Effect Of Acetic Or Citric Acid Ultrafiltration Recycle Streams On Coagulation Processes

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EFFECT OF ACETIC OR CITRIC ACID ULTRAFILTRATION RECYCLE STREAMS ON COAGULATION PROCESSES

by

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B.S. Env.E., University of Central Florida, 2009

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ABSTRACT

Integrating ultrafiltration (UF) membranes in lieu of traditional media filters within conventional surface water coagulation-flocculation-sedimentation processes is growing in popularity. UF systems are able to produce low turbidity filtered water that meets newer drinking water standards. For typical drinking water applications, UF membranes require periodic chemically enhanced backwashes (CEBs) to maintain production; and citric acid is a common chemical used for this purpose. Problems may arise when the backwash recycle stream from a citric acid CEB is blended with raw water entering the coagulation basin, a common practice for conventional surface water plants. Citric acid is a chelating agent capable of forming complexes that interfere with alum or ferric chloride coagulation. Interference with coagulation negatively affects settled water quality. Acetic acid was investigated as a potential substitute for citric acid in CEB applications. A jar testing study was conducted to compare the impacts of both citric acid and acetic acid on the effectiveness of aluminum sulfate (alum) and ferric chloride coagulants. Citric acid was found to adversely affect coagulation at lower acid to coagulant (A/C) molar ratios than acetic acid, and a coagulation interference threshold was identified for both acids based on settled water turbidity goals recommended by the U.S. Environmental Protection Agency (EPA). Pilot testing was conducted to assess the viability of acetic acid as a UF CEB chemical. Acetic acid CEBs maintained pilot performance in combination with sodium hypochlorite CEBs for filtering a raw California surface water. It is believed that this is the first ultrafiltration membrane process application of acetic acid CEBs for municipal potable water production in the United States.
To my parents, Anne and Jim, and my brother Andrew.
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# TABLE OF CONTENTS

LIST OF FIGURES ........................................................................................................... viii
LIST OF TABLES ............................................................................................................... x
LIST OF EQUATIONS ...................................................................................................... xi

## 1 INTRODUCTION

## 2 LITERATURE REVIEW

- An Overview of Ultrafiltration ....................................................................................... 4
- Review of UF CEB Chemicals ........................................................................................ 5
- Coagulation with Hydrolyzing Metal Salts ...................................................................... 5
- Coordination Chemistry and the Chelate Effect ............................................................. 7
- Citric and Acetic: Two Carboxylic Acids ....................................................................... 7
- Interactions of Carboxylic Acids with Coagulants ....................................................... 11
  - Alum .......................................................................................................................... 11
  - Ferric Chloride ........................................................................................................... 13
- Relevant Drinking Water Regulations ........................................................................... 14

## 3 MATERIALS AND METHODS

- Experimental Plan ......................................................................................................... 15
- Water Quality Parameters ............................................................................................. 17
- Pilot Equipment ............................................................................................................ 17
- Methods and Materials ................................................................................................ 19
- Procedures ..................................................................................................................... 21
  - Jar Testing Procedure ............................................................................................. 21
  - Sampling Procedure ............................................................................................... 25
  - UF Pilot Data Analysis ........................................................................................... 25
  - Laboratory Quality Control ................................................................................... 27

## 4 RESULTS AND DISCUSSION

- Alum Coagulation with Citric Acid and Acetic Acid .................................................. 36
  - Turbidity Trends for Alum Jar Tests ......................................................................... 39
  - Total Aluminum and Color Trends for Alum Jar Tests ............................................ 41
- Ferric Chloride Coagulation with Citric Acid and Acetic Acid ................................. 42
  - Turbidity Trends for Ferric Chloride Jar Tests ....................................................... 47
  - Total Iron and Color Trends for Ferric Chloride Jar Tests .................................... 49
<table>
<thead>
<tr>
<th>Chapter</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Possible Impacts of Coagulation Interference</td>
<td>52</td>
</tr>
<tr>
<td>Pilot Scale Evaluation of Acetic Acid CEB Performance</td>
<td>52</td>
</tr>
<tr>
<td>Dilution Considerations for Selecting CEB Chemical Concentrations</td>
<td>56</td>
</tr>
<tr>
<td>5 CONCLUSIONS</td>
<td>57</td>
</tr>
<tr>
<td>6 RECOMMENDATIONS</td>
<td>60</td>
</tr>
<tr>
<td>7 APPENDIX: ADDITIONAL FERRIC CHLORIDE RESULTS</td>
<td>62</td>
</tr>
<tr>
<td>REFERENCES</td>
<td>69</td>
</tr>
</tbody>
</table>
LIST OF FIGURES

Figure 2-1: Carboxyl Functional Group ................................................................. 8
Figure 2-2: Acetic Acid Molecule ........................................................................... 8
Figure 2-3: Citric Acid Molecule ............................................................................ 8
Figure 2-4: Acetic Acid Speciation Diagram ........................................................ 10
Figure 2-5: Citric Acid Speciation Diagram ............................................................ 10
Figure 3-1: Lake Manatee Reservoir, Manatee County, FL ..................................... 16
Figure 3-2: UF Pilot at the Mission San Jose WTP in Alameda County, CA .......... 18
Figure 3-3: Temperature and pH Ranges for Lake Manatee Coagulation with FeCl₃...... 22
Figure 3-4: Temperature and pH Ranges for Lake Manatee Coagulation with Alum..... 22
Figure 3-5: Example Titration Curve for Determining Sodium Hydroxide Doses ...... 23
Figure 3-6: Jar Testing Equipment ......................................................................... 24
Figure 3-7: Control Chart for Turbidity Analyses ................................................ 31
Figure 3-8: Control Chart for Metals Analyses ...................................................... 31
Figure 3-9: Control Chart for Color Analyses ....................................................... 32
Figure 4-1: Jar Test Results for Lake Manatee (Alum) – Turbidity versus A/C Molar Ratio .................................................................................................................. 40
Figure 4-2: Jar Test Results for Lake Manatee (Alum) – Total Aluminum Concentration versus A/C Molar Ratio ................................................................................. 43
Figure 4-3: Jar Test Results for Lake Manatee (Alum) – Color versus A/C Molar Ratio 44
Figure 4-4: Jar Test Results for Lake Manatee (Ferric Chloride) – Turbidity versus A/C Molar Ratio .................................................................................................................. 48
Figure 4-5: Jar Test Results for Lake Manatee (Ferric Chloride) – Total Iron Concentration versus A/C Molar Ratio.................................................................................................................. 50

Figure 4-6: Jar Test Results for Lake Manatee (Ferric Chloride) – Color versus A/C Molar Ratio ....................................................................................................................... 51

Figure 4-7: Pilot Performance Chart: Alameda County UF Pilot (Nov. 23rd, 2010-Jan. 1st, 2011) ........................................................................................................................................... 55

Figure 7-1: Temperature and pH Ranges for Lake Claire Coagulation with FeCl₃......... 64

Figure 7-2: Jar Test Results for Lake Claire (Ferric Chloride) – Turbidity versus A/C Molar Ratio................................................................................................................... 67

Figure 7-3: Jar Test Results for Lake Claire (Ferric Chloride) – Total Iron Concentration versus A/C Molar Ratio ........................................................................................................ 68
LIST OF TABLES

Table 3-1: List of Methods and Equipment ................................................................. 19
Table 3-2: List of Chemicals Used for Jar Testing ....................................................... 20
Table 3-3: Citric and Acetic Acid Dose Ranges ......................................................... 23
Table 3-4: Precision Assessment for Laboratory Quality Control................................. 30
Table 3-5: Accuracy Assessment for Laboratory Quality Control .............................. 33
Table 4-1: Summary Table of the Acid-Coagulant Combinations Tested .................... 35
Table 4-2: Jar Test Results for Lake Manatee with Alum and Citric Acid .................. 37
Table 4-3: Jar Test Results for Lake Manatee with Alum and Acetic Acid ................. 38
Table 4-4: Jar Test Results for Lake Manatee with Ferric Chloride and Citric Acid .... 45
Table 4-5: Jar Test Results for Lake Manatee with Ferric Chloride and Acetic Acid .... 46
Table 5-1: A/C* Molar Ratios Below and Above 2 NTU Interference Threshold .......... 57
Table 7-1: Jar Test Results for Lake Claire with Ferric Chloride and Citric Acid ......... 65
Table 7-2: Jar Test Results for Lake Claire with Ferric Chloride and Acetic Acid ...... 66
LIST OF EQUATIONS

Equation 2-1........................................................................................................6
Equation 2-2........................................................................................................6
Equation 2-3........................................................................................................6
Equation 2-4........................................................................................................6
Equation 3-1........................................................................................................25
Equation 3-2........................................................................................................26
Equation 3-3........................................................................................................26
Equation 3-4........................................................................................................28
Equation 3-5........................................................................................................28
1 INTRODUCTION

Conventional surface water treatment involves the use of coagulation, flocculation and sedimentation followed by filtration to remove colloids, dissolved solids or suspended particles. Traditional filtration methods include the use of sand or media filter beds. However, the implementation of ultrafiltration (UF) membrane systems in lieu of sand or media filters has grown in popularity, because UF membranes can consistently produce filtered water with turbidity values below 0.05 NTU (Duranceau, 2001).

As is the case with conventional sand or media filters, ultrafiltration membranes require regular backwashes to remove particulate matter. Periodically, chemicals may be introduced during backwashes to remove organic, biological or scaling type foulants. These backwashes are referred to as chemically enhanced backwashes (CEBs). Common CEB chemicals used to maintain UF membrane performance include sodium hydroxide, sodium hypochlorite and citric acid (Zondervan and Roffel, 2007). The selected chemical, or chemicals, depends on the type of foulant occurring on the membrane surface.

