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Chemical Treatment of Sludge Return Streams at the Maxson WWTP

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CHEMICAL TREATMENT OF SLUDGE RETURN STREAMS AT THE MAXSON
WWTP

by

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ABSTRACT

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During the treatment of wastewater, many by-products are produced. One of these by-products, the sludge return stream, is produced from the sludge digestion and dewatering process. This high strength wastewater is known as a return stream because it is often returned to the beginning of the treatment plant to be combined with the influent. Because of its high strength, it often has a significant impact on influent concentrations of organics and nutrients. The main focus of this work was to study chemical treatment of the return streams at the Maxson WWTP in order to reduce pollutant loading on the influent. Regarding this, several coagulants and a flocculant were systematically tested on anaerobic lagoon supernatant using jar tests. Results showed that with optimum chemical dosage TSS could be reduced by 88%, VSS could be reduced by 97%, and COD could be reduced by 78%.

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INTRODUCTION

1.1 Background of Sludge Return Streams

In addition to creating a treated effluent stream, wastewater treatment plants

(WWTPs) produce different byproducts depending on the type of treatment process used.

Chemical treatment, biological treatment, and physical treatment are different ways of

treatment that all produce some type of waste. Most municipal wastewater treatment

plants incorporate all three types. Byproducts produced include screenings, grit, scum,

and solids. Most of this can be hauled to the landfill; however, the waste solids need

further treatment prior to landfilling or land application.

One type of treatment for waste solids is sludge digestion. There are two options:

aerobic and anaerobic. Anaerobic digestion involves the decomposition of organic and

inorganic matter in the absence of oxygen. This process occurs over three stages.

Through chemical and biochemical reactions, extracellular enzymes first break down

solid, complex organics into soluble components. Next, microbes also known as acid

formers convert the soluble components into acetic acid, propionic acid, hydrogen, and

carbon dioxide. The last step occurs when methane formers convert the previous stage's

products into methane and bicarbonate (Tchobanoglous 2003).   Aerobic digestion is

different in that microorganisms digest sludge in the presence of supplied oxygen. This

process is similar to that of activated sludge. As the supply of organics and food

diminishes, the microorganisms begin to consume their own protoplasm in order to

obtain energy. The cell tissue that is consumed is converted aerobically to carbon

dioxide, water, and ammonia. There are many advantages and disadvantages to both;

however, anaerobic digestion is primarily used in plants over the size of 5 million gallons

per day (MGD). This is due to the high power cost associated with supplying the required oxygen for aerobic digestion (Tchobanoglous 2003). In both processes, after digestion, sludge is removed and a high strength supernatant remains.

After the sludge solids get treated in the digesters, the sludge is often moved to a dewatering system. Dewatering occurs when the moisture content of the sludge is decreased. There are many reasons to dewater. The cost of trucking sludge to landfills increases with weight. If excess water is not removed prior to landfill disposal, landfill costs will be excessive. Furthermore, dewatered sludge is easier to transport and may better facilitate incineration or composting. With proper dewatering, solids capture can achieve a percentage of greater than 95% (Tchobanoglous 2003). Possible ways to dewater sludge include solid-bowl centrifuges, belt- filter presses, recessed- plate filter presses, sludge drying beds, and sludge lagoons. After dewatering, a high strength wastewater remains and needs to be further treated.

1.2 Characteristics of Sludge Processing Streams

Digester supernatant and dewatering liquor (individually/collectively also known as reject water or sludge liquor) can be characterized in terms of measurable factors or parameters. Some of the most common parameters tested for include: five day biochemical oxygen demand (BOD_5), chemical oxygen demand (COD), ammonia (NH_3), phosphorous, total suspended solids (TSS), volatile suspended solids (VSS), color, alkalinity, pH, and total Kjeldahl nitrogen (TKN).

Organic loadings vary widely in these return flows. Depending on the type of sludge created (primary, trickling filter, and/or activated), total solids in return flows range from 1475 mg/L to 9400 mg/L. Organic carbon and organic nitrogen levels vary

from 1230- 4565 mg/L and 53- 678 mg/L respectively (Sludge Treatment and Disposal 1978). BOD_5 can range from 100- 6000 mg/L (Sludge Treatment and Disposal 1978), while COD levels are even more significant. However, less than 25 % of it is actually biodegradable (Frison et al. 2013). This low percentage of readily biodegradable COD (RBCOD) can unbalance the ratio of COD to nitrogen in the influent wastewater (Caffaz 2006). Proper nutrient and organic ratios are needed by the microorganism population in biological treatment.

Inorganic nutrient levels are very high as well. In a municipal WWTP with anaerobic sludge digestion, 10- 20% of the total nitrogen load may come from the return streams. With ammonia contributing to the majority of the nitrogen, it usually ranges from 600- 1000 mg/L (Caffaz 2006). Other data have shown that it ranges from 253- 853 mg/L (Sludge Treatment and Disposal 1978). Percentages of recirculated phosphorous compared to total phosphorous in the influent are similar (Xu et al. 2012). These can range from 63-143 mg/L (Sludge Treatment and Disposal 1978).

1.3 Purpose of the Study

WWTPs that have sludge digesters or dewatering systems may produce high-strength return streams. This high- strength wastewater must receive adequate treatment prior to its final disposal (Frison et al. 2013). For this reason, it is typical practice to return these wastewaters to the headworks, thus mixing them and the influent. This recycled stream changes the nature of the influent entering the treatment system, and may cause occasional organic overloading if the plant is operating at design loading (Arnold et al. 2002; Arun 1988). The main purpose of this study is to research alternative ways to treat these return streams.

1.4 Features of the Study

The challenging feature that distinguishes this work from other studies carried out in the past is the emphasis on organics removal. A thorough review of the literature shows that most prior research on sludge return streams focuses on nitrogen and phosphorous removal. This is due to the fact that these wastewaters have high nutrient levels and more stringent nutrient discharge limits are being mandated.

Another distinguishing feature of this work is the usage of chemical coagulation to treat return streams. Very little research exists on chemical addition in order to coagulate and flocculate return flows. It is well known that coagulation can reduce organics in both drinking water and wastewater. A review of the literature shows this. However, chemical addition's effect on sludge return streams needed to be reviewed. In this study, different combinations of coagulants, polymers, and flocculants were systematically tested in order to evaluate the efficiency of chemical treatment.

1.5 Contribution of the Study

The contribution of this study will be unique to WWTPs that are concerned about return streams' organic contribution to the influent. For WWTPs without nutrient discharge limits, the phosphorous and nitrogen concentrations in the return streams will be less important. For this reason, treatment options that isolate organics removal are a priority. As a result of this, the author strongly believes that further work is needed in order to define the best and most economical options to reduce organic pollutant loadings in return streams.

