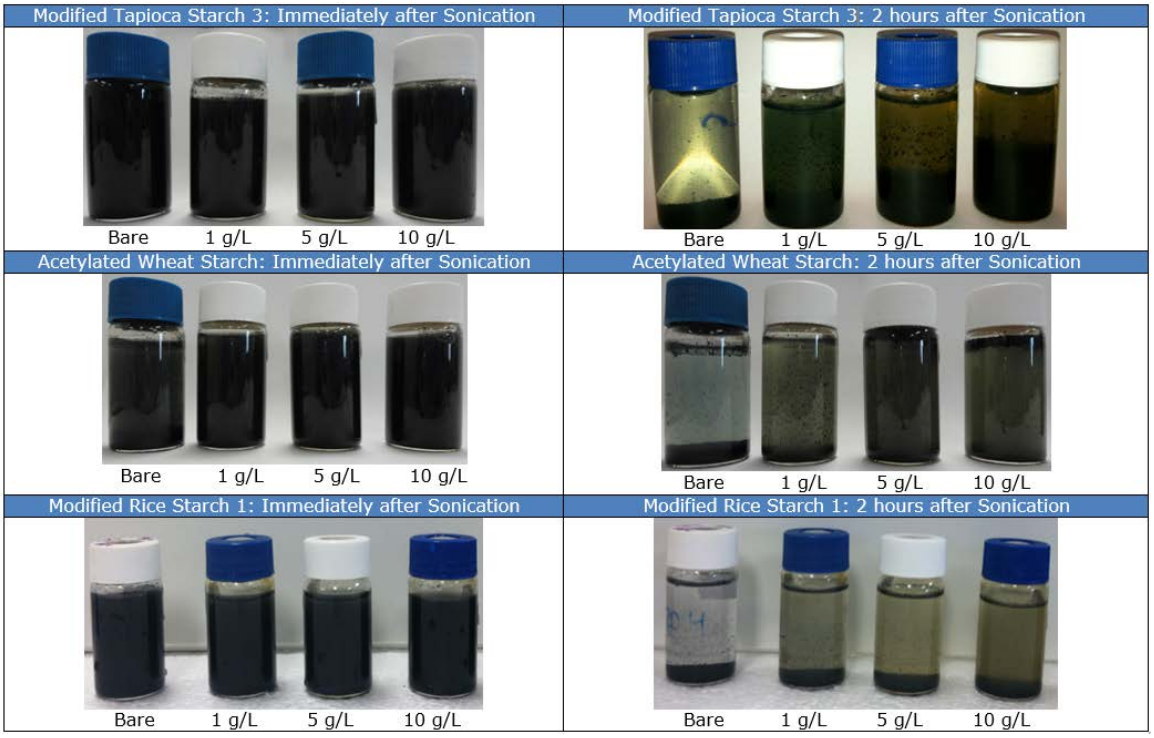


Figure A.5. Visual Sedimentation Study (continued)

A.4. UV Sedimentation for Commercial OSA-modified Tapioca

UV sedimentation tests were conducted for the three commercial OSA-modified tapioca starches at different concentrations (1, 5, and 10 g L^{-1}) to confirm the improved colloidal stability (see Figure A.2.ii.a (a)). One-way ANOVAs were performed for each concentration (α=0.005). The three OSA-modified tapioca starches significantly improved colloidal stability (p=0.000 for all three) for each concentration tested. At higher concentrations, modified tapioca starch 1 was able to keep nearly all NZVI particles suspended, as shown in Figure A.2.i.a (b and c). UV sedimentation data, and statistical results are available in Appendix A-Sections A.5-6.

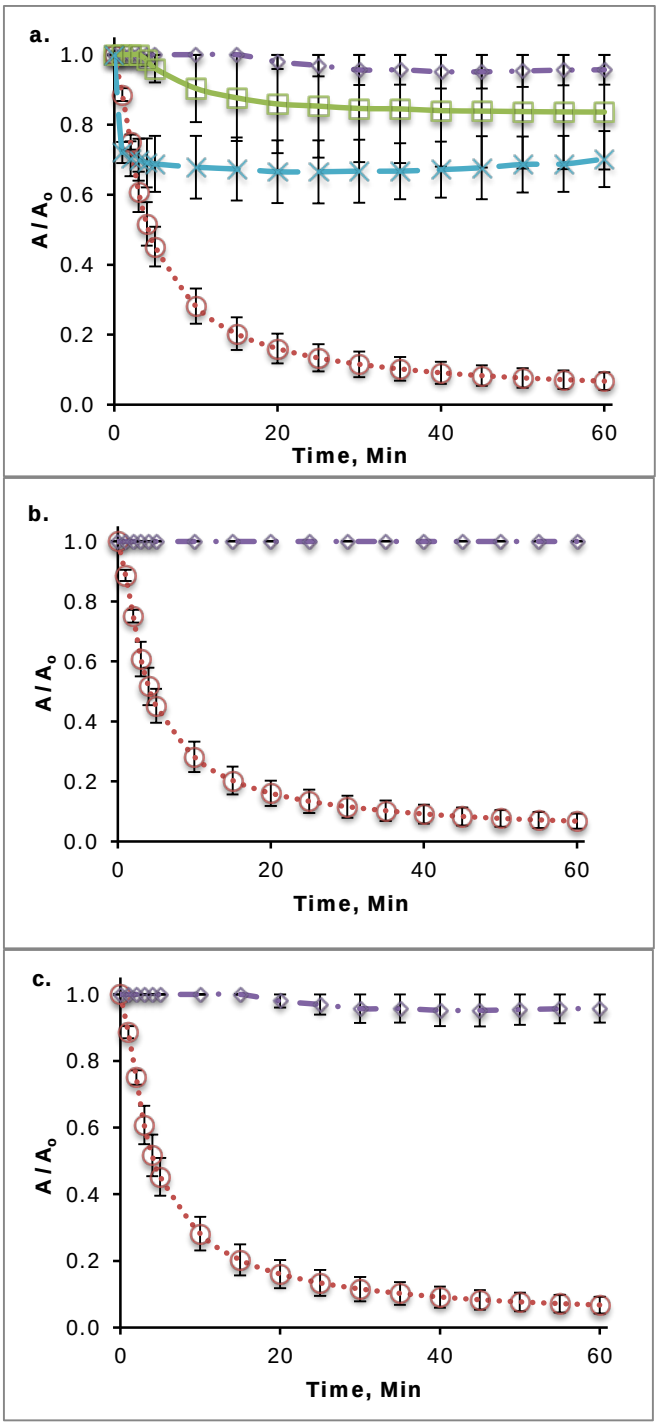


Figure A.6. Commercial Starch Sedimentation Curves
a. All 3 OSA-modified tapioca starches shown; coating concentration = 10 g L^{-1}, and OSA-modified tapioca starch 1 shown in: b. coating concentration = 5 g L^{-1} and b. coating concentration = 10 g L^{-1} -○- Bare NZVI and -◇- OSA-Modified Tapioca Starch 1, -□- OSA-Modified Tapioca Starch 2, and –X– OSA-Modified Tapioca Starch 3.

A.5. Commercial Tapioca Sedimentation Curves

Table A.26. Commercial Tapioca Starch 1 Sedimentation Data (1 g L^{-1})

Commercial Tapioca Starch 1 (1 g L^{-1})											
Sample A			Sample B			Sample C			Ave. A/A_o	Std. Dev.	Std. Error
Time (min)	Abs (A)	A/A_o	Time (min)	Abs (A)	A/A_o	Time (min)	Abs (A)	A/A_o			
0	0.98	1.00	0	3.77	1.00	0	3.77	1.00	1.00	0.00	0.00
1	0.62	0.63	1	3.77	1.00	1	3.77	1.00	0.88	0.22	0.12
2	0.51	0.52	2	3.77	1.00	2	3.77	1.00	0.84	0.28	0.16
3	0.47	0.48	3	3.77	1.00	3	3.77	1.00	0.83	0.30	0.17
4	0.43	0.43	4	3.77	1.00	4	3.77	1.00	0.81	0.33	0.19
5	0.43	0.44	5	3.77	1.00	5	3.22	0.85	0.76	0.29	0.17
10	0.37	0.38	10	3.77	1.00	10	1.94	0.51	0.63	0.33	0.19
15	0.35	0.35	15	3.74	0.99	15	1.56	0.41	0.59	0.35	0.20
20	0.34	0.35	20	3.32	0.88	20	1.38	0.37	0.53	0.30	0.17
25	0.34	0.35	25	3.11	0.83	25	1.34	0.35	0.51	0.27	0.16
30	0.33	0.34	30	3.04	0.81	30	1.31	0.35	0.50	0.27	0.15
35	0.35	0.35	35	2.96	0.78	35	1.28	0.34	0.49	0.25	0.15
40	0.35	0.36	40	2.94	0.78	40	1.28	0.34	0.49	0.25	0.14
45	0.34	0.34	45	2.90	0.77	45	1.28	0.34	0.48	0.25	0.14
50	0.33	0.34	50	2.91	0.77	50	1.28	0.34	0.48	0.25	0.14
55	0.33	0.34	55	2.94	0.78	55	1.30	0.34	0.49	0.25	0.15
60	0.34	0.35	60	2.96	0.79	60	1.31	0.35	0.49	0.25	0.15

Table A.27. Commercial Tapioca Starch 2 Sedimentation Data (1 g L^{-1})

Commercial Tapioca Starch 2 (1 g L^{-1})											
Sample A			Sample B			Sample C			Ave. A/A_o	Std. Dev.	Std. Error
Time (min)	Abs (A)	A/A_o	Time (min)	Abs (A)	A/A_o	Time (min)	Abs (A)	A/A_o			
0	2.18	1.00	0	2.33	1.00	0	1.77	1.00	1.00	0.00	0.00
1	1.55	0.71	1	1.08	0.46	1	1.11	0.62	0.60	0.13	0.07
2	1.34	0.61	2	1.00	0.43	2	0.99	0.56	0.53	0.09	0.05
3	1.28	0.59	3	0.95	0.41	3	0.94	0.53	0.51	0.09	0.05
4	1.21	0.56	4	0.94	0.40	4	0.90	0.51	0.49	0.08	0.05
5	1.20	0.55	5	0.92	0.40	5	0.88	0.50	0.48	0.08	0.04
10	1.00	0.46	10	0.82	0.35	10	0.74	0.42	0.41	0.05	0.03
15	0.86	0.39	15	0.76	0.33	15	0.68	0.38	0.37	0.04	0.02
20	0.76	0.35	20	0.71	0.30	20	0.64	0.36	0.34	0.03	0.02
25	0.70	0.32	25	0.67	0.29	25	0.61	0.35	0.32	0.03	0.02
30	0.66	0.30	30	0.63	0.27	30	0.59	0.33	0.30	0.03	0.02
35	0.63	0.29	35	0.60	0.26	35	0.59	0.33	0.29	0.04	0.02
40	0.63	0.29	40	0.58	0.25	40	0.59	0.33	0.29	0.04	0.02
45	0.62	0.29	45	0.56	0.24	45	0.58	0.33	0.28	0.05	0.03
50	0.62	0.28	50	0.57	0.25	50	0.59	0.33	0.29	0.04	0.03
55	0.62	0.29	55	0.58	0.25	55	0.60	0.34	0.29	0.05	0.03
60	0.61	0.28	60	0.59	0.25	60	0.61	0.34	0.29	0.05	0.03

Table A.28. Commercial Tapioca Starch 3 Sedimentation Data (1 g L^{-1})

Commercial Tapioca Starch 3 (1 g L^{-1})											
Sample A			Sample B			Sample C			Ave. A/A_o	Std. Dev.	Std. Error
Time (min)	Abs (A)	A/A_o	Time (min)	Abs (A)	A/A_o	Time (min)	Abs (A)	A/A_o			
0	2.15	1.00	0	2.66	1.00	0	3.73	1.00	1.00	0.00	0.00
1	1.48	0.69	1	1.29	0.48	1	3.73	1.00	0.72	0.26	0.15
2	1.38	0.64	2	1.02	0.38	2	3.73	1.00	0.67	0.31	0.18
3	1.30	0.60	3	0.96	0.36	3	3.73	1.00	0.65	0.32	0.19
4	1.28	0.59	4	0.92	0.35	4	3.73	1.00	0.65	0.33	0.19
5	1.23	0.57	5	0.89	0.33	5	3.73	1.00	0.64	0.34	0.19
10	1.13	0.53	10	0.84	0.31	10	3.73	1.00	0.61	0.35	0.20
15	1.09	0.50	15	0.81	0.31	15	3.73	1.00	0.60	0.36	0.21
20	1.05	0.49	20	0.81	0.30	20	3.73	1.00	0.60	0.36	0.21
25	1.02	0.48	25	0.77	0.29	25	3.73	1.00	0.59	0.37	0.21
30	1.01	0.47	30	0.81	0.31	30	3.73	1.00	0.59	0.36	0.21
35	1.00	0.46	35	0.77	0.29	35	3.73	1.00	0.58	0.37	0.21
40	0.98	0.46	40	0.76	0.28	40	3.73	1.00	0.58	0.37	0.22
45	0.97	0.45	45	0.75	0.28	45	3.73	1.00	0.58	0.38	0.22
50	0.96	0.45	50	0.75	0.28	50	3.73	1.00	0.58	0.38	0.22
55	0.95	0.44	55	0.74	0.28	55	3.73	1.00	0.57	0.38	0.22
60	0.94	0.44	60	0.74	0.28	60	3.73	1.00	0.57	0.38	0.22

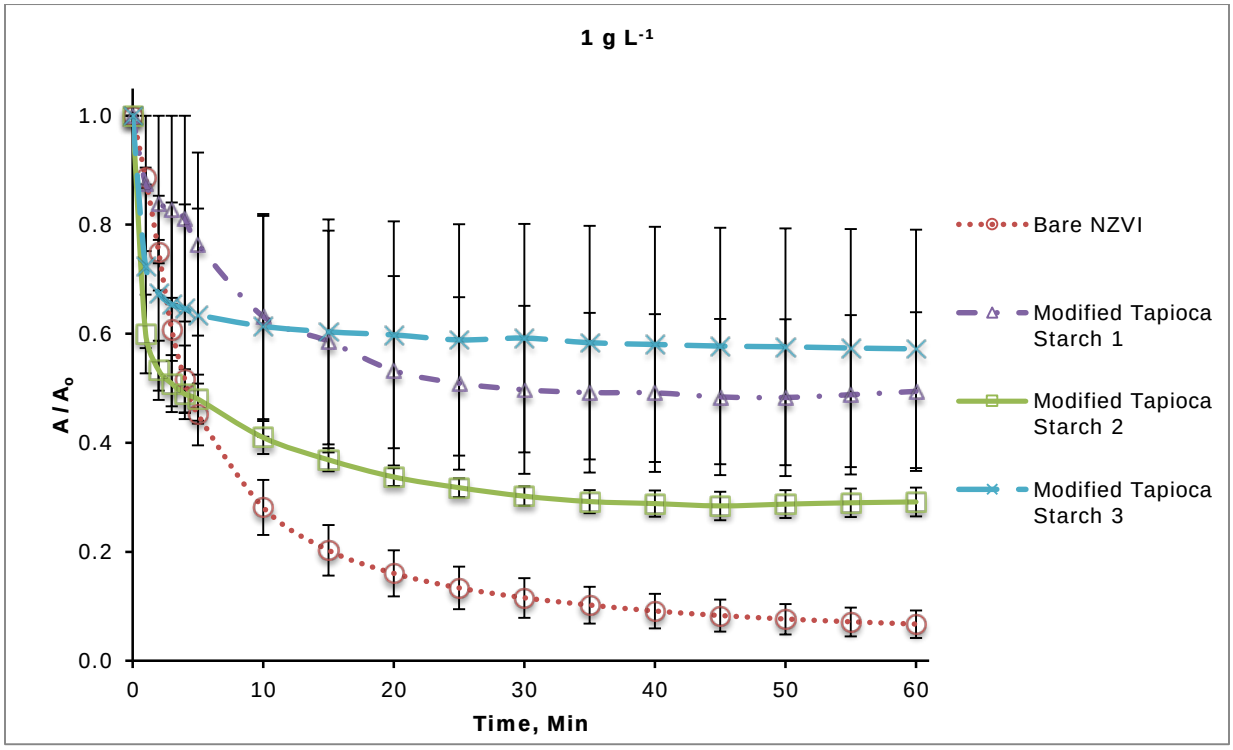


Figure A.7. Commercial Tapioca Starches Sedimentation Data (1 g L^{-1})

Table A.29. Commercial Tapioca Starch 1 Sedimentation Data (5 g L^{-1})

Commercial Tapioca Starch 1 (5 g L^{-1})											
Sample A			Sample B			Sample C			Ave. A/A_o	Std. Dev.	Std. Error
Time (min)	Abs (A)	A/A_o	Time (min)	Abs (A)	A/A_o	Time (min)	Abs (A)	A/A_o			
0	3.78	1.00	0	3.77	1.00	0	3.76	1.00	1.00	0.00	0.00
1	3.78	1.00	1	3.77	1.00	1	3.76	1.00	1.00	0.00	0.00
2	3.78	1.00	2	3.77	1.00	2	3.76	1.00	1.00	0.00	0.00
3	3.78	1.00	3	3.77	1.00	3	3.76	1.00	1.00	0.00	0.00
4	3.78	1.00	4	3.77	1.00	4	3.76	1.00	1.00	0.00	0.00
5	3.78	1.00	5	3.77	1.00	5	3.76	1.00	1.00	0.00	0.00
10	3.78	1.00	10	3.77	1.00	10	3.76	1.00	1.00	0.00	0.00
15	3.78	1.00	15	3.77	1.00	15	3.76	1.00	1.00	0.00	0.00
20	3.78	1.00	20	3.77	1.00	20	3.76	1.00	1.00	0.00	0.00
25	3.78	1.00	25	3.77	1.00	25	3.76	1.00	1.00	0.00	0.00
30	3.78	1.00	30	3.77	1.00	30	3.76	1.00	1.00	0.00	0.00
35	3.78	1.00	35	3.77	1.00	35	3.76	1.00	1.00	0.00	0.00
40	3.78	1.00	40	3.77	1.00	40	3.76	1.00	1.00	0.00	0.00
45	3.78	1.00	45	3.77	1.00	45	3.76	1.00	1.00	0.00	0.00
50	3.78	1.00	50	3.77	1.00	50	3.76	1.00	1.00	0.00	0.00
55	3.78	1.00	55	3.77	1.00	55	3.76	1.00	1.00	0.00	0.00
60	3.78	1.00	60	3.77	1.00	60	3.76	1.00	1.00	0.00	0.00

Table A.30. Commercial Tapioca Starch 2 Sedimentation Data (5 g L^{-1})

Commercial Tapioca Starch 2 (5 g L^{-1})											
Sample A			Sample B			Sample C			Ave. A/A_o	Std. Dev.	Std. Error
Time (min)	Abs (A)	A/A_o	Time (min)	Abs (A)	A/A_o	Time (min)	Abs (A)	A/A_o			
0	2.01	1.00	0	3.77	1.00	0	3.74	1.00	1.00	0.00	0.00
1	1.89	0.94	1	3.77	1.00	1	3.37	0.90	0.95	0.05	0.03
2	1.84	0.91	2	3.77	1.00	2	3.11	0.83	0.92	0.08	0.05
3	1.78	0.89	3	3.77	1.00	3	2.93	0.78	0.89	0.11	0.06
4	1.76	0.88	4	3.77	1.00	4	2.78	0.74	0.87	0.13	0.07
5	1.74	0.86	5	3.77	1.00	5	2.67	0.71	0.86	0.14	0.08
10	1.63	0.81	10	3.29	0.87	10	2.21	0.59	0.76	0.15	0.09
15	1.55	0.77	15	2.84	0.75	15	1.90	0.51	0.68	0.15	0.09
20	1.47	0.73	20	2.62	0.70	20	1.68	0.45	0.63	0.15	0.09
25	1.40	0.70	25	2.52	0.67	25	1.58	0.42	0.60	0.15	0.09
30	1.33	0.66	30	2.49	0.66	30	1.51	0.40	0.57	0.15	0.09
35	1.29	0.64	35	2.44	0.65	35	1.47	0.39	0.56	0.15	0.08
40	1.28	0.64	40	2.42	0.64	40	1.45	0.39	0.55	0.14	0.08
45	1.29	0.64	45	2.41	0.64	45	1.43	0.38	0.55	0.15	0.09
50	1.23	0.61	50	2.40	0.64	50	1.44	0.38	0.54	0.14	0.08
55	1.22	0.61	55	2.39	0.63	55	1.43	0.38	0.54	0.14	0.08
60	1.25	0.62	60	2.38	0.63	60	1.44	0.39	0.55	0.14	0.08

Table A.31. Commercial Tapioca Starch 3 Sedimentation Data (5 g L^{-1})

Commercial Tapioca Starch 3 (5 g L^{-1})											
Sample A			Sample B			Sample C			Ave. A/A_o	Std. Dev.	Std. Error
Time (min)	Abs (A)	A/A_o	Time (min)	Abs (A)	A/A_o	Time (min)	Abs (A)	A/A_o			
0	1.58	1.00	0	2.24	1.00	0	1.52	1.00	1.00	0.00	0.00
1	1.19	0.75	1	2.06	0.92	1	1.07	0.70	0.79	0.05	0.03
2	1.15	0.72	2	1.95	0.87	2	1.04	0.69	0.76	0.08	0.05
3	1.13	0.71	3	1.87	0.84	3	1.04	0.68	0.74	0.11	0.06
4	1.09	0.69	4	1.80	0.80	4	1.03	0.68	0.72	0.13	0.07
5	1.08	0.68	5	1.77	0.79	5	1.01	0.67	0.71	0.14	0.08
10	1.02	0.64	10	1.55	0.69	10	0.99	0.65	0.66	0.15	0.09
15	0.98	0.62	15	1.40	0.63	15	0.98	0.65	0.63	0.15	0.09
20	0.96	0.60	20	1.31	0.58	20	0.98	0.65	0.61	0.15	0.09
25	0.91	0.57	25	1.26	0.56	25	0.98	0.64	0.59	0.15	0.09
30	0.89	0.56	30	1.21	0.54	30	0.98	0.64	0.58	0.15	0.09
35	0.85	0.54	35	1.18	0.53	35	0.98	0.65	0.57	0.15	0.08
40	0.84	0.53	40	1.18	0.53	40	0.99	0.66	0.57	0.14	0.08
45	0.83	0.52	45	1.16	0.52	45	1.01	0.67	0.57	0.15	0.09
50	0.82	0.52	50	1.16	0.52	50	1.02	0.67	0.57	0.14	0.08
55	0.80	0.50	55	1.17	0.52	55	1.17	0.77	0.60	0.14	0.08
60	0.80	0.51	60	1.17	0.52	60.00	1.21	0.80	0.61	0.14	0.08

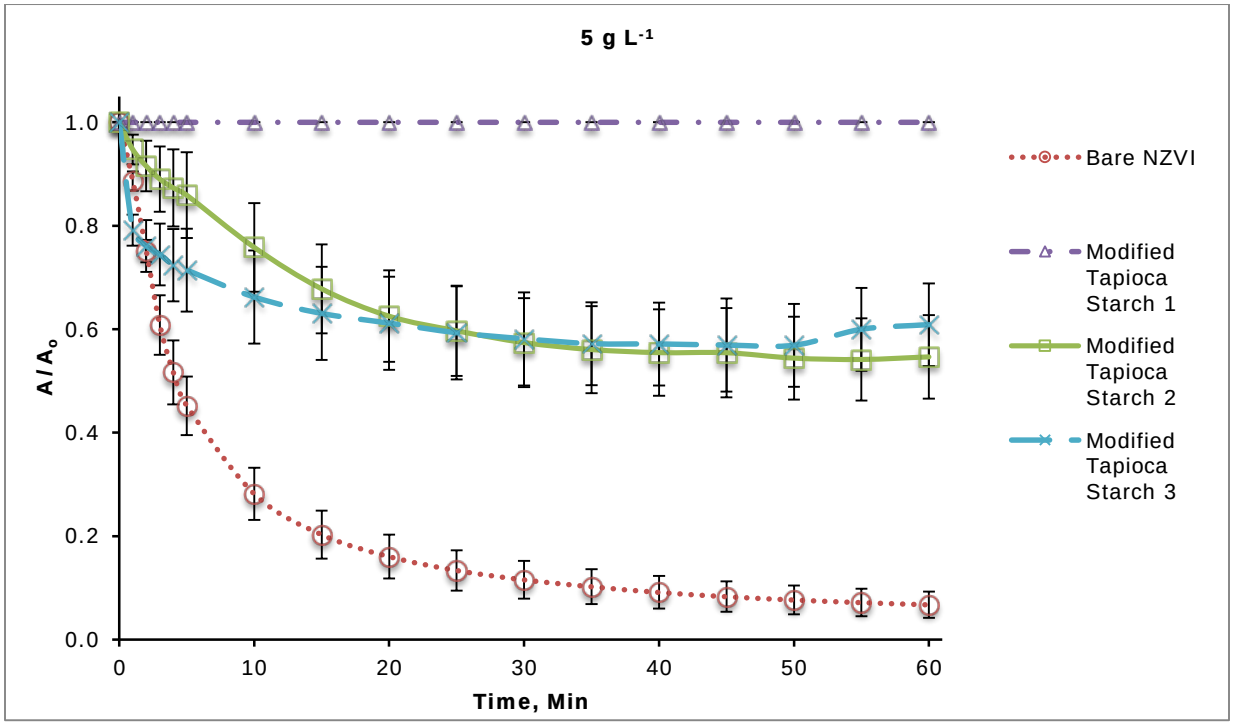


Figure A.8. Commercial Tapioca Starches Sedimentation Data (5 g L^{-1})

Table A.32. Commercial Tapioca Starch 1 Sedimentation Data (10 g L^{-1})

Commercial Tapioca Starch 1 (10 g L^{-1})											
Sample A			Sample B			Sample C			Ave. A/A_o	Std. Dev.	Std. Error
Time (min)	Abs (A)	A/A_o	Time (min)	Abs (A)	A/A_o	Time (min)	Abs (A)	A/A_o			
0	3.77	1.00	0	3.77	1.00	0	3.77	1.00	1.00	0.00	0.00
1	3.77	1.00	1	3.77	1.00	1	3.77	1.00	1.00	0.00	0.00
2	3.77	1.00	2	3.77	1.00	2	3.77	1.00	1.00	0.00	0.00
3	3.77	1.00	3	3.77	1.00	3	3.77	1.00	1.00	0.00	0.00
4	3.77	1.00	4	3.77	1.00	4	3.77	1.00	1.00	0.00	0.00
5	3.77	1.00	5	3.77	1.00	5	3.77	1.00	1.00	0.00	0.00
10	3.77	1.00	10	3.77	1.00	10	3.77	1.00	1.00	0.00	0.00
15	3.77	1.00	15	3.77	1.00	15	3.77	1.00	1.00	0.00	0.00
20	3.54	0.94	20	3.77	1.00	20	3.77	1.00	0.98	0.03	0.02
25	3.43	0.91	25	3.77	1.00	25	3.77	1.00	0.97	0.05	0.03
30	3.28	0.87	30	3.77	1.00	30	3.77	1.00	0.96	0.07	0.04
35	3.29	0.87	35	3.77	1.00	35	3.77	1.00	0.96	0.07	0.04
40	3.23	0.86	40	3.77	1.00	40	3.77	1.00	0.95	0.08	0.05
45	3.23	0.86	45	3.77	1.00	45	3.77	1.00	0.95	0.08	0.05
50	3.25	0.86	50	3.77	1.00	50	3.77	1.00	0.95	0.08	0.05
55	3.28	0.87	55	3.77	1.00	55	3.77	1.00	0.96	0.08	0.04
60	3.29	0.87	60	3.77	1.00	60	3.77	1.00	0.96	0.07	0.04

Table A.33. Commercial Tapioca Starch 2 Sedimentation Data (10 g L^{-1})

Commercial Tapioca Starch 2 (10 g L^{-1})											
Sample A			Sample B			Sample C			Ave. A/A_o	Std. Dev.	Std. Error
Time (min)	Abs (A)	A/A_o	Time (min)	Abs (A)	A/A_o	Time (min)	Abs (A)	A/A_o			
0	3.77	1.00	0	3.77	1.00	0	3.77	1.00	1.00	0.00	0.00
1	3.77	1.00	1	3.77	1.00	1	3.77	1.00	1.00	0.00	0.00
2	3.77	1.00	2	3.77	1.00	2	3.77	1.00	1.00	0.00	0.00
3	3.77	1.00	3	3.77	1.00	3	3.77	1.00	1.00	0.00	0.00
4	3.60	0.95	4	3.77	1.00	4	3.77	1.00	0.98	0.03	0.02
5	3.32	0.88	5	3.77	1.00	5	3.77	1.00	0.96	0.07	0.04
10	2.68	0.71	10	3.77	1.00	10	3.77	1.00	0.90	0.17	0.10
15	2.38	0.63	15	3.77	1.00	15	3.77	1.00	0.88	0.21	0.12
20	2.18	0.58	20	3.77	1.00	20	3.77	1.00	0.86	0.24	0.14
25	2.11	0.56	25	3.77	1.00	25	3.77	1.00	0.85	0.25	0.15
30	2.03	0.54	30	3.77	1.00	30	3.77	1.00	0.85	0.27	0.15
35	2.02	0.54	35	3.77	1.00	35	3.77	1.00	0.85	0.27	0.15
40	1.96	0.52	40	3.77	1.00	40	3.77	1.00	0.84	0.28	0.16
45	1.95	0.52	45	3.77	1.00	45	3.77	1.00	0.84	0.28	0.16
50	1.93	0.51	50	3.77	1.00	50	3.77	1.00	0.84	0.28	0.16
55	1.92	0.51	55	3.77	1.00	55	3.77	1.00	0.84	0.28	0.16
60	1.92	0.51	60	3.77	1.00	60	3.77	1.00	0.84	0.28	0.16

Table A.34. Commercial Tapioca Starch 3 Sedimentation Data (10 g L^{-1})

Commercial Tapioca Starch 3 (5 g L^{-1})											
Sample A			Sample B			Sample C			Ave. A/A_o	Std. Dev.	Std. Error
Time (min)	Abs (A)	A/A_o	Time (min)	Abs (A)	A/A_o	Time (min)	Abs (A)	A/A_o			
0	3.45	1.00	0	3.53	1.00	0	3.77	1.00	1.00	0.00	0.00
1	1.53	0.44	1	2.53	0.72	1	3.77	1.00	0.72	0.05	0.03
2	1.44	0.42	2	2.43	0.69	2	3.77	1.00	0.70	0.08	0.05
3	1.44	0.42	3	2.41	0.68	3	3.77	1.00	0.70	0.11	0.06
4	1.39	0.40	4	2.37	0.67	4	3.77	1.00	0.69	0.13	0.07
5	1.37	0.40	5	2.35	0.67	5	3.77	1.00	0.69	0.14	0.08
10	1.30	0.38	10	2.32	0.66	10	3.77	1.00	0.68	0.15	0.09
15	1.27	0.37	15	2.30	0.65	15	3.77	1.00	0.67	0.15	0.09
20	1.19	0.34	20	2.30	0.65	20	3.77	1.00	0.67	0.15	0.09
25	1.17	0.34	25	2.31	0.66	25	3.77	1.00	0.67	0.15	0.09
30	1.16	0.34	30	2.35	0.67	30	3.77	1.00	0.67	0.15	0.09
35	1.11	0.32	35	2.40	0.68	35	3.77	1.00	0.67	0.15	0.08
40	1.13	0.33	40	2.43	0.69	40	3.77	1.00	0.67	0.14	0.08
45	1.15	0.33	45	2.46	0.70	45	3.77	1.00	0.68	0.15	0.09
50	1.20	0.35	50	2.51	0.71	50	3.77	1.00	0.69	0.14	0.08
55	1.19	0.35	55	2.53	0.72	55	3.77	1.00	0.69	0.14	0.08
60	1.27	0.37	60	2.60	0.74	60	3.77	1.00	0.70	0.14	0.08

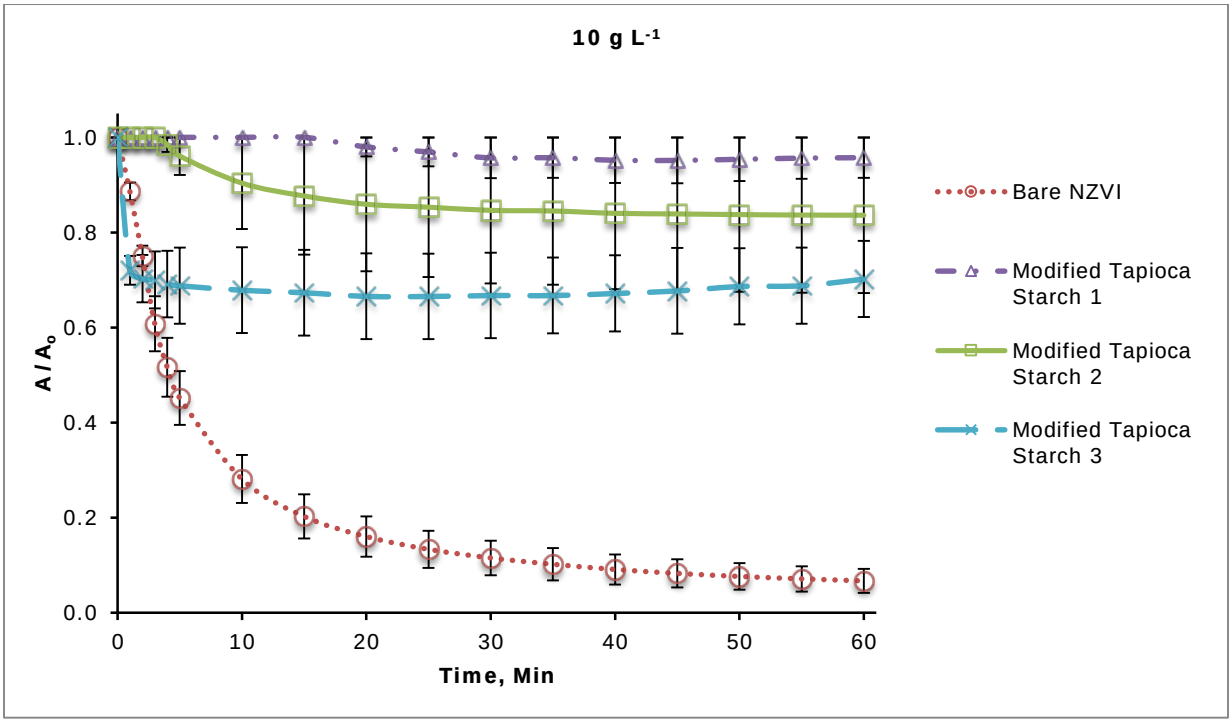


Figure A.9. Commercial Tapioca Starch Sedimentation Data (10 g L^{-1})

A.6. One-Way ANOVA for Commercial Starches

Selection Reason

One-way ANOVA is used to determine if there are significant differences between two or more independent groups. The independent groups in this study are: bare NZVI and NZVI coated with a modified tapioca starch. One-Way ANOVAs were conducted for each coating concentration (1 g L^{-1}, 5 g L^{-1}, and 10 g L^{-1})

Hypothesis

H_o: There is not a significant difference between the mean particle stability of bare NZVI particles and NZVI coated with different commercial starches ($x_0=x_1=x_2=x_3$).