Maintenance of UF membranes through backwashes and CEBs generates a waste stream and can require a substantial volume of water. Therefore, it is both environmentally and financially prudent for water treatment utilities to recycle backwash water to the headworks of the treatment facility for blending with raw water. However, the chemical being recycled may adversely impact treatment objectives. For example, citric acid is a chelating agent commonly used to remove metal salts from membrane surfaces. The
ability of citric acid to complex with metals makes it well suited as a CEB chemical. Unfortunately, this same property can inhibit coagulation by binding with metal atoms in the hydrolyzing iron or aluminum salts commonly used for surface water treatment.

The recycle of backwash water is regulated under the Filter Backwash Recycle Rule (FBRR) promulgated by the U.S. EPA. Interference with coagulation has the potential to impact settled water turbidity and adversely affect settled water quality. Given the possibility of coagulation interference with citric acid, it is desirable to identify an alternative chemical for ultrafiltration membrane CEB applications. Using a concept for an alternative chemical as investigated by Duranceau and co-workers (Gupton et al, 1988), acetic acid is proposed as a substitute for citric acid in membrane CEB applications, because the molecular structure of acetic acid suggests a reduced ability to interfere with metal hydrolysis during coagulation.

This research presents a comparison of acetic acid and citric acid in terms of their respective abilities to impede coagulation. Jar testing was conducted using two Florida surface waters to identify the effects of both acids on ferric chloride and alum coagulation. Preliminary data were collected using water from Lake Claire on the University of Central Florida main campus. Based on the results of the preliminary analysis, a test plan was developed to simulate the impacts of backwash water recycle on full scale coagulation, flocculation and sedimentation. Jar test parameters were selected to imitate the treatment works at the Lake Manatee Water Treatment Plant (WTP) in Manatee County, Florida. Following jar testing, performance data was gathered on the
capability of acetic acid CEBs to maintain membrane performance as part of an ultrafiltration pilot project at the Mission San Jose WTP in Alameda County, California.
2 LITERATURE REVIEW

An Overview of Ultrafiltration

Ultrafiltration (UF) membranes are commonly composed of a bundle of hollow fibers that separate particles from water by a sieving mechanism. Particles larger than the membrane void spaces are rejected and accumulate on the membrane surface. In drinking water treatment, UF systems are typically operated in a dead-end flow regime. In dead-end filtration, feed water flows perpendicularly to the membrane surface without a recycle stream (MWH, 2005).

Transmembrane pressure (TMP) is the pressure difference between the feed and filtrate side of a UF membrane. The TMP is the driving force for flow across the fiber and is affected by water temperature and membrane fouling. Typical TMP values for UF systems are between 3 and 15 psi (MWH, 2005). Membrane performance is often evaluated in terms of specific flux. Specific flux is equal to the temperature corrected flux divided by the TMP.

Particles are removed from the membrane surface by regular backwashing. However, backwashing alone is often insufficient to maintain membrane performance as foulants accumulate on the membrane surface (AWWA, 2010). Chemicals may be used to remove organic, biological or scaling type foulants via chemically enhanced backwashes (CEBs) or chemical clean-in-place (CIP) procedures. The volume of water used to maintain UF membranes determines the recovery of UF systems operated in dead-end filtration mode.
In surface water treatment plants, it is advantageous to recycle backwash water to the head of the treatment works as long as doing so complies with the FBRR.

**Review of UF CEB Chemicals**

Successful foulant removal by CEBs depends on foulant type, chemical type, contact time, flow rate, concentration and chemical solution temperature (Zondervan and Roffel, 2007). Porcelli and Judd (2010) concluded that chemical cleaning is not well understood and that there is significant room for further research. Common CEB chemicals include citric acid, sulfuric acid, sodium hypochlorite and sodium hydroxide. The selection of CEB chemicals is often a trial and error process (Strugholtz et al., 2005).

Citric acid is a chelating agent frequently used to maintain UF membranes in water treatment, because it is well suited to remove organo-metallic foulants. In this research, acetic acid is evaluated as an alternative to citric acid for UF membrane maintenance. The literature search did not identify previous uses of acetic acid for UF membrane maintenance in water treatment applications. However, Mavredaki et al. (2007) reported using acetic acid to remove silicates from membranes in an industrial application.

**Coagulation with Hydrolyzing Metal Salts**

In water treatment, coagulation refers to the raw water addition of a hydrolyzing metal salt to remove dissolved, colloidal and suspended particles. The hydrolyzing metal salts of interest in this study are aluminum sulfate, commonly referred to as alum, and ferric chloride. When either of these metal salts is added to water, a variety of species form
depending on factors such as pH and temperature. However, the nuances of aluminum hydrolytic reactions are not completely understood (Sposito, 1996).

For coagulation purposes, significant reactions of interest are the formation of the amorphous solids presented in Equations 2-1 and 2-2 (MWH, 2005).

\[
Al^{3+} + 3H_2O \leftrightarrow Al(OH)_3(am) \downarrow +3H^+ \quad \text{(Equation 2-1)}
\]

\[
Fe^{3+} + 3H_2O \leftrightarrow Fe(OH)_3(am) \downarrow +3H^+ \quad \text{(Equation 2-2)}
\]

The release of protons during hydrolysis results in the depletion of raw water alkalinity. It is often necessary to add sodium hydroxide or lime to provide supplemental alkalinity to maintain appropriate pH values for amorphous solid formation and particle destabilization. Equations 2-3 and 2-4 illustrate the alkalinity demands of alum and ferric chloride coagulants (MWH, 2005).

\[
Al_2(SO_4)_3 \cdot 14H_2O + 6(HCO_3^-) \rightarrow 2Al(OH)_3(am) \downarrow +3SO_4^{2-} + 14H_2O + 6CO_2 \quad \text{(Equation 2-3)}
\]

\[
FeCl_3 \cdot 6H_2O + 3(HCO_3^-) \rightarrow Fe(OH)_3(am) \downarrow +3Cl^- + 6H_2O + 3CO_2 \quad \text{(Equation 2-4)}
\]

Alum and ferric chloride coagulants operate a different pH ranges. The pH range for alum is between 5.5 and 7.7, while ferric chloride has a broader pH range between 5.0 and 8.5 (MWH, 2005). Alum coagulation has a higher color and turbidity removal efficiency than ferric chloride, but ferric salts show better overall removal of natural organic matter (NOM) (Matilainen et al., 2010).
Coordination Chemistry and the Chelate Effect

Coordination chemistry concerns the formation of complexes consisting of ligands bound around a central metal ion. A ligand is an ion or molecule that bonds (or coordinates) with an aqueous metal. In metal-ligand bonding, the ligand acts as a Lewis base by donating an unshared electron pair to the metal (Brown et al., 2006). Carboxylic acids are common ligands that can coordinate to metal ions via carboxyl groups. Acetic acid is a monodentate ligand, because it possesses only one donor group. Multidentate ligands, such as citric acid, contain more than one donor group.

The thermodynamic stability of complexes formed with citrate versus acetate can be predicted by the chelate effect. The chelate effect describes the thermodynamics of interactions between metals and ligands with differing numbers of donor atoms. The chelate effect states that metal complexes formed with multidentate ligands will be more thermodynamically stable than monodentate ligands (Martell, 1996). Therefore, citric acid complexes are predicted to have increased stability relative to acetic acid complexes.

Citric and Acetic: Two Carboxylic Acids

Carboxylic acids are prevalent in nature and contain the characteristic carboxyl functional group depicted in Figure 2-1, where R represents a carbon chain. In aqueous systems, the hydroxyl (OH) group of a carboxyl functional group can deprotonate and allow for the formation of metal complexes. Acetic and citric acids are common carboxylic acids with extensive industrial applications. Acetic acid (CH₃COOH) is a weak monoprotic acid with the molecular structure depicted in Figure 2-2. The deprotonated form of acetic acid
is the acetate molecule, \( \text{CH}_3\text{COO}^- \). Acetate is a monodentate ligand that acts as a Lewis base when interacting with metal ions such as aluminum or iron. In contrast, citric acid (\( \text{C}_3\text{H}_4\text{O}_7\text{(COOH)}_3 \)) is a polydentate ligand with three carboxyl groups. The molecular structure of citric acid is illustrated in Figure 2-3.

![Figure 2-1: Carboxyl Functional Group](image1)

![Figure 2-2: Acetic Acid Molecule](image2)

![Figure 2-3: Citric Acid Molecule](image3)
The speciation of weak acids in aqueous systems is dependent on solution pH. Figures 2-4 and 2-5 present the speciation of acetic acid and citric acid, respectively. These speciation diagrams show relative constituent concentrations in terms of log(α) values versus solution pH. Note that Ac represents CH₃COO and Cit represents C₃H₄OH(COO)₃. At the pH values commonly desired in surface water treatment coagulation, both acetic acid and citric acid are present in deprotonated forms. The pKₐ value for acetic acid is 4.76; whereas, the pKₐ values for citric acid are 3.13, 4.72 and 6.33 (Benjamin, 2002). As can be seen from the speciation diagram for acetic acid, the dominant species in the pH range typical for coagulation is CH₃COO⁻. Likewise, for pH values between 5 and 8.5, the dominant species for citric acid is either C₃H₄OH(COO)₂(COOH)²⁻ or C₃H₄OH(COO)₃³⁻.
Figure 2-4: Acetic Acid Speciation Diagram

Figure 2-5: Citric Acid Speciation Diagram
Interactions of Carboxylic Acids with Coagulants

In drinking water treatment, coagulation involves the addition of an aluminum or iron salt to an untreated water source. The metal salt dissociates in solution, freeing the metal to coordinate with hydroxyl ligands and form a solid precipitate. Addition of a carboxylic acid into solution creates competition between ligands for coordination sites on the metal. The metal-ligand complexes that form are those thermodynamically favored complexes that lower the potential energy of the system (Benjamin, 2002).