LITERATURE REVIEW

2.1 Overview of Current Treatment Trends for Sludge Return Streams

Anaerobic digester supernatant and dewatered sludge liquor are most commonly sent back to the headworks of the plant to be treated after mixing with the incoming influent. This is the easiest option because of the reduced need for side-stream treatment processes. However, some research has been conducted, mostly on a pilot scale, to treat the sludge return streams separately. Very few WWTPs have gone past the research step. However, the most common configuration for full- scale sludge liquor treatment plants that do exist is sequencing batch reactors (SBRs) (Jardin et al. 2006). This is because of the high flexibility of the design.

The reason for the scarcity of separate treatment processes for reject water is because treatment of these streams is difficult and relatively costly due to the characteristics of the wastewater. Nitrogen and phosphorus levels are extremely high. Therefore, continued research is critical for plants with strict effluent nutrient limits. Accordingly, most of the research focuses on ammonia and phosphorous removal. Furthermore, another difficult characteristic of the sludge return streams previously mentioned is the lack of RBCOD. An additional carbon source due to the lack of RBCOD is often needed (Caffaz 2006).

2.2 Nutrient Background Information in Return Stream Literature

The two major parameters isolated in sludge return stream literature are nitrogen and phosphorous. In order to review the following sludge return stream literature, background information on these nutrients is needed. Both nutrients come in varying forms, and different researchers used different testing parameters depending on the study.

Aqueous nitrogen is very complex. Many different forms of nitrogen combine to equal total nitrogen concentrations in wastewater. These different forms include: ammonium, ammonia, nitrite, nitrate, and organic nitrogen. In both raw influent wastewater and sludge return streams, usually only organic nitrogen, ammonia, and ammonium are present. Each form characteristically effects the environment in different ways. The impact of organic nitrogen on aquatic ecosystems is still in the research phase, as only a portion of this form is bioavailable (Berman and Bronk 2003). The most detrimental form of nitrogen in water is ammonia, while ammonium is basically harmless to aquatic life. Because of this, the relationship between ammonia and ammonium should be reviewed. The chemical equation that shows the relationship between ammonium and ammonia is shown below.

$$NH_3 + H_2O \leftrightarrow NH_4^+ + OH^- \tag{1}$$

The main driving force in this equation is pH. When the pH is low, the reaction is driven to the right. However, as pH increases, the reaction is driven to the left. Many research studies use a mixture of testing parameters to measure for ammonia, ammonium, or the combination of both (Sawyer 2003).

Ammonia is detrimental to receiving streams for several reasons. Primarily, ammonia is toxic to fish and contributes to eutrophication which has negative impacts on aquatic ecosystems. Also, a very common method of wastewater disinfection, chlorination, can produce harmful chloramines when ammonia is present in the wastewater. This is especially of concern when the receiving stream is also used as a

drinking water source. Furthermore, the conversion of ammonia to nitrite produces an oxygen demand (Davis et al. 2009). Because of these reasons, many treatment plants are only concerned with ammonia removal. Other WWTP's continue the process for total nitrogen removal. These concerns drive the research behind sludge return stream treatment.

Aquatic phosphorous is also very complex. In the environment, phosphorous usually exists as a part of a phosphate molecule, PO_4^{3-}. Furthermore, in aquatic systems, phosphorous is sub-divided into organic and inorganic phosphorous. Both forms can be dissolved or suspended. When reviewing the literature, phosphorous is described using several terms. Some of these terms used to describe the different forms of phosphorous are chemistry- based, while others are methods- based. The methods- based terms describe what is measured by a particular test. The most common chemistry- based term used is "orthophosphate" that refers to the phosphate molecule individually. The corresponding method- based term is "reactive phosphorous". There is variability in these terms because the reactive phosphorus test that measures orthophosphate concentrations is not perfect. Tests results provide a majority of orthophosphate; however, a small fraction of the other forms show up as well ("Why is Phosphorous Important?" 2012).

The most harmful effect of phosphorous presence in wastewater is its contribution to algae growth. Often this algae growth, or eutrophication, will occur in excess, and create a large oxygen demand when the algae die and become oxygen demanding organic matter. For this reason, phosphorous levels in wastewater are often a concern (Davis et al. 2009).

2.3 Biological Treatment Trends for Return Streams

Biological treatment of return streams often isolates ammonia removal as the main goal. Nitrification occurs through biological reactions carried out by autotrophic microorganisms most commonly noted as belonging to the genera *Nitrosomonas* and *Nitrobacter*. *Nitrosomonas* bacteria oxidize ammonia to nitrite, while *Nitrobacter* oxidize nitrite to nitrate. These reactions are affected by dissolved oxygen (DO) levels, pH, toxicity, metals content and un-ionized ammonia (Tchobanoglous 2003). Because DO is one of the driving parameters in these reactions, there is limited nitrite and nitrate concentrations in both influent streams and anaerobic sludge liquor. The nitrification formulas are listed below (Tchobanoglous 2003).

$$2 \text{ NH}_3 + 3 \text{ O}_2 \rightarrow 2 \text{ NO}_2^- + 2 \text{ H}_2\text{O} + 2 \text{ H}^+ \text{ (\textit{Nitrosomonas})} \qquad (2)$$

$$2 \text{ NO}_2^- + \text{O}_2 \rightarrow 2 \text{ NO}_3^- \text{ (\textit{Nitrobacter})} \qquad (3)$$
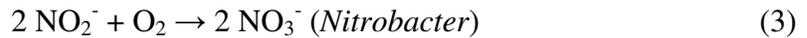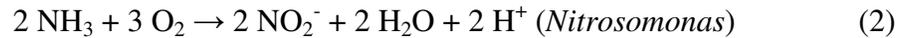
At WWTPs employing complete nitrification for reject water, the main goal is to mitigate ammonia levels of the reject water that are returned to the headworks. One example of reject water treatment using nitrification occurred at the Bromma WWTP in Stockholm. By use of multivariate methodology on a pilot SBR, the researchers found the nitrification rate strongly depended on two factors, the initial concentration of ammonium and the amount of oxygen supplied. They concluded that complete nitrification is possible and that the process is rather easy to control by monitoring measurements of oxygen concentrations, air flow, and pH (Mossakowska et al. 1997). Another example of

nitrification of sludge liquor is known as the *Store and Treat* method. This process begins with a large empty basin. Activated sludge seeds the basin with a sufficient amount of nitrifying bacteria. This initial retained sludge occupies approximately 10-20% of the storage basin. The sludge liquor is then allowed to flow into the basin under constant aeration. The specified aeration allows for a sufficient amount of oxygen to keep the nitrifiers alive; however, the aeration does not allow for a completely mixed system. This design minimizes activated sludge washout when the overflow exits the system via an overflow hopper (Laurich and Gunner 2003).