H_a: at least one mean particle stability is different.

where:

x_0 = bare NZVI

x_1 = NZVI coated with Modified Tapioca Starch 1

x_2 = NZVI coated with Modified Tapioca Starch 2

x_3 = NZVI coated with Modified Tapioca Starch 3

1 g L^{-1}

Table A.35. Data used for One-Way ANOVA Analysis of Modified Tapioca Starches (1 g L^{-1})

Treatment	Sedimentation Data
Bare NZVI	Average C/C_o from Table A.1.i.a (All time periods)
NZVI coated w/ Modified Tapioca Starch 1	Average C/C_o from Table A.3.i.a (All time periods)
NZVI coated w/ Modified Tapioca Starch 2	Average C/C_o from Table A.3.i.b (All time periods)
NZVI coated w/ Modified Tapioca Starch 3	Average C/C_o from Table A.3.i.c (All time periods)

Table A.36. One-Way ANOVA for Modified Tapioca Starches (1 g L^{-1})

Source	DF	Adj. SS	Adj. MS	F-Value	P-Value
Treatment*	3	1.234	0.41150	9.53	0.000
Error	64	2.763	0.04317		
Total	67	3.998			

*The four levels of treatment are presented in the hypothesis section above.

Tukey's test was used after the One-Way ANOVA. Tukey's test compares the means of the groups tested in the One-Way ANOVA and identifies which groups among the samples tested are significantly different.

Table A.37. Tukey Pairwise Comparison for Modified Tapioca Starches (1 g L^{-1})

Treatment	N	Mean	Std. Dev.	99.5% CI	Grouping**
0	17	0.3294	0.3127	(0.1828, 0.4759)	B
1	17	0.6357	0.1758	(0.4891, 0.7822)	A
2	17	0.4165	0.1828	(0.2700, 0.5630)	B
3	17	0.6349	0.1031	(0.4883, 0.7814)	A

** Means that do not share a letter are significantly different.

5 g L^{-1}

Table A.38. Data used for One-Way ANOVA Analysis of Modified Tapioca Starches (5 g L^{-1})

Treatment	Sedimentation Data
Bare NZVI	Average C/C_o from Table A.1.i.a (All time periods)
NZVI coated w/ Modified Tapioca Starch 1	Average C/C_o from Table A.3.i.d (All time periods)
NZVI coated w/ Modified Tapioca Starch 2	Average C/C_o from Table A.3.i.e (All time periods)
NZVI coated w/ Modified Tapioca Starch 3	Average C/C_o from Table A.3.i.f (All time periods)

Table A.39. One-Way ANOVA for Modified Tapioca Starches (5 g L^{-1})

Source	DF	Adj. SS	Adj. MS	F-Value	P-Value
Treatment*	3	3.846	1.28194	36.75	0.000
Error	64	2.232	0.03488		
Total	67	6.078			

*The four levels of treatment are presented in the hypothesis section above.

Tukey's test was used after the One-Way ANOVA. Tukey's test compares the means of the groups tested in the One-Way ANOVA and identifies which groups among the samples tested are significantly different.

Table A.40. Tukey Pairwise Comparison for Modified Tapioca Starches (5 g L^{-1})

Treatment	N	Mean	Std. Dev.	99.5% CI	Grouping**
0	17	0.3294	0.3127	(0.1976, 0.4611)	C
1	17	1.000	0.000	(0.868, 1.132)	A
2	17	0.7070	0.1694	(0.5753, 0.8387)	B
3	17	0.6649	0.1143	(0.5332, 0.7966)	B

** Means that do not share a letter are significantly different.

10 g L^{-1}

Table A.41. Data used for One-Way ANOVA Analysis of Modified Tapioca Starches (10 g L^{-1})

Treatment	Sedimentation Data
Bare NZVI	Average C/C_o from Table A.1.i.a (All time periods)
NZVI coated w/ Modified Tapioca Starch 1	Average C/C_o from Table A.3.i.d (All time periods)
NZVI coated w/ Modified Tapioca Starch 2	Average C/C_o from Table A.3.i.e (All time periods)
NZVI coated w/ Modified Tapioca Starch 3	Average C/C_o from Table A.3.i.f (All time periods)

Table A.42. One-Way ANOVA for Modified Tapioca Starches (10 g L^{-1})

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Treatment*	3	4.289	1.42978	52.29	0.000
Error	64	1.750	0.02734		
Total	67	6.039			

Tukey's test was used after the One-Way ANOVA. Tukey's test compares the means of the groups tested in the One-Way ANOVA and identifies which groups among the samples tested are significantly different.

*The four levels of treatment are presented in the hypothesis section above.

Table A.43. Commercial Starch Tukey Pairwise Comparison (10 g L^{-1})

Treatment	N	Mean	Std. Dev.	99.5% CI	Grouping**
0	17	0.3294	0.3127	(0.2127, 0.4460)	C
1	17	0.97855	0.02185	(0.86193, 1.09516)	A
2	17	0.9012	0.0709	(0.7845, 1.0178)	A
3	17	0.7028	0.0782	(0.5862, 0.8194)	B

** Means that do not share a letter are significantly different.

A.7. FTIR Spectra

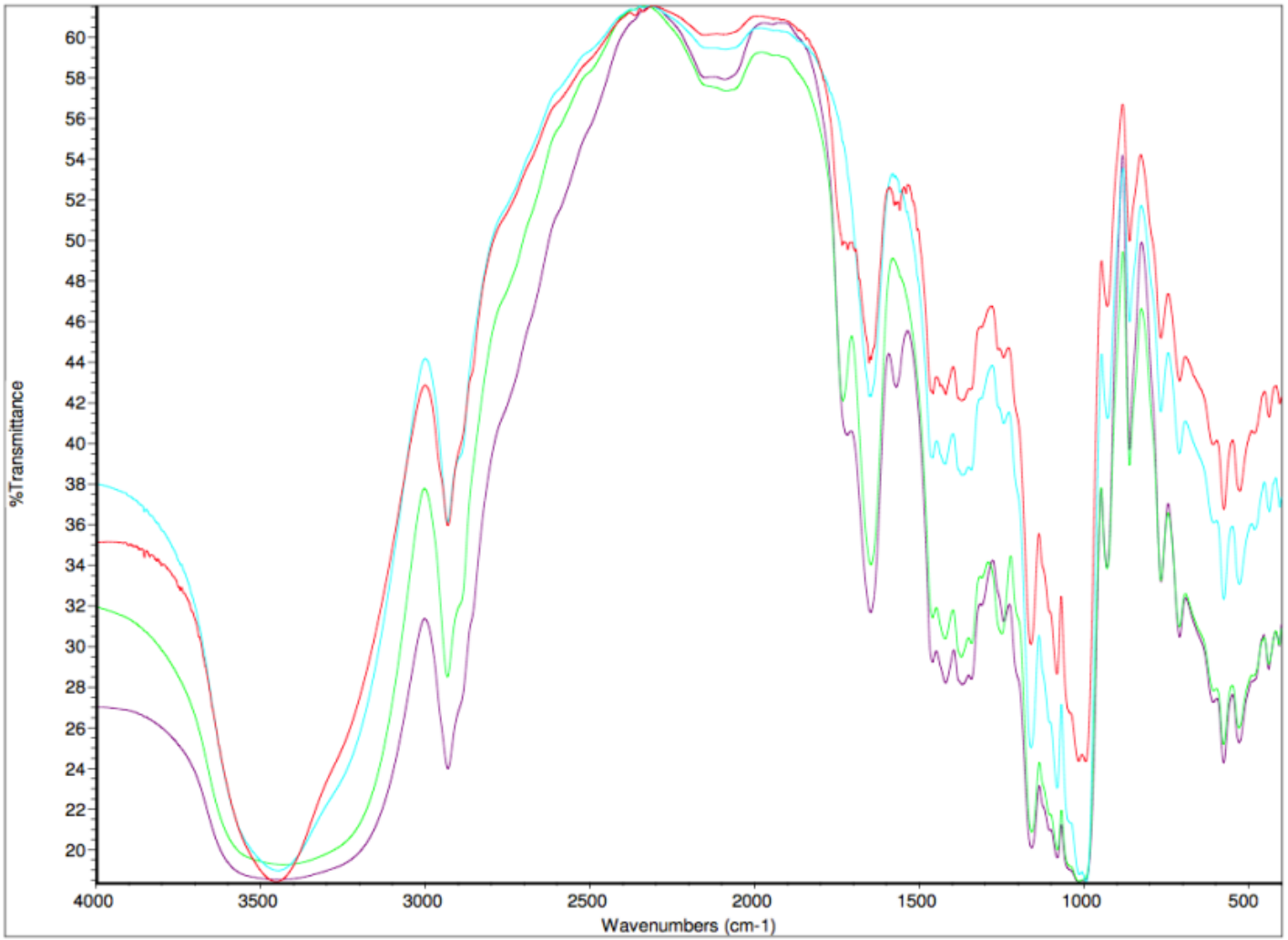


Figure A.10. Combined FTIR Spectra

- *50% OSA*, *–15% OSA*, *–Modified Tapioca Starch 1*, *and –Native Tapioca Starch*.

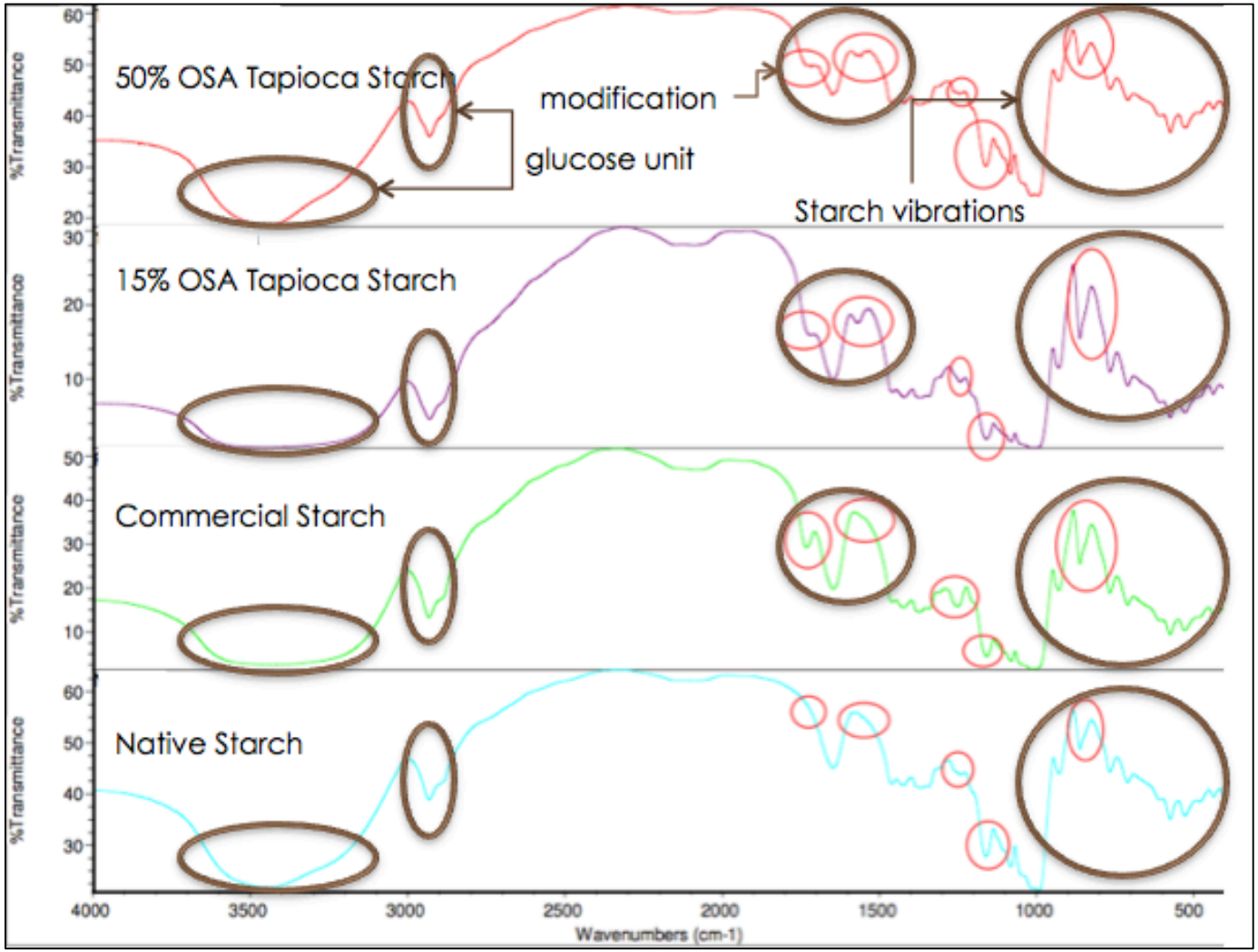


Figure A.11. Separate FTIR Spectra

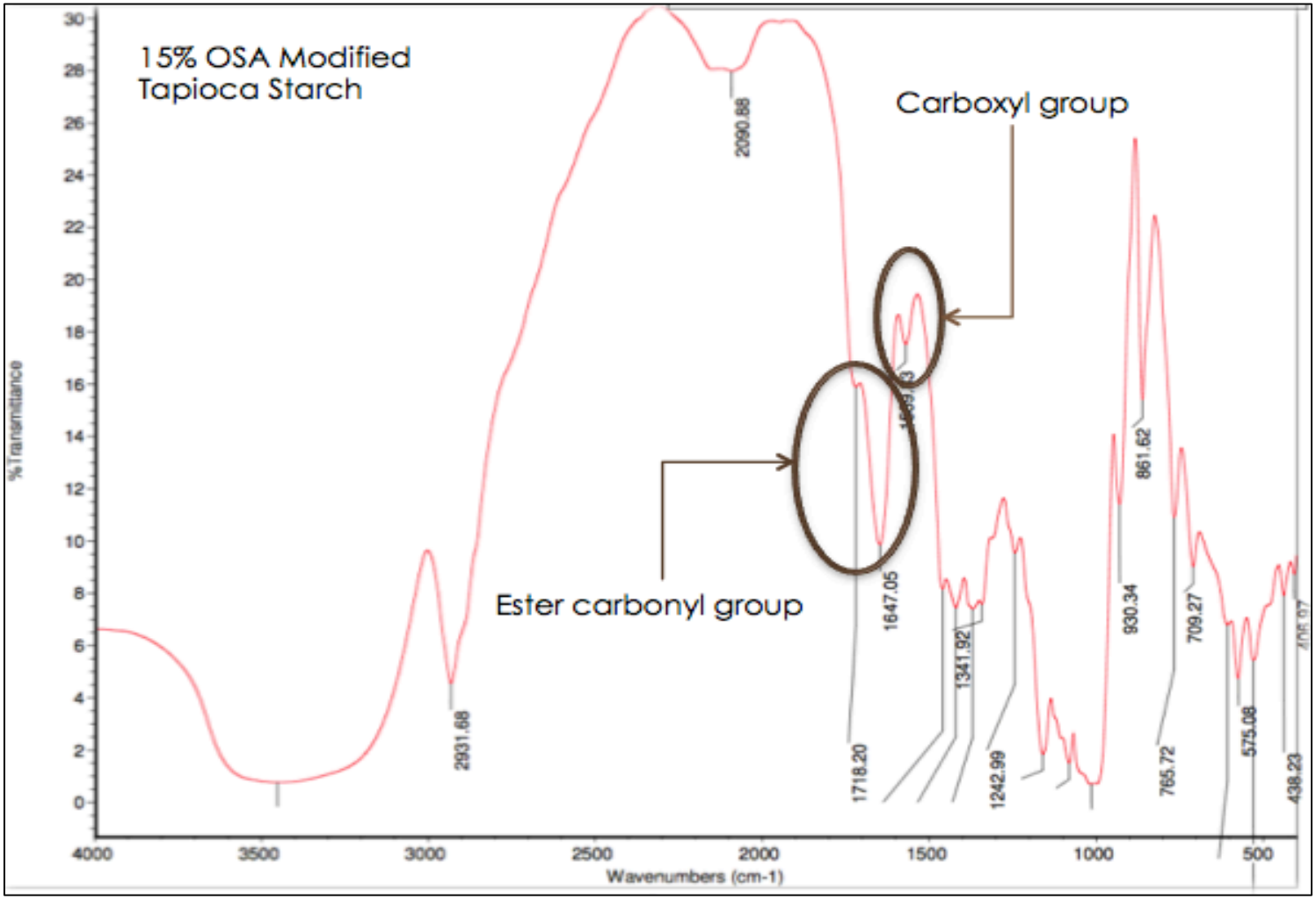


Figure A.12. 15% OSA-Modified Tapioca Starch FTIR Spectra

A.8. NMR Spectra

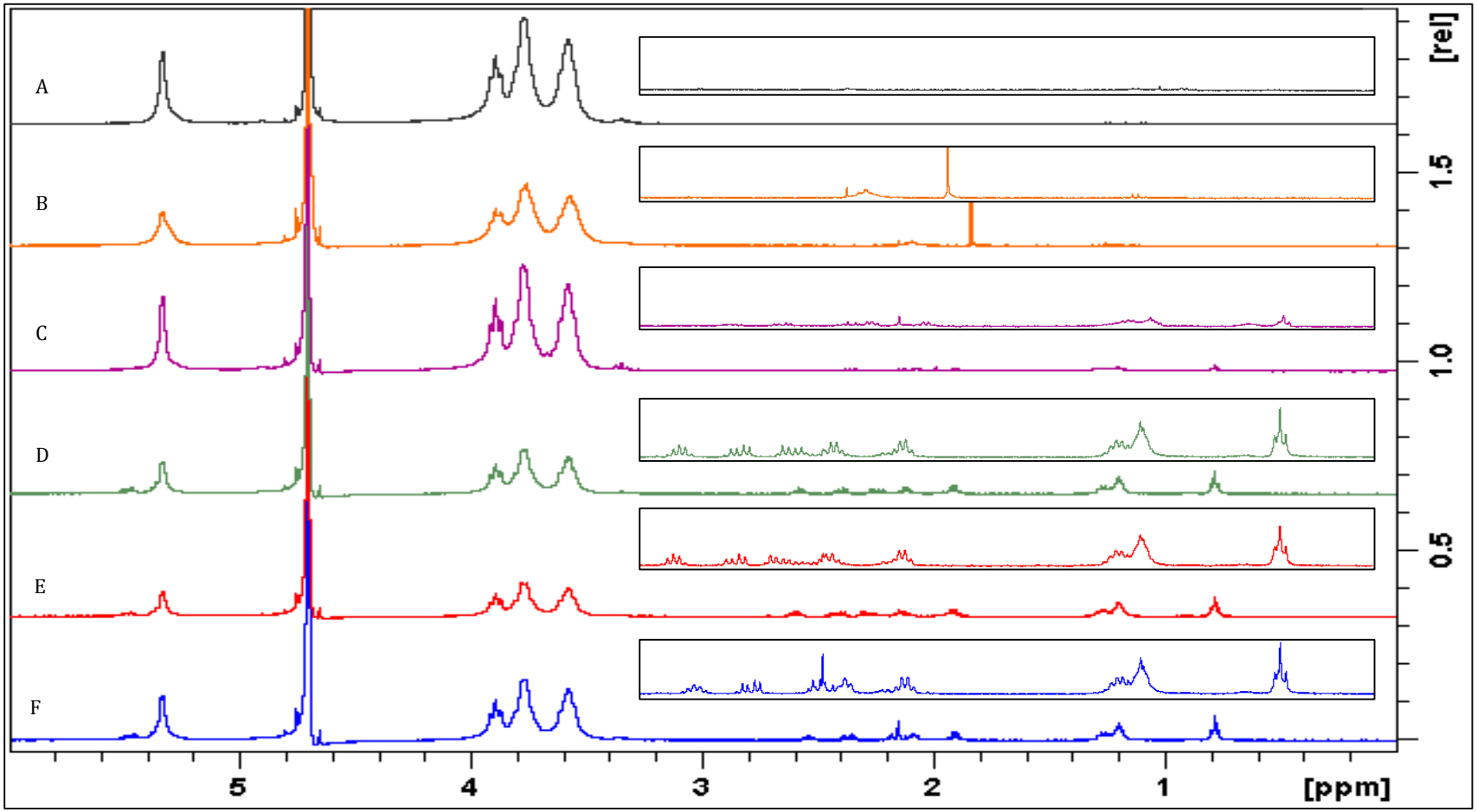


Figure A.13. Separate NMR Spectra
a. Native, b. Modified Tapioca Starch 1, c. 3% OSA, d. 15% OSA, e. 35% OSA, and f. 50% OSA. Inset spectra expansion of 0.5-2.7ppm

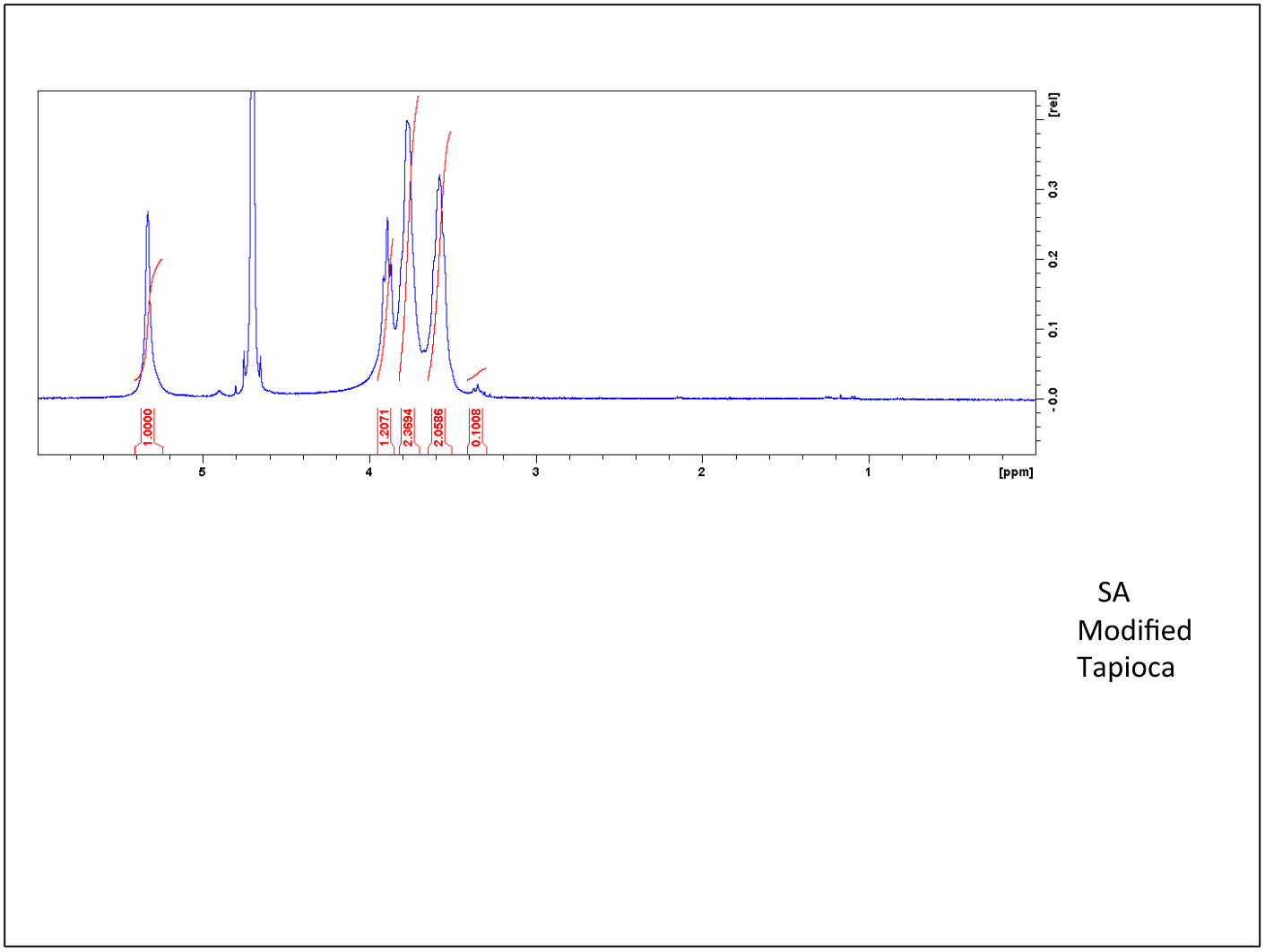


Figure A.14. NMR Integration of Native & Commercial Tapioca Starch
*Red numbers below peaks are the integration of the peak.

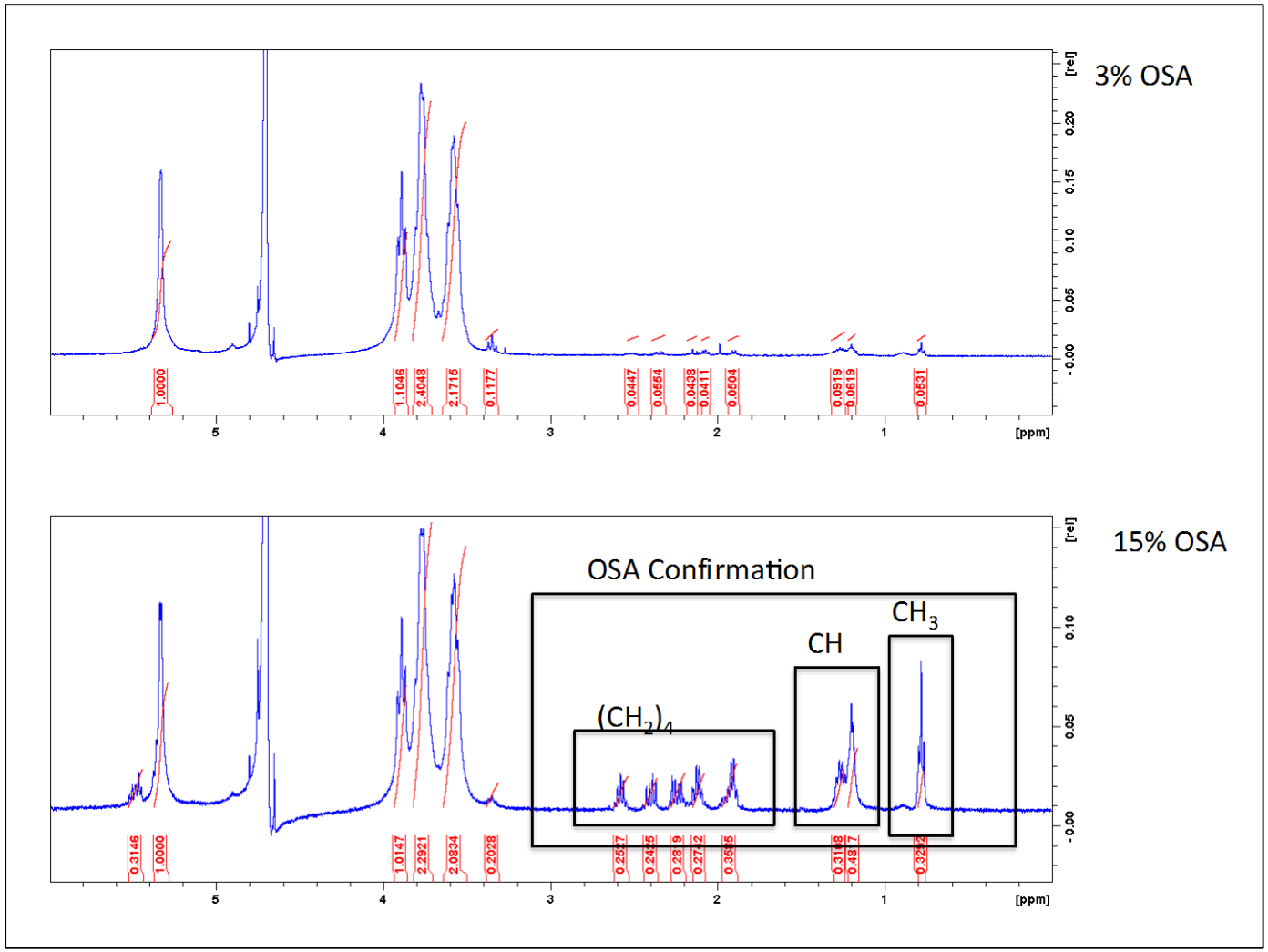


Figure A.15. NMR Integration of 3 & 15% OSA Starch
*Red numbers below peaks are the integration of the peak.

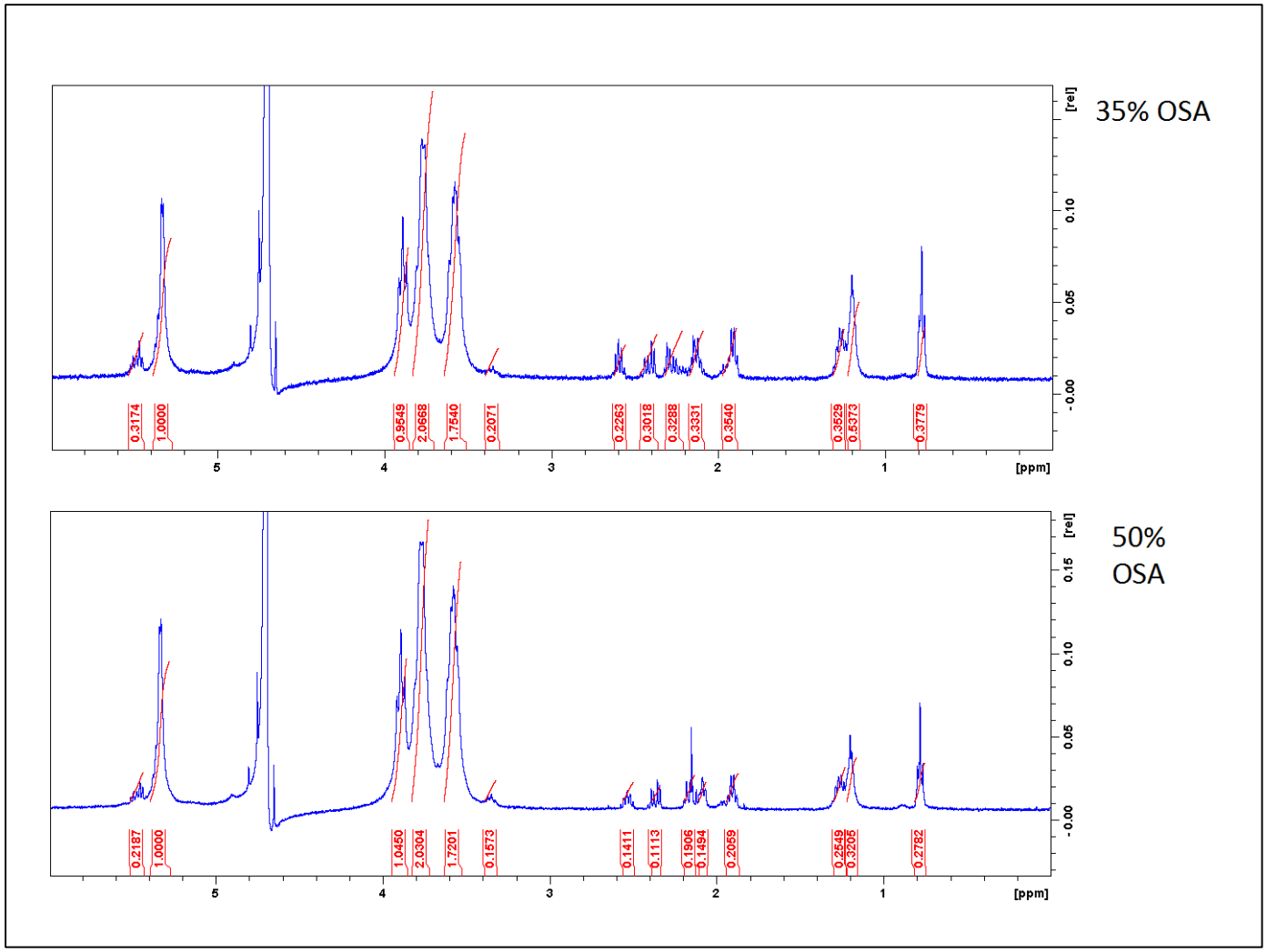


Figure A.16. NMR Integration of 35 & 50% OSA Starch
*Red numbers below peaks are the integration of the peak.