Alum

The interference of a carboxylic acid with aluminum hydrolysis is influenced by factors such as the pH, the ligand/metal molar ratio and the molecular structure of the carboxylic acid (Violante and Violante, 1980). A significant amount of research on the interactions of carboxylic acids with aluminum hydroxides has been presented in soil journals. Aluminum hydroxides are products of soil weathering, and the presence of organic chelates influences the chemical speciation of soil systems (Violante and Violante, 1980). In this research, discussion of the impacts of carboxylic acids on coagulation has been examined through the lens of aqueous soil chemistry.

The ligand/metal molar ratio provides a tool for assessing the viability of coagulation at a given set of ligand and coagulant concentrations. Wang et al (1983) noted the importance of the ligand/metal molar ratio in their work on the interactions of carboxylic acids with aluminum hydroxide. In the Wang et al study, citric acid was evaluated at ligand/metal molar ratios between 0 and 3. Visible solids formation was not observed at values greater
than a ratio of 0.475. Acetic acid was also evaluated at molar ratios between 0 and 3, but no visible impact on solids formation was noted. Violante and Huang (1985) found that weak ligands influence aluminum hydroxide precipitation at sufficiently high ligand/metal molar ratios. Similar studies have also assessed the influence of carboxylic acids at different ligand/metal molar ratios (Violante and Violante; 1980; Kuan et al, 2005; Xu et al, 2010). Generally speaking, the interference of a carboxylic acid with aluminum hydroxide precipitation increases with increasing ligand/metal ratio.

The molecular structure of a carboxylic acid provides information on the potential coordination strength of the acid. As carboxylic acids increase in size and the number of functional groups, an increased possibility exists for alterations to the structure of aluminum hydrolysis products (Violante and Huang, 1985). Low molecular weight ligands, such as oxalic and citric acid, are known to impede the precipitation of Al(OH)$_3$(s) (Violante and Huang, 1985). The interaction of carboxylic ligands with aluminum leads to the formation of poorly crystalline reaction products rather than crystalline Al(OH)$_3$(s) (Violante and Violante, 1980).

Citric acid has been noted as a strong chelator of aluminum with an ability to impede crystallization of aluminum hydroxide species (Kuan et al, 2005; Violante and Violante, 1980). Citric acid readily replaces hydroxyl groups at pH values typical for water treatment applications. In addition to the three carboxyl groups that comprise a citric acid molecule, the molecular structure also contains a hydroxyl group. Motekaitis and Martell (1983) proposed that the hydroxyl group on the citric molecule provides increased
stability to resulting metal-ligand species. Kuan et al. (2005) also concluded that both the carboxyl groups and hydroxyl group can contribute to metal-ligand bonding, with typical reaction products of Al(citrate), AlH(citrate)$^+$ or Al(citrate)$_2^{3-}$.

Acetic acid is a monodentate ligand with one carboxyl group. The chelate effect predicts that acetate will be inferior to citrate in its ability to form metal-ligand complexes. Wang et al. (1983) concluded that citrate forms stronger bonds with aluminum than acetate. Aluminum complexes formed with the acetate anion are weak, and the influence of acetate on the formation of aluminum hydrolytic species is negligible at low molar ratios (Thomas et al, 1991). Motekaitis and Martell (1983) noted that the formation constant for a metal-ligand complex with three acetate molecules is approximately 3.5 orders of magnitude less than complexes with one citrate molecule. This implies that metal-ligand complexes with citrate are significantly more stable than acetate complexes.

Ferric Chloride

A review of the literature did not identify a significant number of articles on the interactions of iron (III) with acetic and citric acids in aqueous solutions. A more thorough search is required to define the chemistry of iron (III) interactions with carboxylic acids. Experiments by Hamm et al. (1954) demonstrated that citric acid acts as a tetrabasic acid in the presence of iron (III) by titrating an iron (III) perchlorate solution with citric acid. As was the case with interactions between aluminum (III) and citric acid, the hydroxyl group contributes to the formation metal-ligand complexes (Warner and Webber, 1953). This implies an increased stability of iron-citrate complexes. As for the
relative influence of citric and acetic acids on the formation of iron complexes, Cornell and Schwertmann (1979) reported that dicarboxylic acids are less efficient at interfering with iron oxide crystallization than hydroxy-carboxylic acids. This conclusion implies that a monocarboxylic acid, such as acetic acid, will be less efficient than citric acid at inhibiting coagulation. This result is in keeping with the chelate effect, which predicts increased stability for multidentate metal-ligand complexes relative to monodentate complexes.

Relevant Drinking Water Regulations
National secondary drinking water regulations define secondary maximum contaminant levels (SMCLs) that deal with the aesthetic quality of drinking water. Although not enforceable at the federal level, enforcement of SMCLs is left to the discretion of the states (AWWA, 2010). SMCLs relevant to coagulation processes include those for iron, aluminum and color. The SMCL for iron is 0.3 mg/L (USEPA, 1991), but iron concentrations as low as 0.1 mg/L can impart a metallic taste and color to water (AWWA, 2010). The SMCL for aluminum is established at 0.05 to 0.2 mg/L (USEPA, 1991). Aluminum also imparts color to water, which can adversely influence public perception of drinking water quality. An SMCL of 15 color units has been specified for color (USEPA, 1991).
3 MATERIALS AND METHODS

Chapter 3 contains information concerning the experimental plan, methods, materials and procedures used to conduct this study. A discussion of jar testing and data analysis procedures is offered for reference purposes. Laboratory quality control monitoring was incorporated into the study, and a summary of the quality control assessment is also presented.

Experimental Plan

The principle goals of this research were to compare the impacts of citric and acetic acid on coagulation and gather data on the performance of acetic acid as an ultrafiltration CEB chemical. To accomplish these goals, two separate experiments were performed. Jar testing was used to evaluate the effects of citric and acetic acid on coagulation with alum and ferric chloride salts. Pilot scale testing was also conducted to gather data on the ability of acetic acid to maintain ultrafiltration membrane performance via chemically enhanced backwashes.

The jar testing experiment was designed to simulate a full scale coagulation – flocculation - sedimentation basin. In this way, jar testing results can be used to identify potential water quality impacts from the recycle of UF backwash water containing citric or acetic acid. Preliminary jar testing data was collected using water from Lake Claire on the University of Central Florida main campus. Using the preliminary data gathered from Lake Claire testing, a more comprehensive test plan was developed to imitate a full scale treatment process. The Lake Manatee WTP was selected as the model for this
experiment, and raw water from the Lake Manatee Reservoir (Figure 3-1) was used to collect the majority of data presented herein. As detailed in this chapter, jar testing with Lake Manatee Reservoir water involved the addition of a coagulant, caustic for pH adjustment and an organic polymer. The organic polymer served as a flocculant aid and is used at the Lake Manatee WTP to improve floc formation.

After jar test results indicated that acetic acid had a lesser effect on coagulation than citric acid at comparable concentrations, a second experiment was designed to gather preliminary data on the CEB performance of acetic acid. Pilot scale evaluations of acetic acid were conducted as part of a pilot testing project at the Mission San Jose WTP in Alameda County, California. The pilot performance data presented in this research is intended to demonstrate the potential for the use of acetic acid as a UF CEB chemical.

Figure 3-1: Lake Manatee Reservoir, Manatee County, FL
Water Quality Parameters

Temperature, pH, turbidity, true color and total aluminum/iron concentrations were the principle water quality parameters collected during jar testing. Temperature and pH were measured during the slow mix phase of jar testing, and it was an experimental goal to maintain relatively constant pH and temperature within the jars for each coagulant. Following the settling phase of jar testing, samples were collected for the measurement of turbidity, true color and total aluminum/iron concentration. These parameters were selected to assess settled water quality changes with increasing citric or acetic acid dose.

Pilot Equipment

The UF pilot, depicted in Figure 3-2, incorporates one Toyobo Durasep UPF0860 ultrafiltration hollow fiber membrane operated in an inside-out dead-end configuration. Toyobo’s membrane fibers are composed of hydrophilic polyethersulfone (PES) modified using blended polyvinylpyrrolidone chemistry. The pilot is controlled electronically by a PLC and is equipped with onboard pressure gauges and transmitters, feed and backwash pumps with variable frequency drives (VFDs), feed and filtrate turbidity meters, flow meters, two chemical feed systems, water sample taps and an air compressor for pneumatic valve operation. Data are logged by the pilot at two minute intervals to facilitate data analysis and pilot evaluation. A touch screen user interface allows for the configuration of pilot operating parameters and the monitoring of pilot status. (Boyd et al., 2010)
The feed water for the UF pilot flows into a 200 gallon tank that serves as a feed water reservoir for the pilot. The UF filtrate stream is stored in a 1000 gallon tank for use during backwash cycles. Two parallel wye strainers provide prescreening of the feed water for removal of large diameter particles and debris. (Boyd et al., 2010)

During normal operation, the UF pilot cycles between forward filtration, backwash and chemically enhanced backwash (CEB) operation modes in a user defined sequence. The pilot actively filters feed water during a forward filtration cycle producing a filtrate stream. Regular backwashes remove particulate matter that has collected on the fiber surface. During backwashes, filtrate water is first pumped through the feed side of the membrane and then through the filtrate side of the membrane at a flux three times greater
than the forward filtration flux. At specified intervals, the pilot will perform a chemically enhanced backwash. During a CEB, a chemical such as sodium hypochlorite or citric acid is injected into the backwash stream to remove a targeted foulant, allowed to soak on the membrane fibers, and then rinsed prior to the restart of forward filtration. (Boyd et al, 2010)

**Methods and Materials**

Table 3-1 presents the methods and equipment used to conduct the laboratory water quality analyses. Table 3-2 provides a list and description of the chemicals used during jar testing.