In treatment plants where total nitrogen levels are of concern, further removal of nitrite and nitrate is needed. This process is known as denitrification, where the nitrate is converted to nitrogen gas. Denitrification in wastewater follows the processes listed below (Tchobanoglous 2003).

$$6NO_3^- + 5CH_3OH \rightarrow 3N_2 + 5CO_2 + 7H_2O + 6OH^- \qquad (4)$$

$$10NO_3^- + C_{10}H_{19}O_3N \rightarrow 5N_2 + 10CO_2 + 3H_2O + NH_3 + 10OH^- \qquad (5)$$
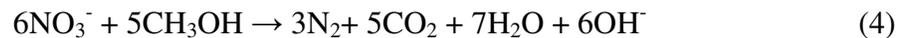
Specifically regarding reject water, conventional denitrification proves to be more difficult than nitrification. Because denitrification depends on the amount of RBCOD, anoxic zones need to be designed with extra capacity or an additional supply of carbon is needed (Teichgraber and Stein 1994). The first denitrification equation above utilizes methanol as a carbon source. This equation more typically characterizes denitrification of a sludge return stream that needs an additional carbon source. This is compared to the

second denitrification equation above that utilizes the typical $C_{10}H_{19}O_3N$ term to represent the biodegradable organic matter in wastewater (Tchobanoglous 2003).

Because complete nitrification and denitrification is rather expensive due to higher oxygen costs, research and treatment options also exist using short-cut nitrogen removal (SCNR) and partial nitrification/denitrification of reject water. Another name for this type of treatment is nitritation and denitritation. The name is derived from the nitrification and denitrification processes that occur via nitrite instead of nitrate (Fux et al. 2006). Benefits of this approach include decreased oxygen demand and 60% less external carbon, as well as decreased sludge production and carbon dioxide, CO_2, production (Abeling and Seyfried 1992; Gustavsson 2010; Van Dongen et al. 2001). In a pilot study conducted in Italy, an SBR operating for SCNR had a total nitrogen reduction of 85% (Frison et al. 2013).

The most common type of treatment system regarding SCNR in reject water is the *Sharon*^{TM} process. This design has been developed at the Delft University of Technology in the Netherlands (Hellinga et al. 1998; Tchobanoglous 2003). The *SHARON*^{TM} process uses partial nitrification in order to reduce supplied oxygen costs. During the process, the single reactor is operated in two cycles. A standard 80 minute aerobic period is followed by a forty minute anoxic cycle. Complete mixing occurs during both cycles. The process takes advantage of the effect of high temperature on nitrification kinetics that favors growth of ammonia- oxidizing bacteria over nitrite-oxidizing bacteria (Van Dongen et al. 2001). Furthermore, hydraulic residence time (HRT) is used to control sludge residence time (SRT) since there is no sludge retention. This detail allows for the washing out of nitrite oxidizers while the ammonium oxidizers

remain in the reactor (Hellinga et al. 1998). In bench scale studies, up to 80-85%

nitrogen removal can be achieved using this process (Tchobanoglous 2003).

The modified denitrification process has been researched for two different

methods. One proposed treatment for reject water is the Annamox^{TM} process. The

bacteria in this process, known as the Annamox bacteria, oxidize ammonia with the

reduction of nitrite under anoxic or anaerobic conditions (Van Dongen et al. 2001;

Tchobanoglous 2003). The name itself is an abbreviation for anaerobic ammonium

oxidation. The chemical formula for modified denitrification or denitritation follows.

$$NH_4^+ + NO_2^- \rightarrow N_2 + 2\ H_2O \qquad\qquad (6)$$

In other words, nitrite is used to oxidize ammonia into nitrogen gas and is the

limiting nutrient for the Annamox^{TM} process to work. This is the reason for further

research into the combination of the *Sharon*^{TM} and the Annamox^{TM} processes (Van

Dongen et al. 2001). Specifically regarding reject water, the *Sharon*^{TM} - Annamox^{TM}

process originated at the S. Colombano WWTP in Florence Italy. The lab-scale pilot

study, under ideal conditions, achieved up to a 98.3% removal of ammonium and 86%

removal of total nitrogen (Caffaz 2006). A different study using denitritation achieved

similar results when using a pilot- scale SBR. This system achieved 85- 90% removal of

nitrogen (Fux et al. 2006).

When biologically treating return streams it is important to do a stream specific

test to determine if there is a need for an additional carbon source. Methanol, added to

increase readily degradable substrate concentrations, is often recommended. Good

design shows that addition occurs in the anoxic zone, prior to the aeration zone. Furthermore, to decrease methanol washout, the anoxic zone should be divided into two separate compartments where the addition occurs in the first basin (Siegrist 1996). Ethanol or acetic acid can also be used as a carbon source (Fux et al. 2006; Peng et al. 2012).

2.4 Physicochemical Treatment Trends for Return Streams

Chemical addition can be useful in removing nutrients from reject water. Most of the literature regarding chemical treatment for reject water isolates phosphorous as the main parameter of concern. Reactions and precipitates can often be controlled by changing the pH or chemical makeup of the wastewater. Following chemical addition, an air stripping step is needed for some proposed treatments. Chemical treatment for nutrient removal is very different from the previously mentioned biological treatment.

The removal of phosphate by addition of modified coal fly ash in digested sludge supernatant was investigated in one such study. The modified coal ash consisted of fly ash and differing amounts of sulfuric acid. The authors proposed that the addition of sulfuric acid to the fly ash, which lowers the pH, could significantly enhance its immobilization ability. The influence of adsorption time, pH, dosage amount, and temperature on the removal of phosphates was investigated using batch adsorption experiments. Results showed that with optimum dosages, phosphorous removal could reach 99% in five minutes (Xu et al. 2012).

Other researchers studied the addition of magnesium to cause magnesium ammonium phosphate (MAP, also commonly called struvite) precipitation. MAP is a naturally occurring crystal of magnesium, ammonium, and phosphate (Munch and Barr

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2001). Specifically designed MAP reactors can optimize precipitation where the volume of precipitate can be used to determine removal of ammonium and phosphate from the supernatant of anaerobic digestion. Considering MAP can be used as a fertilizer, this technique allows for not only removal, but also the recovery of the nutrients (Doyle and Parsons 2002; Momberg and Oellermann 1992; Siegrist 1996). The background for the optimization of MAP precipitation is known from prior research. Increased levels of magnesium, Mg^{2+}, can help increase percentages of ammonium and phosphorus removal. This is because one of the major ions in MAP formation is magnesium and it is usually in the lowest concentration compared to ammonium and phosphate (Doyle and Parsons 2002). The following formula shows the precipitation of struvite (Celen and Tuker 2001).