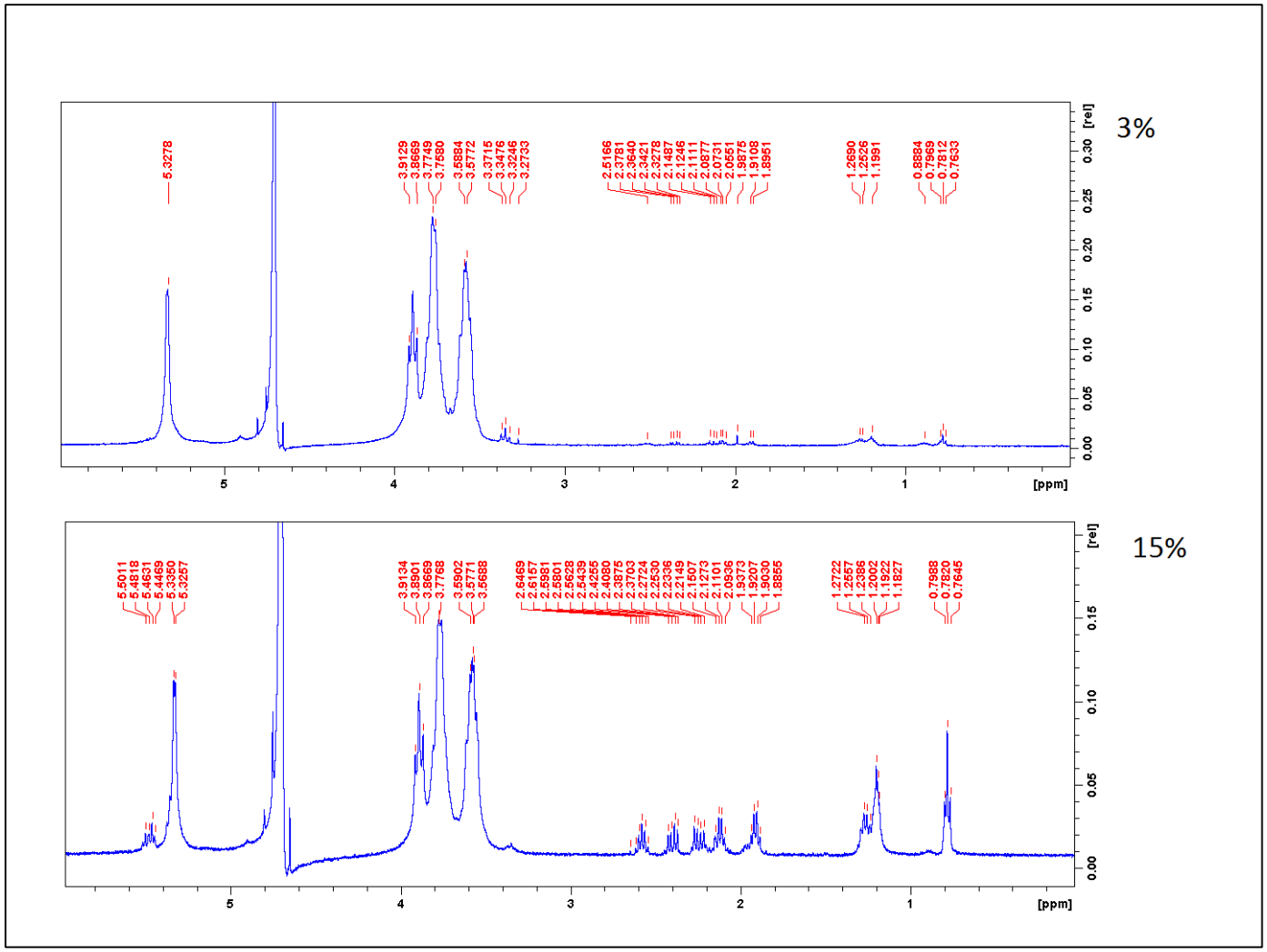


Figure A.17. Peak Assignments of 3 & 15% OSA Starch

* Red numbers above peaks are peak assignments.

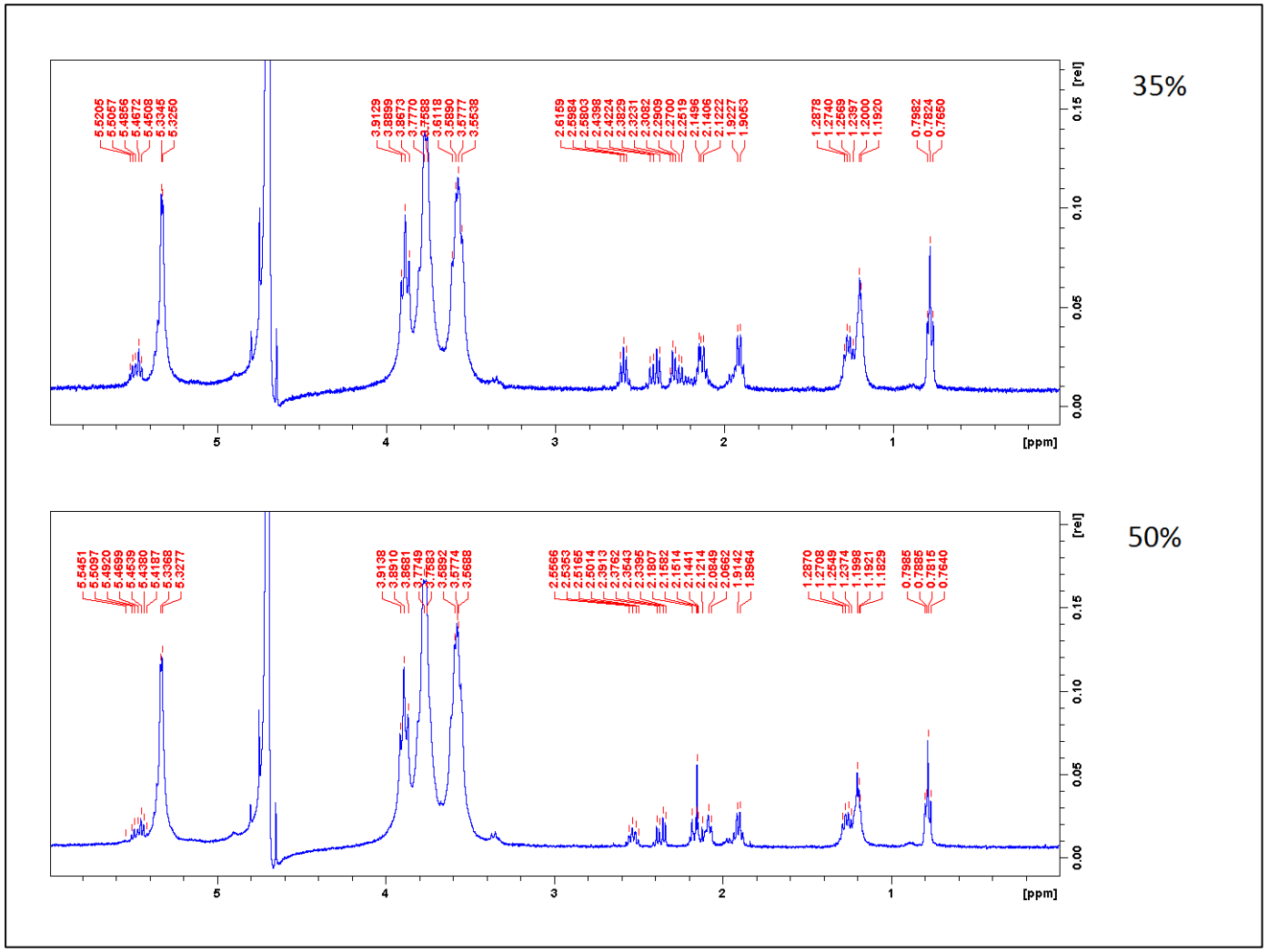


Figure A.18. Peak Assignments of 35 & 50% OSA Starch

* Red numbers above peaks are peak assignments.

A.9. Molecular Weight

Table A.44. Molecular Weight Data for Starches

	Amylopectin	Amylose	Amylopectin	Amylose
	%	%	Mw (Da)	Mw (Da)
Native	74.62877	25.37123	1.74E+07	1.39E+06
	73.6968	26.3032	1.74E+07	1.39E+06
Commercial	73.379	26.621	1.33E+07	3.20E+06
	73.4608	26.5692	1.34E+07	3.19E+06
3% OSA	75.2222	24.7778	1.22E+07	8.60E+05
	75.8401	24.1599	1.22E+07	8.66E+05
15 % OSA	76.0324	23.9676	9.83E+06	1.79E+06
	76.0679	23.9321	9.84E+06	1.79E+06
35% OSA	77.7583	22.2417	8.95E+06	2.06E+06
	77.5548	22.4452	8.96E+06	2.07E+06
50% OSA	79.4435	20.5565	7.63E+06	2.42E+06
	79.3377	20.6623	7.63E+06	2.42E+06

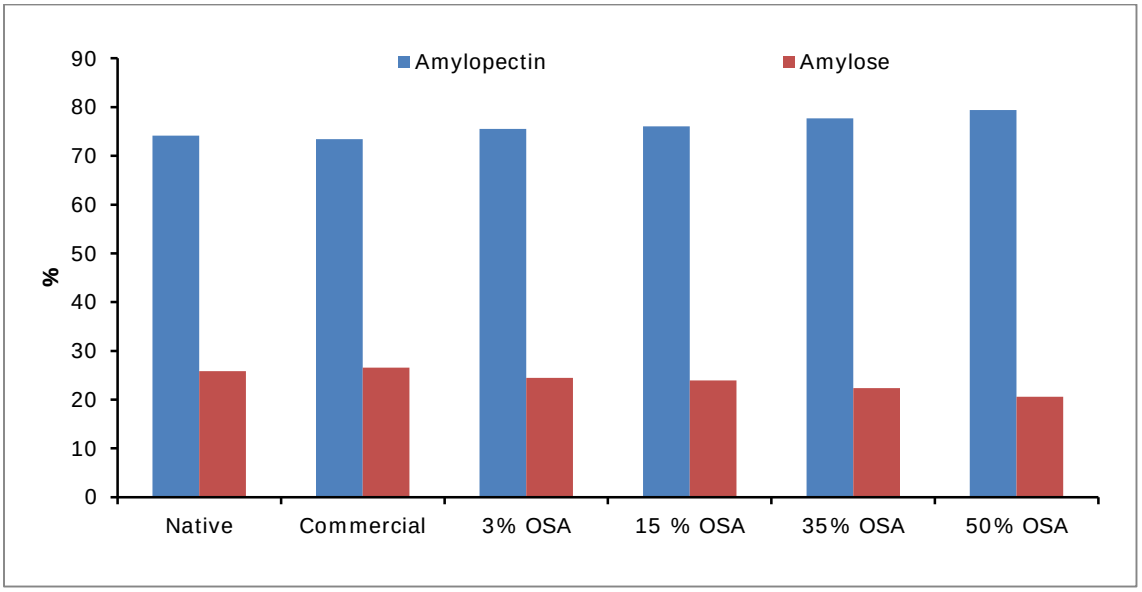


Figure A.19. Amylopectin/Amylose Percentages per Sample

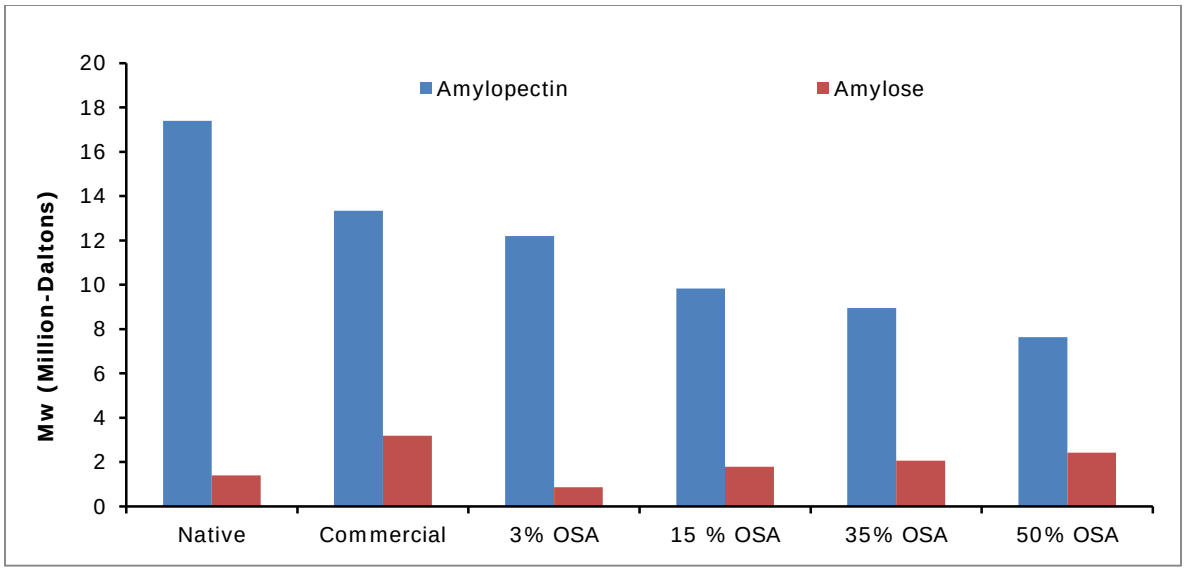


Figure A.20. Amylopectin/Amylose MW per Sample

A.10. Molecular Weigh ANOVA

Hypothesis

H_o: There is not a significant difference between the mean molecular weight of amylopectin/amylose in each sample ($x_0=x_1=x_2=x_3= x_4=x_5$).

H_a: at least one mean molecular weight is different.

where:

x_0 = bare NZVI

x_1 = unmodified tapioca starch

x_2 = 3% OSA modified tapioca starch

x_3 = 15% OSA modified tapioca starch

x_4 = 35% OSA modified tapioca starch

x_5 = 50% OSA modified tapioca starch

Percentage Amylopectin/Amylose

Table A.45. One-Way ANOVA of % Amylopectin/Amylose

Source	DF	Adj. SS	Adj. MS	F-Value	P-Value
Treatment*	1.00	24.57	24.57	788294.67	0.00
Error	4.00	0.00	0.00		
Total	5.00	24.57			

Table A.46. One-Way ANOVA of MW Amylopectin/Amylose

Source	DF	Adj. SS	Adj. MS	F-Value	P-Value
Treatment*	1	2.07626E+11	2.07626E+11	0.268940984	0.631
Error	4	3.08806E+12	7.72015E+11		
Total	5	3.29569E+12			

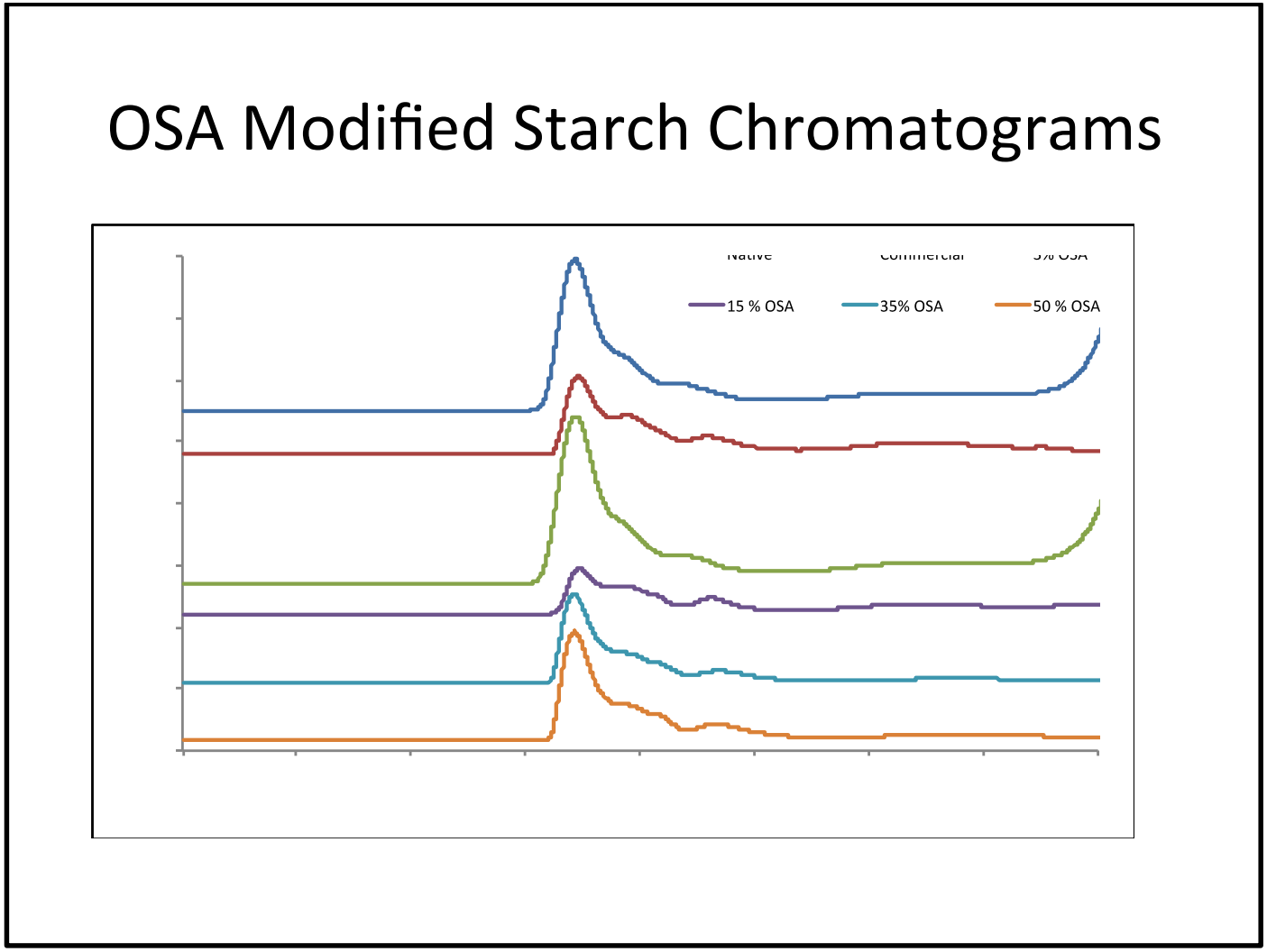


Figure A.21. OSA Modified Starch Chromatograms

A.11. OSA-Modified Tapioca Sedimentation Curves

Table A.47. Bare NZVI Sedimentation Data (2 Hours)

Bare NZVI											
Sample A			Sample B			Sample C			Ave. A/A_o	Std. Dev.	Std. Error
Time (min)	Abs (A)	A/A_o	Time (min)	Abs (A)	A/A_o	Time (min)	Abs (A)	A/A_o			
0	2.97	1.00	0	2.69	1.00	0	4.61	1.00	1.00	0.00	0.00
1	2.59	0.87	1	2.33	0.86	1	4.26	0.92	0.89	0.03	0.02
2	2.27	0.76	2	2.10	0.78	2	3.27	0.71	0.75	0.04	0.02
3	2.00	0.67	3	1.77	0.66	3	2.27	0.49	0.61	0.10	0.06
4	1.80	0.60	4	1.48	0.55	4	1.83	0.40	0.52	0.11	0.06
5	1.62	0.54	5	1.25	0.46	5	1.61	0.35	0.45	0.10	0.06
10	1.13	0.38	10	0.67	0.25	10	0.99	0.22	0.28	0.09	0.05
15	0.88	0.30	15	0.43	0.16	15	0.70	0.15	0.20	0.08	0.05
20	0.73	0.25	20	0.31	0.12	20	0.55	0.12	0.16	0.07	0.04
25	0.63	0.21	25	0.24	0.09	25	0.46	0.10	0.13	0.07	0.04
30	0.56	0.19	30	0.20	0.07	30	0.39	0.08	0.12	0.06	0.04
35	0.50	0.17	35	0.17	0.06	35	0.34	0.07	0.10	0.06	0.03
40	0.46	0.15	40	0.15	0.06	40	0.29	0.06	0.09	0.05	0.03
45	0.42	0.14	45	0.13	0.05	45	0.26	0.06	0.08	0.05	0.03
50	0.39	0.13	50	0.12	0.05	50	0.24	0.05	0.08	0.05	0.03
55	0.37	0.12	55	0.11	0.04	55	0.22	0.05	0.07	0.05	0.03
60	0.35	0.12	60	0.11	0.04	60	0.20	0.04	0.07	0.04	0.03
65	0.33	0.11	65	0.10	0.04	65	0.19	0.04	0.06	0.04	0.02
70	0.32	0.11	70	0.10	0.04	70	0.18	0.04	0.06	0.04	0.02
75	0.31	0.10	75	0.09	0.03	75	0.17	0.04	0.06	0.04	0.02
80	0.30	0.10	80	0.09	0.03	80	0.16	0.03	0.06	0.04	0.02
85	0.28	0.10	85	0.09	0.03	85	0.15	0.03	0.05	0.04	0.02
90	0.27	0.09	90	0.08	0.03	90	0.15	0.03	0.05	0.03	0.02
95	0.25	0.08	95	0.08	0.03	95	0.14	0.03	0.05	0.03	0.02
100	0.24	0.08	100	0.08	0.03	100	0.14	0.03	0.05	0.03	0.02
105	0.23	0.08	105	0.08	0.03	105	0.14	0.03	0.05	0.03	0.02
110	0.22	0.07	110	0.08	0.03	110	0.13	0.03	0.04	0.03	0.02
115	0.22	0.07	115	0.07	0.03	115	0.13	0.03	0.04	0.03	0.02
120	0.21	0.07	120	0.07	0.03	120	0.13	0.03	0.04	0.03	0.01

Table A.48. Native Tapioca Starch Sedimentation Data (1 g L^{-1})

Unmodified Tapioca Starch											
Sample A			Sample B			Sample C			Ave. A/A_o	Std. Dev.	Std. Error
Time (min)	Abs (A)	A/A_o	Time (min)	Abs (A)	A/A_o	Time (min)	Abs (A)	A/A_o			
0	3.78	1.00	0	3.77	1.00	0	2.89	1.00	1.00	0.00	0.00
1	2.35	0.62	1	3.77	1.00	1	1.27	0.44	0.69	0.29	0.17
2	1.31	0.35	2	1.99	0.53	2	0.99	0.34	0.41	0.11	0.06
3	1.16	0.31	3	1.60	0.42	3	0.89	0.31	0.35	0.07	0.04
4	0.98	0.26	4	1.46	0.39	4	0.82	0.28	0.31	0.07	0.04
5	0.87	0.23	5	1.37	0.36	5	0.74	0.26	0.28	0.07	0.04
10	0.62	0.16	10	1.06	0.28	10	0.60	0.21	0.22	0.06	0.03
15	0.59	0.15	15	1.01	0.27	15	0.52	0.18	0.20	0.06	0.03
20	0.56	0.15	20	1.00	0.26	20	0.51	0.18	0.20	0.06	0.03
25	0.56	0.15	25	0.97	0.26	25	0.51	0.18	0.19	0.06	0.03
30	0.57	0.15	30	0.98	0.26	30	0.49	0.17	0.19	0.06	0.03
35	0.56	0.15	35	0.98	0.26	35	0.51	0.18	0.19	0.06	0.03
40	0.56	0.15	40	0.98	0.26	40	0.50	0.17	0.19	0.06	0.03
45	0.57	0.15	45	1.00	0.26	45	0.51	0.18	0.20	0.06	0.03
50	0.59	0.16	50	1.00	0.27	50	0.52	0.18	0.20	0.06	0.03
55	0.60	0.16	55	1.01	0.27	55	0.53	0.18	0.20	0.06	0.03
60	0.61	0.16	60	1.02	0.27	60	0.53	0.18	0.20	0.06	0.03
65	0.62	0.16	65	1.02	0.27	65	0.54	0.19	0.21	0.06	0.03
70	0.63	0.17	70	1.03	0.27	70	0.54	0.19	0.21	0.06	0.03
75	0.63	0.17	75	1.04	0.28	75	0.55	0.19	0.21	0.06	0.03
80	0.64	0.17	80	1.05	0.28	80	0.56	0.19	0.21	0.06	0.03
85	0.65	0.17	85	1.06	0.28	85	0.56	0.19	0.22	0.06	0.03
90	0.66	0.18	90	1.07	0.28	90	0.57	0.20	0.22	0.06	0.03
95	0.67	0.18	95	1.08	0.29	95	0.57	0.20	0.22	0.06	0.03
100	0.68	0.18	100	1.09	0.29	100	0.58	0.20	0.22	0.06	0.03
105	0.69	0.18	105	1.10	0.29	105	0.59	0.20	0.23	0.06	0.03
110	0.70	0.19	110	1.11	0.29	110	0.59	0.20	0.23	0.06	0.03
115	0.71	0.19	115	1.12	0.30	115	0.60	0.21	0.23	0.06	0.03
120	0.72	0.19	120	1.13	0.30	120	0.60	0.21	0.23	0.06	0.03

Table A.49. 3% OSA-modified Tapioca Starch Sedimentation Data (1 g L^{-1})

3% OSA Tapioca Starch											
Sample A			Sample B			Sample C			Ave. A/A_0	Std. Dev.	Std. Error
Time (min)	Abs (A)	A/A_0	Time (min)	Abs (A)	A/A_0	Time (min)	Abs (A)	A/A_0			
0	2.88	1.00	0	3.76	1.00	0	2.15	1.00	1.00	0.00	0.00
1	0.91	0.32	1	3.76	1.00	1	1.02	0.47	0.60	0.36	0.21
2	0.66	0.23	2	2.72	0.72	2	0.82	0.38	0.44	0.25	0.15
3	0.53	0.18	3	2.17	0.58	3	0.69	0.32	0.36	0.20	0.12
4	0.46	0.16	4	1.86	0.49	4	0.62	0.29	0.31	0.17	0.10
5	0.41	0.14	5	1.57	0.42	5	0.58	0.27	0.28	0.14	0.08
10	0.32	0.11	10	1.17	0.31	10	0.43	0.20	0.21	0.10	0.06
15	0.34	0.12	15	1.01	0.27	15	0.40	0.18	0.19	0.08	0.04
20	0.36	0.13	20	0.96	0.26	20	0.40	0.19	0.19	0.07	0.04
25	0.38	0.13	25	0.93	0.25	25	0.40	0.18	0.19	0.06	0.03
30	0.41	0.14	30	0.92	0.24	30	0.40	0.19	0.19	0.05	0.03
35	0.42	0.15	35	0.92	0.24	35	0.42	0.19	0.19	0.05	0.03
40	0.44	0.15	40	0.91	0.24	40	0.42	0.20	0.20	0.04	0.03
45	0.46	0.16	45	0.91	0.24	45	0.43	0.20	0.20	0.04	0.02
50	0.47	0.16	50	0.91	0.24	50	0.44	0.20	0.20	0.04	0.02
55	0.49	0.17	55	0.92	0.24	55	0.45	0.21	0.21	0.04	0.02
60	0.50	0.17	60	0.91	0.24	60	0.45	0.21	0.21	0.04	0.02
65	0.51	0.18	65	0.92	0.24	65	0.46	0.21	0.21	0.03	0.02
70	0.52	0.18	70	0.92	0.24	70	0.46	0.21	0.21	0.03	0.02
75	0.52	0.18	75	0.92	0.24	75	0.47	0.22	0.22	0.03	0.02
80	0.53	0.18	80	0.92	0.24	80	0.47	0.22	0.22	0.03	0.02
85	0.54	0.19	85	0.92	0.24	85	0.48	0.22	0.22	0.03	0.02
90	0.54	0.19	90	0.92	0.24	90	0.48	0.23	0.22	0.03	0.02
95	0.54	0.19	95	0.92	0.24	95	0.49	0.23	0.22	0.03	0.02
100	0.54	0.19	100	0.91	0.24	100	0.49	0.23	0.22	0.03	0.02
105	0.54	0.19	105	0.91	0.24	105	0.49	0.23	0.22	0.03	0.02
110	0.54	0.19	110	0.91	0.24	110	0.49	0.23	0.22	0.03	0.02
115	0.53	0.18	115	0.90	0.24	115	0.50	0.23	0.22	0.03	0.02
120	0.53	0.18	120	0.90	0.24	120	0.50	0.23	0.22	0.03	0.02

Table A.50. 15% OSA-modified Tapioca Starch (1 g L^{-1})

15% OSA Tapioca Starch											
Sample A			Sample B			Sample C			Ave. A/A_o	Std. Dev.	Std. Error
Time (min)	Abs (A)	A/A_o	Time (min)	Abs (A)	A/A_o	Time (min)	Abs (A)	A/A_o			
0	2.09	1.00	0	3.77	1.00	0	3.78	1.00	1.00	0.00	0.00
1	1.52	0.73	1	2.25	0.60	1	3.78	1.00	0.77	0.21	0.12
2	1.24	0.59	2	1.93	0.51	2	2.40	0.63	0.58	0.06	0.04
3	1.15	0.55	3	1.71	0.45	3	2.13	0.56	0.52	0.06	0.03
4	1.08	0.52	4	1.57	0.42	4	1.97	0.52	0.49	0.06	0.03
5	1.05	0.50	5	1.48	0.39	5	1.89	0.50	0.46	0.06	0.04
10	1.00	0.48	10	1.28	0.34	10	1.64	0.43	0.42	0.07	0.04
15	1.01	0.48	15	1.23	0.33	15	1.56	0.41	0.41	0.08	0.05
20	1.02	0.49	20	1.21	0.32	20	1.52	0.40	0.40	0.08	0.05
25	1.04	0.50	25	1.21	0.32	25	1.48	0.39	0.40	0.09	0.05
30	1.06	0.51	30	1.24	0.33	30	1.49	0.39	0.41	0.09	0.05
35	1.07	0.51	35	1.25	0.33	35	1.50	0.40	0.41	0.09	0.05
40	1.09	0.52	40	1.28	0.34	40	1.48	0.39	0.42	0.09	0.05
45	1.11	0.53	45	1.29	0.34	45	1.49	0.39	0.42	0.10	0.06
50	1.12	0.54	50	1.30	0.34	50	1.51	0.40	0.43	0.10	0.06
55	1.14	0.55	55	1.32	0.35	55	1.51	0.40	0.43	0.10	0.06
60	1.16	0.55	60	1.34	0.36	60	1.51	0.40	0.44	0.10	0.06
65	1.17	0.56	65	1.38	0.37	65	1.53	0.40	0.44	0.10	0.06
70	1.19	0.57	70	1.39	0.37	70	1.54	0.41	0.45	0.11	0.06
75	1.21	0.58	75	1.41	0.37	75	1.55	0.41	0.45	0.11	0.06
80	1.22	0.59	80	1.43	0.38	80	1.57	0.41	0.46	0.11	0.06
85	1.24	0.59	85	1.45	0.39	85	1.58	0.42	0.47	0.11	0.06
90	1.25	0.60	90	1.46	0.39	90	1.58	0.42	0.47	0.11	0.07
95	1.27	0.61	95	1.48	0.39	95	1.59	0.42	0.47	0.12	0.07
100	1.28	0.61	100	1.50	0.40	100	1.61	0.43	0.48	0.12	0.07
105	1.29	0.62	105	1.52	0.40	105	1.62	0.43	0.48	0.12	0.07
110	1.30	0.62	110	1.53	0.41	110	1.63	0.43	0.49	0.12	0.07
115	1.31	0.63	115	1.55	0.41	115	1.64	0.43	0.49	0.12	0.07
120	1.32	0.63	120	1.57	0.42	120	1.65	0.44	0.49	0.12	0.07

Table A.51. 35% OSA-modified Tapioca Starch (1 g L^{-1})

35% OSA Tapioca Starch											
Sample A			Sample B			Sample C			Ave. A/A_0	Std. Dev.	Std. Error
Time (min)	Abs (A)	A/A_0	Time (min)	Abs (A)	A/A_0	Time (min)	Abs (A)	A/A_0			
0	3.78	1.00	0	1.91	1.00	0	3.78	1.00	1.00	0.00	0.00
1	1.54	0.41	1	0.74	0.39	1	1.36	0.36	0.39	0.02	0.01
2	1.08	0.28	2	0.55	0.29	2	1.04	0.27	0.28	0.01	0.00
3	0.90	0.24	3	0.44	0.23	3	0.86	0.23	0.23	0.01	0.00
4	0.79	0.21	4	0.38	0.20	4	0.78	0.20	0.20	0.01	0.00
5	0.70	0.19	5	0.33	0.17	5	0.68	0.18	0.18	0.01	0.00
10	0.46	0.12	10	0.24	0.13	10	0.49	0.13	0.13	0.00	0.00
15	0.34	0.09	15	0.21	0.11	15	0.39	0.10	0.10	0.01	0.01
20	0.28	0.08	20	0.20	0.11	20	0.38	0.10	0.09	0.02	0.01
25	0.25	0.07	25	0.20	0.11	25	0.35	0.09	0.09	0.02	0.01
30	0.21	0.06	30	0.21	0.11	30	0.34	0.09	0.09	0.03	0.02
35	0.20	0.05	35	0.21	0.11	35	0.34	0.09	0.08	0.03	0.02
40	0.22	0.06	40	0.22	0.11	40	0.33	0.09	0.09	0.03	0.02
45	0.20	0.05	45	0.22	0.12	45	0.33	0.09	0.09	0.03	0.02
50	0.21	0.06	50	0.23	0.12	50	0.33	0.09	0.09	0.03	0.02
55	0.21	0.06	55	0.24	0.13	55	0.33	0.09	0.09	0.04	0.02
60	0.22	0.06	60	0.25	0.13	60	0.33	0.09	0.09	0.04	0.02
65	0.22	0.06	65	0.26	0.13	65	0.34	0.09	0.09	0.04	0.02
70	0.22	0.06	70	0.26	0.14	70	0.34	0.09	0.10	0.04	0.02
75	0.23	0.06	75	0.27	0.14	75	0.34	0.09	0.10	0.04	0.02
80	0.23	0.06	80	0.28	0.15	80	0.35	0.09	0.10	0.04	0.02
85	0.24	0.06	85	0.28	0.15	85	0.36	0.09	0.10	0.04	0.03
90	0.24	0.06	90	0.29	0.15	90	0.36	0.09	0.10	0.04	0.03
95	0.24	0.06	95	0.29	0.15	95	0.29	0.08	0.10	0.05	0.03
100	0.25	0.07	100	0.30	0.15	100	0.29	0.08	0.10	0.05	0.03
105	0.25	0.07	105	0.30	0.16	105	0.29	0.08	0.10	0.05	0.03
110	0.25	0.07	110	0.30	0.16	110	0.29	0.08	0.10	0.05	0.03
115	0.26	0.07	115	0.31	0.16	115	0.29	0.08	0.10	0.05	0.03
120	0.26	0.07	120	0.31	0.16	120	0.28	0.07	0.10	0.05	0.03