**Table 3-1: List of Methods and Equipment**

<table>
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<tr>
<td>Temperature</td>
<td>Lab</td>
<td>Hach HQ40d; pH Testr 30</td>
<td>0.01 °C</td>
</tr>
<tr>
<td>Turbidity</td>
<td>Lab</td>
<td>Hach 2100 Q Portable Turbidimeter</td>
<td>0.01 NTU</td>
</tr>
<tr>
<td>Color</td>
<td>Lab</td>
<td>SM 2120 C; Hach DR 2700</td>
<td>1 CU/0.005 abs</td>
</tr>
<tr>
<td>Iron</td>
<td>Lab</td>
<td>Perkin Elmer Optima 2100 DV ICP-OES</td>
<td>0.001 mg/L</td>
</tr>
<tr>
<td>Aluminum</td>
<td>Lab</td>
<td>Perkin Elmer Optima 2100 DV ICP-OES</td>
<td>0.001 mg/L</td>
</tr>
</tbody>
</table>
Table 3-2: List of Chemicals Used for Jar Testing

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium Hydroxide</td>
<td>Solid, 97.8% NaOH</td>
</tr>
<tr>
<td>Alum</td>
<td>Provided by the Lake Manatee WTP in Manatee County, Florida</td>
</tr>
<tr>
<td>Ferric Chloride</td>
<td>Provided by the Mission San Jose WTP in Alameda County, California</td>
</tr>
<tr>
<td>Organic Polymer</td>
<td>CedarFloc 510 produced by CedarChem, LLC, Sample provided by the Lake Manatee WTP in Manatee County, Florida</td>
</tr>
<tr>
<td>Citric Acid</td>
<td>Anhydrous Citric Acid</td>
</tr>
<tr>
<td>Acetic Acid</td>
<td>25% Volume/Volume</td>
</tr>
<tr>
<td>Turbidity Standards</td>
<td>10, 20, 100 and 800 NTU Standards</td>
</tr>
<tr>
<td>pH Buffer Solns.</td>
<td>pH 4, 7 and 10 Buffer Solutions</td>
</tr>
<tr>
<td>Color Standard</td>
<td>500 Platinum Cobalt Units</td>
</tr>
<tr>
<td>Nitric Acid</td>
<td>15.8 Normal</td>
</tr>
</tbody>
</table>
Procedures

Jar Testing Procedure

Before an evaluation of coagulation interference could be made, it was first necessary to select a coagulant dose and pH for coagulation. It is desirable to keep the pH and temperature constant so that direct comparisons can be made between individual jars. If pH is not held constant, acid speciation and complex formation could vary between jars and confound results. Figures 3-3 and 3-4 present the pH and temperature values measured during Lake Manatee jar testing in this experiment.

Ferric chloride doses were determined through jar testing by evaluating different coagulant dose and pH combinations and comparing the settled water turbidity values. Lake Manatee water jar tests with ferric chloride used a ferric chloride dose of 75 mg/L with a target coagulation pH of 5.0. The alum dose (100 mg/L) and target pH (5.5) values for coagulation of Lake Manatee water were selected based on the actual operating conditions of the Lake Manatee WTP at the time of jar testing.

In order to maintain a relatively constant pH during coagulation, titrations were conducted to determine the required sodium hydroxide dose for each sample. Figure 3-5 displays an example titration curve for alum coagulation in the presence of citric acid. To create this curve, citric acid doses between 0.25mg/L and 70 mg/L were added to beakers filled with 100 mL of lake water. The appropriate coagulant dose was added into the beaker just prior to titration with sodium hydroxide. Titration curves were prepared for the each combination of acid and coagulant.
Figure 3-3: Temperature and pH Ranges for Lake Manatee Coagulation with FeCl₃

Figure 3-4: Temperature and pH Ranges for Lake Manatee Coagulation with Alum
The jar testing apparatus consisted of six 2-liter square jars commonly referred to as gator jars. The water used for testing was brought to room temperature and mixed before use. Jars were spiked with the appropriate concentration of citric or acetic acid prior to the addition of the coagulant, sodium hydroxide and polymer (if applicable). Table 3-3 presents the acid dose ranges tested with both alum and ferric chloride coagulants.

**Table 3-3: Citric and Acetic Acid Dose Ranges**

<table>
<thead>
<tr>
<th>Water Source</th>
<th>Coagulant</th>
<th>Coagulant Dose (mg/L)</th>
<th>Citric Acid Ranges (mg/L)</th>
<th>Acetic Acid Ranges (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lake Claire</td>
<td>Ferric Chloride</td>
<td>114</td>
<td>0.25 - 70</td>
<td>0.25 - 50</td>
</tr>
<tr>
<td>Lake Manatee</td>
<td>Alum</td>
<td>100</td>
<td>0.25 - 70</td>
<td>0.25 - 3000</td>
</tr>
<tr>
<td>Lake Manatee</td>
<td>Ferric Chloride</td>
<td>75</td>
<td>0.25 - 70</td>
<td>0.5 - 2750</td>
</tr>
</tbody>
</table>

**Figure 3-5: Example Titration Curve for Determining Sodium Hydroxide Doses**

\[
y = 0.01x + 0.42 \\
R^2 = 0.97
\]
The jar tests conducted with Lake Manatee water were intended to model operations at the Lake Manatee WTP. Jar tests consisted of one rapid mix stage, three slow mix stages and one settling stage. Coagulant and sodium hydroxide doses were added (either by vial or septa) just prior to the start of a 32 second rapid mix at 142 revolutions per minute (rpm). At the conclusion of the first slow mix stage, which lasted 3 minutes and 09 seconds at 60 rpm, an organic polymer dose of 0.18 mg/L was added to facilitate the agglomeration of flocs. Temperature and pH measurements were taken during the second slow mix stage which operated at 37 rpm for 14 minutes and 17 seconds. The final slow mix stage lasted 11 minutes at 10 rpm. These mixing times and speeds were provided by the Lake Manatee WTP. To facilitate sampling, a uniform settling time of 15 minutes was selected based on ASTM guidelines (ASTM, 2003). Figure 3-6 presents a photo of the jar testing equipment.

Figure 3-6: Jar Testing Equipment
Sampling Procedure

At the conclusion of the 15 minute settling period, 400 mL samples were collected from each jar for turbidity, color and metals testing. Jar sample taps were flushed for several seconds prior to sampling, and turbidity measurements were taken immediately after sample collection. Metals analysis vials were filled with sample, acidified in a 2 percent nitric acid solution, and stored at 4°C for analysis by ICP-OES. Remaining sample volumes were filtered through glass microfiber filters using a vacuum pump. Sodium hydroxide was then used to pH adjust each sample to 7.6 prior to color measurement.

UF Pilot Data Analysis

The Alameda County UF pilot records data electronically at 2-minute intervals into Excel spreadsheets. Before data was graphed for presentation, a statistical analysis and averaging of the applicable data was conducted to reduce the size of the data set and remove erroneous instrument readings. Data outside +/- 3 standard deviations from the mean (99th percentile) were excluded from the data set.

UF membrane performance is determined by monitoring trends in specific flux and transmembrane pressure (TMP). In the United States, flux and specific flux are typically presented in units of gallons/ft$^2$-day and gallons/ft$^2$-day-psi, respectively. Equation 3-1 presents the flux calculation.

\[
J_M = \frac{Q_F}{SA}
\]

(Equation 3-1)

\[J_M = \text{Flux (gal/ft}^2\text{-day)}\]
Q_F = Filtrate Flow (gal/day)

SA = Membrane Surface Area (ft²)

Equations 3-2 and 3-3 for the calculation of temperature corrected flux and specific flux are presented in the Membrane Filtration chapter of Water Treatment Principles and Design by MWH (2005). Flux values were corrected to 20°C for the UF pilot data analysis presented in this research, which is the typical correction temperature for UF membranes.

\[ J_s = J_M (1.03)^{T_s - T_M} \]  
\[J_{SP,20°C} = \frac{J_s}{\Delta P}\]

\( J_s \) = Flux at 20°C (gal/ft²-day)

\( T_s \) = Standard Temperature (°C)

\( T_M \) = Measured Temperature (°C)

\( J_{SP,20°C} \) = Specific Flux at 20°C (gal/ft²-day-psi)

\( \Delta P \) = Transmembrane Pressure (psi)

The UF pilot performance charts presented in this research consist of specific flux, filtrate flow and TMP plotted versus runtime. The runtime of the pilot is equal to the amount of time the pilot is actively filtering water. Downtimes associated with backwashing, CEB cycles or unanticipated stoppages are not included in the runtime.
Laboratory Quality Control

Laboratory quality control measures were taken to monitor and assess the data collection process. Glassware used in the course of data collection were washed thoroughly with 1:1 hydrochloric acid and rinsed with distilled water prior to use. Samples requiring storage were kept in a cooler at 4°C. Sample collection, storage and analytical equipment maintenance activities were conducted in accordance with the recommendations of the Standard Methods for the Examination of Water and Wastewater (Eaton et al, 2005).