$$Mg^{2+} + PO_4^{3-} + NH_4^+ + 6\ H_2O \leftrightarrow MgNH_4PO_4 \cdot 6H_2O \qquad (7)$$
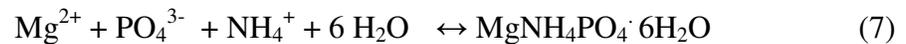
One example of MAP precipitation research on reject water used two major mechanisms to test for removal percentages of ammonium. The first, the control experiment, included volatilization of the dissolved ammonia gas under constant aeration. The control corresponded with a 19% removal of ammonium (Ulidag- Demirer and Othman 2009). The second experiment addressed the removal of ammonium with the addition of Mg^{2+}. Aeration was again used. The increased percentage of ammonium removal was 38% and showed that the MAP formation was better for removal of ammonium than aeration alone. Percentages of phosphate removal from MAP formation were even higher. These experiments were conducted on a bench scale (Ulidag- Demirer and Othman 2009). A

continuously operated pilot- scale study also showed significant phosphorous removal when magnesium was added. A MAP reactor was specifically built to optimize phosphorus removal. This process achieved an orthophosphate reduction of 94% when treating an influent of anaerobic digester supernatant with 61 mg/L of orthophosphate (Munch and Barr 2001).

A different study showed that magnesium hydroxide application can reduce phosphorous concentrations in anaerobic digestion supernatant. The pilot scale digesters were each 32 liters and the supernatant was supplied by a nearby sludge dewatering facility. After chemical addition, a 60 minute cycle of aeration and a 60 minute period of settling followed. In varying doses between 50 and 400 mg/L, phosphorous removal showed an increase in percentage removal as the dosage of magnesium hydroxide increased. Best results obtained 93% removal of phosphorous. This is compared to the control removal percentage of 56% (Wu et al. 2001).

Treatment processes that utilize aeration after anaerobic digestion encourage precipitation of various minerals from the treated supernatant. The process begins when the aeration strips off the CO_2. This increases the pH. Minerals that precipitate at higher pHs include struvite ($MgNH_4PO_4$), newberyite ($MgHPO_4$), amorphous calcium phosphate, $CaCO_3$ and $MgCO_3$. Simultaneous ammonia stripping occurs as well (Musvoto et al. 2000; Battistoni et al. 2001). This process allows for removal of high concentrations of nitrogen and phosphorous when proper settling clarifiers are designed into the process (Musvoto et al. 2000). Otherwise, pipe blockage can occur.

2.5 Chemical Treatment for Organics Removal in Various Waste Streams

The majority of return sludge stream research does not acknowledge chemical coagulation in order to reduce organics. However, chemical coagulation has given excellent results regarding treatment of other wastewater. In fact, chemical coagulation is one of the most important physiochemical treatment processes regarding organic pollutant removal (Bag et al. 2008).

Colloidal particles are solids in dispersion that do not settle out of solution. These particles are negatively charged and range in size from .01 to 1 μm. Brownian motion or random movement usually keeps these particles in suspension because the attractive body forces between particles are less than the repelling forces of the negative electrical charge (Tchobanoglous 2003).

Chemical coagulation is a common treatment of wastewater that needs removal of colloidal particles and organics. The coagulation and flocculation process often has objectives for achieving reduction in turbidity, color, microorganisms, and THM and TOX precursors. Three of these four are related to organic material (Rebhun and Lurie 1993). The chemical coagulation process is aimed at destabilizing these negative particles so that particle growth can occur from particle collisions. This particle growth is known as floc formation. The flocculation process that follows coagulation describes the process where the floc formation increases in size. This increase in size occurs due to particle aggregation during slow mixing, and also when larger floc particles entangle smaller particles. Flocculation can be further classified into two types: perikinetic and orthokinetic.   Perikinetic flocculation occurs from the Brownian motion of constant bombardment from the other molecules in solution. Orthokinetic flocculation occurs

when colloidal particles collide with one another after a velocity gradient (mixing) is introduced (Tchobanoglous 2003).

To determine the effectiveness of coagulants, there are multiple methods to analyze the coagulation and flocculation process. The first method employs jar tests which are conducted in a laboratory in order to determine approximate dosage. During the jar test procedure, comparing sizes of floc and sludge volumes after settling gives a good indication of the best results. Typical jar test procedure has three stages: rapid mix (coagulation), slow mix (flocculation), and settling. A different method of analyzing coagulation is with a Zeta-potential test. This test involves determining the speed at which particles move through an electric field after subjecting the water to a direct current (Salvato 1972).

Typical coagulants contain certain characteristics. The most important characteristic of a wastewater coagulant is the presence of a trivalent cation. These cations are required to achieve destabilization and charge neutralization. Furthermore, research shows that trivalent cations are much more effective than monovalent or divalent cations (David and Masten 2009). Another good coagulant characteristic is that it is insoluble in water in the neutral pH range. This is important because after coagulant addition, a decently settled sludge is imperative. Other coagulant characteristics become important when treatment is for the production of potable water. Nontoxicity is an example of one of these.

There are many different types of coagulants. Some of the different types of coagulants include: aluminum sulfate (alum), aluminum chlorohydrate, lime, ferrous sulfate, ferric chloride, ferric sulfate, and various clays (Salvato 1972; Tchobanoglous

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2003; Leentvaar et al. 1978). These chemicals can also be blended together to form unique coagulants.

The two most commonly used metallic coagulants are aluminum (Al^{3+}) and ferric iron (Fe^{3+}) (David and Masten 2009). The most common coagulant of the aluminum compounds is alum. Alum addition reacts with alkalinity and precipitates as aluminum hydroxide. The process follows the following reaction (Rich 1973).

$$Al_2(SO_4)_3 \cdot 18H_2O + 6(HCO_3) \leftrightarrow 3SO_4 + 2Al(OH)_3 + 6CO_2 + 18H_2O \qquad (8)$$
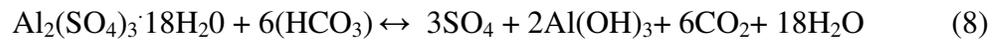
Alum treatment has shown to obtain 92-94% removal of TSS, and 59- 65% removal of COD in industrial wastewater (Bag et al. 2008). One of the most common iron coagulants is ferric chloride. Ferric chloride addition in the presence of alkalinity reacts to precipitate bernalite, or iron (III) hydroxide. The process follows the following reaction (David and Masten 2009).

$$FeCl_3 \cdot 7H_2O + 3HCO_3^- \leftrightarrow Fe(OH)_3 + 3CO_2 + 3Cl^- + 7H_2O \qquad (9)$$
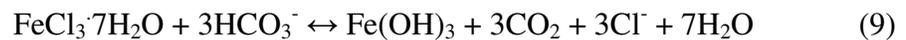
Ferric chloride treatment has shown to reduce COD by 86% and TSS by 80% when optimally mixed with a coagulant aid (Poon and Chu 1999; Abdessemed et al. 2000). Other iron compounds such as copperas (ferrous sulfate), ferrate salt, and ferric sulfate can also be used as coagulants (Rich 1973; Tchobanoglous 2003; Jiang and Lloyd 2002).