Table A.52. 50% OSA-modified Tapioca Starch (1 g L^{-1})

50% OSA Tapioca Starch											
Sample A			Sample B			Sample C			Ave. A/A_o	Std. Dev.	Std. Error
Time (min)	Abs (A)	A/A_o	Time (min)	Abs (A)	A/A_o	Time (min)	Abs (A)	A/A_o			
0	3.79	1.00	0	3.78	1.00	0	2.23	1.00	1.00	0.00	0.00
1	2.85	0.75	1	2.13	0.56	1	1.87	0.84	0.72	0.14	0.08
2	1.95	0.51	2	1.69	0.45	2	1.46	0.65	0.54	0.11	0.06
3	1.62	0.43	3	1.46	0.39	3	1.27	0.57	0.46	0.10	0.06
4	1.37	0.36	4	1.35	0.36	4	1.14	0.51	0.41	0.09	0.05
5	1.22	0.32	5	1.28	0.34	5	1.09	0.49	0.38	0.09	0.05
10	0.97	0.26	10	1.07	0.28	10	0.90	0.40	0.31	0.08	0.05
15	0.88	0.23	15	1.00	0.27	15	0.88	0.39	0.30	0.08	0.05
20	0.85	0.22	20	0.97	0.26	20	0.86	0.38	0.29	0.08	0.05
25	0.79	0.21	25	0.96	0.25	25	0.86	0.38	0.28	0.09	0.05
30	0.78	0.21	30	0.97	0.26	30	0.86	0.38	0.28	0.09	0.05
35	0.77	0.20	35	0.98	0.26	35	0.87	0.39	0.28	0.10	0.06
40	0.76	0.20	40	0.99	0.26	40	0.88	0.40	0.29	0.10	0.06
45	0.76	0.20	45	1.01	0.27	45	0.90	0.40	0.29	0.10	0.06
50	0.76	0.20	50	1.03	0.27	50	0.91	0.41	0.29	0.11	0.06
55	0.75	0.20	55	1.03	0.27	55	0.91	0.41	0.29	0.11	0.06
60	0.75	0.20	60	1.05	0.28	60	0.93	0.42	0.30	0.11	0.06
65	0.74	0.20	65	1.06	0.28	65	0.95	0.42	0.30	0.12	0.07
70	0.74	0.20	70	1.08	0.29	70	0.95	0.43	0.30	0.12	0.07
75	0.74	0.20	75	1.09	0.29	75	0.96	0.43	0.30	0.12	0.07
80	0.74	0.20	80	1.11	0.29	80	0.96	0.43	0.31	0.12	0.07
85	0.74	0.19	85	1.12	0.30	85	0.97	0.43	0.31	0.12	0.07
90	0.74	0.19	90	1.14	0.30	90	0.98	0.44	0.31	0.12	0.07
95	0.74	0.19	95	1.16	0.31	95	0.98	0.44	0.31	0.12	0.07
100	0.74	0.19	100	1.16	0.31	100	0.99	0.44	0.32	0.12	0.07
105	0.74	0.19	105	1.18	0.31	105	1.00	0.45	0.32	0.13	0.07
110	0.73	0.19	110	1.20	0.32	110	1.01	0.45	0.32	0.13	0.07
115	0.74	0.19	115	1.21	0.32	115	1.02	0.46	0.32	0.13	0.08
120	0.73	0.19	120	1.23	0.32	120	1.02	0.46	0.33	0.13	0.08

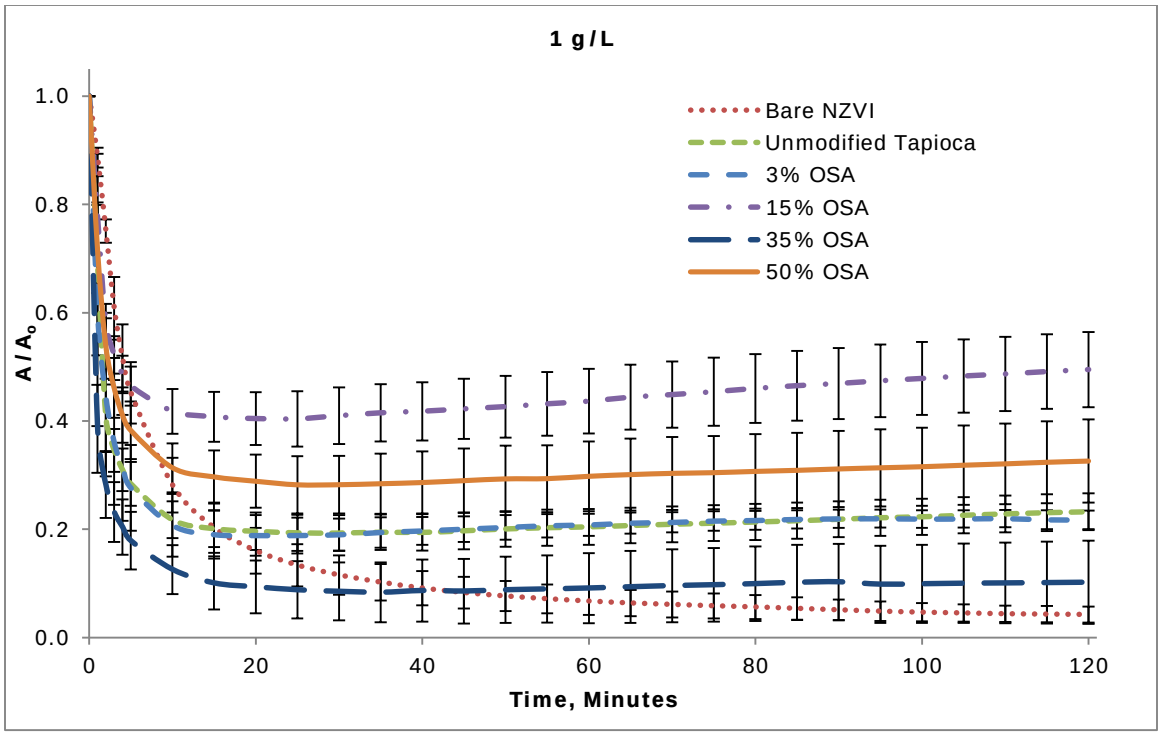


Figure A.22. Modified Tapioca Starch Sedimentation Curves (1 g L^{-1})

Table A.53. Native Tapioca Starch Sedimentation Data (5 g L^{-1})

Unmodified Tapioca Starch											
Sample A			Sample B			Sample C			Ave. A/A_o	Std. Dev.	Std. Error
Time (min)	Abs (A)	A/A_o	Time (min)	Abs (A)	A/A_o	Time (min)	Abs (A)	A/A_o			
0	1.86	1.00	0	3.78	1.00	0	3.03	1.00	1.00	0.00	0.00
1	1.61	0.87	1	1.14	0.30	1	1.13	0.37	0.51	0.31	0.18
2	1.09	0.59	2	0.87	0.23	2	0.87	0.29	0.37	0.19	0.11
3	0.80	0.43	3	0.73	0.19	3	0.74	0.24	0.29	0.13	0.07
4	0.65	0.35	4	0.63	0.17	4	0.63	0.21	0.24	0.10	0.06
5	0.54	0.29	5	0.53	0.14	5	0.56	0.19	0.21	0.08	0.04
10	0.39	0.21	10	0.36	0.10	10	0.33	0.11	0.14	0.06	0.04
15	0.32	0.17	15	0.32	0.08	15	0.29	0.10	0.12	0.05	0.03
20	0.30	0.16	20	0.25	0.07	20	0.27	0.09	0.10	0.05	0.03
25	0.30	0.16	25	0.25	0.06	25	0.25	0.08	0.10	0.05	0.03
30	0.30	0.16	30	0.25	0.07	30	0.25	0.08	0.10	0.05	0.03
35	0.31	0.17	35	0.25	0.07	35	0.26	0.09	0.11	0.05	0.03
40	0.32	0.17	40	0.25	0.07	40	0.27	0.09	0.11	0.06	0.03
45	0.33	0.18	45	0.25	0.07	45	0.28	0.09	0.11	0.06	0.03
50	0.35	0.19	50	0.26	0.07	50	0.29	0.10	0.12	0.06	0.04
55	0.36	0.19	55	0.27	0.07	55	0.31	0.10	0.12	0.06	0.04
60	0.37	0.20	60	0.27	0.07	60	0.32	0.11	0.13	0.07	0.04
65	0.38	0.20	65	0.28	0.07	65	0.33	0.11	0.13	0.07	0.04
70	0.38	0.21	70	0.29	0.08	70	0.33	0.11	0.13	0.07	0.04
75	0.39	0.21	75	0.29	0.08	75	0.34	0.11	0.13	0.07	0.04
80	0.40	0.21	80	0.30	0.08	80	0.35	0.12	0.14	0.07	0.04
85	0.40	0.22	85	0.31	0.08	85	0.36	0.12	0.14	0.07	0.04
90	0.41	0.22	90	0.31	0.08	90	0.36	0.12	0.14	0.07	0.04
95	0.42	0.22	95	0.31	0.08	95	0.37	0.12	0.14	0.07	0.04
100	0.42	0.23	100	0.31	0.08	100	0.38	0.12	0.15	0.07	0.04
105	0.43	0.23	105	0.32	0.08	105	0.38	0.13	0.15	0.08	0.04
110	0.43	0.23	110	0.32	0.08	110	0.39	0.13	0.15	0.08	0.04
115	0.44	0.24	115	0.32	0.08	115	0.39	0.13	0.15	0.08	0.04
120	0.44	0.24	120	0.32	0.09	120	0.40	0.13	0.15	0.08	0.05

Table A.54. 3% OSA-modified Tapioca Starch Sedimentation Data (5 g L^{-1})

3% OSA Tapioca Starch											
Sample A			Sample B			Sample C			Ave. A/A_o	Std. Dev.	Std. Error
Time (min)	Abs (A)	A/A_o	Time (min)	Abs (A)	A/A_o	Time (min)	Abs (A)	A/A_o			
0	3.76	1.00	0	2.30	1.00	0	1.55	1.00	1.00	0.00	0.00
1	3.76	1.00	1	2.21	0.96	1	1.19	0.77	0.91	0.12	0.07
2	3.59	0.96	2	2.16	0.94	2	0.98	0.63	0.84	0.18	0.11
3	2.78	0.74	3	2.10	0.92	3	0.86	0.55	0.74	0.18	0.11
4	2.52	0.67	4	2.02	0.88	4	0.76	0.49	0.68	0.20	0.11
5	2.33	0.62	5	1.91	0.83	5	0.70	0.45	0.63	0.19	0.11
10	1.91	0.51	10	1.49	0.65	10	0.57	0.37	0.51	0.14	0.08
15	1.77	0.47	15	1.39	0.61	15	0.54	0.35	0.47	0.13	0.07
20	1.67	0.44	20	1.33	0.58	20	0.53	0.34	0.46	0.12	0.07
25	1.64	0.44	25	1.29	0.56	25	0.53	0.34	0.45	0.11	0.06
30	1.61	0.43	30	1.28	0.56	30	0.53	0.34	0.44	0.11	0.06
35	1.60	0.43	35	1.27	0.55	35	0.55	0.35	0.44	0.10	0.06
40	1.60	0.43	40	1.27	0.55	40	0.56	0.36	0.45	0.10	0.06
45	1.60	0.42	45	1.28	0.56	45	0.56	0.36	0.45	0.10	0.06
50	1.59	0.42	50	1.29	0.56	50	0.58	0.37	0.45	0.10	0.06
55	1.60	0.43	55	1.29	0.56	55	0.58	0.38	0.46	0.10	0.06
60	1.60	0.43	60	1.31	0.57	60	0.60	0.38	0.46	0.10	0.06
65	1.61	0.43	65	1.32	0.57	65	0.60	0.39	0.46	0.10	0.06
70	1.61	0.43	70	1.33	0.58	70	0.61	0.39	0.47	0.10	0.06
75	1.62	0.43	75	1.34	0.58	75	0.61	0.39	0.47	0.10	0.06
80	1.63	0.43	80	1.36	0.59	80	0.62	0.40	0.47	0.10	0.06
85	1.64	0.44	85	1.37	0.60	85	0.62	0.40	0.48	0.10	0.06
90	1.65	0.44	90	1.38	0.60	90	0.63	0.40	0.48	0.10	0.06
95	1.65	0.44	95	1.40	0.61	95	0.63	0.41	0.48	0.11	0.06
100	1.67	0.44	100	1.41	0.62	100	0.63	0.41	0.49	0.11	0.06
105	1.68	0.45	105	1.42	0.62	105	0.63	0.40	0.49	0.11	0.07
110	1.69	0.45	110	1.43	0.62	110	0.62	0.40	0.49	0.12	0.07
115	1.69	0.45	115	1.45	0.63	115	0.61	0.39	0.49	0.12	0.07
120	1.70	0.45	120	1.45	0.63	120	0.61	0.39	0.49	0.12	0.07

Table A.55. 15% OSA-modified Tapioca Starch (5 g L^{-1})

15% OSA Tapioca Starch											
Sample A			Sample B			Sample C			Ave. A/A_o	Std. Dev.	Std. Error
Time (min)	Abs (A)	A/A_o	Time (min)	Abs (A)	A/A_o	Time (min)	Abs (A)	A/A_o			
0	1.62	1.00	0	1.51	1.00	0	1.39	1.00	1.00	0.00	0.00
1	1.25	0.78	1	1.24	0.82	1	0.95	0.68	0.76	0.07	0.04
2	1.09	0.67	2	0.96	0.64	2	0.85	0.61	0.64	0.03	0.02
3	1.00	0.62	3	0.84	0.55	3	0.79	0.57	0.58	0.03	0.02
4	0.95	0.59	4	0.74	0.49	4	0.76	0.54	0.54	0.05	0.03
5	0.91	0.56	5	0.68	0.45	5	0.75	0.54	0.52	0.06	0.03
10	0.84	0.52	10	0.55	0.36	10	0.76	0.55	0.48	0.10	0.06
15	0.85	0.53	15	0.55	0.36	15	0.77	0.55	0.48	0.10	0.06
20	0.85	0.53	20	0.57	0.38	20	0.77	0.56	0.49	0.10	0.05
25	0.86	0.53	25	0.58	0.38	25	0.79	0.56	0.49	0.10	0.06
30	0.86	0.53	30	0.59	0.39	30	0.80	0.57	0.50	0.10	0.06
35	0.88	0.54	35	0.61	0.40	35	0.81	0.58	0.51	0.09	0.05
40	0.89	0.55	40	0.63	0.41	40	0.81	0.59	0.52	0.09	0.05
45	0.89	0.55	45	0.64	0.42	45	0.82	0.59	0.52	0.09	0.05
50	0.90	0.56	50	0.65	0.43	50	0.83	0.60	0.53	0.09	0.05
55	0.91	0.57	55	0.66	0.44	55	0.84	0.61	0.54	0.09	0.05
60	0.92	0.57	60	0.67	0.44	60	0.85	0.61	0.54	0.09	0.05
65	0.93	0.58	65	0.69	0.45	65	0.86	0.62	0.55	0.08	0.05
70	0.94	0.58	70	0.70	0.46	70	0.87	0.62	0.55	0.08	0.05
75	0.95	0.59	75	0.71	0.47	75	0.87	0.63	0.56	0.08	0.05
80	0.96	0.59	80	0.72	0.47	80	0.88	0.63	0.57	0.08	0.05
85	0.96	0.60	85	0.73	0.48	85	0.88	0.64	0.57	0.08	0.05
90	0.97	0.60	90	0.74	0.49	90	0.89	0.64	0.58	0.08	0.05
95	0.98	0.61	95	0.75	0.49	95	0.89	0.64	0.58	0.08	0.04
100	0.99	0.61	100	0.76	0.50	100	0.90	0.65	0.59	0.08	0.04
105	0.99	0.61	105	0.76	0.50	105	0.90	0.65	0.59	0.08	0.04
110	1.00	0.62	110	0.77	0.51	110	0.91	0.65	0.59	0.08	0.04
115	1.00	0.62	115	0.78	0.51	115	0.91	0.66	0.60	0.07	0.04
120	1.01	0.62	120	0.78	0.52	120	0.92	0.66	0.60	0.07	0.04

Table A.56. 35% OSA-modified Tapioca Starch (5 g L^{-1})

35% OSA Tapioca Starch											
Sample A			Sample B			Sample C			Ave. A/A_o	Std. Dev.	Std. Error
Time (min)	Abs (A)	A/A_o	Time (min)	Abs (A)	A/A_o	Time (min)	Abs (A)	A/A_o			
0	1.70	1.00	0	1.60	1.00	0	2.90	1.00	1.00	0.00	0.00
1	1.38	0.81	1	1.57	0.98	1	2.10	0.72	0.84	0.13	0.08
2	1.11	0.65	2	1.54	0.96	2	1.64	0.56	0.73	0.21	0.12
3	0.95	0.56	3	1.52	0.95	3	1.37	0.47	0.66	0.25	0.15
4	0.82	0.48	4	1.50	0.94	4	1.16	0.40	0.61	0.29	0.17
5	0.72	0.42	5	1.47	0.92	5	1.02	0.35	0.57	0.31	0.18
10	0.48	0.28	10	1.37	0.86	10	0.69	0.24	0.46	0.35	0.20
15	0.37	0.22	15	1.20	0.75	15	0.56	0.19	0.39	0.32	0.18
20	0.31	0.18	20	1.07	0.67	20	0.51	0.18	0.34	0.28	0.16
25	0.28	0.16	25	1.00	0.62	25	0.50	0.17	0.32	0.26	0.15
30	0.26	0.15	30	0.93	0.58	30	0.48	0.17	0.30	0.25	0.14
35	0.23	0.14	35	0.89	0.56	35	0.48	0.17	0.29	0.24	0.14
40	0.22	0.13	40	0.84	0.53	40	0.46	0.16	0.27	0.22	0.13
45	0.21	0.12	45	0.83	0.52	45	0.44	0.15	0.27	0.22	0.13
50	0.22	0.13	50	0.79	0.49	50	0.44	0.15	0.26	0.21	0.12
55	0.22	0.13	55	0.77	0.48	55	0.43	0.15	0.25	0.20	0.11
60	0.22	0.13	60	0.74	0.46	60	0.44	0.15	0.25	0.19	0.11
65	0.21	0.13	65	0.74	0.47	65	0.44	0.15	0.25	0.19	0.11
70	0.23	0.13	70	0.74	0.47	70	0.45	0.15	0.25	0.19	0.11
75	0.21	0.13	75	0.74	0.46	75	0.45	0.15	0.25	0.19	0.11
80	0.21	0.13	80	0.74	0.46	80	0.45	0.15	0.25	0.19	0.11
85	0.22	0.13	85	0.74	0.46	85	0.45	0.15	0.25	0.18	0.11
90	0.21	0.13	90	0.73	0.46	90	0.45	0.15	0.25	0.18	0.11
95	0.21	0.13	95	0.73	0.46	95	0.46	0.16	0.25	0.18	0.11
100	0.22	0.13	100	0.73	0.46	100	0.46	0.16	0.25	0.18	0.11
105	0.22	0.13	105	0.73	0.46	105	0.46	0.16	0.25	0.18	0.11
110	0.22	0.13	110	0.73	0.46	110	0.46	0.16	0.25	0.18	0.11
115	0.22	0.13	115	0.73	0.46	115	0.47	0.16	0.25	0.18	0.11
120	0.22	0.13	120	0.73	0.46	120	0.47	0.16	0.25	0.18	0.10

Table A.57. 50% OSA-modified Tapioca Starch (5 g L^{-1})

50% OSA Tapioca Starch											
Sample A			Sample B			Sample C			Ave. A/A_o	Std. Dev.	Std. Error
Time (min)	Abs (A)	A/A_o	Time (min)	Abs (A)	A/A_o	Time (min)	Abs (A)	A/A_o			
0	3.79	1.00	0	3.77	1.00	0	2.52	1.00	1.00	0.00	0.00
1	2.57	0.68	1	2.70	0.72	1	1.44	0.57	0.65	0.08	0.04
2	1.59	0.42	2	1.73	0.46	2	1.23	0.49	0.45	0.04	0.02
3	1.31	0.35	3	1.52	0.40	3	1.12	0.44	0.40	0.05	0.03
4	1.15	0.30	4	1.29	0.34	4	1.05	0.42	0.35	0.06	0.03
5	1.05	0.28	5	1.19	0.31	5	1.00	0.40	0.33	0.06	0.04
10	0.84	0.22	10	0.89	0.23	10	0.89	0.35	0.27	0.07	0.04
15	0.76	0.20	15	0.80	0.21	15	0.83	0.33	0.25	0.07	0.04
20	0.72	0.19	20	0.74	0.20	20	0.81	0.32	0.24	0.07	0.04
25	0.71	0.19	25	0.73	0.19	25	0.79	0.31	0.23	0.07	0.04
30	0.70	0.18	30	0.73	0.19	30	0.78	0.31	0.23	0.07	0.04
35	0.69	0.18	35	0.74	0.20	35	0.78	0.31	0.23	0.07	0.04
40	0.69	0.18	40	0.75	0.20	40	0.78	0.31	0.23	0.07	0.04
45	0.69	0.18	45	0.75	0.20	45	0.79	0.31	0.23	0.07	0.04
50	0.69	0.18	50	0.72	0.19	50	0.78	0.31	0.23	0.07	0.04
55	0.69	0.18	55	0.74	0.20	55	0.79	0.31	0.23	0.07	0.04
60	0.70	0.18	60	0.74	0.20	60	0.79	0.31	0.23	0.07	0.04
65	0.70	0.18	65	0.75	0.20	65	0.80	0.32	0.23	0.07	0.04
70	0.70	0.19	70	0.75	0.20	70	0.80	0.32	0.23	0.07	0.04
75	0.70	0.19	75	0.75	0.20	75	0.81	0.32	0.24	0.07	0.04
80	0.71	0.19	80	0.76	0.20	80	0.81	0.32	0.24	0.07	0.04
85	0.71	0.19	85	0.76	0.20	85	0.82	0.32	0.24	0.07	0.04
90	0.72	0.19	90	0.77	0.20	90	0.82	0.32	0.24	0.07	0.04
95	0.73	0.19	95	0.78	0.21	95	0.82	0.32	0.24	0.07	0.04
100	0.73	0.19	100	0.80	0.21	100	0.83	0.33	0.24	0.07	0.04
105	0.74	0.19	105	0.80	0.21	105	0.83	0.33	0.24	0.07	0.04
110	0.74	0.20	110	0.81	0.22	110	0.83	0.33	0.25	0.07	0.04
115	0.75	0.20	115	0.82	0.22	115	0.84	0.33	0.25	0.07	0.04
120	0.76	0.20	120	0.83	0.22	120	0.84	0.33	0.25	0.07	0.04

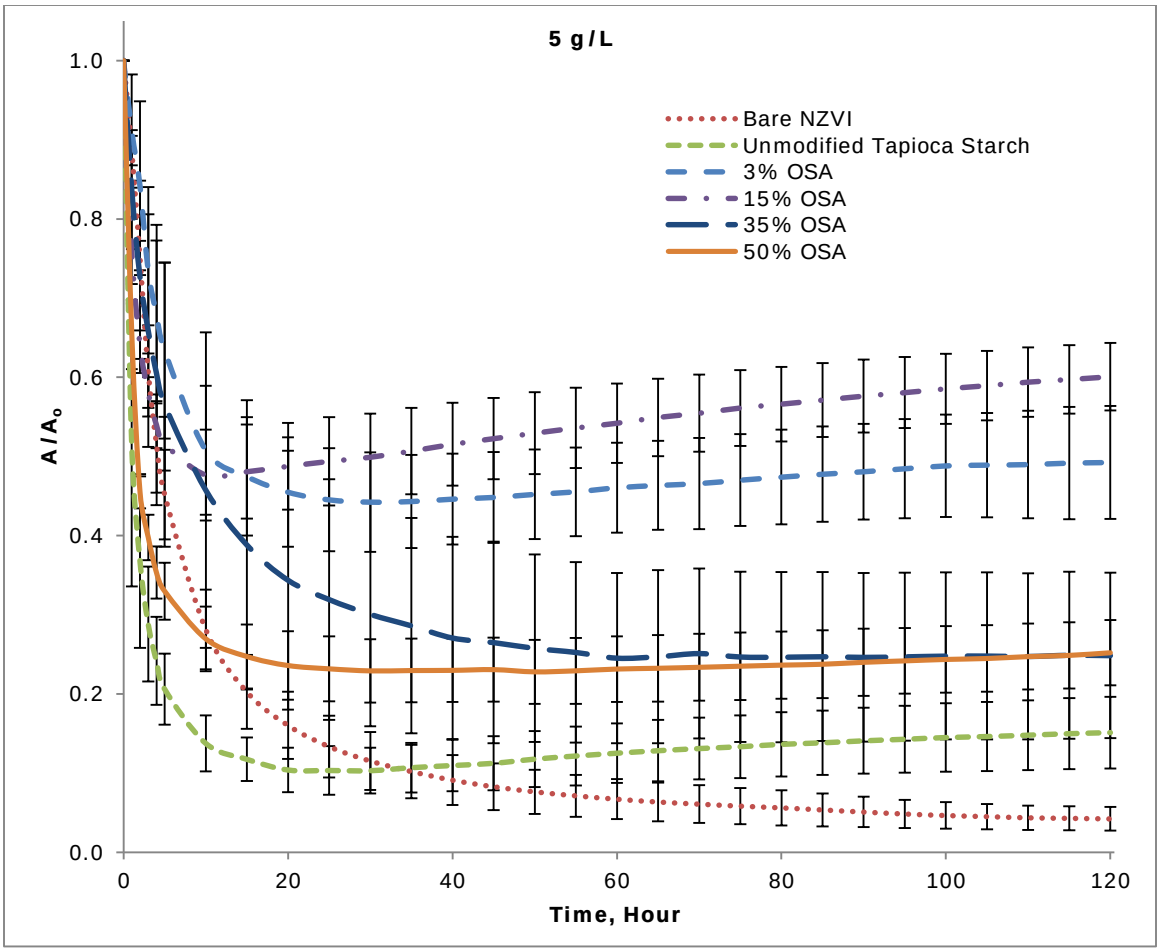


Figure A.23. Modified Tapioca Starch Sedimentation Curves (5 g L^{-1})

Table A.58. NativeTapioca Starch Sedimentation Data (10 g L^{-1})

Unmodified Tapioca Starch											
Sample A			Sample B			Sample C			Ave. A/A_o	Std. Dev.	Std. Error
Time (min)	Abs (A)	A/A_o	Time (min)	Abs (A)	A/A_o	Time (min)	Abs (A)	A/A_o			
0	3.78	1.00	0	3.78	1.00	0	3.78	1.00	1.00	0.00	0.00
1	3.78	1.00	1	3.78	1.00	1	3.44	0.91	0.97	0.05	0.03
2	2.76	0.73	2	2.74	0.73	2	2.43	0.64	0.70	0.05	0.03
3	2.41	0.64	3	2.23	0.59	3	1.80	0.48	0.57	0.08	0.05
4	2.16	0.57	4	1.85	0.49	4	1.58	0.42	0.49	0.08	0.04
5	1.98	0.52	5	1.65	0.44	5	1.40	0.37	0.44	0.08	0.04
10	1.47	0.39	10	1.29	0.34	10	1.12	0.30	0.34	0.05	0.03
15	1.32	0.35	15	1.13	0.30	15	0.98	0.26	0.30	0.05	0.03
20	1.22	0.32	20	1.07	0.28	20	0.91	0.24	0.28	0.04	0.02
25	1.16	0.31	25	1.06	0.28	25	0.88	0.23	0.27	0.04	0.02
30	1.12	0.30	30	1.05	0.28	30	0.87	0.23	0.27	0.03	0.02
35	1.08	0.28	35	1.04	0.28	35	0.87	0.23	0.26	0.03	0.02
40	1.07	0.28	40	1.03	0.27	40	0.86	0.23	0.26	0.03	0.02
45	1.04	0.28	45	1.03	0.27	45	0.87	0.23	0.26	0.02	0.01
50	1.02	0.27	50	1.02	0.27	50	0.87	0.23	0.26	0.02	0.01
55	1.00	0.26	55	1.04	0.28	55	0.88	0.23	0.26	0.02	0.01
60	1.02	0.27	60	1.03	0.27	60	0.89	0.23	0.26	0.02	0.01
65	1.01	0.27	65	1.04	0.28	65	0.89	0.23	0.26	0.02	0.01
70	1.02	0.27	70	1.04	0.27	70	0.89	0.24	0.26	0.02	0.01
75	1.03	0.27	75	1.05	0.28	75	0.91	0.24	0.26	0.02	0.01
80	1.01	0.27	80	1.06	0.28	80	0.92	0.24	0.26	0.02	0.01
85	1.01	0.27	85	1.07	0.28	85	0.93	0.24	0.27	0.02	0.01
90	1.03	0.27	90	1.08	0.28	90	0.93	0.25	0.27	0.02	0.01
95	1.03	0.27	95	1.09	0.29	95	0.95	0.25	0.27	0.02	0.01
100	1.03	0.27	100	1.09	0.29	100	0.95	0.25	0.27	0.02	0.01
105	1.04	0.28	105	1.10	0.29	105	0.97	0.26	0.27	0.02	0.01
110	1.04	0.27	110	1.11	0.29	110	0.98	0.26	0.28	0.02	0.01
115	1.04	0.28	115	1.11	0.29	115	0.99	0.26	0.28	0.02	0.01
120	1.05	0.28	120	1.12	0.30	120	0.99	0.26	0.28	0.02	0.01

Table A.59. 3% OSA-modified Tapioca Starch Sedimentation Data (10 g L^{-1})

3% OSA Tapioca Starch											
Sample A			Sample B			Sample C			Ave. A/A_o	Std. Dev.	Std. Error
Time (min)	Abs (A)	A/A_o	Time (min)	Abs (A)	A/A_o	Time (min)	Abs (A)	A/A_o			
0.00	2.28	1.00	0.00	3.76	1.00	0.00	1.61	1.00	1.00	0.00	0.00
1.00	2.23	0.98	1.00	3.76	1.00	1.00	1.55	0.97	0.98	0.02	0.01
2.00	2.20	0.97	2.00	3.24	0.86	2.00	1.52	0.94	0.92	0.06	0.03
3.00	2.16	0.95	3.00	2.79	0.74	3.00	1.49	0.93	0.87	0.11	0.07
4.00	2.13	0.93	4.00	2.47	0.66	4.00	1.45	0.90	0.83	0.15	0.09
5.00	2.08	0.91	5.00	2.30	0.61	5.00	1.41	0.88	0.80	0.16	0.09
10.00	1.80	0.79	10.00	1.93	0.51	10.00	1.23	0.76	0.69	0.15	0.09
15.00	1.66	0.73	15.00	1.77	0.47	15.00	1.01	0.63	0.61	0.13	0.07
20.00	1.54	0.68	20.00	1.71	0.45	20.00	0.90	0.56	0.56	0.11	0.06
25.00	1.51	0.66	25.00	1.68	0.45	25.00	0.83	0.51	0.54	0.11	0.06
30.00	1.48	0.65	30.00	1.66	0.44	30.00	0.77	0.48	0.52	0.11	0.06
35.00	1.46	0.64	35.00	1.66	0.44	35.00	0.74	0.46	0.52	0.11	0.06
40.00	1.45	0.64	40.00	1.65	0.44	40.00	0.73	0.46	0.51	0.11	0.06
45.00	1.49	0.65	45.00	1.65	0.44	45.00	0.73	0.45	0.51	0.12	0.07
50.00	1.46	0.64	50.00	1.66	0.44	50.00	0.72	0.45	0.51	0.11	0.07
55.00	1.49	0.66	55.00	1.66	0.44	55.00	0.72	0.45	0.52	0.12	0.07
60.00	1.50	0.66	60.00	1.66	0.44	60.00	0.72	0.45	0.52	0.12	0.07
65.00	1.50	0.66	65.00	1.67	0.44	65.00	0.72	0.45	0.52	0.12	0.07
70.00	1.51	0.66	70.00	1.68	0.45	70.00	0.72	0.45	0.52	0.12	0.07
75.00	1.52	0.67	75.00	1.70	0.45	75.00	0.72	0.45	0.52	0.13	0.07
80.00	1.53	0.67	80.00	1.70	0.45	80.00	0.73	0.45	0.52	0.13	0.07
85.00	1.54	0.68	85.00	1.71	0.45	85.00	0.73	0.45	0.53	0.13	0.07
90.00	1.55	0.68	90.00	1.72	0.46	90.00	0.73	0.46	0.53	0.13	0.07
95.00	1.57	0.69	95.00	1.73	0.46	95.00	0.73	0.46	0.53	0.13	0.08
100.00	1.57	0.69	100.00	1.74	0.46	100.00	0.74	0.46	0.54	0.13	0.08
105.00	1.58	0.69	105.00	1.75	0.46	105.00	0.74	0.46	0.54	0.13	0.08
110.00	1.60	0.70	110.00	1.76	0.47	110.00	0.75	0.47	0.54	0.14	0.08
115.00	1.61	0.71	115.00	1.77	0.47	115.00	0.76	0.47	0.55	0.14	0.08
120.00	1.63	0.72	120.00	1.77	0.47	120.00	0.76	0.47	0.55	0.14	0.08

Table A.60. 15% OSA-modified Tapioca Starch (10 g L^{-1})