Precision and accuracy in the lab were assessed by preparation of duplicates and spikes. For quality control purposes, approximately one out of every five samples was duplicated to monitor precision via calculation of the industrial (I) statistic. It should be noted that a portion of the samples collected yielded results below detection limits or could not be analyzed. This is most notable with the reporting of color values, because a large percentage of the color measurements taken yielded values below the color calibration curve for the experiment.

Equation 3-4 presents the calculation for the industrial statistic as described in the Handbook for Quality Control in Water and Wastewater Laboratories (EPA, 1979). Upper control limits (UCL) and upper warning limits (UWL) were established for turbidity, total metal and color analyses. The UCL was defined to be the average I-statistic value plus three standard deviations from the mean. The UWL was defined to be the average I-statistic value plus two standard deviations from the mean. Duplicate samples were said to be in compliance if they did not exceed the UCL or two consecutive
samples did not exceed the UWL. Accuracy was monitored by calculating the percent recovery for spiked metals samples. Equation 3-5 presents the percent recovery calculation for a laboratory-fortified matrix sample. Spiked samples were said to be in compliance if the percent recovery fell within the range of 80 to 120% (Eaton et al., 2005).

\[ I = \frac{|A-B|}{(A+B)} \]  \hspace{1cm} \text{(Equation 3-4)}

\[ \% \text{Recovery} = \frac{\text{Concentration}_{\text{sample+spike}} - \text{Concentration}_{\text{sample}}}{\text{Concentration}_{\text{spike}}} \times 100\% \] \hspace{1cm} \text{(Equation 3-5)}

Table 3-4 presents the results of the laboratory precision assessment conducted for this experiment. Control charts for the turbidity, metals and color analyses are presented in Figures 3-7 through 3-9. The industrial statistic values did not exceed the UCL or UWL compliance guidelines for the samples tested. Table 3-5 presents the results of the laboratory accuracy assessment conducted for this experiment. Three of the percent recovery values violate the percent recovery compliance range of 80% to 120%.

There is a degree of variability in the I-statistic and percent recovery values determined as part of the quality control plan for this experiment. This variability is attributed to several factors including the non-homogeneity of the surface water used in jar testing and the variable application of chemicals associated with pouring reagents from vials. Human error in preparing sample spikes is a potential cause for the errant percent recovery values shown in Table 3-5. Another possible source of error may be attributed to the jar testing equipment. The jar testing apparatus was not calibrated prior to the start of testing,
because the necessary calibration equipment was not available. It is possible that the individual paddles used in the jar testing apparatus were not rotating at the same speed during the experiment resulting in variable mixing. However, the trends in the data show a strong correlation between carboxylic acid concentration and settled water quality impacts that are worthy of consideration.
Table 3-4: Precision Assessment for Laboratory Quality Control

<table>
<thead>
<tr>
<th>Set #</th>
<th>Turbidity (NTU)</th>
<th>Metals (mg/L)</th>
<th>Color (abs)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Duplicate A</td>
<td>Duplicate B</td>
<td>I-Statistic</td>
</tr>
<tr>
<td>1</td>
<td>1.84</td>
<td>1.02</td>
<td>0.287</td>
</tr>
<tr>
<td>2</td>
<td>4.57</td>
<td>5.23</td>
<td>0.067</td>
</tr>
<tr>
<td>3</td>
<td>0.62</td>
<td>0.70</td>
<td>0.061</td>
</tr>
<tr>
<td>4</td>
<td>0.59</td>
<td>0.52</td>
<td>0.063</td>
</tr>
<tr>
<td>5</td>
<td>0.42</td>
<td>0.45</td>
<td>0.034</td>
</tr>
<tr>
<td>6</td>
<td>1.20</td>
<td>0.72</td>
<td>0.250</td>
</tr>
<tr>
<td>7</td>
<td>0.36</td>
<td>0.43</td>
<td>0.089</td>
</tr>
<tr>
<td>8</td>
<td>0.66</td>
<td>0.50</td>
<td>0.138</td>
</tr>
<tr>
<td>9</td>
<td>0.60</td>
<td>0.61</td>
<td>0.008</td>
</tr>
<tr>
<td>10</td>
<td>0.76</td>
<td>0.80</td>
<td>0.026</td>
</tr>
<tr>
<td>11</td>
<td>9.89</td>
<td>9.06</td>
<td>0.044</td>
</tr>
<tr>
<td>12</td>
<td>1.18</td>
<td>1.17</td>
<td>0.004</td>
</tr>
<tr>
<td>13</td>
<td>0.59</td>
<td>0.74</td>
<td>0.113</td>
</tr>
<tr>
<td>14</td>
<td>2.46</td>
<td>2.23</td>
<td>0.049</td>
</tr>
<tr>
<td>15</td>
<td>23.4</td>
<td>17.4</td>
<td>0.147</td>
</tr>
<tr>
<td>16</td>
<td>0.43</td>
<td>0.39</td>
<td>0.049</td>
</tr>
<tr>
<td>17</td>
<td>0.29</td>
<td>0.38</td>
<td>0.134</td>
</tr>
<tr>
<td>18</td>
<td>0.31</td>
<td>0.34</td>
<td>0.046</td>
</tr>
<tr>
<td>19</td>
<td>0.50</td>
<td>0.45</td>
<td>0.053</td>
</tr>
<tr>
<td>20</td>
<td>0.51</td>
<td>0.41</td>
<td>0.109</td>
</tr>
<tr>
<td>21</td>
<td>0.93</td>
<td>0.94</td>
<td>0.005</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Duplicate A</th>
<th>Duplicate B</th>
<th>I-Statistic</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average</td>
<td>0.085</td>
<td>0.079</td>
<td>0.084</td>
</tr>
<tr>
<td>Standard Deviation</td>
<td>0.075</td>
<td>0.109</td>
<td>0.074</td>
</tr>
<tr>
<td>Minimum</td>
<td>0.004</td>
<td>0.001</td>
<td>0.000</td>
</tr>
<tr>
<td>Maximum</td>
<td>0.287</td>
<td>0.406</td>
<td>0.200</td>
</tr>
<tr>
<td>Upper Warning Limit</td>
<td>0.234</td>
<td>0.297</td>
<td>0.231</td>
</tr>
<tr>
<td>Upper Control Limit</td>
<td>0.308</td>
<td>0.406</td>
<td>0.305</td>
</tr>
</tbody>
</table>
Figure 3-7: Control Chart for Turbidity Analyses

Figure 3-8: Control Chart for Metals Analyses
Figure 3-9: Control Chart for Color Analyses
Table 3-5: Accuracy Assessment for Laboratory Quality Control

<table>
<thead>
<tr>
<th>Sample</th>
<th>Spiked Sample</th>
<th>% Recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.09</td>
<td>1.08</td>
<td>101</td>
</tr>
<tr>
<td>0.19</td>
<td>1.20</td>
<td>103</td>
</tr>
<tr>
<td>1.92</td>
<td>2.92</td>
<td>102</td>
</tr>
<tr>
<td>0.07</td>
<td>1.10</td>
<td>105</td>
</tr>
<tr>
<td>0.11</td>
<td>1.10</td>
<td>102</td>
</tr>
<tr>
<td>0.10</td>
<td>1.12</td>
<td>104</td>
</tr>
<tr>
<td>4.63</td>
<td>5.34</td>
<td>72.3</td>
</tr>
<tr>
<td>0.30</td>
<td>2.08</td>
<td>90.8</td>
</tr>
<tr>
<td>0.53</td>
<td>2.35</td>
<td>92.9</td>
</tr>
<tr>
<td>25.4</td>
<td>26.7</td>
<td>63.8</td>
</tr>
<tr>
<td>0.37</td>
<td>2.27</td>
<td>96.7</td>
</tr>
<tr>
<td>0.15</td>
<td>2.05</td>
<td>97.0</td>
</tr>
<tr>
<td>0.96</td>
<td>2.67</td>
<td>87.0</td>
</tr>
<tr>
<td>12.7</td>
<td>13.2</td>
<td>28.5</td>
</tr>
<tr>
<td>0.01</td>
<td>1.82</td>
<td>92.6</td>
</tr>
<tr>
<td>0.15</td>
<td>1.98</td>
<td>93.0</td>
</tr>
<tr>
<td>0.11</td>
<td>1.96</td>
<td>94.6</td>
</tr>
<tr>
<td>0.14</td>
<td>1.97</td>
<td>93.6</td>
</tr>
<tr>
<td>0.09</td>
<td>1.96</td>
<td>95.4</td>
</tr>
</tbody>
</table>

Average 90.2
Standard Deviation 18.1
4 RESULTS AND DISCUSSION

Integrating ultrafiltration (UF) membranes in lieu of traditional media filters within conventional surface water coagulation-flocculation-sedimentation processes is growing in popularity. UF systems are able to produce low turbidity filtered water that meets newer drinking water standards. For typical drinking water applications, UF membranes require periodic chemically enhanced backwashes (CEBs) to maintain production; and citric acid is a common chemical used for this purpose. Problems may arise when the backwash recycle stream from a citric acid CEB is blended with raw water entering the coagulation basin, a common practice for conventional surface water plants. Acetic acid is a potential substitute for citric acid in CEB applications.