Sometimes chemicals are added in order to enhance the performance of an individual coagulant. Chemicals that aid in the coagulation process are known as

coagulant aids. These may include activated silica, bentonite clay, various polymers, or additional coagulants. One coagulant aid that shows promise for organics removal is polyDADMAC. PolyDADMAC is a cationic polymer and organic coagulant that has performed well when compared to alum (Yu et al. 2010). Razali et al. (2011) showed that multiple different dosages and molecular weights of polyDADMAC achieved COD reduction of 90% and higher. When mixed with alum, dosages of polyDADMAC improved dissolved organic matter removal by 15- 20% when compared to alum treatment alone. Researchers also concluded that accurate alum to polyDADMAC ratio is imperative. This is because polyDADMAC addition had negligible effect on the removal of organics when alum dosages were too high (Lee and Westerhoff 2006). A different polymer, polyamine also shows promise as a coagulant aid. Polyamine, like polyDADMAC, is a cationic organic coagulant. It has shown to reduce COD concentrations by 89% in dye wastewater (Yu et al. 2008). Furthermore, Choi et al. (2001) showed that mixing polyamine with alum can improve removal efficiencies for certain parameters and reduce alum dosages by more than 50%.

Flocculants have also shown to assist in organic solids removal. Poon and Chu (1999) showed large scale tests utilizing coagulants and flocculants achieved a TSS reduction of 80%. The study used raw wastewater collected from two separate municipal WWTPs. Initial one- liter jar tests were conducted to determine optimum flocculant dosage for the following larger scaled test. Using 30 mg/L of ferric chloride with 0.5 mg/L of anionic flocculant, the test was performed in a 10L metal container where a motor driven paddle was used for mixing. After thirty minutes of settling, supernatants were analyzed for TSS. A control container was also analyzed in a similar manner

without chemical treatment. The control achieved a 55% percent removal of TSS, while the chemical treatment achieved an 80% removal of TSS.

For chemically treating sludge return streams, it is also important to acknowledge how chemical treatment processes will affect biological process. Treatment plants that employ a chemical treatment process prior to biological processes do exist. This process is known as Chemically Enhanced Primary Treatment (CEPT) or Chemically Assisted Primary Sedimentation Process (CAPS) and takes place in the primary clarifier. It has been shown that CEPT is effective in organic pollutant removal and can even decrease needed volume for the following aeration tanks in biological treatment (Galil and Rebhun 1990). Similar results showed that CEPT can reduce organic pollutant concentrations prior to attached growth systems (Newbigging et al. 1995; Parker et al. 1998).

MATERIALS AND METHODS

3.1 Preliminary Analysis of Return Streams

In order to optimize experimentation, a preliminary analysis was conducted. Initially, tests were planned for all three return streams at the Maxson WWTP. The return flows are identified as the number one manhole, the 24 inch outfall, and the Horn Lake ditch. The number one manhole carries only sludge lagoon supernatant, while the composition of the 24 inch outfall and the Horn Lake ditch vary. Unlike the sludge lagoon which is a closed anaerobic system, the 24 inch outfall and the Horn Lake ditch are open ditches. In addition to anaerobic lagoon overflow, the 24 inch outfall consists of sludge dewatering liquor and some rainwater. The Horn Lake Ditch, however, varies the most. The flow in the Horn Lake Ditch usually consists of anaerobic lagoon overflow, rainwater, and varying amounts of run off from the sludge disposal site. During sample collection, the flow in the number one manhole was always significant. However, this was not true for the 24 inch outfall and the Horn Lake Ditch. The flow rates at these two sampling points were typically extremely low because of minimal rainfall during the study. The belt press filtrate stream was sampled separately. However, this stream has already been chemically treated with a strongly cationic emulsion polymer and has significantly large floc particles that settle relatively quickly. These observations and facts led experimentation to focus primarily on the supernatant from the number one manhole. However, some chemical treatment of the belt press filtrate and raw influent was examined. Figure 3-1 shows a flow diagram for the Maxson WWTP.
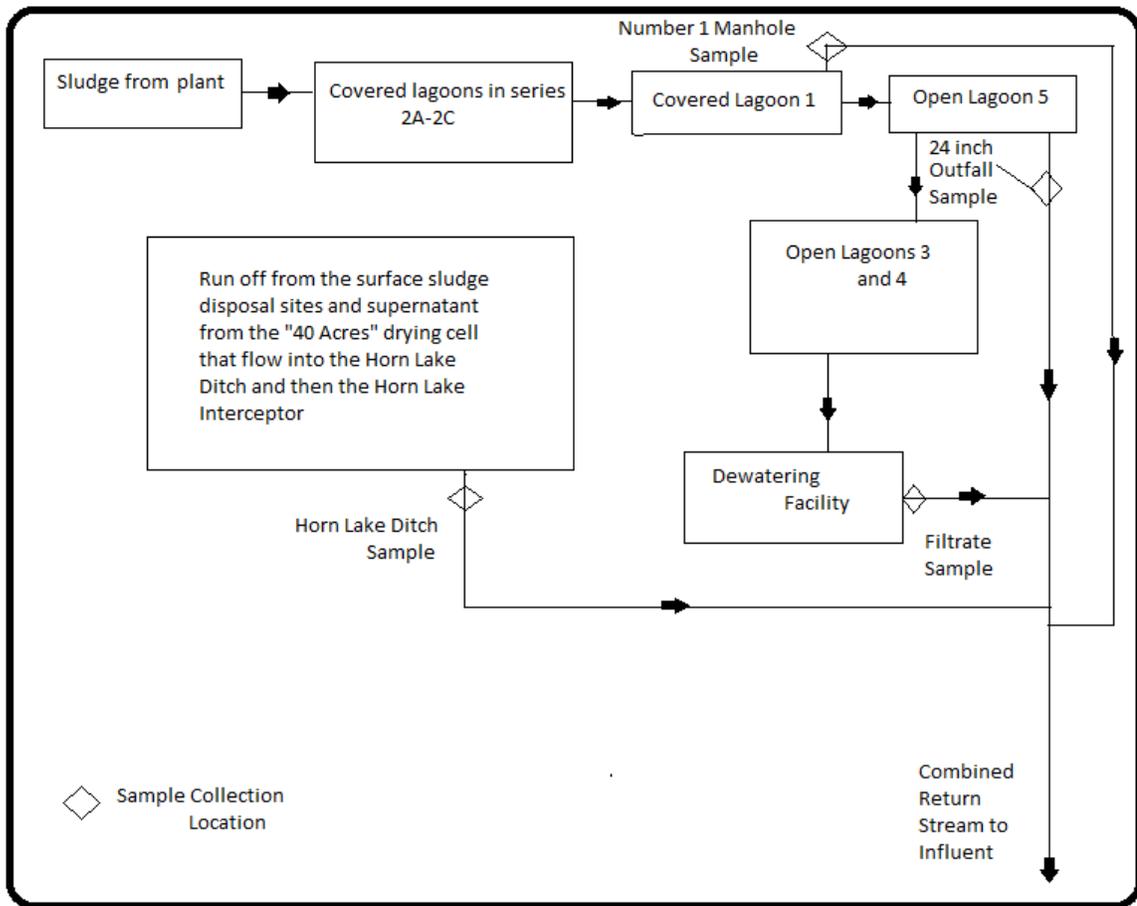
Figure 3-1. Flow Diagram of Return Streams for the Maxson WWTP