15% OSA Tapioca Starch											
Sample A			Sample B			Sample C			Ave. A/A_o	Std. Dev.	Std. Error
Time (min)	Abs (A)	A/A_o	Time (min)	Abs (A)	A/A_o	Time (min)	Abs (A)	A/A_o			
0.00	3.77	1.00	0.00	3.78	1.00	0.00	3.78	1.00	1.00	0.00	0.00
1.00	3.77	1.00	1.00	3.78	1.00	1.00	2.54	0.67	0.89	0.19	0.11
2.00	3.77	1.00	2.00	2.99	0.79	2.00	1.89	0.50	0.76	0.25	0.15
3.00	3.77	1.00	3.00	2.39	0.63	3.00	1.55	0.41	0.68	0.30	0.17
4.00	3.77	1.00	4.00	2.03	0.54	4.00	1.37	0.36	0.63	0.33	0.19
5.00	3.76	1.00	5.00	1.85	0.49	5.00	1.26	0.33	0.61	0.35	0.20
10.00	2.21	0.59	10.00	1.41	0.37	10.00	1.00	0.27	0.41	0.16	0.09
15.00	1.85	0.49	15.00	1.28	0.34	15.00	0.91	0.24	0.36	0.12	0.07
20.00	1.70	0.45	20.00	1.22	0.32	20.00	0.84	0.22	0.33	0.11	0.07
25.00	1.55	0.41	25.00	1.19	0.32	25.00	0.83	0.22	0.32	0.10	0.06
30.00	1.50	0.40	30.00	1.18	0.31	30.00	0.81	0.21	0.31	0.09	0.05
35.00	1.46	0.39	35.00	1.18	0.31	35.00	0.81	0.21	0.31	0.09	0.05
40.00	1.42	0.38	40.00	1.17	0.31	40.00	0.80	0.21	0.30	0.08	0.05
45.00	1.42	0.38	45.00	1.17	0.31	45.00	0.80	0.21	0.30	0.08	0.05
50.00	1.39	0.37	50.00	1.18	0.31	50.00	0.80	0.21	0.30	0.08	0.05
55.00	1.39	0.37	55.00	1.18	0.31	55.00	0.81	0.21	0.30	0.08	0.05
60.00	1.38	0.37	60.00	1.18	0.31	60.00	0.81	0.21	0.30	0.08	0.04
65.00	1.38	0.37	65.00	1.18	0.31	65.00	0.81	0.21	0.30	0.08	0.04
70.00	1.37	0.36	70.00	1.19	0.31	70.00	0.82	0.22	0.30	0.08	0.04
75.00	1.36	0.36	75.00	1.19	0.32	75.00	0.82	0.22	0.30	0.07	0.04
80.00	1.36	0.36	80.00	1.19	0.32	80.00	0.83	0.22	0.30	0.07	0.04
85.00	1.34	0.36	85.00	1.20	0.32	85.00	0.83	0.22	0.30	0.07	0.04
90.00	1.35	0.36	90.00	1.20	0.32	90.00	0.83	0.22	0.30	0.07	0.04
95.00	1.35	0.36	95.00	1.20	0.32	95.00	0.84	0.22	0.30	0.07	0.04
100.00	1.34	0.35	100.00	1.21	0.32	100.00	0.84	0.22	0.30	0.07	0.04
105.00	1.33	0.35	105.00	1.21	0.32	105.00	0.85	0.22	0.30	0.07	0.04
110.00	1.33	0.35	110.00	1.21	0.32	110.00	0.85	0.23	0.30	0.07	0.04
115.00	1.32	0.35	115.00	1.22	0.32	115.00	0.86	0.23	0.30	0.07	0.04
120.00	1.32	0.35	120.00	1.23	0.33	120.00	0.86	0.23	0.30	0.06	0.04

Table A.61. 35% OSA-modified Tapioca Starch (10 g L^{-1})

35% OSA Tapioca Starch											
Sample A			Sample B			Sample C			Ave. A/A_o	Std. Dev.	Std. Error
Time (min)	Abs (A)	A/A_o	Time (min)	Abs (A)	A/A_o	Time (min)	Abs (A)	A/A_o			
0.00	3.77	1.00	0.00	3.78	1.00	0.00	3.78	1.00	1.00	0.00	0.00
1.00	3.77	1.00	1.00	3.78	1.00	1.00	3.78	1.00	1.00	0.00	0.00
2.00	3.77	1.00	2.00	3.31	0.88	2.00	3.78	1.00	0.96	0.07	0.04
3.00	3.77	1.00	3.00	2.86	0.76	3.00	3.78	1.00	0.92	0.14	0.08
4.00	3.40	0.90	4.00	2.68	0.71	4.00	3.78	1.00	0.87	0.15	0.09
5.00	3.25	0.86	5.00	2.57	0.68	5.00	3.62	0.96	0.83	0.14	0.08
10.00	2.81	0.74	10.00	2.25	0.60	10.00	2.95	0.78	0.71	0.10	0.06
15.00	2.72	0.72	15.00	2.12	0.56	15.00	2.78	0.74	0.67	0.10	0.06
20.00	2.70	0.71	20.00	2.06	0.55	20.00	2.70	0.72	0.66	0.10	0.06
25.00	2.67	0.71	25.00	2.04	0.54	25.00	2.64	0.70	0.65	0.09	0.05
30.00	2.66	0.70	30.00	2.03	0.54	30.00	2.59	0.69	0.64	0.09	0.05
35.00	2.66	0.70	35.00	2.02	0.53	35.00	2.54	0.67	0.64	0.09	0.05
40.00	2.65	0.70	40.00	2.02	0.53	40.00	2.53	0.67	0.64	0.09	0.05
45.00	2.66	0.70	45.00	2.01	0.53	45.00	2.54	0.67	0.64	0.09	0.05
50.00	2.66	0.71	50.00	2.01	0.53	50.00	2.52	0.67	0.64	0.09	0.05
55.00	2.67	0.71	55.00	2.02	0.54	55.00	2.53	0.67	0.64	0.09	0.05
60.00	2.68	0.71	60.00	2.02	0.54	60.00	2.53	0.67	0.64	0.09	0.05
65.00	2.68	0.71	65.00	2.03	0.54	65.00	2.53	0.67	0.64	0.09	0.05
70.00	2.69	0.71	70.00	2.04	0.54	70.00	2.53	0.67	0.64	0.09	0.05
75.00	2.70	0.72	75.00	2.05	0.54	75.00	2.53	0.67	0.64	0.09	0.05
80.00	2.71	0.72	80.00	2.05	0.54	80.00	2.54	0.67	0.64	0.09	0.05
85.00	2.72	0.72	85.00	2.06	0.55	85.00	2.54	0.67	0.65	0.09	0.05
90.00	2.74	0.73	90.00	2.07	0.55	90.00	2.55	0.67	0.65	0.09	0.05
95.00	2.75	0.73	95.00	2.07	0.55	95.00	2.54	0.67	0.65	0.09	0.05
100.00	2.76	0.73	100.00	2.08	0.55	100.00	2.56	0.68	0.65	0.09	0.05
105.00	2.77	0.73	105.00	2.09	0.55	105.00	2.56	0.68	0.65	0.09	0.05
110.00	2.78	0.74	110.00	2.09	0.55	110.00	2.56	0.68	0.66	0.09	0.05
115.00	2.79	0.74	115.00	2.10	0.56	115.00	2.57	0.68	0.66	0.09	0.05
120.00	2.80	0.74	120.00	2.11	0.56	120.00	2.56	0.68	0.66	0.09	0.05

Table A.62. 50% OSA-modified Tapioca Starch (10 g L^{-1})

50% OSA Tapioca Starch											
Sample A			Sample B			Sample C			Ave. A/A_o	Std. Dev.	Std. Error
Time (min)	Abs (A)	A/A_o	Time (min)	Abs (A)	A/A_o	Time (min)	Abs (A)	A/A_o			
0.00	1.48	1.00	0.00	1.22	1.00	0.00	1.78	1.00	1.00	0.00	0.00
1.00	0.68	0.46	1.00	0.90	0.74	1.00	1.26	0.71	0.64	0.15	0.09
2.00	0.54	0.37	2.00	0.82	0.67	2.00	1.05	0.59	0.54	0.16	0.09
3.00	0.47	0.32	3.00	0.76	0.62	3.00	0.91	0.51	0.48	0.15	0.09
4.00	0.41	0.28	4.00	0.71	0.58	4.00	0.83	0.47	0.44	0.15	0.09
5.00	0.37	0.25	5.00	0.69	0.56	5.00	0.80	0.45	0.42	0.16	0.09
10.00	0.26	0.18	10.00	0.60	0.49	10.00	0.65	0.37	0.34	0.16	0.09
15.00	0.22	0.15	15.00	0.57	0.47	15.00	0.60	0.34	0.32	0.16	0.09
20.00	0.20	0.13	20.00	0.57	0.47	20.00	0.58	0.33	0.31	0.17	0.10
25.00	0.24	0.16	25.00	0.59	0.48	25.00	0.58	0.32	0.32	0.16	0.09
30.00	0.24	0.16	30.00	0.58	0.48	30.00	0.58	0.32	0.32	0.16	0.09
35.00	0.24	0.16	35.00	0.58	0.48	35.00	0.59	0.33	0.32	0.16	0.09
40.00	0.24	0.16	40.00	0.59	0.48	40.00	0.60	0.34	0.33	0.16	0.09
45.00	0.24	0.16	45.00	0.63	0.51	45.00	0.61	0.34	0.34	0.17	0.10
50.00	0.24	0.16	50.00	0.64	0.52	50.00	0.62	0.35	0.34	0.18	0.10
55.00	0.26	0.18	55.00	0.64	0.52	55.00	0.63	0.35	0.35	0.17	0.10
60.00	0.27	0.18	60.00	0.67	0.55	60.00	0.64	0.36	0.36	0.18	0.11
65.00	0.28	0.19	65.00	0.68	0.56	65.00	0.65	0.36	0.37	0.18	0.11
70.00	0.29	0.19	70.00	0.69	0.56	70.00	0.66	0.37	0.38	0.18	0.11
75.00	0.29	0.20	75.00	0.70	0.57	75.00	0.68	0.38	0.38	0.19	0.11
80.00	0.30	0.20	80.00	0.71	0.58	80.00	0.68	0.38	0.39	0.19	0.11
85.00	0.31	0.21	85.00	0.73	0.59	85.00	0.71	0.40	0.40	0.19	0.11
90.00	0.31	0.21	90.00	0.75	0.61	90.00	0.73	0.41	0.41	0.20	0.12
95.00	0.32	0.22	95.00	0.76	0.62	95.00	0.73	0.41	0.42	0.20	0.12
100.00	0.32	0.22	100.00	0.78	0.64	100.00	0.76	0.43	0.43	0.21	0.12
105.00	0.33	0.22	105.00	0.79	0.65	105.00	0.78	0.44	0.44	0.21	0.12
110.00	0.34	0.23	110.00	0.80	0.66	110.00	0.79	0.44	0.44	0.21	0.12
115.00	0.34	0.23	115.00	0.82	0.67	115.00	0.81	0.46	0.45	0.22	0.13
120.00	0.34	0.23	120.00	0.84	0.69	120.00	0.82	0.46	0.46	0.23	0.13

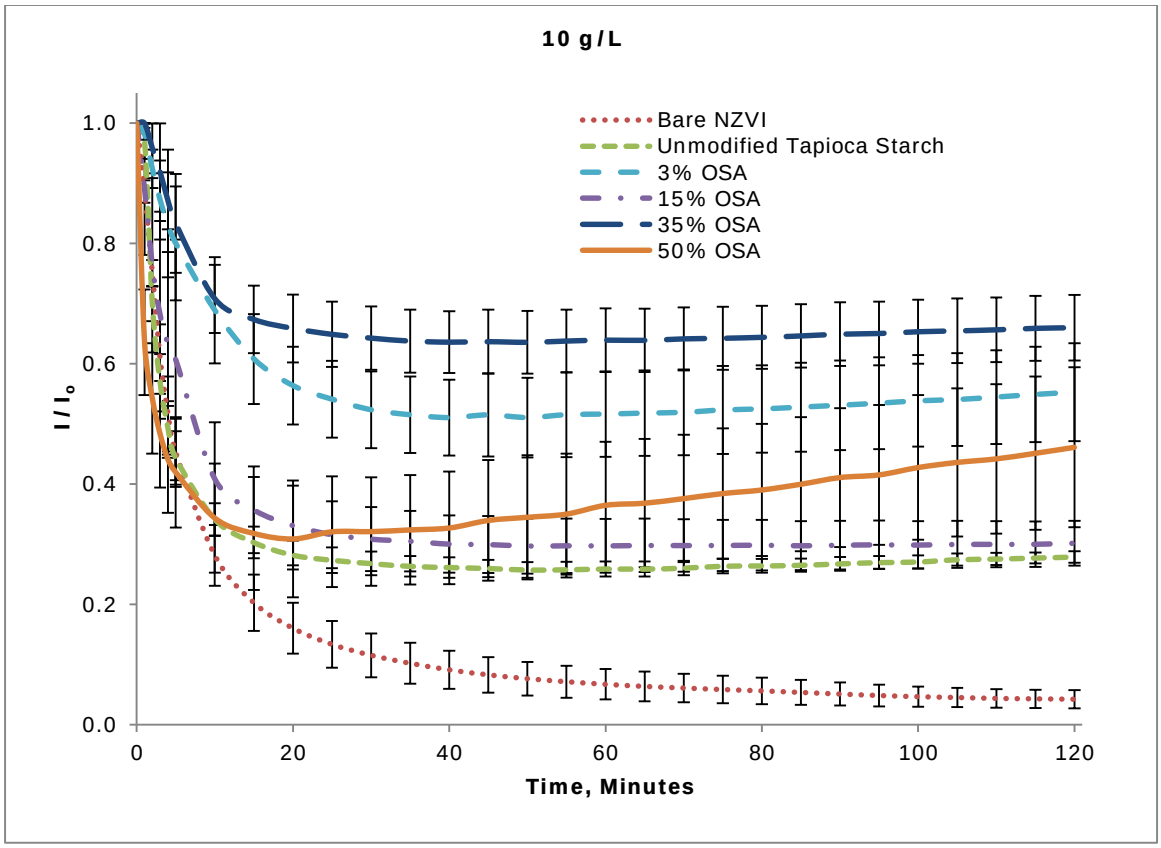


Figure A.24. Modified Tapioca Starch Sedimentation Curves (10 g L^{-1})

A.12. One-Way ANOVA for OSA-Modified Tapioca

Selection Reason:

One-way ANOVA is used to determine if there are significant differences between two or more independent groups. The independent groups in this study are: bare NZVI, NZVI coated with native tapioca, and NZVI coated with an OSA modified tapioca. A One-Way was preformed separately for each coating concentration (1 g L^{-1}, 5 g L^{-1}, and 10 g L^{-1}).

Hypothesis

H_o: There is not a significant difference between the mean particle stability of bare NZVI particles and NZVI coated with different concentrations of OSA modified tapioca starches ($x_0=x_1=x_2=x_3= x_4=x_5$).

H_a: at least one mean particle stability is different.

where:

x_0 = bare NZVI

x_1 = unmodified tapioca starch

x_2 = 3% OSA modified tapioca starch

x_3 = 15% OSA modified tapioca starch

x_4 = 35% OSA modified tapioca starch

x_5 = 50% OSA modified tapioca starch

1 g L^{-1}

Table A.63. Data used for One-Way ANOVA Analysis of OSA Tapioca Starches (1 g L^{-1})

Treatment	Sedimentation Data
Bare NZVI	Average C/C_o from Table A.5.i.a (All time periods)
NZVI coated w/ Unmodified Tapioca Starch	Average C/C_o from Table A.5.i.b (All time periods)
NZVI coated w/ 3% OSA Tapioca Starch	Average C/C_o from Table A.5.i.c (All time periods)
NZVI coated w/ 15% OSA Tapioca Starch	Average C/C_o from Table A.5.i.d (All time periods)
NZVI coated w/ 35% OSA Tapioca Starch	Average C/C_o from Table A.5.i.e (All time periods)
NZVI coated w/ 50% OSA Tapioca Starch	Average C/C_o from Table A.5.i.f (All time periods)

Table A.64. One-Way ANOVA for OSA Tapioca Starch (1 g L^{-1})

Source	DF	Adj. SS	Adj. MS	F-Value	P-Value
Treatment*	5	1.97	0.3941	11.71	0.000
Error	168	5.65	0.0337		
Total	173	7.62			

*The four levels of treatment are presented in the hypothesis section above.

Tukey's test was used after the One-Way ANOVA w. Tukey's test compares the means of the groups tested in the One-Way ANOVA and identifies which groups among the samples tested are significantly different.

Table A.65. Tukey Pairwise Comparison for OSA Tapioca Starch (1 g L^{-1})

Treatment	N	Mean	Std. Dev.	99.5% CI	Grouping**
0	29	0.2142	0.2745	(0.1173, 0.3111)	C
1	29	0.2712	0.1710	(0.1743, 0.3680)	B, C
2	29	0.2679	0.1660	(0.1710, 0.3648)	B, C
3	29	0.4851	0.1220	(0.3882, 0.5820)	A
4	29	0.1549	0.1766	(0.0580, 0.2518)	C
5	29	0.3611	0.1538	(0.2642, 0.4580)	A, B

** Means that do not share a letter are significantly different.

5 g L^{-1}

Table A.66. Data used for One-Way ANOVA Analysis of OSA Tapioca Starches (5 g L^{-1})

Treatment	Sedimentation Data
Bare NZVI	Average C/C_o from Table A.5.i.a (All time periods)
NZVI coated w/ Unmodified Tapioca Starch	Average C/C_o from Table A.5.i.g (All time periods)
NZVI coated w/ 3% OSA Tapioca Starch	Average C/C_o from Table A.5.i.h (All time periods)
NZVI coated w/ 15% OSA Tapioca Starch	Average C/C_o from Table A.5.i.i (All time periods)
NZVI coated w/ 35% OSA Tapioca Starch	Average C/C_o from Table A.5.i.j (All time periods)
NZVI coated w/ 50% OSA Tapioca Starch	Average C/C_o from Table A.5.i.k (All time periods)

Table A.67. One-Way ANOVA for OSA Tapioca Starch (5 g L^{-1})

Source	DF	Adj. SS	Adj. MS	F-Value	P-Value
Treatment*	5	3.748	0.7410	21.55	0.000
Error	168	5.843	0.0348		
Total	173	9.592			

*The four levels of treatment are presented in the hypothesis section above.

Tukey's test was used after the One-Way ANOVA w. Tukey's test compares the means of the groups tested in the One-Way ANOVA and identifies which groups among the samples tested are significantly different.

Table A.68. Tukey Pairwise Comparison for OSA Tapioca Starch (5 g L^{-1})

Treatment	N	Mean	Std. Dev.	99.5% CI	Grouping**
0	29	0.2142	0.2745	(0.1157, 0.3127)	C
1	29	0.1922	0.1792	(0.0937, 0.2907)	C
2	29	0.5380	0.1498	(0.4395, 0.6365)	A
3	29	0.5708	0.1001	(0.4723, 0.6694)	A
4	29	0.3709	0.2057	(0.2724, 0.4694)	B
5	29	0.2992	0.1627	(0.2007, 0.3977)	B, C

** Means that do not share a letter are significantly different.

10 g L^{-1}

Table A.69. Data used for One-Way ANOVA Analysis of OSA Tapioca Starches (10 g L^{-1})

Treatment	Sedimentation Data
Bare NZVI	Average C/C_o from Table A.5.i.a (All time periods)
NZVI coated w/ Unmodified Tapioca Starch	Average C/C_o from Table A.5.i.l (All time periods)
NZVI coated w/ 3% OSA Tapioca Starch	Average C/C_o from Table A.5.i.m (All time periods)
NZVI coated w/ 15% OSA Tapioca Starch	Average C/C_o from Table A.5.i.n (All time periods)
NZVI coated w/ 35% OSA Tapioca Starch	Average C/C_o from Table A.5.i.o (All time periods)
NZVI coated w/ 50% OSA Tapioca Starch	Average C/C_o from Table A.5.i.p (All time periods)

Table A.70. One-Way ANOVA for OSA Tapioca Starch (10 g L^{-1})

Source	DF	Adj. SS	Adj. MS	F-Value	P-Value
Treatment*	5	4.653	0.93066	26.21	0.000
Error	168	5.965	0.03551		
Total	173	10.618			

*The four levels of treatment are presented in the hypothesis section above.

Tukey's test was used after the One-Way ANOVA w. Tukey's test compares the means of the groups tested in the One-Way ANOVA and identifies which groups among the samples tested are significantly different.

Table A.71. Tukey Pairwise Comparison for OSA Tapioca Starch (10 g L^{-1})

Treatment	N	Mean	Std. Dev.	99.5% CI	Grouping**
0	29	0.2142	0.2745	(0.1147, 0.3138)	C
1	29	0.3596	0.2028	(0.2600, 0.4591)	B
2	29	0.6144	0.1570	(0.5149, 0.7139)	A
3	29	0.4028	0.1994	(0.3033, 0.5023)	B
4	29	0.7079	0.1198	(0.6084, 0.8074)	A
5	29	0.4189	0.1335	(0.3193, 0.5184)	B

** Means that do not share a letter are significantly different.

A.13. SEM/EDS Data

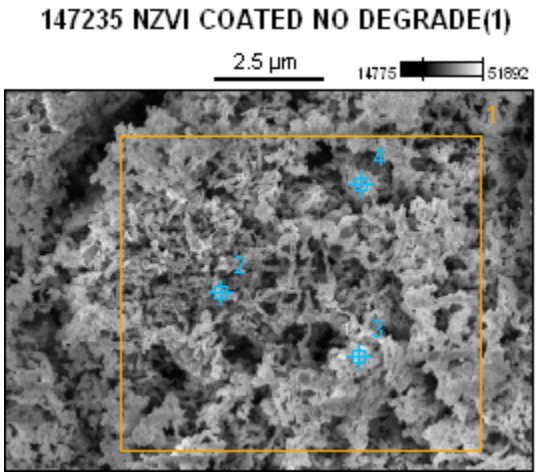
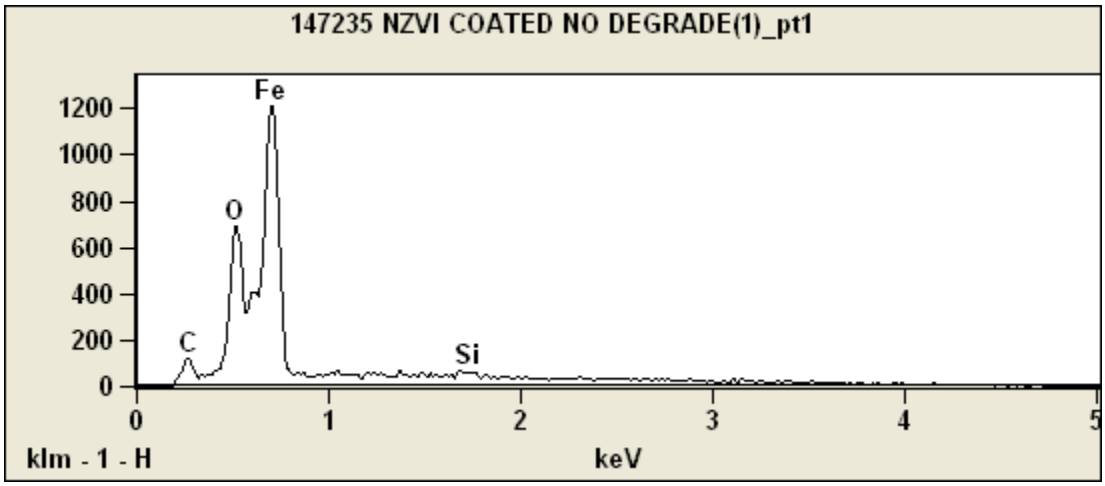


Image Name: 147235 NZVI COATED NO DEGRADE(1)

Accelerating Voltage: 5.0 kV

Magnification: 10000



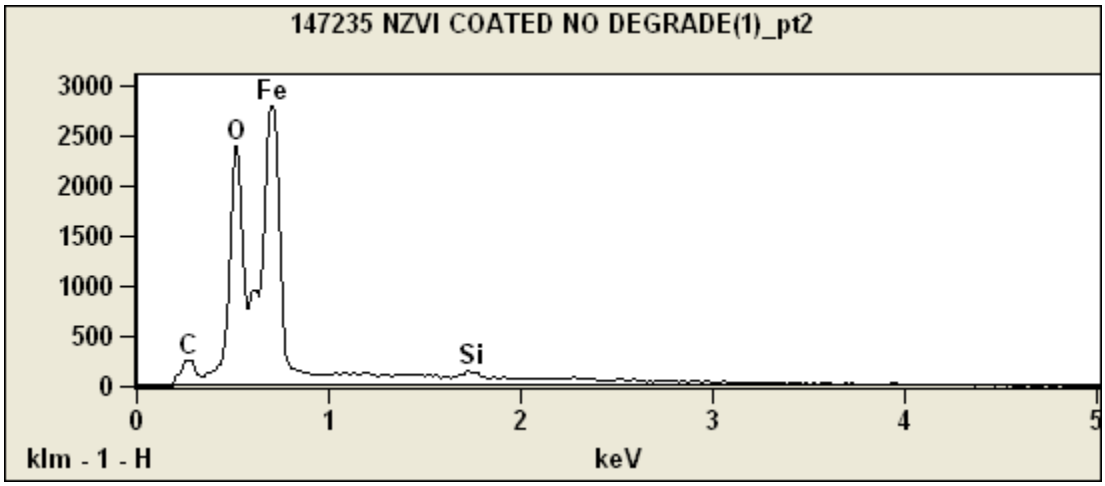
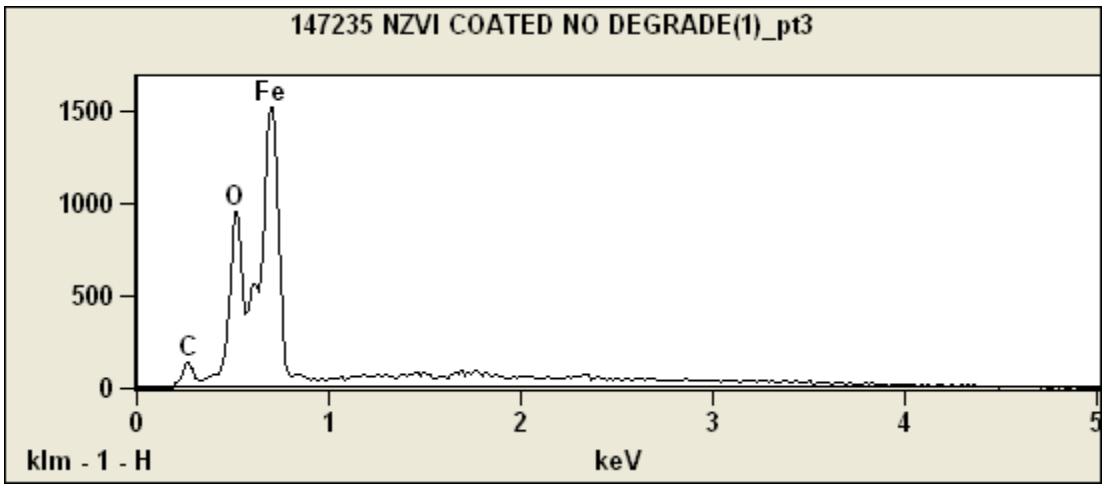


Figure A.25. Fresh CNZVI EDS Graphs



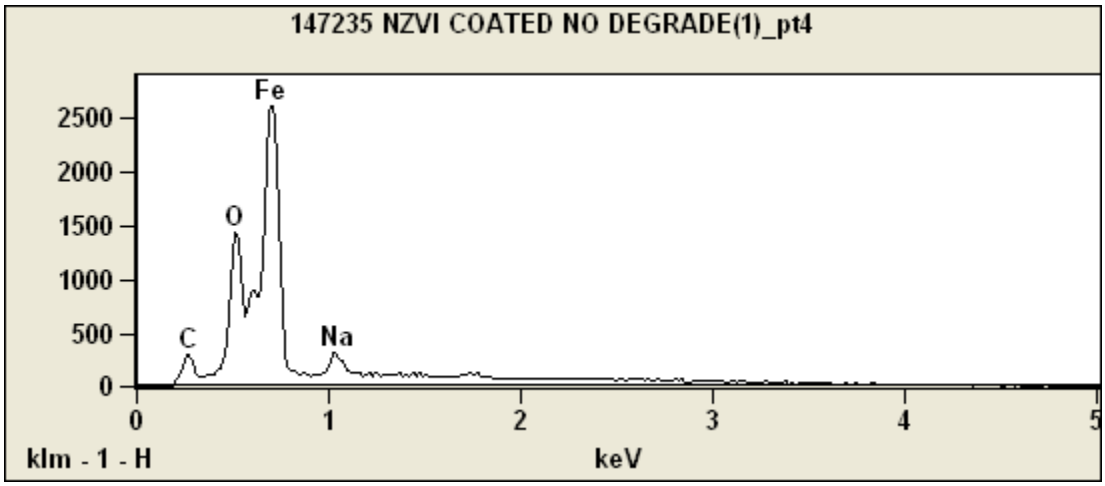


Figure A.25. Fresh CNZVI EDS Graphs (continued)

Table A.72. Fresh CNZVI EDS Weight %
Weight %

	C-K	O-K	Na-K	Si-K	Fe-L
147235 NZVI COATED NO DEGRADE(1)_pt1	2.35	9.09		0.60	87.96
147235 NZVI COATED NO DEGRADE(1)_pt2	2.04	11.95		0.83	85.18
147235 NZVI COATED NO DEGRADE(1)_pt3	1.81	8.98			89.21
147235 NZVI COATED NO DEGRADE(1)_pt4	2.56	8.23	1.91		87.30

Table A.73. Fresh CNZVI EDS Weight % Error
Weight % Error (+/- 3 Sigma)

	C-K	O-K	Na-K	Si-K	Fe-L
147235 NZVI COATED NO DEGRADE(1)_pt1	+/- 0.30	+/- 0.82		+/- 0.43	+/- 3.41
147235 NZVI COATED NO DEGRADE(1)_pt2	+/- 0.23	+/- 0.57		+/- 0.45	+/- 2.32
147235 NZVI COATED NO DEGRADE(1)_pt3	+/- 0.31	+/- 0.77			+/- 3.08
147235 NZVI COATED NO DEGRADE(1)_pt4	+/- 0.25	+/- 0.57	+/- 0.54		+/- 2.41

Table A.74. Fresh CNZVI EDS Atom %
Atom %

	C-K	O-K	Na-K	Si-K	Fe-L
147235 NZVI COATED NO DEGRADE(1)_pt1	8.28	24.07		0.91	66.74
147235 NZVI COATED NO DEGRADE(1)_pt2	6.87	30.21		1.20	61.71
147235 NZVI COATED NO DEGRADE(1)_pt3	6.52	24.31			69.17
147235 NZVI COATED NO DEGRADE(1)_pt4	8.99	21.66	3.50		65.85

Table A.75. Fresh CNZVI EDS Atom % Error
Atom % Error (+/- 3 Sigma)

	C-K	O-K	Na-K	Si-K	Fe-L
147235 NZVI COATED NO DEGRADE(1)_pt1	+/- 1.07	+/- 2.17		+/- 0.65	+/- 2.59
147235 NZVI COATED NO DEGRADE(1)_pt2	+/- 0.77	+/- 1.44		+/- 0.66	+/- 1.68
147235 NZVI COATED NO DEGRADE(1)_pt3	+/- 1.11	+/- 2.08			+/- 2.39
147235 NZVI COATED NO DEGRADE(1)_pt4	+/- 0.88	+/- 1.51	+/- 0.99		+/- 1.82

Particle Size Distribution

The particle size distribution was determined by measuring the diameters of 200 CNZVI particles.