In this research, a jar testing study was conducted to compare the impacts of both citric acid and acetic acid on the effectiveness of aluminum sulfate (alum) and ferric chloride coagulants. Turbidity, color and total metal concentration measurements were taken to assess coagulation performance on the basis of changes in settled water quality. Monitoring changes in settled water quality provides a useful method for quantifying the extent of coagulation interference by carboxylic acids.

Surface water from the Lake Manatee Reservoir was used to conduct the majority of the jar tests. Preliminary data were also collected using water from Lake Claire. An effort was made to simulate the operations of the Lake Manatee WTP by selecting jar test mixing times, speeds and chemical additions that approximated the operation of the full scale facility. An organic polymer (CedarFloc 510) was added as a flocculant aid during
jar testing. Flocculant aids are advantageous in water treatment, because they improve floc formation (MWH, 2005). It is therefore reasonable to assume that the organic polymer addition created a best case scenario for floc formation and settling. Table 4-1 presents a summary of the acid-coagulant combinations tested.

Table 4-1: Summary Table of the Acid-Coagulant Combinations Tested

<table>
<thead>
<tr>
<th>Acid/Coagulant Combination</th>
<th>Alum</th>
<th>Ferric Chloride</th>
</tr>
</thead>
<tbody>
<tr>
<td>Citric Acid</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>Acetic Acid</td>
<td>✓</td>
<td>✓</td>
</tr>
</tbody>
</table>

Based on the findings of this research, there is a threshold beyond which significant deteriorations in settled water quality are observed. This threshold has been defined in terms of settled water turbidity values, because the quality of sedimentation basin effluent has a direct impact on downstream processes. The U.S. EPA has recommended individual sedimentation basin performance goals for surface water treatment facilities. For facilities with average annual raw water turbidity values greater than 10 NTU, the settled water turbidity goal is less than 2 NTU 95% of the time (USEPA, 1998). The Lake Manatee WTP has adopted this settled water turbidity goal for sedimentation basin effluent, and this study defines the coagulation interference threshold as the acid to coagulant (A/C) molar ratio beyond which settled water turbidity values exceed 2 NTU.
Interference with coagulation has the potential to impact settled water turbidity and adversely affect settled water quality. In this study, the impacts of citric and acetic acids on coagulation were evaluated in terms of A/C molar ratios. The ratio of acid to coagulant provides a simple tool for water purveyors to assess the possible coagulation impacts of UF CEB recycle streams. A range of A/C molar ratios were tested to identify changes in settled water quality with increasing acid concentration. Additional testing was conducted to gather preliminary data on the performance of acetic acid CEBs. Acetic acid may be a viable alternative to citric acid for maintaining UF membranes in drinking water applications.

**Alum Coagulation with Citric Acid and Acetic Acid**

The interference effects of citric acid and acetic acid on alum coagulation were evaluated using water from the Lake Manatee Reservoir. The Lake Manatee jar test runs modeled full scale operations at Lake Manatee WTP, including the addition of an organic polymer. Alum coagulation with citric acid was evaluated at acid/coagulant molar ratios between 0.008 and 2.17. These values correspond to a range of 0.25 mg/L to 70 mg/L of citric acid at an alum dose of approximately 100 mg/L. Acetic acid was evaluated at A/C molar ratios between 0.025 and 297, corresponding to a range of 0.25 mg/L to 3000 mg/L of acetic acid. Tables 4-2 and 4-3 present the results for alum jar tests with citric and acetic acid.
Table 4-2: Jar Test Results for Lake Manatee with Alum and Citric Acid

<table>
<thead>
<tr>
<th>Citric Acid/Alum Molar Ratio</th>
<th>Citric Acid/Alm Molar Ratio</th>
<th>Citric Acid Concentration (mg/L)</th>
<th>pH</th>
<th>Temperature (°C)</th>
<th>Turbidity (NTU)</th>
<th>True Color (PCU)</th>
<th>Total Al Concentration (mg/L Al)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.000</td>
<td>0.000</td>
<td>0</td>
<td>5.74</td>
<td>19.9</td>
<td>0.59</td>
<td>11</td>
<td>0.45</td>
</tr>
<tr>
<td>0.008</td>
<td>0.004</td>
<td>0.25</td>
<td>5.95</td>
<td>20.5</td>
<td>0.60</td>
<td>&lt;10</td>
<td>0.48</td>
</tr>
<tr>
<td>0.015</td>
<td>0.008</td>
<td>0.5</td>
<td>5.96</td>
<td>19.7</td>
<td>0.69</td>
<td>13</td>
<td>0.47</td>
</tr>
<tr>
<td>0.023</td>
<td>0.012</td>
<td>0.75</td>
<td>5.89</td>
<td>19.8</td>
<td>0.49</td>
<td>&lt;10</td>
<td>0.44</td>
</tr>
<tr>
<td>0.031</td>
<td>0.015</td>
<td>1</td>
<td>5.90</td>
<td>19.7</td>
<td>1.30</td>
<td>13</td>
<td>0.68</td>
</tr>
<tr>
<td>0.062</td>
<td>0.031</td>
<td>2</td>
<td>5.85</td>
<td>19.7</td>
<td>1.43</td>
<td>12</td>
<td>0.80</td>
</tr>
<tr>
<td>0.124</td>
<td>0.062</td>
<td>4</td>
<td>5.86</td>
<td>20.6</td>
<td>0.95</td>
<td>&lt;10</td>
<td>0.99</td>
</tr>
<tr>
<td>0.155</td>
<td>0.077</td>
<td>5</td>
<td>5.94</td>
<td>20.4</td>
<td>1.40</td>
<td>&lt;10</td>
<td>1.41</td>
</tr>
<tr>
<td>0.310</td>
<td>0.155</td>
<td>10</td>
<td>6.04</td>
<td>20.2</td>
<td>13.80</td>
<td>72</td>
<td>8.30</td>
</tr>
<tr>
<td>0.619</td>
<td>0.310</td>
<td>20</td>
<td>6.02</td>
<td>19.9</td>
<td>11.30</td>
<td>116</td>
<td>10.53</td>
</tr>
<tr>
<td>0.929</td>
<td>0.464</td>
<td>30</td>
<td>5.88</td>
<td>20.4</td>
<td>7.58</td>
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Turbidity Trends for Alum Jar Tests

Figure 4-1 presents the turbidity trends observed for alum coagulation with citric and acetic acid. Turbidity values for citric acid spiked jars remained below the 2 NTU threshold between A/C molar ratios of 0.0 and 0.155. A sharp rise in turbidity was recorded at an A/C ratio of 0.310 corresponding to the formation of tiny non-settling floc particles. Citric acid molecules at the citric acid/alum ratio of 0.310 began to severely limit the agglomeration of aluminum hydroxide flocs characteristic of typical coagulation. A gradual reduction in turbidity was observed at A/C molar ratios between 0.310 and 2.17. Declining turbidity values may indicate the formation of soluble metal-citric complexes and an increased inhibition of Al(OH)₃ precipitation. Visual settling was not observed at A/C ratios of 0.310 or higher.

Acetic acid had a significantly lower inhibitory effect on alum coagulation than citric acid. Coagulation, flocculation and sedimentation were observed at each acetic acid/alum ratio tested. A/C molar ratios between 0.025 and 39.6 yielded turbidity values below the 2 NTU threshold. Turbidity values increased above the 2 NTU threshold at an A/C molar ratio of 49.5; however, the maximum turbidity recorded for acetic acid spiked jars was 4.23 NTU compared with 13.8 NTU for citric acid. This result implies that acetic acid has a reduced potential for pin floc formation with alum coagulation. Interestingly, turbidity values dipped below the 2 NTU turbidity threshold between A/C values of 198 and 297. Visual observation of jars at these molar ratios indicated that floc density was reduced as compared to reference jars (i.e. jars without acetic acid addition).
Figure 4-1: Jar Test Results for Lake Manatee (Alum) – Turbidity versus A/C Molar Ratio
Total Aluminum and Color Trends for Alum Jar Tests

Figure 4-2 presents the trends for total aluminum concentrations in settled water samples. A gradual increase in the total aluminum concentration for citric acid spiked jars was observed between A/C molar ratios of 0.0 and 0.155. The total aluminum concentration then increased significantly between A/C ratios of 0.155 and 0.310 from 1.14 mg/L to 8.30 mg/L. A comparison with the turbidity data shows that the increased total aluminum concentration at an A/C ratio of 0.310 corresponded to pin floc formation, high turbidity values and negligible particle settling. Total aluminum concentrations ranged between 10.53 mg/L and 9.09 mg/L for A/C ratios of 0.619 and higher.

The maximum total aluminum concentration (6.97 mg/L) in acetic acid spiked jars was less than the maximum total aluminum concentration (10.5 mg/L) in citric acid spiked jars within the range of A/C molar ratios tested. This result is explained by the partial removal of aluminum from suspension by floc formation and settling in acetic acid spiked jars. As noted previously, the agglomeration of flocs at varying floc densities was observed at acetic acid/alum molar ratios between 0.0 and 297. It is anticipated that total aluminum concentrations would continue to increase at acetic acid/alum molar ratios in excess of 297.

Figure 4-3 presents the color trends for the alum jar tests. Citric acid spiked jars showed a significant increase in color at an A/C ratio of 0.310. The increase in settled water color corresponded to the observed turbidity and total aluminum concentration increases at the same A/C ratio. Maximum color values for acetic acid spiked jars were approximately
half of the maximum color values for jars containing citric acid. Additionally, color values for acetic acid spiked jars did not correlate as well with turbidity and total aluminum trends. The data shows that color values remained relatively stable until an A/C ratio of 149 despite increases in turbidity and total aluminum concentrations at lower A/C ratios. These results imply that color is not a clear and reliable indicator of coagulation interference with acetic acid.