3.2 Supernatant Collection and Preparation

Samples of number one manhole supernatant were collected on a weekly basis for two months at the Maxson WWTP in south Memphis. The samples were stored at 4 °C in 10- liter Nalgene containers. Before performing each test, samples were allowed to reach room temperature. The sample containers were shaken before each test to mix any settled solids so as to produce a representative sample.

3.3 Laboratory Analysis

Laboratory analysis is essential to determine optimum chemical dosage for coagulants, polymers, and flocculants. Jar tests were performed using the *Phipps and Bird PB-700 Jartester*. The jartester contains six two- liter containers where

experimentation can be performed. Accordingly, each set of jar tests contained one control and five jars for experimentation. One liter was poured into each of the six jars and placed into the apparatus. The prescribed dosages of primary coagulant were then added to the samples. If coagulant aids were used, the coagulants and coagulant aids were premixed prior to dispersion into the jar tests. Rapid mix followed for 60 seconds at 175 revolutions per minute (rpm). If a flocculant was used, it was then added at this time. Flocculation then followed for an additional 15 minutes at 30 rpm. After this, the jartester was turned off and the samples were allowed to settle for thirty minutes. Visual observations and sludge levels were recorded.

3.4 Preliminary Analysis of Coagulants, Polymers, and Flocculants

Several coagulant chemicals were evaluated as part of the preliminary research. These initial tests followed the jar test process above. Dan Thompson, from Ideal Chemical and Supply Company supervised the preliminary testing and supplied the needed chemicals. Chemicals included aluminum sulfate (alum), aluminum chlorohydrate, ferric chloride, and an Ideal Chemical and Supply Company coagulant blend. These coagulants were tested both individually and blended with varying percentages of PolyDADMAC and polyamine, which have potential to work well when blended with alum. After rapid mix, different concentrations of anionic flocculant were added to induce flocculation for further comparison. During each test, treatment was visually judged for floc size, floc characteristics, and clarity of the supernatant remaining. The best results were included in the experimental design.

Preliminary jar tests included:

1. Alum ranging from 1 mg/L to 500 mg/L

2. Alum at 500mg/L with an anionic flocculant ranging from 2 to 4 mg/L

3. Alum and polyDADMAC blend with ratio ranging from 90/10 to 95/5 and total dosage ranging from 100 to 500 mg/L

4. Alum and polyDADMAC blend with ratio ranging from 90/10 to 95/5 and total dosage ranging from 100 to 500 mg/L with an anionic flocculant ranging from 2-4 mg/L

5. Alum and polyamine blend with ratios ranging from 90/10 to 95/5 and total dosage ranging from 100 to 500 mg/L

6. Alum and polyamine blend with ratios ranging from 90/10 to 95/5 and total dosage ranging from 100 to 500 mg/L with an anionic flocculant ranging from 2 to 4 mg/L

7. Ideal Chemical coagulant blend ranging from 1 to 500 mg/L

8. Aluminum chlorohydrate ranging from 1 to 500 mg/L

9. Ferric chloride ranging from 40 to 320 mg/L

10. Ferric chloride ranging from 40 to 320 mg/L with 4 mg/L of anionic flocculant

The ratios of the blends represent the percentage makeup of total dosage each chemical contributed.

3.5 Experimental Design

The main purpose of the experiment was to find a coagulant or combination of coagulants and a flocculant that would achieve effective removal of various pollutants from the anaerobic lagoon supernatant. Second, the best treatment found for organics removal would then be tested on the influent. During the preliminary analysis, different treatments were visually judged for floc size, floc characteristic, thirty minute sludge

volume, and clarity of the supernatant remaining. The author found that the following

chemicals offered the greatest promise.

Anaerobic Lagoon Supernatant Jar Tests

1. Alum dosages 20, 40, 60, 80, 320 mg/L

2. Alum dosages 200, 400, 600, 800, 1000 mg/L with 4 mg/L of anionic flocculant

3. Alum and PolyDADMAC blends with ratios 95/5, 90/10, 85/15, 80/20, and 75/25
    of a total dosage of 300 mg/L with 4 mg/L of anionic flocculant

4. Ferric chloride dosages 40, 80, 120, 160, and 320 mg/L

5. Ferric chloride dosages 40, 80, 120, 160, and 320 mg/L with 4 mg/L of anionic
    flocculant

Influent Jar Test

1. Alum and PolyDADMAC 75/25 blend with dosages 50, 100, 150, 200, 250 mg/L

Following each jar test, the samples were allowed to settle for thirty minutes.

Supernatants were then carefully drawn from the middle of the jars. In some cases,

floating floc particles (floaters) were present on the very top layer of the jar. Extreme

care was taken to minimize the floater uptake into the drawn supernatants. Analytical

tests were run on each supernatant within twenty four hours to ensure reliable results.

For the tests not examined immediately following the jar test, the samples were stored

overnight at 4 °C.   The following tests were run on each supernatant:

- Five- Day Biochemical Oxygen Demand (BOD_5)

  BOD_5 values were determined according to *Method 5210 B* of *Standard Methods*

  for Examination of Water and Wastewater.   Dissolved oxygen (DO) was

  measured using *YSI 5100 Dissolved Oxygen Meter*, and 300 mL BOD_5 specific

  bottles were used. Aerated, distilled water was seeded with the proper nutrients

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and volume and then used as dilution water. As a quality control check, only the samples resulting in a minimum DO depletion of 2.0 mg/L with at least 1.0 mg/L of residual DO were considered valid. DO depletion in the three blank controls also needed to be less than 0.2 mg/L. Three replicates of each dilution were used with two different dilutions for each sample. Three standard solutions using a glucose- glutamic acid standard were also included in each BOD_5 test. The samples were incubated for five days at 20˚ Celsius in a *Fisher Scientific* incubator.