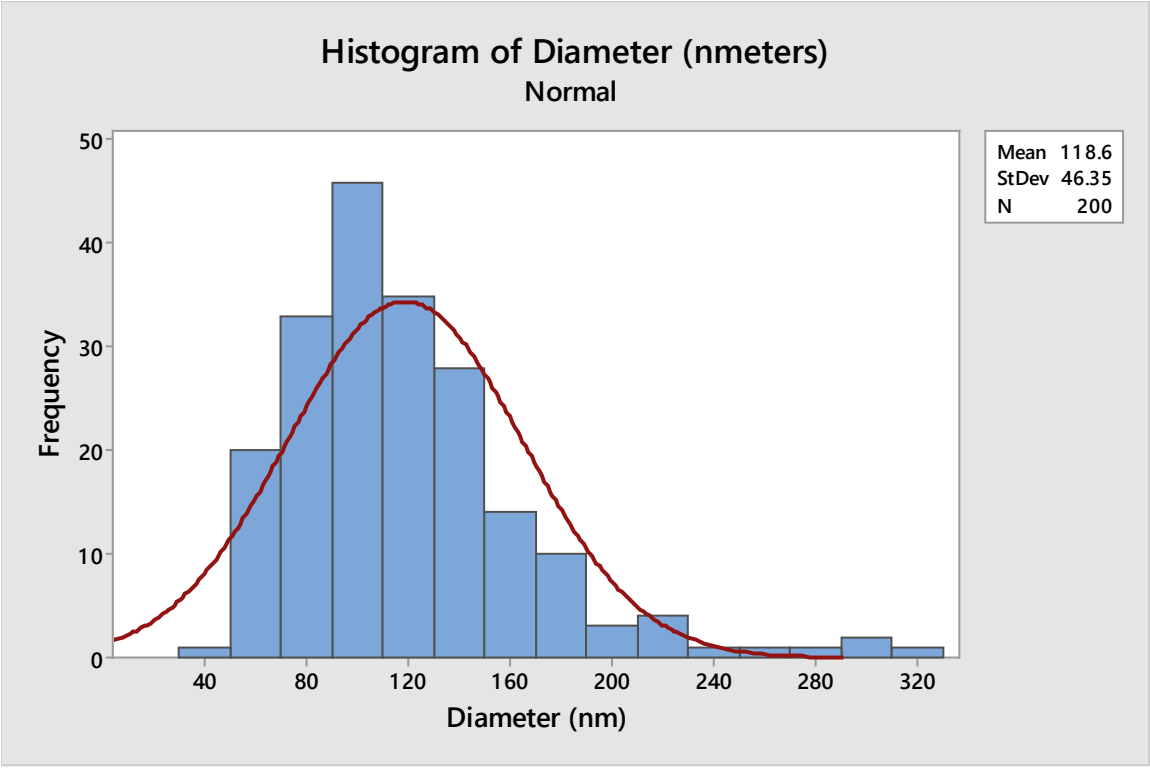


Figure A.26. Fresh CNZVI Particle Size Histogram

Particle size range: 47.5-325 nm

APPENDIX B. SUPPORTING DATA FOR CHAPTER 3

B.1. Nitrate Reduction Studies

Table B.1. Blank Nitrate Reduction Data (20 mg L^{-1})

Blank									
	Sample A			Sample B			Sample C		
Time (hr)	pH	NO_3^--N ppm	C/C_o	pH	NO_3^--N ppm	C/C_o	pH	NO_3^--N ppm	C/C_o
0	6.88	28.92	1.00	6.89	28.88	1.00	7.50	28.92	1.00
2	7.59	28.08	0.97	6.59	28.44	0.98	7.67	28.44	0.98
4	6.86	27.38	0.95	6.52	28.08	0.97	6.68	26.93	0.93
6	6.50	26.15	0.90	6.31	26.93	0.93	7.46	28.92	1.00
12	6.00	26.59	0.92	6.00	26.59	0.92	6.31	26.26	0.91

Table B.2. Blank Nitrate Statistical Data (20 mg L^{-1})

Blank			
	NO_3^--N		
Time (hrs)	Ave C/C_o	Std. Dev.	Std. Error
0	1.00	0.00	0.00
2	0.98	0.01	0.00
4	0.96	0.02	0.01
6	0.95	0.05	0.03
12	0.92	0.01	0.00

Table B.3. OSA-modified Tapioca Starch Nitrate Reduction Data (20 mg L^{-1})

OSA-modified Tapioca Starch									
	Sample A			Sample B			Sample C		
Time (hr)	pH	NO_3^--N ppm	C/C_o	pH	NO_3^--N ppm	C/C_o	pH	NO_3^--N ppm	C/C_o
0	7.47	20.42	1.00	7.48	20.53	1.00	7.45	20.36	1.00
2	5.81	19.80	0.97	5.66	19.88	0.97	5.57	19.63	0.96
4	5.46	20.05	0.98	5.31	19.88	0.97	5.44	19.80	0.97
6	5.35	19.19	0.94	5.18	19.19	0.93	5.24	20.06	0.99
12	6.04	19.63	0.96	5.56	19.05	0.93	5.91	19.55	0.96

Table B.4. OSA-modified Tapioca Starch Nitrate Statistical Data (20 mg L^{-1})

OSA-modified Tapioca Starch			
	NO_3^--N		
Time (hrs)	Ave C/C_o	Std. Dev.	Std. Error
0	1.00	0.00	0.00
2	0.97	0.00	0.00
4	0.97	0.01	0.00
6	0.95	0.03	0.02
12	0.95	0.02	0.01

Table B.5. CNZVI Nitrate Reduction Data (20 mg L^{-1})

CNZVI									
	Sample A			Sample B				Sample C	
Time (hrs)	pH	NO_3^--N ppm	C/C_o	pH	NO_3^--N ppm	C/C_o	pH	NO_3^--N ppm	C/C_o
0	7.84	19.94	1.00	6.88	19.96	1.00	7.85	19.94	1.00
0.5	9.32	12.86	0.65	9.22	12.92	0.65	9.15	12.86	0.64
1	9.57	10.10	0.51	9.47	13.41	0.67	9.56	11.45	0.57
2	9.48	11.99	0.60	9.99	10.53	0.53	10.28	11.35	0.57
4	10.25	9.23	0.46	9.81	10.75	0.54	10.14	10.02	0.50
6	9.94	7.44	0.37	10.10	7.41	0.37	10.14	6.87	0.34
12	10.02	6.52	0.33	10.02	5.23	0.26	9.95	5.68	0.28

Table B.6. CNZVI Nitrate Statistical Data (20 mg L^{-1})

CNZVI			
	NO_3^--N		
Time (hrs)	Ave C/C_o	Std. Dev.	Std. Error
0	1.00	0.00	0.00
0.5	0.65	0.00	0.00
1	0.58	0.08	0.05
2	0.57	0.04	0.02
4	0.50	0.04	0.02
6	0.36	0.02	0.01
12	0.29	0.03	0.02

Table B.7. NZVI Nitrate Reduction Data (20 mg L^{-1})

NZVI									
	Sample A			Sample B			Sample C		
Time (hrs)	pH	NO_3^--N ppm	C/C_o	pH	NO_3^--N ppm	C/C_o	pH	NO_3^--N ppm	C/C_o
0	7.67	17.09	1.00	7.60	17.98	1.00	7.78	17.45	1.00
0.5	9.34	13.87	0.81	9.30	14.32	0.80	9.28	14.72	0.84
1	9.40	11.91	0.70	9.31	11.46	0.64	9.66	11.06	0.63
2	9.69	10.52	0.62	9.70	9.00	0.50	9.78	8.56	0.49
4	9.65	5.92	0.35	9.66	5.38	0.30	9.64	5.74	0.33
6	9.70	4.62	0.27	9.64	4.58	0.25	9.70	3.91	0.22
12	9.62	0.24	0.01	9.66	0.20	0.01	9.69	0.11	0.01

Table B.8. NZVI Nitrate Statistical Data (20 mg L^{-1})

NZVI			
	NO_3^--N		
Time (hrs)	Ave C/C_o	Std. Dev.	Std. Error
0	1.00	0.00	0.00
0.5	0.82	0.02	0.01
1	0.66	0.04	0.02
2	0.54	0.07	0.04
4	0.32	0.02	0.01
6	0.25	0.02	0.01
12	0.01	0.00	0.00

Table B.9. Blank Nitrate Reduction Data (40 mg L^{-1})

Blank									
	Sample A			Sample B			Sample C		
Time (hrs)	pH	NO_3^--N ppm	C/C_o	pH	NO_3^--N ppm	C/C_o	pH	NO_3^--N ppm	C/C_o
0	6.25	40.30	1.00	6.25	45.60	1.00	6.25	45.63	1.00
2	6.31	40.22	1.00	6.29	44.23	0.97	8.10	45.63	1.00
4	8.43	35.46	0.88	8.23	43.77	0.96	8.25	43.19	0.95
6	6.25	39.00	0.97	6.19	43.77	0.96	7.32	42.90	0.94
12	6.46	35.06	0.87	6.34	43.32	0.95	6.55	40.61	0.89

Table B.10. Blank Nitrate Statistical Data (40 mg L^{-1})

Blank			
	NO_3^--N		
Time (hrs)	Ave C/C_o	Std. Dev.	Std. Error
0	1.00	0.00	0.00
2	0.98	0.02	0.01
4	0.93	0.04	0.02
6	1.00	0.01	0.01
12	0.91	0.04	0.02

Table B.11. OSA-modified Tapioca Starch Nitrate Reduction Data (40 mg L^{-1})

OSA-modified Tapioca Starch									
	Sample A			Sample B			Sample C		
Time (hrs)	pH	NO_3^--N ppm	C/C_o	pH	NO_3^--N ppm	C/C_o	pH	NO_3^--N ppm	C/C_o
0	6.09	40.71	1.00	6.09	40.64	1.00	6.09	40.65	1.00
2	6.12	39.79	0.98	5.47	39.12	0.96	5.88	39.62	0.97
4	5.26	39.62	0.97	5.32	39.28	0.97	5.33	39.62	0.97
6	5.54	40.11	0.99	5.40	39.16	0.96	5.44	39.79	0.98
12	5.50	37.00	0.91	5.43	37.32	0.92	5.57	36.53	0.90

Table B.12. OSA-modified Tapioca Starch Nitrate Statistical Data (40 mg L^{-1})

OSA-modified Tapioca Starch			
	NO_3^--N		
Time (hrs)	Ave C/C_o	Std. Dev.	Std. Error
0	1.00	0.00	0.00
2	0.97	0.01	0.00
4	0.97	0.00	0.00
6	0.98	0.01	0.01
12	0.91	0.01	0.00

Table B.13. CNZVI Nitrate Reduction Data (40 mg L^{-1})

CNZVI									
	Sample A			Sample B			Sample C		
Time (hrs)	pH	NO_3^--N ppm	C/C_o	pH	NO_3^--N ppm	C/C_o	pH	NO_3^--N ppm	C/C_o
0	7.85	37.88	1.00	7.84	37.85	1.00	7.84	38.00	1.00
0.5	9.04	36.42	0.96	9.01	35.46	0.94	9.17	36.14	0.95
1	9.41	34.25	0.90	9.71	29.94	0.79	9.88	30.40	0.80
2	9.78	24.54	0.65	9.71	25.06	0.66	9.80	20.51	0.54
4	10.05	22.51	0.59	9.97	23.40	0.62	9.99	20.93	0.55
6	9.80	23.00	0.61	9.93	17.41	0.46	10.08	16.47	0.43
12	10.11	12.86	0.34	10.16	11.02	0.29	10.13	11.16	0.29

Table B.14. CNZVI Nitrate Statistical Data (40 mg L^{-1})

CNZVI			
	NO_3^--N		
Time (hrs)	Ave C/C_o	Std. Dev.	Std. Error
0	1.00	0.00	0.00
0.5	0.94	0.01	0.00
1	0.82	0.05	0.03
2	0.61	0.06	0.04
4	0.58	0.03	0.02
6	0.49	0.08	0.05
12	0.31	0.02	0.01

Table B.15. NZVI Nitrate Reduction Data (40 mg L^{-1})

NZVI									
	Sample A			Sample B			Sample C		
Time (hrs)	pH	NO_3^--N ppm	C/C_o	pH	NO_3^--N ppm	C/C_o	pH	NO_3^--N ppm	C/C_o
0	6.45	40.91	1.00	6.45	40.05	1.00	6.45	41.88	1.00
0.5	9.57	32.58	0.80	9.67	28.71	0.72	9.58	31.89	0.76
1	9.48	27.11	0.66	9.80	29.54	0.74	9.62	31.17	0.74
0	N/A	29.37	1.00	N/A	30.43	1.00	N/A	28.41	1.00
2	9.68	19.17	0.65	9.75	20.30	0.67	9.72	20.41	0.72
4	9.68	11.81	0.40	9.67	15.08	0.50	9.63	14.72	0.52
0	N/A	40.41	1.00	N/A	41.71	1.00	N/A	40.36	1.00
6	9.98	17.04	0.42	9.89	14.83	0.36	9.90	18.98	0.47
0	N/A	30.04	1.00	N/A	24.98	1.00	N/A	25.09	1.00
12	10.00	7.50	0.25	9.91	8.58	0.34	10.09	7.91	0.32

Table B.16. NZVI Nitrate Statistical Data (40 mg L^{-1})

NZVI			
	NO_3^--N		
Time (hrs)	Ave C/C_o	Std. Dev.	Std. Error
0	1.00	0.00	0.00
0.5	0.76	0.04	0.02
1	0.71	0.05	0.03
2	0.68	0.03	0.02
4	0.47	0.06	0.04
6	0.42	0.06	0.03
12	0.30	0.05	0.03

Table B.17. Blank Nitrate Reduction Data (60 mg L^{-1})

Blank									
	Sample A			Sample B			Sample C		
Time (hrs)	pH	NO_3^--N ppm	C/C_o	pH	NO_3^--N ppm	C/C_o	pH	NO_3^--N ppm	C/C_o
0	7.50	63.58	1.00	7.50	63.58	1.00	7.50	63.85	1.00
2	7.37	61.74	0.97	7.24	63.58	1.00	7.24	63.84	1.00
4	8.90	60.97	0.96	8.00	62.52	0.98	7.18	63.31	0.99
6	8.98	58.71	0.92	8.31	63.84	1.00	7.14	63.31	0.99
12	6.68	59.23	0.93	6.40	58.08	0.91	6.45	59.23	0.93

Table B.18. Blank Nitrate Statistical Data (60 mg L^{-1})

Blank			
	NO_3^--N		
Time (hrs)	Ave C/C_o	Std. Dev.	Std. Error
0	1.00	0.00	0.00
2	1.00	0.02	0.01
4	0.98	0.02	0.01
6	0.98	0.05	0.03
12	0.93	0.01	0.01

Table B.19. OSA-modified Tapioca Starch Reduction Degradation Data (60 mg L^{-1})

OSA-modified Tapioca Starch									
	Sample A			Sample B			Sample C		
Time (hrs)	pH	NO_3^--N ppm	C/C_o	pH	NO_3^--N ppm	C/C_o	pH	NO_3^--N ppm	C/C_o
0	6.48	61.39	1.00	6.48	61.41	1.00	6.50	61.38	1.00
2	5.27	59.52	0.97	5.35	59.26	0.96	5.36	59.52	0.97
4	6.17	59.17	0.96	6.21	59.40	0.97	6.18	59.40	0.97
6	6.53	59.48	0.97	6.94	59.73	0.97	9.69	59.48	0.97
12	5.42	56.54	0.92	5.59	59.26	0.96	5.49	60.29	0.98

Table B.20. OSA-modified Tapioca Starch Nitrate Statistical Data (60 mg L^{-1})

OSA-modified Tapioca Starch			
	NO_3^--N		
Time (hrs)	Ave C/C_o	Std. Dev.	Std. Error
0	1.00	0.00	0.00
2	0.97	0.00	0.00
4	0.97	0.00	0.00
6	0.97	0.00	0.00
12	0.96	0.03	0.02

Table B.21. CNZVI Nitrate Reduction Data (60 mg L^{-1})

CNZVI									
	Sample A			Sample B			Sample C		
Time (hrs)	pH	NO_3^--N ppm	C/C_o	pH	NO_3^--N ppm	C/C_o	pH	NO_3^--N ppm	C/C_o
0	7.85	62.32	1.00	7.85	62.32	1.00	7.86	62.32	1.00
0.5	9.17	45.85	0.74	9.54	45.66	0.73	9.41	46.04	0.74
1	9.38	46.05	0.74	9.36	46.77	0.75	9.78	45.00	0.72
2	9.71	43.98	0.71	9.65	46.24	0.74	9.74	42.72	0.69
4	10.02	41.89	0.67	9.95	44.29	0.71	10.07	43.72	0.70
6	10.41	35.78	0.57	10.28	38.71	0.62	10.43	38.71	0.62
12	10.09	27.12	0.44	9.97	31.51	0.51	10.20	26.56	0.43

Table B.22. CNZVI Nitrate Statistical Data (60 mg L^{-1})

CNZVI			
	NO_3^--N		
Time (hrs)	Ave C/C_o	Std. Dev.	Std. Error
0	1.00	0.00	0.00
0.5	0.74	0.00	0.00
1	0.74	0.01	0.01
2	0.71	0.03	0.02
4	0.69	0.02	0.01
6	0.61	0.03	0.02
12	0.46	0.04	0.03

Table B.23. NZVI Nitrate Reduction Data (60 mg L^{-1})

NZVI									
	Sample A			Sample B			Sample C		
Time (hrs)	pH	NO_3^--N ppm	C/C_o	pH	NO_3^--N ppm	C/C_o	pH	NO_3^--N ppm	C/C_o
0	6.31	66.38	1.00	6.33	69.65	1.00	6.31	68.87	1.00
0.5	9.64	67.05	1.01	9.63	60.80	0.87	9.34	71.03	1.03
1	9.77	58.53	0.88	9.86	63.06	0.91	9.37	55.21	0.80
2	9.97	54.38	0.82	10.05	53.05	0.76	9.37	57.09	0.83
4	10.25	54.38	0.82	10.20	53.05	0.76	9.66	57.09	0.83
0	N/A	80.10	1.00	N/A	87.35	1.00	N/A	78.05	1.00
6	10.02	52.33	0.65	10.12	44.76	0.51	9.92	57.48	0.74
12	10.20	19.59	0.24	10.18	43.48	0.50	10.20	43.04	0.55

Table B.24. NZVI Nitrate Statistical Data (60 mg L^{-1})

NZVI			
	NO_3^--N		
Time (hrs)	Ave C/C_o	Std. Dev.	Std. Error
0	0.00	0.00	1.00
0.5	0.00	0.00	0.97
1	0.01	0.01	0.86
2	0.03	0.02	0.80
4	0.02	0.01	0.80
6	0.03	0.02	0.63
12	0.04	0.03	0.43

B.2. One-Way ANOVA for Nitrate Reduction

Selection Reason:

One-way ANOVA is used to determine if there are significant differences between two or more independent groups. The independent groups in this study are: bare NZVI, and NZVI coated 35% OSA modified tapioca. A One-Way was preformed separately for each nitrate concentration (20 g L^{-1}, 40 g L^{-1}, and 60 g L^{-1}).

Hypothesis:

H_o: There is not a significant difference in nitrate degradation between bare NZVI particles and NZVI coated with 35%-OSA tapioca starch ($x_0 = x_1$).

H_a: there is a significant difference between nitrate degradation.

X_0 = bare NZVI

X_1 = NZVI coated with 35%-OSA tapioca starch

$\alpha = 0.05$

20 mg L^{-1}

Table B.25. Data used for One-Way ANOVA Analysis of Nitrate Reduction (20 mg L^{-1})

Treatment	C/C_o @ 12 hours
Bare NZVI	0.01, 0.01, 0.01
Coated NZVI	0.33, 0.26, 0.28

Table B.26. One-Way ANOVA for 20 mg L^{-1} Nitrate Reduction (NZVI vs. CNZVI)

Source	DF	Adj. SS	Adj. MS	F-Value	P-Value
Treatment*	1	0.118165	0.118165	0.118165 214.26	0.000
Error	4	0.002206	0.000551		
Total	5	.120371			

*The four levels of treatment are presented in the hypothesis section above.

Tukey's test was used after the One-Way ANOVA w. Tukey's test compares the means of the groups tested in the One-Way ANOVA and identifies which groups among the samples tested are significantly different.

Table B.27. Tukey Pairwise Comparison for 20 mg L^{-1} Reduction (NZVI vs. CNZVI)

Treatment	N	Mean	Std. Dev	99.5% CI	Grouping**
0	3	0.01060	0.00401	(-0.06529, 0.08650)	A
1	3	0.2913	0.0330	(0.2154, 0.3672)	B

** Means that do not share a letter are significantly different.

40 ppm

Table B.28. Data used for One-Way ANOVA Analysis of Nitrate Reduction (40 mg L^{-1})

Treatment	C/C_o @ 12 hours
Bare NZVI	.249, .343, .315
Coated NZVI	.33, .291, .293

Table B.29 One-Way ANOVA for 40 mg L^{-1} Nitrate Reduction (NZVI vs. CNZVI)

Source	DF	Adj. SS	Adj. MS	F-Value	P-Value
Treatment*	1	0.000009	0.000009	0.01	0.939
Error	4	0.005614	0.001403		
Total	8	0.005623			

*The four levels of treatment are presented in the hypothesis section above.

Tukey's test was used after the One-Way ANOVA w. Tukey's test compares the means of the groups tested in the One-Way ANOVA and identifies which groups among the samples tested are significantly different.

Table B.30. Tukey Pairwise Comparison for 40 mg L^{-1} Reduction (NZVI vs. CNZVI)

Treatment	N	Mean	Std. Dev	99.5% CI	Grouping**
0	3	0.3028	0.0481	(0.1817, 0.4239)	A
1	3	0.3053	0.0221	(0.1842, 0.4263)	A

** Means that do not share a letter are significantly different.

60 ppm

Table B.31. Data used for One-Way ANOVA Analysis of Nitrate Reduction (60 mg L^{-1})

Treatment	C/C_o @ 12 hours
Bare NZVI	.224, .497, .551
Coated NZVI	.435, .506, .426

Table B.32. One-Way ANOVA for 60 mg L^{-1} Nitrate Reduction (NZVI vs. CNZVI)

Source	DF	Adj. SS	Adj. MS	F-Value	P-Value
Treatment*	1	0.000895	0.000895	0.06	0.815
Error	4	0.057524	0.014381		
Total	5	0.058419			

*The four levels of treatment are presented in the hypothesis section above.

Tukey's test was used after the One-Way ANOVA w. Tukey's test compares the means of the groups tested in the One-Way ANOVA and identifies which groups among the samples tested are significantly different.

Table B.33. One-Way ANOVA for 60 mg L^{-1} Nitrate Reduction (NZVI vs. CNZVI)

Treatment	N	Mean	Std. Dev	99.5% CI	Grouping**
0	21	0.4313	0.1639	(0.0437, 0.8188)	A
1	21	0.4557	0.0435	(0.0681, 0.8432)	A

** Means that do not share a letter are significantly different.

B.3. Nitrate Degradation Kinetics

Table B.34. NZVI Zero Order Reaction Data (20 mg L^{-1})

	Sample A	Sample B	Sample C	Ave. C
Time (hrs)				
0	1.00	1.00	1.00	1.00
0.5	0.81	0.80	0.84	0.82
1	0.70	0.64	0.63	0.66
2	0.62	0.50	0.49	0.54
4	0.35	0.30	0.33	0.32
6	0.27	0.25	0.22	0.25
12	0.01	0.01	0.01	0.01

Table B.35. NZVI 1st Order Reaction Data (20 mg L^{-1})

	Sample A	Sample B	Sample C	ln(Ave C)
Time (hrs)				
0	1.00	1.00	1.00	0.00
0.5	0.81	0.80	0.84	-0.20
1	0.70	0.64	0.63	-0.42
2	0.62	0.50	0.49	-0.62
4	0.35	0.30	0.33	-1.12
6	0.27	0.25	0.22	-1.39
12	0.01	0.01	0.01	-4.55

Table B.36. NZVI 2nd Order Reaction Data (20 mg L^{-1})

	Sample A	Sample B	Sample C	1/(Ave C)
Time (hrs)				
0	1.00	1.00	1.00	1.00
0.5	0.81	0.80	0.84	1.22
1	0.70	0.64	0.63	1.52
2	0.62	0.50	0.49	1.87
4	0.35	0.30	0.33	3.08
6	0.27	0.25	0.22	4.00
12	0.01	0.01	0.01	94.33

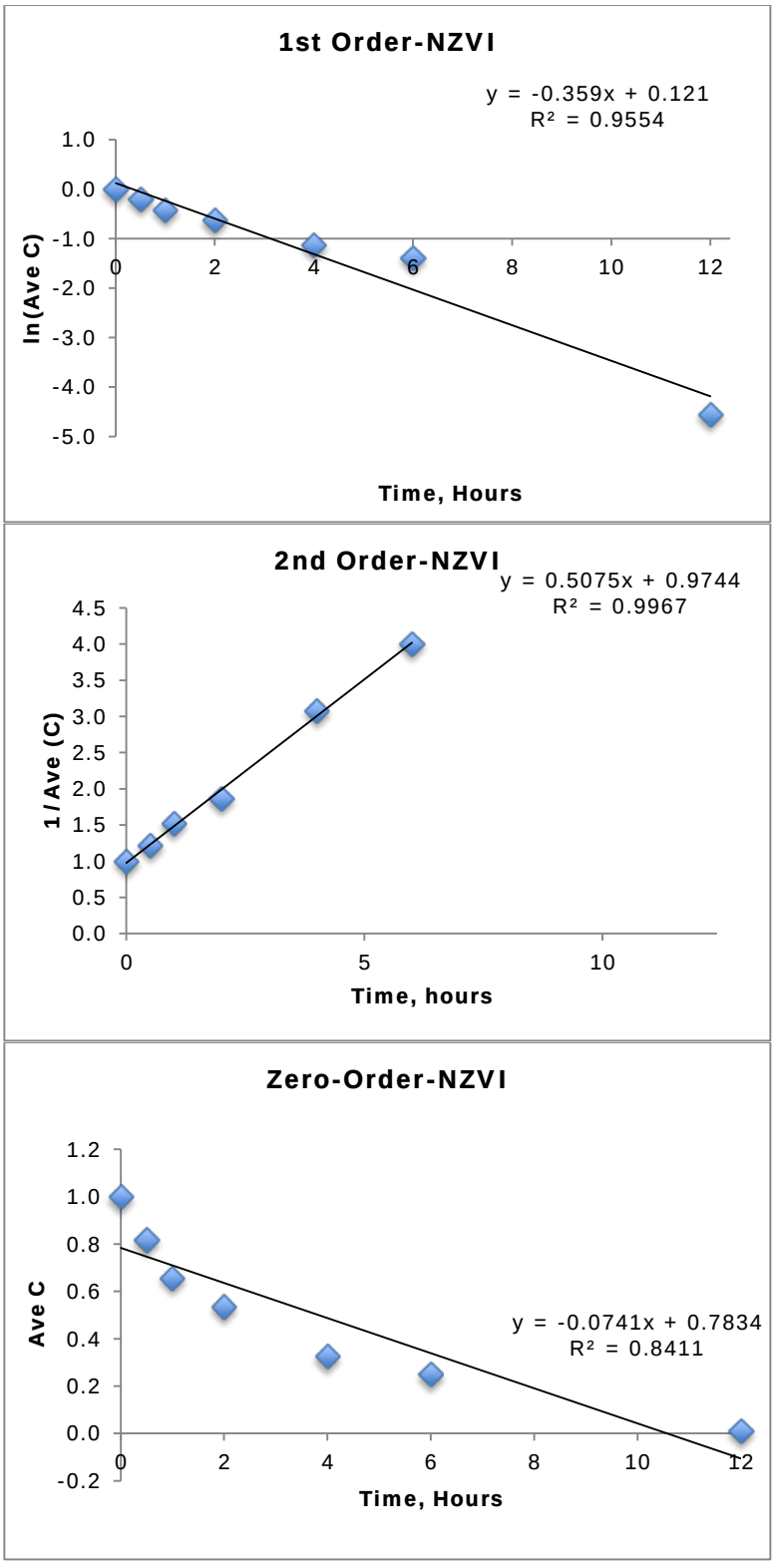


Figure B.1. Reaction Kinetic Graphs for Bare NZVI (20 mg L^{-1})

Table B.37. CNZVI Zero Order Reaction Data (20 mg L^{-1})

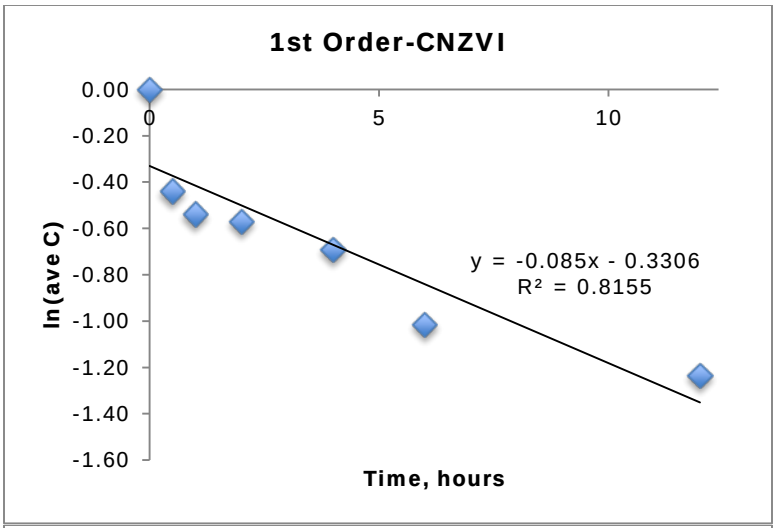
	Sample A	Sample B	Sample C	Ave. C
Time (hrs)				
0	1.00	1.00	1.00	1.00
0.5	0.64	0.65	0.64	0.65
1	0.51	0.67	0.57	0.58
2	0.60	0.53	0.57	0.57
4	0.46	0.54	0.50	0.50
6	0.37	0.37	0.34	0.36
12	0.33	0.26	0.28	0.29

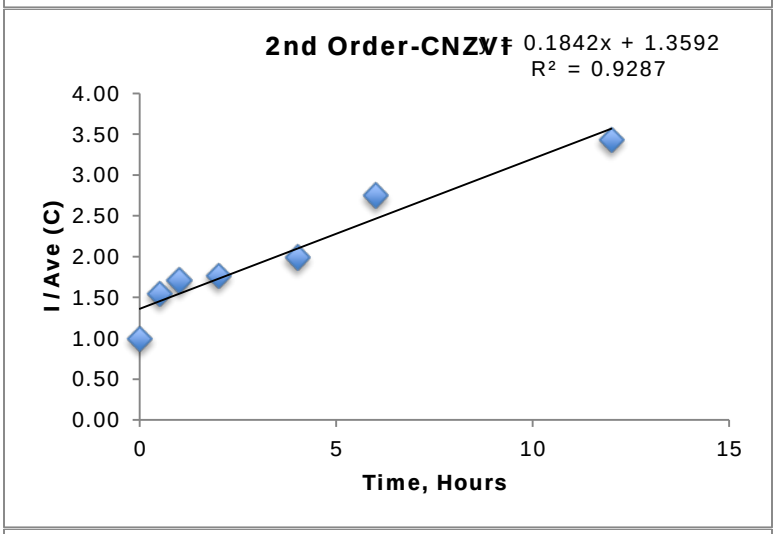
Table B.38. CNZVI 1st Order Reaction Data (20 mg L^{-1})

	Sample A	Sample B	Sample C	ln(Ave C)
Time (hrs)				
0	1.00	1.00	1.00	0.00
0.5	0.64	0.65	0.84	-0.44
1	0.51	0.67	0.63	-0.54
2	0.60	0.53	0.49	-0.57
4	0.46	0.54	0.33	-0.69
6	0.37	0.37	0.22	-1.01
12	0.33	0.26	0.01	-1.23

Table B.39. CNZVI 2nd Order Reaction Data (20 mg L^{-1})

	Sample A	Sample B	Sample C	1/(Ave C)
Time (hrs)				
0	1.00	1.00	1.00	1.00
0.5	0.64	0.65	0.84	1.55
1	0.51	0.67	0.63	1.71
2	0.60	0.53	0.49	1.77
4	0.46	0.54	0.33	1.99
6	0.37	0.37	0.22	2.76
12	0.33	0.26	0.01	3.43





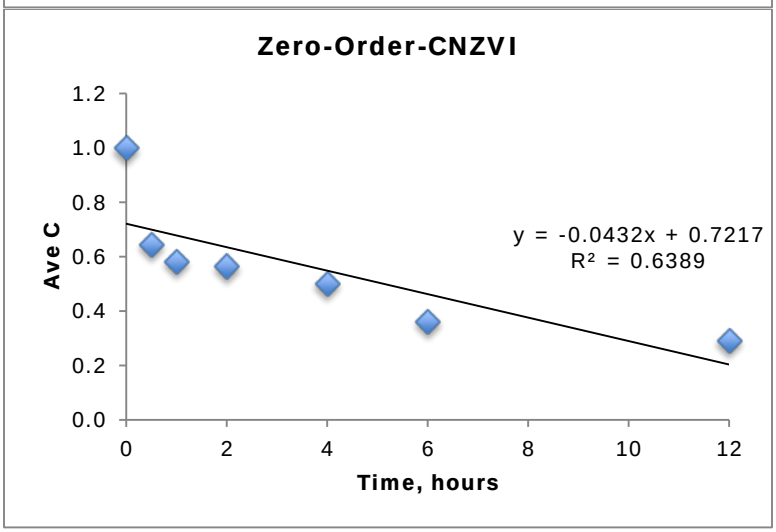


Figure B.2. Reaction Kinetic Graphs for CNZVI (20 mg L^{-1})

Table B.40. NZVI Zero Order Reaction Data (40 mg L^{-1})

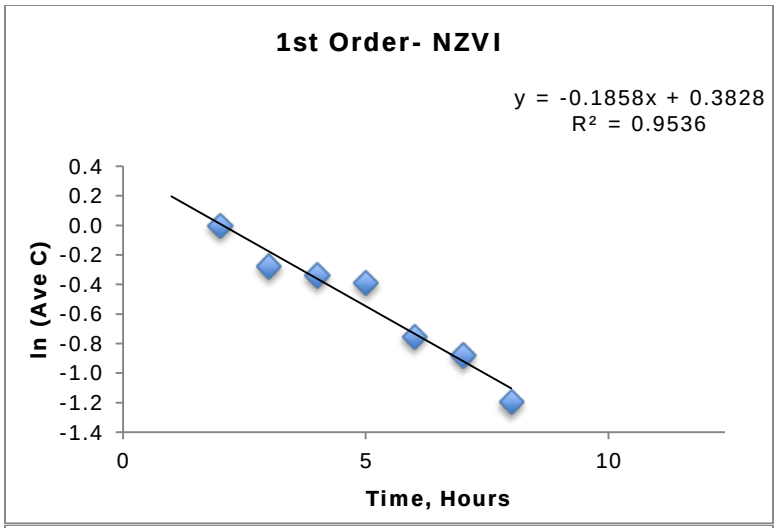
	Sample A	Sample B	Sample C	Ave. C
Time (hrs)				
0	1.00	1.00	1.00	1.00
0.5	0.80	0.72	0.76	0.76
1	0.66	0.74	0.74	0.71
2	0.65	0.67	0.72	0.68
4	0.40	0.50	0.52	0.47
6	0.42	0.36	0.47	0.42
12	0.25	0.34	0.32	0.30

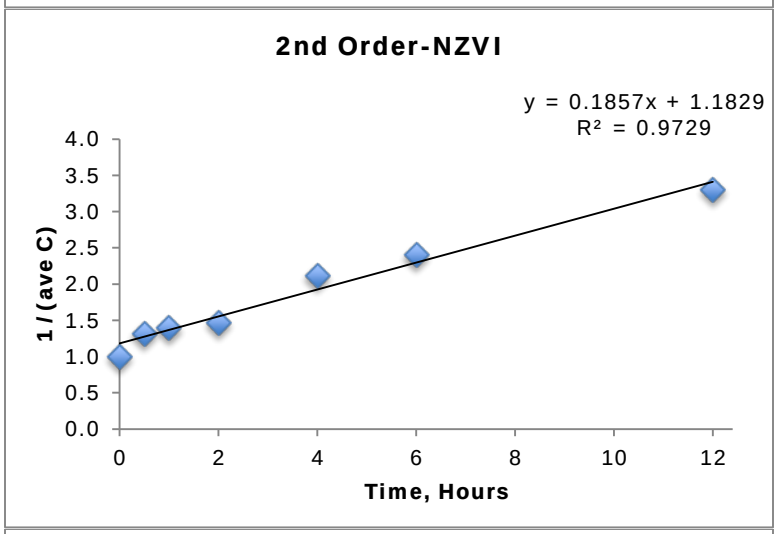
Table B.41. NZVI 1st Order Reaction Data (40 mg L^{-1})