Ferric Chloride Coagulation with Citric Acid and Acetic Acid

Two different Florida surface waters were used to test the effects of citric acid and acetic acid on ferric chloride coagulation. Preliminary data was gathered using water from Lake Claire on the University of Central Florida campus. The results for the Lake Claire jar tests are presented in the Appendix. A more comprehensive analysis was conducted using water from the Lake Manatee Reservoir. The Lake Manatee jar test runs modeled full scale operations at the Lake Manatee WTP at the time of testing, including the addition of an organic polymer. Ferric chloride coagulation with citric acid was evaluated at A/C molar ratios between 0.003 and 0.788. These values correspond to a range of 0.25 mg/L to 70 mg/L of citric acid at a ferric chloride dose of 75 mg/L. Acetic acid was evaluated at A/C molar ratios between 0.018 and 106, corresponding to a range of 0.50 mg/L to 2750 mg/L of acetic acid. Tables 4-4 and 4-5 present the results for the Lake Manatee ferric chloride jar tests.
Figure 4-2: Jar Test Results for Lake Manatee (Alum) – Total Aluminum Concentration versus A/C Molar Ratio
Figure 4-3: Jar Test Results for Lake Manatee (Alum) – Color versus A/C Molar Ratio
Table 4-4: Jar Test Results for Lake Manatee with Ferric Chloride and Citric Acid

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<th>pH</th>
<th>Temperature (°C)</th>
<th>Turbidity (NTU)</th>
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## Table 4-5: Jar Test Results for Lake Manatee with Ferric Chloride and Acetic Acid

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<td>2500</td>
<td>4.87</td>
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<td>106</td>
<td>2750</td>
<td>4.86</td>
<td>19.7</td>
<td>24.7</td>
<td>192</td>
<td>19.0</td>
</tr>
</tbody>
</table>
Turbidity Trends for Ferric Chloride Jar Tests

Figure 4-4 presents the turbidity trends for ferric chloride coagulation with citric and acetic acids. Turbidity values for jars spiked with citric acid remained below the 2 NTU threshold between A/C molar ratios of 0.0 and 0.113. Settled water turbidity then rose sharply at an A/C molar ratio of 0.169 to 28.9 NTU corresponding to pin floc formation. The increase in settled water turbidity from 1.07 NTU to 28.9 NTU indicates the potential for significant changes in settled water quality over a narrow range of citric acid concentrations. Similar turbidity trends were observed during both the Lake Manatee alum and Lake Claire ferric chloride jar tests. Visual settling was not observed between A/C molar ratios of 0.169 and 0.788. As with alum coagulation, turbidity values began to decline after reaching a maximum value, which may indicate a transition from particulate iron complexes to soluble iron complexes at increasing A/C molar ratios.

Acetic acid had a lower inhibitory effect on ferric chloride coagulation than citric acid. A/C molar ratios between 0.0 and 10.8 yielded turbidity values below the 2 NTU threshold. Unlike the other acid-coagulant combinations tested, the turbidity did not rapidly spike to a maximum value and begin to decline. Instead, turbidity values gradually increased in a linear fashion within the range of A/C ratios tested. This implies that significant acetic acid concentrations are required to fully impede the visible formation of Fe(OH)$_3$(s). However, pin floc formation was observed between molar ratios of 57.9 and 106 with reduced particle settling. In contrast, alum jar tests with acetic acid showed some floc formation and settling within the range of A/C ratios tested.
Figure 4-4: Jar Test Results for Lake Manatee (Ferric Chloride) – Turbidity versus A/C Molar Ratio
Total Iron and Color Trends for Ferric Chloride Jar Tests

Figure 4-5 presents the trends for total iron concentrations in settled water samples. A gradual increase in the total iron concentration for citric acid spiked jars was observed between A/C molar ratios of 0.0 and 0.113. The total iron concentration then increased significantly between A/C ratios of 0.113 and 0.169 from 1.76 to 25.2 mg/L. Based on a mass balance calculation, the settled water iron concentration for samples with A/C ratios of 0.169 and greater approximated the amount of iron added with the ferric chloride coagulant. A comparison with the turbidity data shows that the increased total iron concentration at an A/C ratio of 0.169 corresponded to pin floc formation, high turbidity values and negligible particle settling.

Acetic acid spiked jars showed a gradual linear increase in total iron concentrations up to a value of 19.0 mg/L at an A/C ratio of 106. The sudden spike in the total iron concentration characteristic of citric acid spiked jars was not observed. A similar trend was noted with acetic acid and alum, where total aluminum concentrations gradually increased with increasing acetic acid dose. It is anticipated that total iron concentrations would continue to increase at A/C ratios in excess of 106.

Iron complexes imparted significant color to settled water samples at high A/C molar ratios. Figure 4-6 shows the color trends for the ferric chloride jar tests. Citric acid spiked jars showed a significant increase in color at an A/C ratio of 0.169. This sudden increase in color corresponded to observed turbidity and total iron concentration increases at the same A/C ratio.
Figure 4-5: Jar Test Results for Lake Manatee (Ferric Chloride) – Total Iron Concentration versus A/C Molar Ratio
Figure 4-6: Jar Test Results for Lake Manatee (Ferric Chloride) – Color versus A/C Molar Ratio
Color values for acetic acid spiked jars did not correlate as well with turbidity and total aluminum trends. Color values remained relatively stable until an A/C ratio of 54.1, despite increases in turbidity and total iron concentration at lower A/C ratios. These results reinforce the idea that color is not a clear and reliable indicator of coagulation interference with acetic acid.

Possible Impacts of Coagulation Interference

As demonstrated in this study, coagulation interference can lead to increased settled water turbidity. If the A/C molar ratio is such that pin flocs form in the coagulation basin, then the mass loading on downstream UF filters may increase resulting in shorter filter runs and the need for more frequent backwashes and CEBs. Additionally, coagulation interference could possibly have negative impacts on compliance with secondary water quality standards. In this study, settled water total aluminum (for alum coagulation) or total iron (for ferric chloride coagulation) concentrations were demonstrated to increase at appreciable A/C molar ratios. Depending on the solubility of the metal-ligand complexes formed, it is possible that a fraction of the metal added with the coagulant could pass through downstream filters. Settled water color values were also demonstrated to increase at appreciable A/C molar ratios.

Pilot Scale Evaluation of Acetic Acid CEB Performance

Citric acid is commonly used in the water treatment industry as a CEB chemical for maintaining synthetic membranes. However, citric acid can significantly affect the performance of coagulation processes in surface water treatment. Acetic acid is proposed
as an alternative to citric acid for maintaining UF membranes in drinking water applications. As demonstrated in this study, the impact of acetic acid on both alum and ferric chloride coagulation is less than that of citric acid at comparable concentrations. Therefore, it is advantageous to consider acetic acid as a CEB chemical because of the reduced possibility for coagulation interference during CEB water recycle.

Pilot scale testing of acetic acid was conducted at the Mission San Jose WTP in Alameda County, California. The intent of the acetic acid test was to gather preliminary data on the CEB performance of acetic acid using a Toyobo Durasep UPF0860 hollow fiber ultrafiltration membrane. The UF pilot filtered surface water directly from Lake Del Valle in northern California between November 23rd, 2010 and January 1st, 2011.

Maintaining stable membrane performance was the principle goal of pilot testing at the Mission San Jose WTP. In light of this goal, sodium hypochlorite CEBs were used in conjunction with acetic acid CEBs to remove possible biological or organic foulants. With the exception of a ten day period, a back-to-back sodium hypochlorite/acetic acid CEB sequence was used during which a sodium hypochlorite CEB was followed by an acetic acid CEB. This combined CEB sequence prohibits isolation of the benefits of acetic acid as a CEB chemical. However, it can be stated that the pilot experienced stable operation using the combined sodium hypochlorite and acetic acid CEB sequence.

Figure 4-7 presents the UF pilot performance chart for the Alameda County UF pilot. Specific flux and filtrate flow are plotted on the primary (left) y-axis. Filtration transmembrane pressure is plotted on the secondary (right) y-axis, and CEB events are
indicated by vertical lines on the graphs. Refer to the legend for details on the type or
types of CEB chemicals used during a given CEB event. For quality control purposes, a
minimum of one month of runtime was required to demonstrate the CEB performance of
acetic acid.

No pretreatment of Lake Del Valle water was provided prior to the UF pilot’s pre-
screeners. A conservative operating flux of 30 gal/ft\(^2\)-day was selected because of the
difficulty associated with treating this surface water source. As can be seen in Figure 4-7,
the high fouling nature of the surface water resulted in a specific flux decline from
approximately 28 gal/ft\(^2\)-day-psi to 15 gal/ft\(^2\)-day-psi before a stable operating condition
was established.

During the first ten days of pilot runtime, acetic acid and sodium hypochlorite CEBs were
attempted separately on a once per day interval. However, the specific flux trends
indicated that neither chemical was sufficient in isolation to deal with the foulants
accumulating on the membrane surface. A combination of acetic acid and sodium
hypochlorite CEBs was needed to maintain membrane performance. Stable operation was
established with back-to-back sodium hypochlorite/acetic acid CEBs between a specific
flux range of 10 to 20 gal/ft\(^2\)-day-psi.