- Chemical Oxygen Demand

  COD of each supernatant was measured using the *Hach DR 6000 UV VIS Spectrophotometer with RFID Technology.* The process was carried out according to the United States Environmental Protection Agency (USEPA) - approved *Method 8000,* described on the Hach website. COD Digestion Reagent vials used are accurate between 20 and 1500 mg/L. A *Hach COD Reactor* was used to heat the vials for a 2-hour digestion period at 150˚ Celsius. Tests were run in duplicate. For high COD samples, appropriate dilutions were prepared. Standards were run using a potassium hydrogen phthalate (KHP) solution for each test.

- TSS and VSS

  Total Suspended Solids (TSS) and Volatile Suspended Solids (VSS) were measured using *Whatman 934-AH Glass* microfiber filters. Filters were inserted into the filtration apparatus and the vacuum was initiated.   Distilled water was used to moisten and wash the filters before the samples were filtered. The filters

have a particle retention of 1.5 μm, and each test was run in triplicate according to

Method 2540 D and *2450 E* of *Standard Methods for the Examination of Water*

and Wastewater (*2005*). The pads containing the supernatant solids were dried in

the oven with a temperature of 105 °C for one hour, cooled in a desiccator for at

least fifteen minutes, and then weighed. After the TSS measurements were

obtained, the solids were ignited at 550 °C for 15 minutes, cooled in the

desiccator for at least 15 minutes, and then weighed again. During the drying

process, the ignition process, and the weight measurements, filters were placed in

inert aluminum weighing dishes.

- pH

  The pH of all samples was determined using *Orion 920A+ pH Meter*. The meter

  was calibrated using three standard buffer solutions with pH of 4, 7, and 10.

- Alkalinity

  Alkalinity of the samples was determined by potentiometric titration. Fifty mL of

  each sample was used and a 1.0 N sulfuric acid solution was prepared from *Fisher*

  Scientific Certified A.C.S Plus Sulfuric Acid stock. The samples were titrated

  against the acid solution using a buret. The pH was monitored continuously using

  the pH meter until the proper endpoint was reached. The endpoint was selected as

  4.5 according to *Standard Methods for the Examination of Water and Wastewater*

  (*2005*).

- Ammonia

  Ammonia was measured according to the ammonia-selective electrode method in

  Standard Methods for the Examination of Water and Wastewater (2005). The

electrode of choice was the *Orion 920A+ Ammonia Meter.* Stock ammonium

chloride solution was made with *Fisher Scientific Certified* ammonium chloride.

The electrometer was calibrated using standards of 10, 100, 500, and 1000 mg/L.

For the test samples, 50 mL of sample was used and 0.5 mL of 10*N* NaOH

solution was used to raise the pH above 11. Samples were gently stirred and the

electrometer was inserted into each sample prior to NaOH addition.

- Total- Kjeldahl Nitrogen (TKN)

  TKN tests were conducted according to the USEPA-approved Micro Kjeldahl

  system test. Fifty mL of sample was placed in a 100 mL Kjeldahl flask and 10

  mL of sulfuric sulfate-potassium sulfate solution was added. Flasks were placed

  in the TKN specific digestion apparatus underneath the vent hood. Samples were

  digested until the solution gave off SO_3 fumes and the solution turned colorless or

  pale yellow. From this point samples were digested an additional 30 minutes

  before the residue was cooled. Next, the residue was mixed with 44 mL of

  distilled water before 6 mL of 10N NaOH solution was added. Samples were

  again cooled to room temperature before transferring each one to a 100 mL

  beaker. The *Orion 920A+ Ammonia Meter* was immersed in each solution and

  4mL of NaOH-NaI-EDTA reagent was added. Measurements were recorded.

  Standards of 200, 400, and 600 mg/L were run for each test.

- Phosphorous

  Phosphorous was recorded according to the USEPA- approved TNTplus 845

  method described on the Hach website. Dilution factors of 6, 8, and 10 were

  used. The method has nine steps.

a. Remove DosiCap Zip cap foil and then remove the cap from the vial.

b. Add 0.4 mL of sample needing testing.

c. Replace DosiCap Zip cap with proper side up.

d. Shake the vial 2- 3 times.

e. Heat for 60 minutes at 100˚ Celsius in the *Hach COD Reactor*.

f. Allow the vial to reach room temperature, then add 0.5 mL of the
    packaged sulfuric acid and ammonium molybdate solution.

g. Apply the second DosiCap cap.

h. Invert the vial several times. After ten minutes, invert the vial several
    more times.

i. Record results using the *Hach DR 6000 UV VIS Spectrophotometer with
    RFID Technology*.

RESULTS AND DISCUSION

4.1 Raw Test Results

The anaerobic lagoon supernatant, also known as the number one manhole, is a high strength, black wastewater with an intense odor. The characteristics of the first lagoon supernatant sample are summarized in the Table 4-1.

Table 4-1. Raw Lagoon Supernatant Sample

Sample	pH	Alkalinity, mg/L	TSS, mg/L	VSS, mg/L	BOD_5, mg/L	COD, mg/L	Total P, mg/L	TKN, mg/L	NH_3-N, mg/L
Raw	7.4	2600	1147	717	81	1631	243	745	590

Each week fresh samples of the supernatant were collected. At times, the phosphorous concentration exceeded the maximum value for the given dilution. The dilution amount was changed on several occasions; however, phosphorous results continued to vary. In most cases, the test could not be repeated because of limited sample volume of the supernatant from the jar test procedure.

For the BOD_5 test, quality control checks are needed to produce a statistically valid BOD_5 test. Numerous attempts were made to limit DO depletion in the blanks to 0.2 mg/L. Several precautions were used to solve this problem. Initial tests were run using deionized water obtained from the University of Memphis Biomedical Engineering lab. This water was replaced with deionized water obtained from the University of Memphis Environmental Engineering lab. Initial BOD_5 buffer reagents were prepared during a previous semester. These buffers showed no signs of precipitation or biological growth; however, they were replaced with new solutions. All tubing and containers for dilution water were replaced. The DO membrane was replaced. The oxygen filter was

adjusted. These steps were taken in addition to the constant thorough cleaning of the

BOD_5 bottles prior to testing. The second quality control check for the BOD_5 test is a

minimum DO sample depletion of 2 mg/L. BOD_5 was initially overestimated because of

the previously cited literature ranges. Test results showed BOD_5 values were typically

between 5- 15% of the COD values, yielding BOD_5 values in the range of 30-100 mg/L.

These low concentrations of BOD_5 would not have a significant impact on the WWTP

influent. For this reason organic removal was evaluated based on COD results, which

were more consistent for measuring refractory organics.

Other than a slight pH change variation from sample to sample, chemical

coagulation did not change pH. This is because the alkalinity of the waste stream was

very high.