	Sample A	Sample B	Sample C	ln(Ave C)
Time (hrs)				
0	1.00	1.00	1.00	0.00
0.5	0.80	0.72	0.76	-0.28
1	0.66	0.74	0.74	-0.34
2	0.65	0.67	0.72	-0.39
4	0.40	0.50	0.52	-0.75
6	0.42	0.36	0.47	-0.88
12	0.25	0.34	0.32	-1.19

Table B.42. NZVI 2nd Order Reaction Data (40 mg L^{-1})

	Sample A	Sample B	Sample C	1/(Ave C)
Time (hrs)				
0	1.00	1.00	1.00	1.00
0.5	0.80	0.72	0.76	1.32
1	0.66	0.74	0.74	1.40
2	0.65	0.67	0.72	1.47
4	0.40	0.50	0.52	2.12
6	0.42	0.36	0.47	2.41
12	0.25	0.34	0.32	3.30





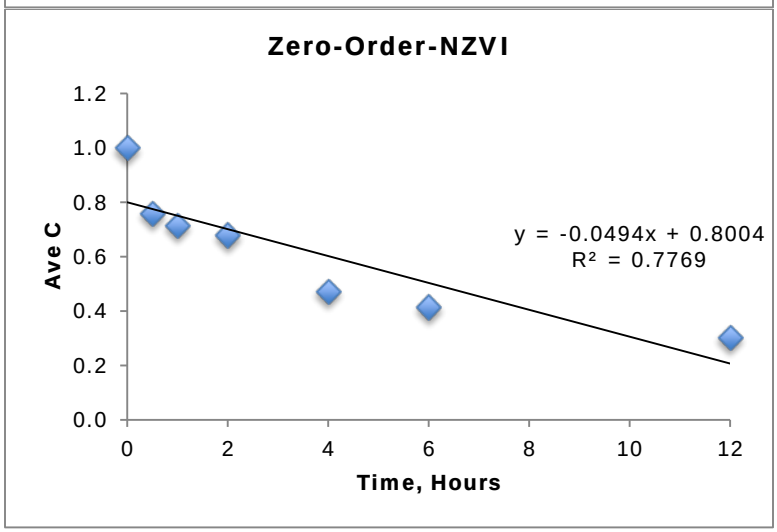


Figure B.3. Reaction Kinetic Graphs for Bare NZVI (40 mg L^{-1})

Table B.43. CNZVI Zero Order Reaction Data (40 mg L^{-1})

	Sample A	Sample B	Sample C	Ave. C
Time (hrs)				
0	1.00	1.00	1.00	1.00
0.5	0.94	0.94	0.95	0.94
1	0.88	0.79	0.80	0.82
2	0.63	0.66	0.54	0.61
4	0.58	0.62	0.55	0.58
6	0.59	0.46	0.43	0.49
12	0.33	0.29	0.29	0.31

Table B.44. CNZVI 1st Order Reaction Data (40 mg L^{-1})

	Sample A	Sample B	Sample C	ln(Ave C)
Time (hrs)				
0	1.00	1.00	1.00	0.00
0.5	0.94	0.94	0.95	-0.06
1	0.88	0.79	0.80	-0.19
2	0.63	0.66	0.54	-0.49
4	0.58	0.62	0.55	-0.54
6	0.59	0.46	0.43	-0.70
12	0.33	0.29	0.29	-1.19

Table B.45. CNZVI 2nd Order Reaction Data (40 mg L^{-1})

	Sample A	Sample B	Sample C	1/(Ave C)
Time (hrs)				
0	1.00	1.00	1.00	1.00
0.5	0.94	0.94	0.95	1.06
1	0.88	0.79	0.80	1.21
2	0.63	0.66	0.54	1.64
4	0.58	0.62	0.55	1.72
6	0.59	0.46	0.43	2.02
12	0.33	0.29	0.29	3.28

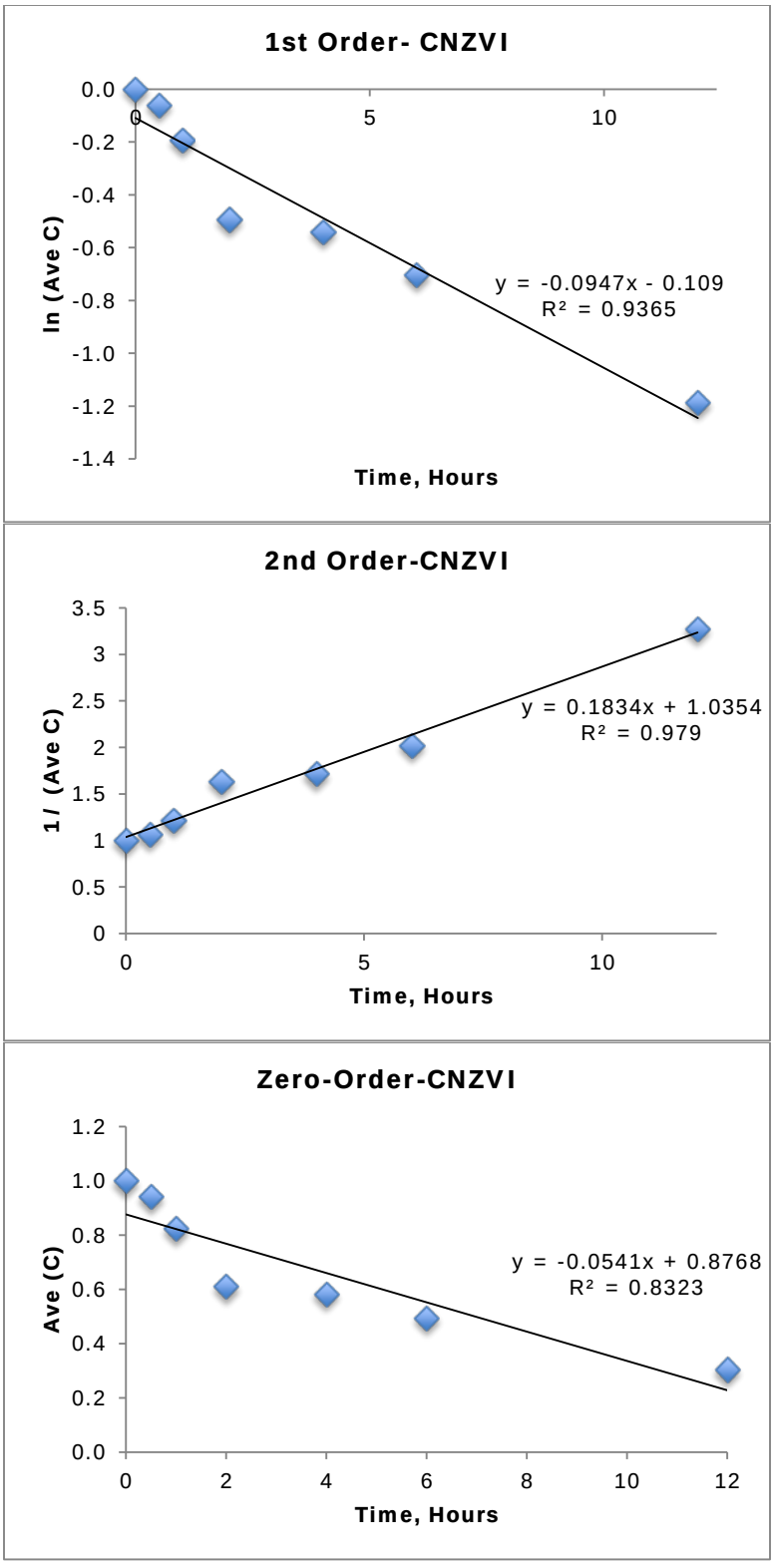


Figure B.4. Reaction Kinetic Graphs for CNZVI (40 mg L^{-1})

Table B.46. NZVI Zero Order Reaction Data (60 mg L^{-1})

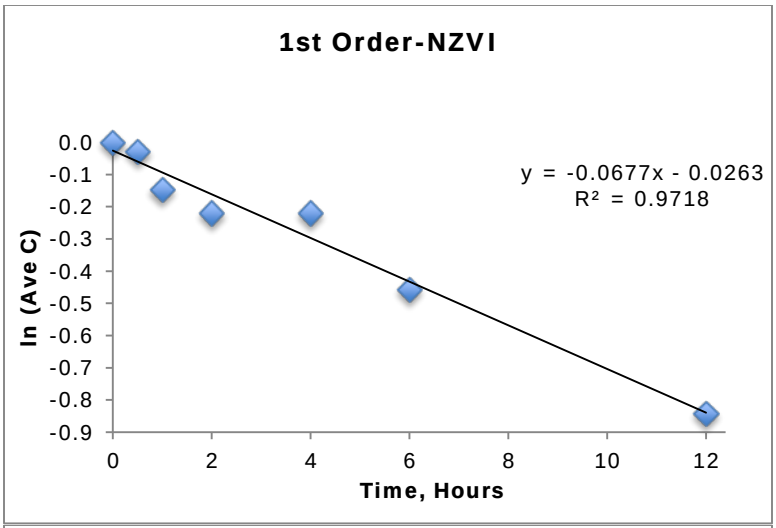
	Sample A	Sample B	Sample C	Ave. C
Time (hrs)				
0	1.00	1.00	1.00	1.00
0.5	1.01	0.87	1.03	0.97
1	0.88	0.91	0.80	0.86
2	0.82	0.76	0.83	0.80
4	0.82	0.76	0.83	0.80
6	0.65	0.51	0.74	0.63
12	0.24	0.50	0.55	0.43

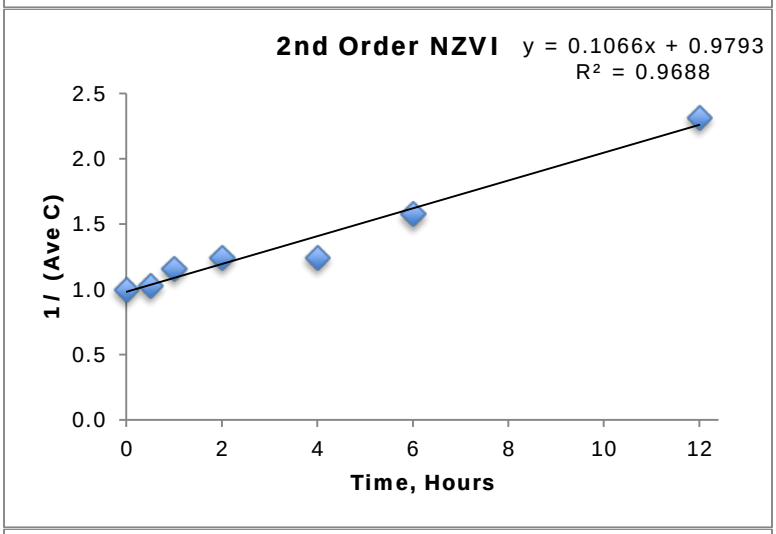
Table B.47. NZVI 1st Order Reaction Data (60 mg L^{-1})

	Sample A	Sample B	Sample C	ln(Ave C)
Time (hrs)				
0	1.00	1.00	1.00	0.00
0.5	1.01	0.87	1.03	-0.03
1	0.88	0.91	0.80	-0.15
2	0.82	0.76	0.83	-0.22
4	0.82	0.76	0.83	-0.22
6	0.65	0.51	0.74	-0.46
12	0.24	0.50	0.55	-0.84

Table B.48. NZVI 2nd Order Reaction Data (60 mg L^{-1})

	Sample A	Sample B	Sample C	1/(Ave C)
Time (hrs)				
0	1.00	1.00	1.00	1.00
0.5	1.01	0.87	1.03	1.03
1	0.88	0.91	0.80	1.16
2	0.82	0.76	0.83	1.24
4	0.82	0.76	0.83	1.24
6	0.65	0.51	0.74	1.58
12	0.24	0.50	0.55	2.32





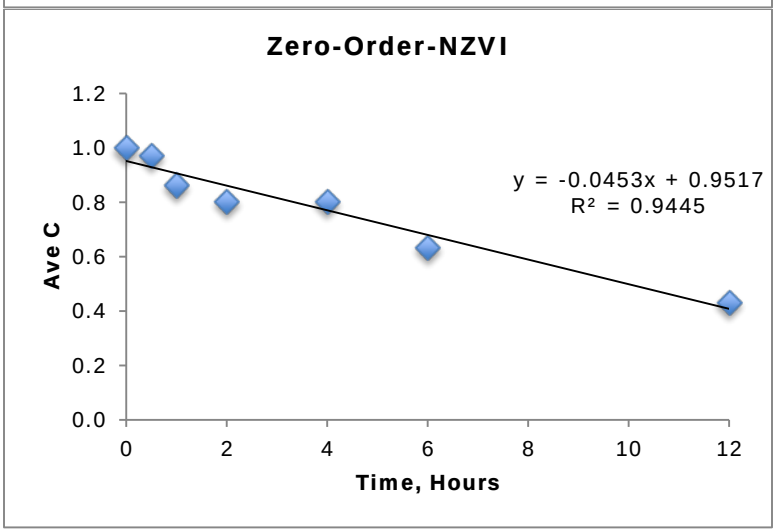


Figure B.5. Reaction Kinetic Graphs for Bare NZVI (60 mg L^{-1})

Table B.49. CNZVI Zero Order Reaction Data (60 mg L^{-1})

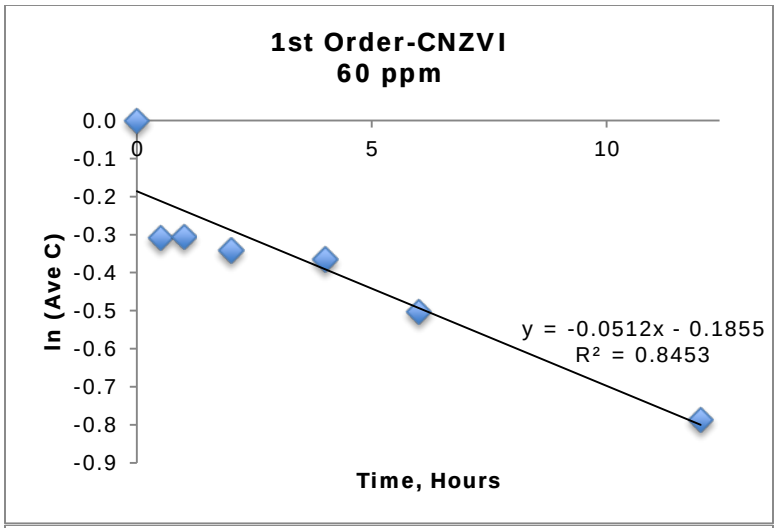
	Sample A	Sample B	Sample C	Ave. C
Time (hrs)				
0	1.00	1.00	1.00	1.00
0.5	0.74	0.73	0.74	0.74
1	0.74	0.75	0.72	0.74
2	0.71	0.74	0.69	0.71
4	0.67	0.71	0.70	0.69
6	0.57	0.62	0.62	0.61
12	0.44	0.51	0.43	0.46

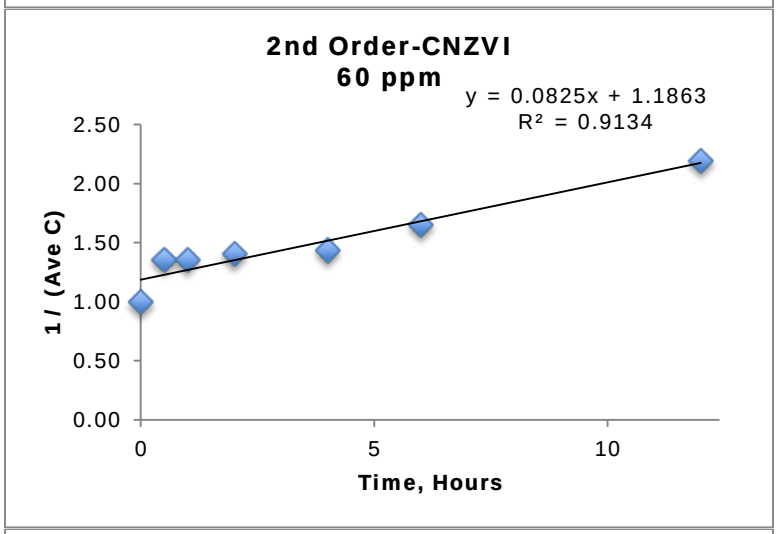
Table B.50. CNZVI 1st Order Reaction Data (60 mg L^{-1})

	Sample A	Sample B	Sample C	ln(Ave C)
Time (hrs)				
0	1.00	1.00	1.00	0.00
0.5	0.74	0.73	0.74	-0.31
1	0.74	0.75	0.72	-0.30
2	0.71	0.74	0.69	-0.34
4	0.67	0.71	0.70	-0.36
6	0.57	0.62	0.62	-0.50
12	0.44	0.51	0.43	-0.79

Table B.51. CNZVI 2nd Order Reaction Data (60 mg L^{-1})

	Sample A	Sample B	Sample C	1/(Ave C)
Time (hrs)				
0	1.00	1.00	1.00	1.00
0.5	0.74	0.73	0.74	1.36
1	0.74	0.75	0.72	1.36
2	0.71	0.74	0.69	1.41
4	0.67	0.71	0.70	1.44
6	0.57	0.62	0.62	1.65
12	0.44	0.51	0.43	2.19





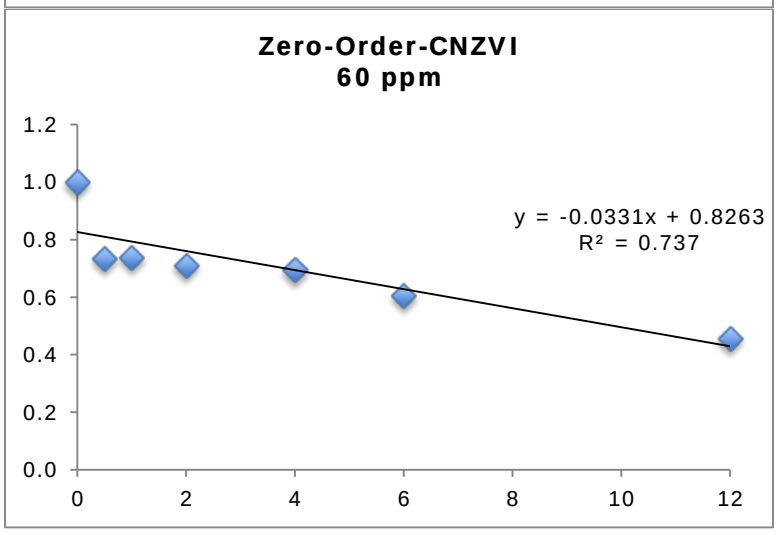


Figure B.6. Reaction Kinetic Graphs for CNZVI (60 mg L^{-1})

B.4. Nitrogen Species

Table B.52. NZVI NO_2^--N Data (20 mg L^{-1})

Nitrite NO_2^--N (ppm)									
	Sample A		Sample B		Sample C				
Time	C	C/TN*	C	C/TN*	C	C/TN*	Ave. C/TN	Std. Dev	Std. Error
0	0.51	0.02	0.53	0.02	0.59	0.02	0.02	0.00	0.00
1	0.40	0.01	0.52	0.02	0.38	0.01	0.01	0.00	0.00
2	0.24	0.01	0.13	0.00	0.23	0.01	0.01	0.00	0.00
6	0.14	0.00	0.10	0.00	0.21	0.01	0.00	0.00	0.00
12	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Table B.53. NZVI NH_4^+-N Data (20 mg L^{-1})

Ammonium NH_4^+-N (ppm)									
	Sample A		Sample B		Sample C				
Time	C	C/TN*	C	C/TN*	C	C/TN*	Ave. C/TN	Std. Dev	Std. Error
0	1.82	0.06	1.53	0.05	1.71	0.06	0.06	0.01	0.00
1	6.66	0.22	10.03	0.31	6.31	0.22	0.25	0.05	0.03
2	19.41	0.65	19.20	0.59	20.31	0.72	0.65	0.06	0.04
6	20.60	0.69	23.00	0.71	17.10	0.61	0.67	0.05	0.03
12	22.30	0.75	22.60	0.70	22.40	0.79	0.74	0.05	0.03

Table B.54. NZVI NO_3-N Data (20 mg L^{-1})

Nitrate NO_3-N (ppm)									
	Sample A		Sample B		Sample C				
Time	C	C/TN*	C	C/TN*	C	C/TN*	Ave. C/TN	Std. Dev	Std. Error
0	27.60	0.92	30.30	0.94	25.90	0.92	0.93	0.01	0.01
1	6.66	0.22	10.03	0.31	6.31	0.22	0.25	0.05	0.03
2	5.06	0.17	2.68	0.08	3.63	0.13	0.13	0.04	0.02
6	2.86	0.10	1.87	0.06	2.99	0.11	0.09	0.03	0.01
12	0.80	0.03	0.10	0.00	0.10	0.00	0.01	0.01	0.01

* Corresponding starting (time =0) TN concentration for the samples (from following table)

Table B.55. NZVI Total Nitrogen Data (20 mg L^{-1})

Nitrate NO_3-N (ppm)									
	Sample A		Sample B		Sample C				
Time	C	C/TN*	C	C/TN*	C	C/TN*	Ave. C/TN	Std. Dev	Std. Error
0	29.93	1.00	32.36	1.00	28.20	1.00	0.00	0.00	29.93
1	13.72	0.46	20.58	0.64	13.00	0.46	0.10	0.06	13.72
2	24.71	0.83	22.01	0.68	24.17	0.86	0.09	0.05	24.71
6	23.60	0.79	24.97	0.77	20.30	0.72	0.04	0.02	23.60
12	23.11	0.77	22.70	0.70	22.50	0.80	0.05	0.03	23.11

Table B.56. CNZVI NO_2^--N Data (20 mg L^{-1})

Nitrite NO_2^--N (ppm)									
	Sample A		Sample B		Sample C				
Time	C	C/TN*	C	C/TN*	C	C/TN*	Ave. C/TN	Std. Dev	Std. Error
0	0.47	0.02	0.55	0.02	0.54	0.02	0.02	0.00	0.00
1	0.51	0.02	0.66	0.03	0.50	0.02	0.02	0.00	0.00
2	0.28	0.01	0.52	0.02	0.31	0.01	0.02	0.01	0.00
6	0.29	0.01	0.26	0.01	0.24	0.01	0.01	0.00	0.00
12	0.17	0.01	0.20	0.01	0.22	0.01	0.01	0.00	0.00

Table B.57. CNZVI NH_4^+-N Data (20 mg L^{-1})

Ammonium NH_4^+-N (ppm)									
	Sample A		Sample B		Sample C				
Time	C	C/TN*	C	C/TN*	C	C/TN*	Ave. C/TN	Std. Dev	Std. Error
0	1.90	0.08	2.57	0.12	2.90	0.13	0.11	0.03	0.02
1	6.20	0.25	4.34	0.20	5.39	0.24	0.23	0.03	0.02
2	10.70	0.44	5.25	0.24	9.70	0.43	0.37	0.11	0.07
6	12.40	0.51	10.35	0.47	11.95	0.53	0.50	0.03	0.02
12	14.90	0.61	13.05	0.59	12.55	0.56	0.59	0.03	0.02

Table B.58. CNZVI NO_3-N Data (20 mg L^{-1})

Nitrate NO_3-N (ppm)									
	Sample A		Sample B		Sample C				
Time	C	C/TN*	C	C/TN*	C	C/TN*	Ave. C/TN	Std. Dev	Std. Error
0	22.04	0.90	18.99	0.86	19.13	0.85	0.87	0.03	0.02
1	13.62	0.56	19.40	0.88	14.76	0.65	0.69	0.16	0.09
2	11.23	0.46	18.99	0.86	11.16	0.49	0.60	0.22	0.13
6	9.41	0.39	8.93	0.40	9.36	0.41	0.40	0.01	0.01
12	6.91	0.28	8.24	0.37	8.81	0.39	0.35	0.06	0.03

* Corresponding starting (time =0) TN concentration for the samples (from following table)

Table B.59. CNZVI Total Nitrogen Data (20 mg L^{-1})

Nitrate NO_3-N (ppm)									
	Sample A		Sample B		Sample C				
Time	C	C/TN*	C	C/TN*	C	C/TN*	Ave. C/TN	Std. Dev	Std. Error
0	24.41	1.00	22.11	1.00	22.57	1.00	1.00	0.00	0.00
1	20.33	0.83	24.40	1.10	20.65	0.91	0.95	0.14	0.08
2	22.21	0.91	24.76	1.12	21.17	0.94	0.99	0.11	0.07
6	22.10	0.91	19.54	0.88	21.55	0.95	0.91	0.04	0.02
12	21.98	0.90	21.49	0.97	21.58	0.96	0.94	0.04	0.02

B.5. One-Way ANOVA for Nitrogen Species

Nitrite

H_o: There is not a significant difference in nitrite generation between bare NZVI particles and NZVI coated with 35%-OSA tapioca starch ($x_0 = x_1$).

H_a: there is a significant difference between nitrite generation.

X_0 = bare NZVI

X_1 = NZVI coated with 35%-OSA tapioca starch

$\alpha = 0.05$

Table B.60. One-Way ANOVA for Nitrite (CNZVI vs. NZVI)

Source	DF	Adj. SS	Adj. MS	F-Value	P-Value
Treatment*	1	0.5223	0.5223	4.44	0.044
Error	28	3.2935	0.1176		
Total	29	3.8158			

*The four levels of treatment are presented in the hypothesis section above.

Table B.61. Nitrite (CNZVI vs. NZVI) Tukey Pairwise Comparison

Treatment	N	Mean	Std. Dev	99.5% CI	Grouping**
0	15	0.4903	0.3835	(0.2204, 0.7601)	A
1	15	0.7542	0.2970	(0.4843, 1.0240)	B

** Means that do not share a letter are significantly different.

Ammonium

H_o: There is not a significant difference in ammonium generation between bare NZVI particles and NZVI coated with 35%-OSA tapioca starch ($x_0 = x_1$).

H_a: there is a significant difference between ammonium generation.

X_0 = bare NZVI

X_1 = NZVI coated with 35%-OSA tapioca starch

$\alpha = 0.05$

Table B.62. One-Way ANOVA for Ammonium (CNZVI vs. NZVI)

Source	DF	Adj. SS	Adj. MS	F-Value	P-Value
Treatment*	1	198.1	198.08	12.66	0.001
Error	28	438.2	15.65		
Total	29	636.3			

*The four levels of treatment are presented in the hypothesis section above.

Table B.63. 20 ppm (CNZVI vs. NZVI) Tukey Pairwise Comparison

Treatment	N	Mean	Std. Dev	99.5% CI	Grouping**
0	15	8.56	5.20	(5.45, 11.68)	A
1	15	3.426	2.058	(0.313, 6.538)	B

** Means that do not share a letter are significantly different.

Nitrate

H_0: There is not a significant difference in nitrate generation between bare NZVI particles and NZVI coated with 35%-OSA tapioca starch ($x_0 = x_1$).

H_a: there is a significant difference between nitrate generation.

X_0 = bare NZVI

X_1 = NZVI coated with 35%-OSA tapioca starch

$\alpha = 0.05$

Table B.64. One-Way ANOVA for Nitrate (NZVI vs. CNZVI)

Source	DF	Adj. SS	Adj. MS	F-Value	P-Value
Treatment*	1	0.8551	0.8551	7.29	0.012
Error	28	3.2861	0.1174		
Total	29	4.1412			

*The four levels of treatment are presented in the hypothesis section above.

Table B.65. Nitrate (NZVI vs. CNZVI) Tukey Pairwise Comparison

Treatment	N	Mean	Std. Dev	99.5% CI	Grouping**
0	15	0.3030	0.3722	(0.0335, 0.5725)	A
1	15	0.6406	0.3101	(0.3711, 0.9102)	B

** Means that do not share a letter are significantly different.

B.6. Spent CNZVI SEM/EDS Data

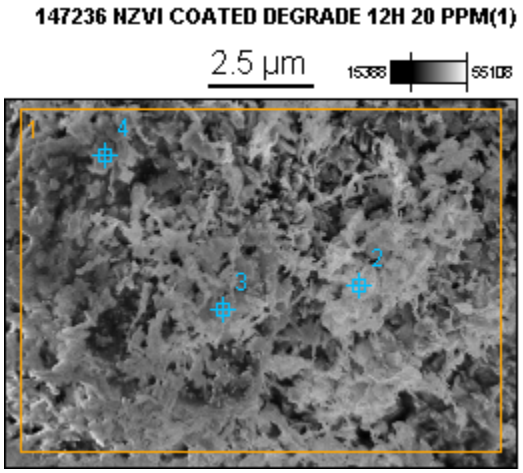
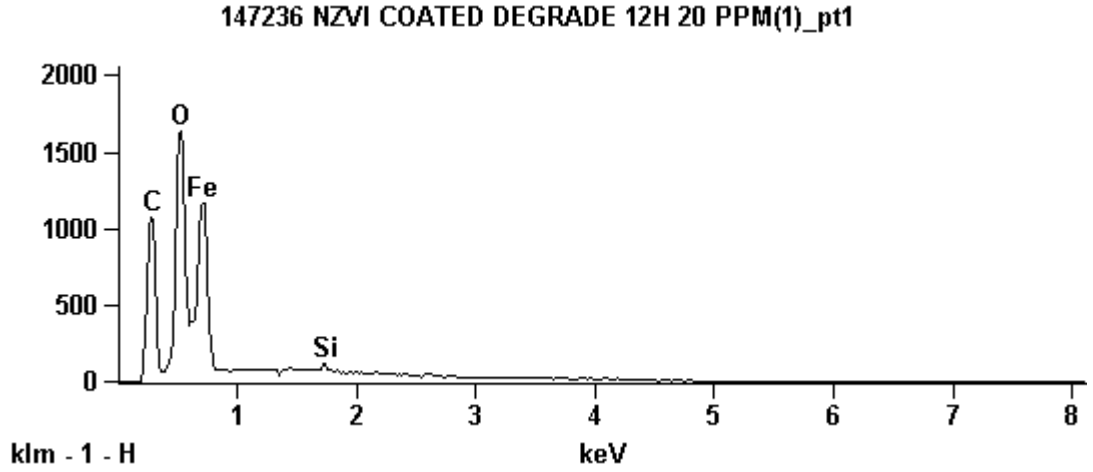


Image Name: 147236 NZVI COATED DEGRADE 12H 20 PPM(1)

Accelerating Voltage: 5.0 kV



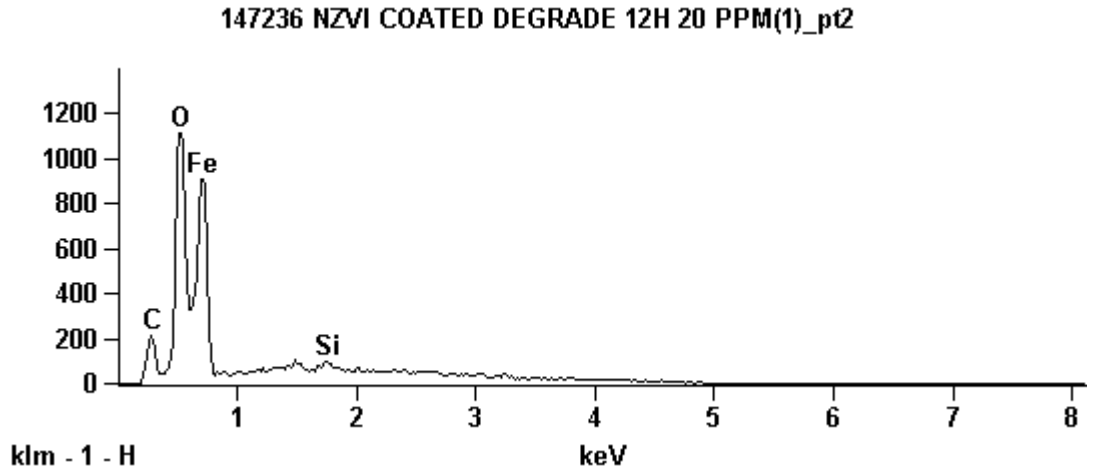


Figure B.7. Spent CNZVI EDS Graphs

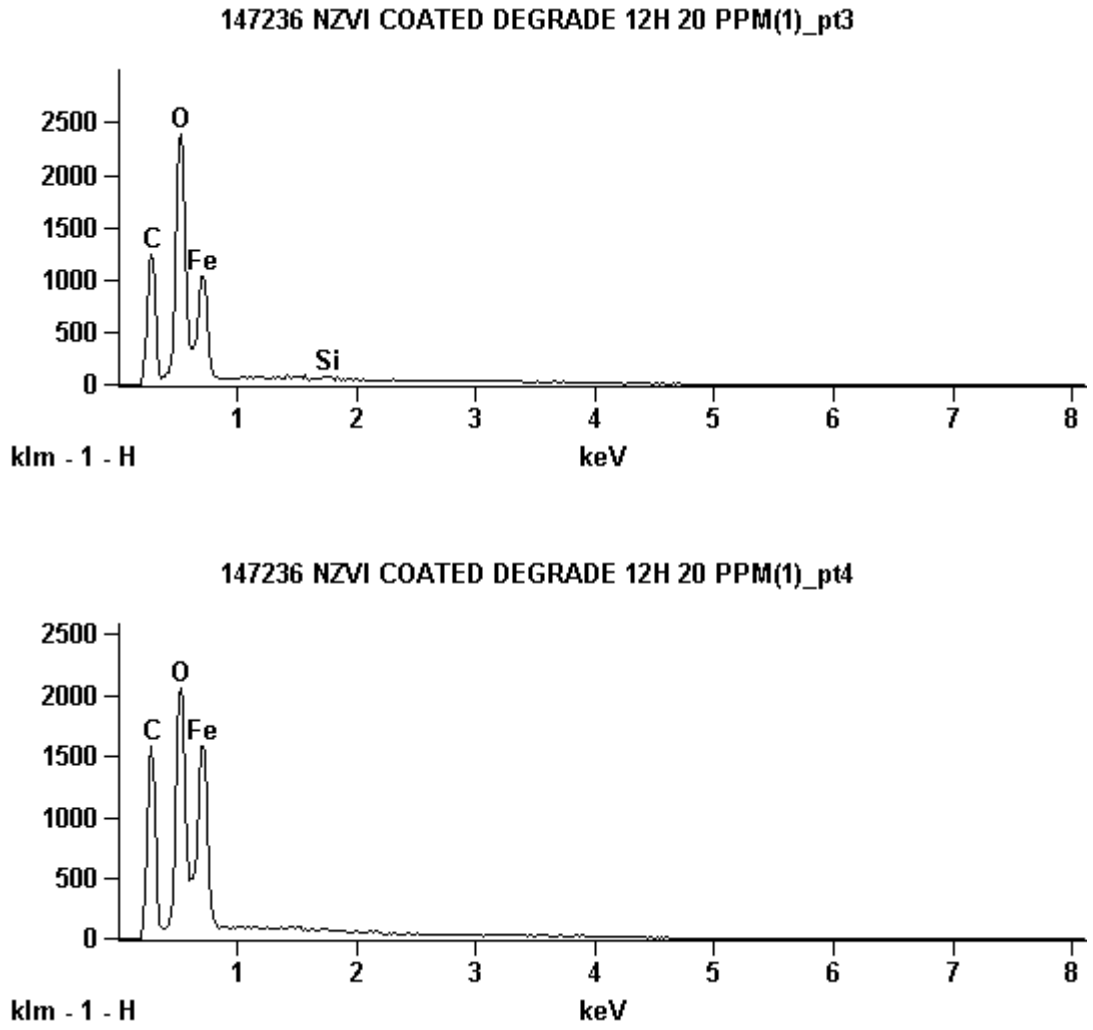


Figure B.7. Spent CNZVI EDS Graphs (continued)