The acetic acid solution concentration in contact with membrane fibers during a CEB is
an important design consideration. During pilot testing at the Mission San Jose WTP, the
concentration of acetic acid during a CEB soak was approximately 1500 mg/L.
Additional testing is needed to evaluate different acetic acid chemical strengths.
Figure 4-7: Pilot Performance Chart: Alameda County UF Pilot (Nov. 23rd, 2010-Jan. 1st, 2011)
Note: CEB Chemical Key: A = Acetic Acid; B = Sodium Hypochlorite
Dilution Considerations for Selecting CEB Chemical Concentrations

The chemicals used to maintain membranes during CEB sequences undergo a series of dilutions following initial chemical injection. The first dilution occurs when the chemical is injected into the backwash flow. If a backwash water storage pond or tank is installed as part of the UF system, a second dilution of the chemical will occur within this volume when the CEB waste stream is mixed with other plant water streams. Further dilution will occur when the decanted backwash holding water is pumped ahead of the coagulation basin and blended with water entering the WTP. The concentration of citric or acetic acid in contact with the membrane fibers during a CEB is limited, in part, by the amount of dilution provided at the WTP following CEB maintenance. The available dilution influences the concentration of citric or acetic acid entering the coagulation basin. Therefore, it is important that the dilution of the chemical be a factor in selecting CEB chemical concentrations.
5 CONCLUSIONS

In this study, the impacts of citric and acetic acids on alum and ferric chloride coagulation were evaluated in terms of A/C molar ratios. The ratio of acid to coagulant provides a simple tool for water purveyors to assess the possible coagulation impacts of UF CEB recycle streams. Citric acid was found to adversely affect coagulation at lower acid/coagulant (A/C) molar ratios than acetic acid. Based on the findings of this research, there is a threshold beyond which significant deteriorations in settled water quality are observed. This threshold has been defined in terms of settled water turbidity values. Table 5-1 presents the coagulation interference results for Lake Manatee jar tests with alum and ferric chloride coagulants.

Table 5-1: A/C* Molar Ratios Below and Above 2 NTU Interference Threshold

<table>
<thead>
<tr>
<th>Coagulant</th>
<th>Acid</th>
<th>A/C Molar Ratios (Below 2 NTU Threshold)</th>
<th>A/C Molar Ratios (Above 2 NTU Threshold)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alum</td>
<td>Citric Acid</td>
<td>&lt; 0.155</td>
<td>0.310 to 2.17</td>
</tr>
<tr>
<td>Alum</td>
<td>Acetic Acid</td>
<td>&lt; 39.6</td>
<td>49.5 to 297</td>
</tr>
<tr>
<td>Ferric Chloride</td>
<td>Citric Acid</td>
<td>&lt; 0.113</td>
<td>0.169 to 0.788</td>
</tr>
<tr>
<td>Ferric Chloride</td>
<td>Acetic Acid</td>
<td>&lt; 10.8</td>
<td>18.0 to 106</td>
</tr>
</tbody>
</table>

* A/C = acid to coagulant molar ratio

This research identified general water quality trends for the interference of coagulation by citric acid and acetic acid. Significant changes in turbidity, total metal concentrations and color values were observed with citric acid addition over a narrow concentration range, and citric acid was found to prevent the formation of settleable floc particles for both alum and ferric chloride coagulants. Changes in settled water quality with acetic acid
were generally more gradual. Acetic acid prevented the formation of settleable floc particles with ferric chloride at high A/C molar ratios, but floc formation was still noted with alum at high A/C ratios despite increases in total aluminum concentrations.

Turbidity trends varied depending on the A/C molar ratio and coagulant type. Jar test results indicated a general range of A/C molar ratios over which turbidity values increased. Visual observations of jars showed the formation of pin floc within this region of increasing turbidity. Turbidity then trended downward from a maximum turbidity value as greater concentrations of acid were added. However, this downward trend was not observed for the combination of ferric chloride and acetic acid. Total metals concentrations and color values generally increased with increasing A/C molar ratio, but color was not a clear and reliable indicator of coagulation interference. Importantly, observations of jars at A/C molar ratios in excess of the interference threshold did not exhibit coagulation, flocculation and settling characteristics typically observed in surface water treatment coagulation plants.

As demonstrated in this study, coagulation interference can lead to increased settled water turbidity. If the A/C molar ratio is such that pin flocs form in the coagulation basin, then the mass loading on downstream UF filters may increase resulting in shorter filter runs and the need for more frequent backwashes and CEBs. Additionally, coagulation interference could possibly have negative impacts on compliance with secondary water quality standards. In this study, settled water total aluminum (for alum coagulation) or total iron (for ferric chloride coagulation) concentrations were demonstrated to increase
at appreciable A/C molar ratios. Depending on the solubility of the metal-ligand complexes formed, it is possible that a fraction of the metal added with the coagulant could pass through downstream filters. Settled water color values were also demonstrated to increase at appreciable A/C molar ratios.

Acetic acid showed a reduced tendency for interfering with coagulation relative to citric acid. This means that higher concentrations of acetic acid may be used to maintain UF membranes before the 2 NTU settled water turbidity threshold is exceeded during backwash water recycle. Based on these findings, acetic acid appears to be advantageous for use in conventional surface water treatment applications. Acetic acid was able to maintain membrane performance for filtering raw northern California surface water in conjunction with sodium hypochlorite CEBs. It is believed that this is the first ultrafiltration membrane process application of acetic acid CEBs for municipal potable water production in the United States. Further evaluation is needed to assess the CEB performance of acetic acid for removing a variety of foulants, as well as the ability for acetic acid to be used independently of sodium hypochlorite CEBs.
6 RECOMMENDATIONS

Jar tests are strongly recommended to evaluate the possible coagulation impacts of chemical recycle streams at surface water treatment plants. If citric or acetic acid CEB waste streams are recycled to the head of the treatment works, it is important to identify the site specific A/C molar ratio at which unacceptable interference is observed. The A/C molar ratio selected will depend on the water quality goals of the individual facility as well as applicable drinking water regulations. Jar tests conducted to identify coagulation interference thresholds should simulate actual treatment plant operations.

The design of citric or acetic acid UF CEB systems must account for the concentration of the acid when it enters the coagulation basin. The concentration of citric or acetic acid used for maintaining membranes is limited by the site specific conditions at the water treatment plant, including the amount of dilution provided after initial chemical injection. It is recommended that acid concentrations entering the coagulation basin be below the identified interference threshold. Failure to maintain citric or acetic acid concentrations below interference levels may result in significant settled water quality impacts.

Consideration should also be given to the interactions of citric or acetic acid with disinfectants such as chlorine or chloramines. The possibility exists for the formation of disinfection by-products (DBPs) such as Trihalomethanes (THMs) or Haloacetic Acids (HAAs) as a result of citric or acetic acid CEB water recycle. An evaluation of the impacts of backwash water recycle should investigate DBP formation potentials.
Acetic acid shows promise as a CEB chemical for maintaining UF membranes, but further testing is needed. Pilot scale testing using acetic acid for CEBs is recommended to assess the performance of acetic acid on maintaining UF membranes for the source water being filtered. A thorough evaluation of acetic acid should be conducted to identify appropriate operating conditions prior to the implementation of acetic acid CEBs.
APPENDIX: ADDITIONAL FERRIC CHLORIDE RESULTS
The Appendix contains the data collected during jar tests using Lake Claire water with ferric chloride coagulation. Lake Claire jars received a ferric chloride dose of approximately 114 mg/L at a target pH of 5.5. The jar test settings were selected based on the guidelines of ASTM D 2035 – 80 (ASTM, 2003). Coagulant and sodium hydroxide volumes were added just prior to the start of a one minute rapid mix cycle at 120 rpm. The temperature and pH of each jar were measured during a 20 minutes slow mix cycle at 35 rpm. Jars were then allowed to settle for 15 minutes prior to sample collection and testing. Polymer addition was not included for Lake Claire jars.
Figure 7-1: Temperature and pH Ranges for Lake Claire Coagulation with FeCl₃
Table 7-1: Jar Test Results for Lake Claire with Ferric Chloride and Citric Acid

<table>
<thead>
<tr>
<th>Citric Acid/FeCl₃ Molar Ratio</th>
<th>Citric Acid/Fe Molar Ratio</th>
<th>Citric Acid Concentration (mg/L)</th>
<th>pH</th>
<th>Temperature (°C)</th>
<th>Turbidity (NTU)</th>
<th>Total Fe Concentration (mg/L Fe)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.000</td>
<td>0.000</td>
<td>0</td>
<td>5.55</td>
<td>18.6</td>
<td>0.42</td>
<td>0.77</td>
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<tr>
<td>0.002</td>
<td>0.002</td>
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<td>0.59</td>
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<td>0.94</td>
<td>37.2</td>
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</tbody>
</table>
Table 7-2: Jar Test Results for Lake Claire with Ferric Chloride and Acetic Acid

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<th>Acetic Acid/FeCl₃ Molar Ratio</th>
<th>Acetic Acid/Fe Molar Ratio</th>
<th>Acetic Acid Concentration (mg/L)</th>
<th>pH</th>
<th>Temperature (°C)</th>
<th>Turbidity (NTU)</th>
<th>Total Fe Concentration (mg/L Fe)</th>
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<td>19.8</td>
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Figure 7-2: Jar Test Results for Lake Claire (Ferric Chloride) – Turbidity versus A/C Molar Ratio
Figure 7-3: Jar Test Results for Lake Claire (Ferric Chloride) – Total Iron Concentration versus A/C Molar Ratio
REFERENCES