Table B.66. Spent CNZVI Net Count
Net Counts

	C-K	O-K	Si-K	Fe-L
147236 NZVI COATED DEGRADE 12H 20 PPM(1)_pt1	7231	11186	394	12138
147236 NZVI COATED DEGRADE 12H 20 PPM(1)_pt2	1228	7643	356	9569
147236 NZVI COATED DEGRADE 12H 20 PPM(1)_pt3	8087	16629	255	10485
147236 NZVI COATED DEGRADE 12H 20 PPM(1)_pt4	10293	14087		16246

Table B.67. Spent CNZVI EDS Weight %
Weight %

	C-K	O-K	Si-K	Fe-L
147236 NZVI COATED DEGRADE 12H 20 PPM(1)_pt1	16.26	16.30	1.03	66.42
147236 NZVI COATED DEGRADE 12H 20 PPM(1)_pt2	4.49	15.94	1.43	78.14
147236 NZVI COATED DEGRADE 12H 20 PPM(1)_pt3	17.23	23.65	0.65	58.47
147236 NZVI COATED DEGRADE 12H 20 PPM(1)_pt4	17.24	15.59		67.16

Table B.68. Spent CNZVI EDS Weight % Error
Weight % Error (+/- 3 Sigma)

	C-K	O-K	Si-K	Fe-L
147236 NZVI COATED DEGRADE 12H 20 PPM(1)_pt1	+/- 0.55	+/- 0.94	+/- 0.36	+/- 2.82
147236 NZVI COATED DEGRADE 12H 20 PPM(1)_pt2	+/- 0.45	+/- 1.01	+/- 0.54	+/- 3.50
147236 NZVI COATED DEGRADE 12H 20 PPM(1)_pt3	+/- 0.55	+/- 0.99	+/- 0.33	+/- 2.79
147236 NZVI COATED DEGRADE 12H 20 PPM(1)_pt4	+/- 0.48	+/- 0.81		+/- 2.47

Table B.69. Spent CNZVI EDS Atom %
Atom %

	C-K	O-K	Si-K	Fe-L
147236 NZVI COATED DEGRADE 12H 20 PPM(1)_pt1	37.62	28.31	1.02	33.05
147236 NZVI COATED DEGRADE 12H 20 PPM(1)_pt2	13.26	35.33	1.80	49.60
147236 NZVI COATED DEGRADE 12H 20 PPM(1)_pt3	36.02	37.11	0.58	26.29
147236 NZVI COATED DEGRADE 12H 20 PPM(1)_pt4	39.74	26.97		33.29

Table B.70. Spent CNZVI EDS Atom % Error
Atom % Error (+/- 3 Sigma)

	C-K	O-K	Si-K	Fe-L
147236 NZVI COATED DEGRADE 12H 20 PPM(1)_pt1	+/- 1.26	+/- 1.62	+/- 0.36	+/- 1.41
147236 NZVI COATED DEGRADE 12H 20 PPM(1)_pt2	+/- 1.33	+/- 2.25	+/- 0.68	+/- 2.22
147236 NZVI COATED DEGRADE 12H 20 PPM(1)_pt3	+/- 1.15	+/- 1.55	+/- 0.29	+/- 1.26
147236 NZVI COATED DEGRADE 12H 20 PPM(1)_pt4	+/- 1.11	+/- 1.40		+/- 1.22

APPENDIX C. FATE AND TRANSPORT OF COATED NZVI

C.1. Introduction

Groundwater remediation is critical to meeting current and future water needs[1]. Traditionally, pump and treat systems (PTS) were used for restoring groundwater quality[1,2]. When first installed, PTS systems are able to quickly reduce contamination concentrations, but are unable to meet long-term cleanup goals[1,2]. Additionally, PTS systems require the excavation of contaminated soil/water for treatment and disposal elsewhere[3]. To reduce greenhouse gases and landfill use, along with improving remediation efficiency, significant research has been devoted to improving *in-situ* remediation technologies[3]. PRBs are of particular interest because they utilized the natural hydraulic gradient to treat contaminants[1-5].

Granular ZVI particles have been used in PRBs since the early 1990s and are effective at reducing contaminant concentrations[2,6]. However, ZVI PRBs have limited applications due to construction restrictions (depth of wall and cost), limited mobility due to size, pore blocking (caused by particle size), and large mass of iron required for treatment[6-8]. The development of NZVI was critical to improving *in situ* remediation techniques because NPs can be injected into groundwater under pressure and transported by groundwater flow[7]. However, NZVI tends to aggregate and settle in aqueous systems, limiting delivery to deep groundwater systems[9-11] unless NZVI's surface is modified[12-15].

Extensive research has been conducted on the mobility of surface modified NZVI particles in porous media. Many studies have reported increased mobility of surface-modified NZVI in column studies[10,11,16-18]. Kanel et al. [9] found PAA coated NZVI moved downward and horizontally when injected into a bench scale reactor. The two-dimensional transport indicates density-driven flow is a significant factor for delivery particles to deep aquifers[9]. A field study by He et al. [19] CMC-stabilized NZVI injected under gravity and pressurized conditions were able to travel up to 1.5 meters down-gradient. This

characteristic is ideal for treating heavily contaminated source areas[7] and targeting contaminants[14,20-22]. Henn et al. [23] injected modified NZVI into saturated subsurface using a closed-loop recirculating system; recirculating systems increase groundwater velocity, which improves NZVI's advective and dispersive transport[23]. Geochemistry analysis indicated the injected NZVI particles were able to migrate 20 feet down gradient from the recirculating system[23].

The previous studies successfully transported surface modified NZVI, but other studies report difficulty injecting and transporting the particles. Several field studies report non-uniform transport and limited mobility of surface modified NZVI[6,24]. Wei et al. [24] found surface modified NZVI was mobile in the unsaturated zone of medium to coarse stand. However, the NZVI was unable to move into the saturated zone, resulting in a large accumulation of NZVI in the soil's upper layer[24]. This resulted in high degradation efficiencies in the upper layers and lower degradation in the bottom layers[24]. In a push-pull field test, Bennett et al.[25] found CMC modified NZVI was virtually immobile 13 hours under ambient conditions. Henn et al.[23] found NZVI was not transported uniformly through the test site in their recirculating field study.

The irregular mobility and distribution of NZVI in aquifers makes it difficult to design effective groundwater treatments. However, very few studies have focused on using NZVI as the reactive media in PRBs because NZVI particles are not easily contained in PRBs due to their miniscule particle size[26]. PRBs are commonly designed as continuous trenches and funnel-and-gate design[4]. A continuous trench is a reactive wall installed across the entire path of a plume[27]. Funnel-and-gate PRBs use impermeable walls to direct the contaminant plume to a single/series of permeable containers filled with reactive media[4,27]. Hosseini et al.[8] tested a bench scale PRB with a funnel-and-gate configuration to see if NZVI would remain in the PRB. Several flow studies indicated the PRB remained porous and was able to reduce nitrate concentrations by approximately 20% with 8 g/L of NZVI injected[8]. Liu et al.

[26] found chitosan bead-supported NZVI were an effective reactive material for PRBs because of the beads large (19.2-138.6μm) size maintained porosity in the PRB and ability to NZVI suspended.

The goal of this work is to determine if CNZVI particles would work as reactive material in PRBs. Previous studies have reported limited mobility for starch-stabilized NZVI particles[11,28]. This is likely because the starch matrix binds to the surface of aquifer materials, thus preventing significant movement of NZVI, which makes it an ideal candidate for PRB material. This study was conducted to see how CNZVI particles move in a bench scale reactor. Specific goals are: 1) use a bench scale reactor to monitor the transport of bare NZVI and CNZVI, and 2) determine the biodegradability of OSA-starch stabilized NZVI particles.

C.2. Materials and Methods

C.2.1. Materials

$FeSO_4 7H_20$ (Aldrich Chemical), $NaBH_4$ (ACS grade, Alfa Aesar), methanol (95+%, BDH), NaOH (ACS grade, BDH), 2-Octen-l-ylsuccinic anhydride (OSA) (Dixie Chemical Company), HCL (EMD Millipore), Na_2SO_4 (Sigma-Aldrich), native tapioca starch (Ingredion Company), BOD Nutrient Pillows (Hach, USA), lithium hydroxide pillows (LiOH, Hach, USA), and N_2 gas (Praxair) were used as obtained. Silica sand was purchased from Petco.

C.2.2 NZVI Synthesis

NZVI was synthesized by borohydride reduction of ferrous iron in $FeSO_4 7H_20$ according to the Liu et al.. method[14,29,30]. The synthesis procedure is described in section 2.2.2.

C.2.3. Coating NZVI

NZVI was coated with 35% OSA tapioca starch. Native tapioca starch was modified as described by Bai et al. [31,32]. Starch was modified as described in Section 2.2.4. To coat

NZVI, a 10 g L^{-1} solution of 35% tapioca starch was prepared in deoxygenated-DI water. The starch solution was prepared as described in Section 2.2.3. Glass vials (20 mL) were filled with NZVI particles (6 g L^{-1}) and 20 mL of the starch. The vials were capped after the headspace was filled with nitrogen and sonicated for 30 minutes to disperse the particles[14]. Immediately following sonication, the reactors were placed in a custom end-over-end shaker (28 rpm) and rotated for 72 hours[14]. Following shaking, the particles were washed three times with deoxygenated-DI water and immediately used for the transport study.

C.2.4. Two-Dimensional Flow Study

C.2.4.1. Tank Setup

Transport of bare and coated NZVI was studied using a two-dimensional flow container provided by Sushil Kanel[9]. The dimensions of the tank, shown in Figure C.2.i, are 50 cm (length) X 2 cm (width) X 28.5 cm (height)[9]. Overflow chambers (5 cm wide) were built at both ends to set constant-head boundary conditions[9]; the overflow chambers were separated from the main chamber by US Mesh #16. Each chamber had a series of overflow orifices to drain excess fluid and maintain water level in the main chamber[9]. The orifices established a head difference of 0.7 cm (1.4% gradient) between the left and right chamber[9] Water level was maintained at lowest orifice hole (23 cm) and flowed from left to right during experiments. Steady state flow was maintained for 10 minutes before starting each experiment[9]; flow velocity was 0.017 cm/sec. Silica sand was used as a porous media and the sand height was 34 cm. The mean particle diameter was 0.6 mm with a variation of ± 0.1 mm and the average porosity of the packed system was 0.212.

Starch-stabilized NZVI particles are reported to have limited soil mobility[11,28], it is unlikely the CNZVI particles will be mobile at typical groundwater velocities (approximately 30 cm/day[33]). Since NZVI mobility increases with short resident times and high pore velocities[23,25], a higher flow velocity was used in the study. Higher velocities, which are achieved through recirculation systems, can enhance *in situ* remediation because they

increase the mass transfer of a sorbed DNAPL plume into the dissolved phase[25]. Once a contaminant plume is in the dissolved phase, it can be easily treated by NZVI particles in the aquifer. Testing CNZVI particle mobility at a high groundwater velocity is ideal for determining if particles could create an iron wall in a recirculating system.

Tracer, bare NZVI, and coated NZVI solutions were injected into the tank using an injection apparatus. The injection apparatus was composed of a hard plastic tube (inner diameter = 0.25 cm, height = 15 cm) attached to a 20 mL syringe. All samples were injected 15 cm from the left end and 16 cm from container's bottom[9]; solutions were injected at a rate of 1.25 mL s^{-1}. The sand was washed between each transportation study.

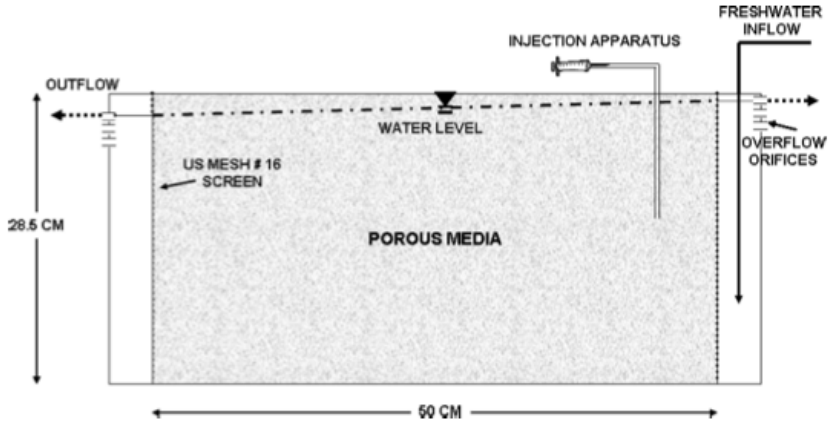


Figure C.1. Conceptual Diagram of Two-Dimensional Flow Container. Picture from Kanel et al.[9].

C.2.4.2. Tracer Study

The optical tracer for this study was non-reactive red dye (FD&C Red 40)[11]. Once steady state conditions were established, 20 mL of dyed tap water was injected into the porous. A high-resolution camera was used to record transport over a 30-minute interval by taking pictures at designated intervals. A 3 cm X 3 cm grid was placed over the tank to track movement.

C.2.4.3. Bare and Coated NZVI Studies

Freshly synthesized bare NZVI was injected into the system at a concentration of 6 g L^{-1}. Particle transport was recorded with digital images obtained from a high-resolution camera at set intervals for 30 minutes. CNZVI particles were injected into the tank immediately after they were wash. The coated particles were also injected at a concentration of 6 g L^{-1}.

C.2.5. Starch Biodegradation

Unmodified NZVI will oxidize and age into nontoxic iron forms in a few months[34]. Surface modification can prevent NZVI from oxidizing for at least 6 months[14,35]. In order to prevent human exposure to un-oxidized NZVI, surface modifiers must be biodegradable[35,36]. Coating polymers onto NZVI can affect/limit the polymer's biodegradation[37]. Since coatings can remain on NZVI for months[35], both the polymers and polymer coated NZVI need to be tested for biodegradation[37].

Biodegradation can be measured by direct measurement of parent compound concentrations or by indirect measure of parent compound bioconversion (i.e. biochemical oxygen demand (BOD), dissolved organic carbon (DOC), and chemical oxygen demand (COD))[38]. An accurate representation of the biodegradation process can be easily done by monitoring the production of BOD using a respirometer[38]. The biodegradation behavior of OSA-modified starch and CNZVI particles were obtained using respirometric experiments following the OCED 301 C modified MITI test (I)[39].

BOD was monitored using an automated closed-system respirometer (BODTrak Apparatus, Hach, USA). BODTrak tests the quantity of oxygen consumed by monitoring changes in headspace pressure[40]. Headspace pressure will decrease as the sample's bacteria consumes organic matter[40]. BOD data was automatically collected and stored on a computer connected to the instrument during the 28-day test period. Mixed liquor

suspended solids (MLSS) was collected from the City of Moorhead Wastewater Treatment Plant (Moorhead, MN) and used immediately as see for microorganisms.

The biodegradation studies were conducted in 500 mL amber bottles and ran in duplicate. BOD nutrient solution was prepared by mixing a BOD nutrient capsule with 6L of DI water and aerated for 24 hours. Next, each reactor was filled as described in Table C.2.5. Upon filling each reactor, a seal cup was placed on the reactor and LiOH was added to adsorb CO_2 generated; the LiOH was carefully added to ensure it did not spill into the solution.

Table C.1. Biodegradation Study Reactors

Sample Type	OSA-Modified Starch (mg)	NZVI (mg)	BOD Nutrient (mL)	MLSS (mL)
CNZVI*	100	100	155	5
Bare NZVI		100	155	5
OSA-Modified Starch	100		155	5
Control**			155	5

*NZVI particles were coated as described in section C.1.3

**This reactor did not contain OSA-Modified Starch or NZVI.

BOD values obtained from the respirometer were converted into percent (%) biodegradation by the following equations[39]:

$$BOD = \frac{mg\ O_2\ uptake\ by\ test\ substance - mg\ O_2\ uptake\ by\ blank}{mg\ test\ substance\ in\ vessel} \quad \text{(C-1)}$$

Equation C-1 was modified to Equation C-2 for OSA-starch and to Equation C-3 for CNZVI.

$$BOD = \frac{mg\ O_2\ uptake\ by\ OSA\ Starch - mg\ O_2\ uptake\ by\ control}{100\ mg\ OSA\ starch} \quad \text{(C-2)}$$

$$BOD = \frac{mg\ O_2\ uptake\ by\ CNZVI - mg\ O_2\ uptake\ by\ NZVI}{100\ mg\ CNZVI} \quad \text{(C-3)}$$

$$\%\, Biodegradation = \%\, ThOD = \frac{BOD\left(\frac{mg\ O_2}{mg\ of\ substance}\right)}{ThOD\left(\frac{mg\ O_2}{mg\ of\ substance}\right)} \quad \text{(C-4)}$$

ThOD = theoretical oxygen demand of the organic compound.

For a compound with an elemental composition of $C_cH_hO_o$, ThOD is calculated by the following equation:

$$ThOD = \frac{\left(16*[2c+0.5h-o]\frac{mg}{mg}\right)}{MW} \quad \text{(C-5)}$$

MW = molecular weight.

Equation C-5 can be modified to calculate the ThOD of a polymer with a repeating unit, as shown in Equation C-6.

$$ThOD = \frac{\left(16*[2c+0.5h-o]\frac{mg}{mg}\right)}{MW\ of\ Repeating\ Unit} \quad \text{(C-6)}$$

Biodegradation studies were conducted in duplicate and average values reported. One-way ANOVA (α = 0.005) was used to determine statistical differences.

C.3. Results and Discussion

C.3.1. Two-Dimensional Tank Flow

Results from the tracer, bare NZVI, and CNZVI transport studies are shown in Table C.3.1.i. Pictures in the first column represent the location of the plumes immediately after injection, while subsequent columns depict plume location at various times. Table C.3.1.i a shows the dyed freshwater easily dispersed and moved horizontally across the tank in 30 minutes; Kanel et al. [9] reported similar behavior in his tracer study. Throughout the 30-minute study, bare NZVI particles, shown in Table C.3.1.i b, were transported approximately 3 centimeters from the injection point. Limited movement of bare NZVI is commonly reported in literature[10,16,41,42]. In addition to limited horizontal movement, particle sedimentation was also evident during the observation period. Particle sedimentation is visible at the bottom of the NZVI plume, which slowly gets darker as the study progressed.

Table C.2. Transportation Results

Time	0 min	5 min	10 min	20 min	30 min
Tracer (a)					
Bare (b)					
CNZVI (c)					

CNZVI remained stationary and suspended throughout the experiment, as shown in Table C.3.1.i c. However, unlike bare NZVI particles, it does not appear that particle sedimentation occurred during the study period. To confirm the coated particles did not settle, an additional 6-hour transport study was run. During the 6-hour study, shown in Appendix D-Section D.1, the CNZVI particles also appeared to remain suspended and stationary. The immobilization of CNZVI particles may have been caused by adsorption of the starch onto the silica sand[43] or the coated particle size prohibited movement through the pore space[26,43].

Since the CNZVI remains stationary in high flow velocities, they are ideal candidates for iron walls in PRBs and/or recirculating systems. In shallow aquifers, where nitrate contamination is common[44], the CNZVI particles could be injected to create an iron wall. For recirculating systems, the stationary CNZVI particles would immobilize contaminants as they enter the dissolved phase. The immobilized contaminants would be sorbed/reduced by the CNZVI iron wall, preventing the contaminants from being transported downstream.

Installing CNZVI iron walls by injection offers several construction and economic benefits compared to continuous trench PRBs. Continuous trench PRBs require the removal of significant volumes of soil, which requires the trench to be supported with temporary sheet walls or filled immediately with the reactive material, which complicates

construction[45]. Injecting particles would reduce cost, construction difficulties, and potentially reduce the potential for creating an impermeable barrier.

C.3.2. Starch Biodegradation

Respirometric experiments were conducted for 28 days using continuous monitoring. Continuous monitoring produces better biodegradation curves than monitoring at specified times[38]. The BOD production from the respirometric experiments is shown in Figure C.3.2.i. One-way ANOVA ($\alpha = 0.005$) showed there was a significant difference ($p = 0.000$) of BOD produced between the control (seed only) and bare NZVI. The increase in BOD production indicates NZVI does not prohibit microbial activity, which is necessary for testing biodegradation. Statistical data is presented in Appendix D-Section D.2.

BOD values of OSA-starch and CNZVI were obtained using Equation C-2 and Equation C-3. There was a significant increase ($p = 0.000$) in BOD with the addition of either OSA starch or CNZVI particles (Figure B.3.2.i). The increase in BOD production suggests that OSA-starch boosts the microbial population in the reactors. CNZVI particles also produced significantly ($p = 0.000$) more BOD than just OSA-starch, which also suggests NZVI furthers microbial activity. Increased microbial populations in the presence of bare NZVI and/or modified NZVI has been reported by He et al.[19], Kirschling et al. [37], and Gu et al.[46].

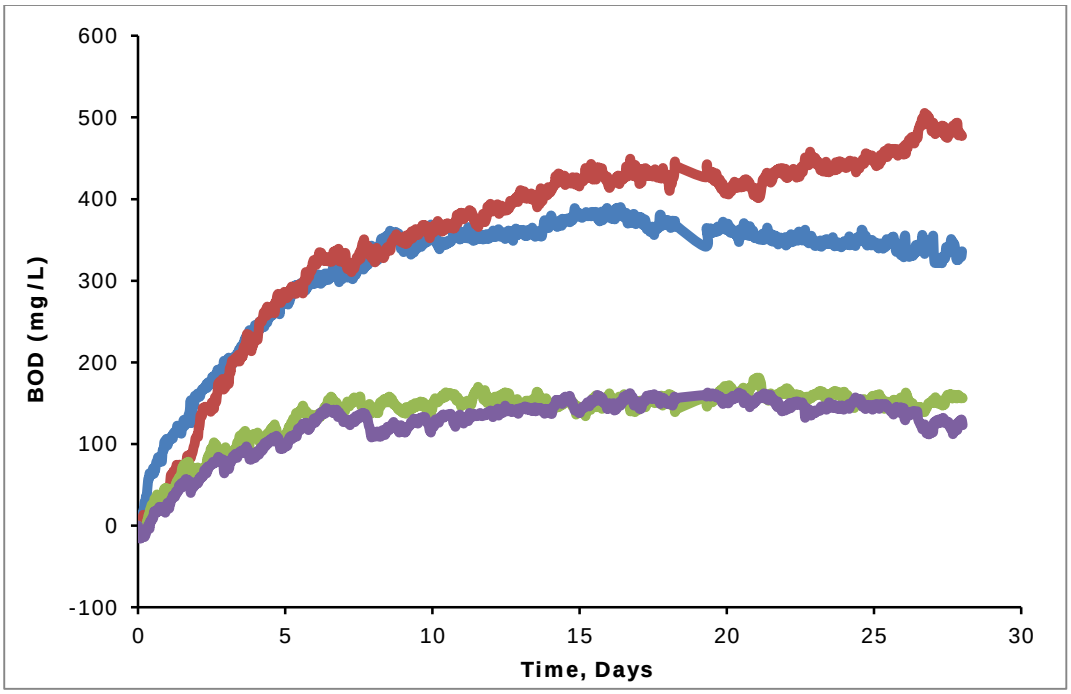


Figure C.2. BOD Production
– CNZVI, – OSA Starch, – NZVI, and – Seed.

Biodegradability of OSA-starch was determined using Equation C-4 and Equation C-6. The molecular formula of the repeating unit was determined to be $C_{18}H_{27}O_8$ (MW = 499 g/mol) based on NMR (presented in Chapter 2, Section 2.3.3) and literature[47,48]. For 100 mg of OSA-starch, the ThOD is 133 mg/L. The %-biodegradation for OSA-starch and CNZVI is presented in Figure C.3.2.ii. By OCDE a standard, a polymer is considered biodegradable if the % biodegradation is greater than 60% within the first 10 testing days[39]; Figure C.3.2.ii shows both OSA-starch and CNZVI met this requirement. There was a significant difference ($p = 0.000$) between the biodegradability of just OSA-starch and CNZVI (approximately 67% and 97% of biodegradation, respectively). This suggests that NZVI stimulates the microorganisms in the reactors, which results in improved biodegradation of OSA starch.

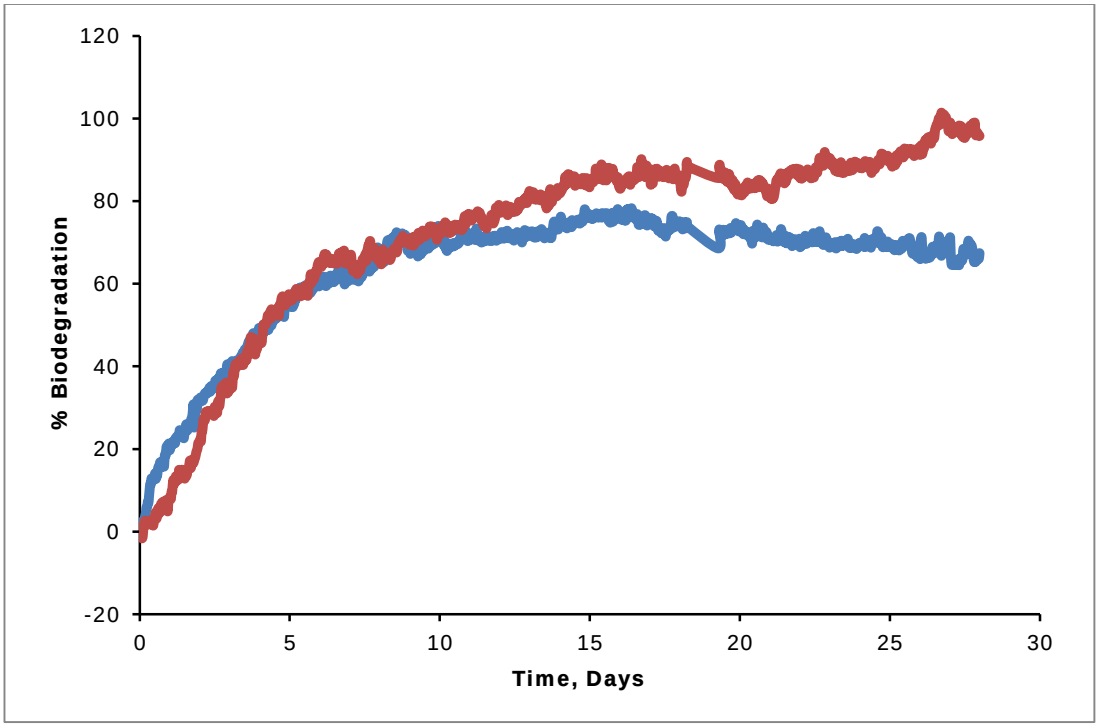


Figure C.3. % Biodegradation
– CNZVI and – OSA Starch

C.4. Conclusion

In situ treatments with surface-modified NZVI particles are limited because the mobility and distribution of modified particles is difficult to predict pre-injection. Using surface-modified NZVI particles as the reactive material in PRBs would reduce design uncertainties (i.e. non-uniform distribution and unexpected mobility). Surface-modified NZVI particles must remain stationary to be used in a PRB. This study monitored the 2-D transport of CNZVI particles (coated with 35% OSA-modified tapioca starch) to determine if they are applicable for use in PRBs.

The transportation studies indicate the CNZVI particles remain stationary and suspended when injected (for up to 6 hours). Injecting these particles into groundwater systems to create iron walls could reduce the cost of construction PRBs, which would improve the usability of PRBs. The OSA-starch is also biodegradable, which will necessary for injecting in groundwater systems.

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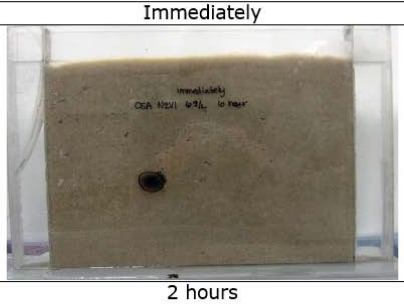
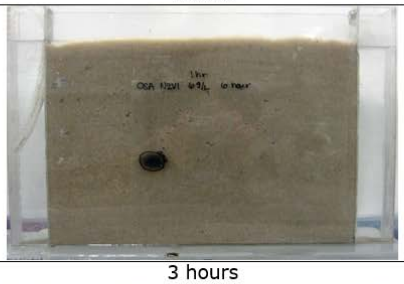
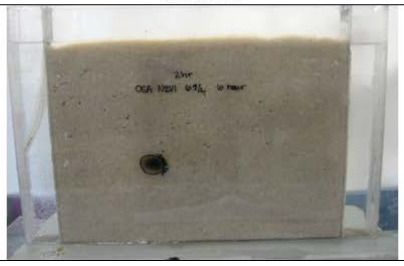
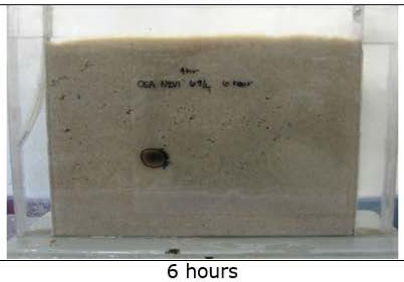
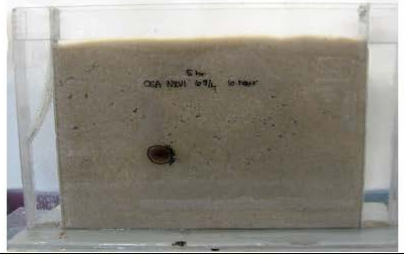
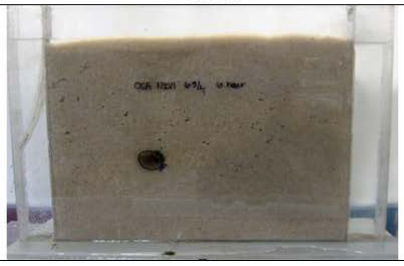
APPENDIX D. SUPPORTING DATA FOR APPENDIX C

D.1. 6-hour CNZVI Transport Study

Table D.1.6-hour CNZVI Transport Study

OSA Coated NZVI (6 g/L)	
Immediately	1 hour
	
2 hours	3 hours
	

4 hours	5 hours
	
6 hours	
	

D.2. One-Way ANOVA for BOD & Biodegradability

Hypothesis

H_o: There is not a significant difference between the biodegradability of bare NZVI particles and seed ($x_0 = x_1$).

H_a: There is a significant difference in biodegradability.

where:

x_0 = bare NZVI

x_1 = Seed

Table D.2. One-Way ANOVA (NZVI vs. Seed)

Source	DF	Adj. SS	Adj. MS	F-Value	P-Value
Treatment*	1	109032	109032	86.74	0.000
Error	2594	3260739	1257		
Total	2595	3369772			

*The four levels of treatment are presented in the hypothesis section above.

Table D.3. Seed vs. NZVI Tukey Pairwise Comparison

Treatment	N	Mean	Std. Dev	99.5% CI	Grouping**
0	1298	125.080	35.982	(122.315, 127.845)	B
1	1298	138.042	34.919	(135.277, 140.806)	A

** Means that do not share a letter are significantly different.

Hypothesis

H_o: There is not a significant difference between the biodegradability of CNZVI particles and starch ($x_0 = x_1$)

H_a: There is a significant difference in biodegradability.

x_0 = CNZVI

x_1 = Starch

Table D.4. One-Way ANOVA (CNZVI vs. Starch)

Source	DF	Adj. SS	Adj. MS	F-Value	P-Value
Treatment*	1	1925093	1925093	107.03	0.000
Error	2594	46657597	17987		
Total	2595	48584690			

*The four levels of treatment are presented in the hypothesis section above.

Table D.5. Seed vs. NZVI Tukey Pairwise Comparison

Treatment	N	Mean	Std. Dev	99.5% CI	Grouping**
0	1298	440.07	114.88	(429.62, 450.53)	B
1	1298	494.54	150.92	(484.08, 505.00)	A

** Means that do not share a letter are significantly different