Nitrogen concentrations, both organic nitrogen and ammonia, remained relatively

constant through each test. Results indicate that chemical coagulation did not have a

significant impact on nitrogen concentrations.

The three main parameters needed to indicate organics removal were TSS, VSS,

and COD. Each test returned valid data. For most jar tests, better removal percentages

correlated with higher chemical dosages.

4.2 Alum Results- Jar Test 1

The first coagulation experiment was conducted using different dosages of alum.

As the alum dosage increased, the supernatant appeared lighter in color. Visually, the

320 mg/L looked to be the best treatment. Figure 4-1 shows the sludge volume after

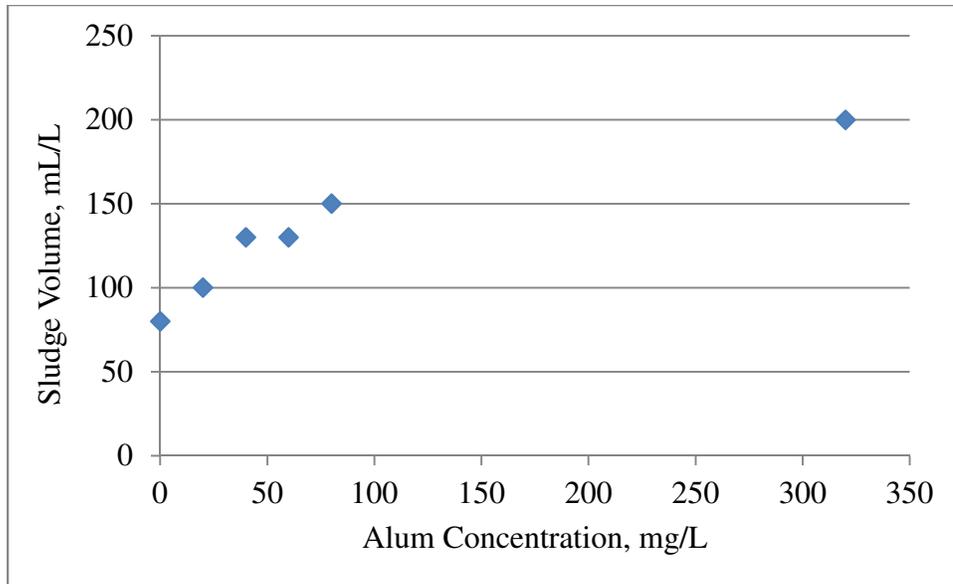thirty minutes of settling, while Table 4-2 shows the analytical results.

Figure 4-1. Sludge Volume after 30 Minutes of Settling for Alum Treatment

Table 4-2. Jar Test 1 Analytical Results

Jar	Coagulant	Dosage, mg/L	pH	Alkalinity, mg/L	TSS, mg/L	VSS, mg/L	COD, mg/L	Total P, mg/L	TKN, mg/L	NH₃-N, mg/L
Raw	Alum	0	7.4	2600	1147	717	1631	>120	745	590
Control	Alum	0	7.4	2300	613	383	1134	>120	720	580
2	Alum	20	7.4	2300	513	377	1082	>120	-	580
3	Alum	40	7.4	2400	527	383	1071	>120	700	580
4	Alum	60	7.4	2500	467	210	1033	>120	660	580
5	Alum	80	7.4	2400	527	330	997	>120	750	580
6	Alum	320	7.2	2200	267	150	770	>120	830	580

Table 4-2 shows the results using alum as the sole coagulant. BOD_5 data are not included because it did not meet quality control checks. Blank oxygen depletion averaged 1.9 mg/L. This is much higher than the needed maximum depletion of 0.2 mg/L. However, BOD_5 concentrations could be estimated at less than 600 mg/L due to amount of dilution used. Phosphorous concentrations were underestimated as can be seen by the results. Also, one error occurred during the TKN test for 20 mg/L alum dosage. The other results for TKN and ammonia showed that chemical coagulation did

not have a significant impact on nitrogen removal. The following figures show solids

and organic removal compared to chemical dosages.

Figures 4-2 through 4-4 (see appendix) show better removal percentages correlate

with higher dosages of alum.   This is true for every dosage except 40 mg/L. For that jar,

a slight decrease in TSS and VSS removal percentages occurred. The best alum

treatment was the 320 mg/L dosage. For this test, 77% of TSS, 79% of VSS, and 53% of

COD were removed.

4.3 Alum with an Anionic Flocculant Results- Jar Test 2

Alum dosages were increased for the second coagulation experiment. Four mg/L

of anionic flocculant was also added to each jar. Visual analysis during the flocculation

period showed larger floc particles compared to jar test 1. Further visual analysis showed

floaters began to appear at the 400 mg/L concentration. Floater abundancy continued to

increase as dosage increased. Visual clarity of each chemically treated supernatant

appeared similar in all jars. The control jar showed a large concentration of suspended

particles, while none of the others did. Figure 4-2 shows the sludge volume after thirty
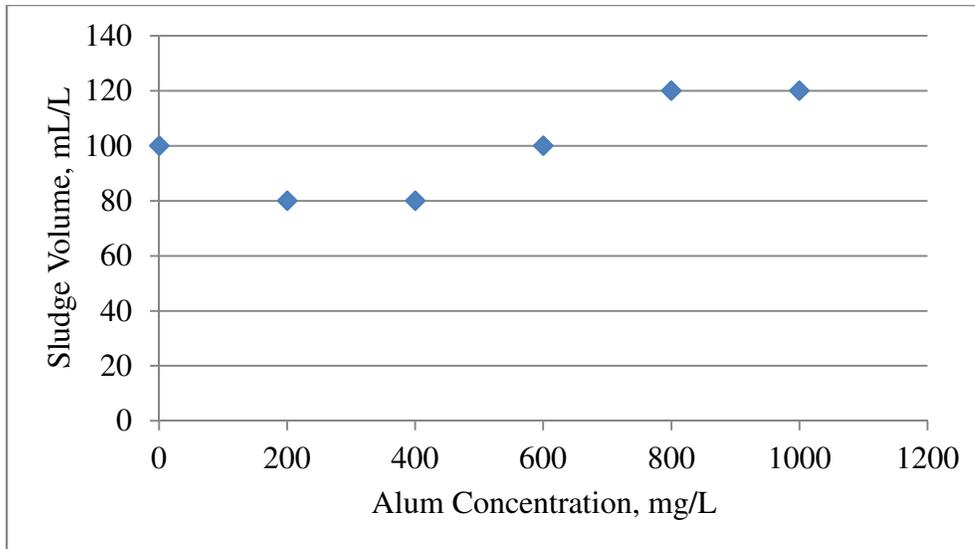
minutes of settleability.

Figure 4-5. Sludge Volume after 30 Minutes of Settling for Alum and Flocculant
Treatment

Figure 4-5 shows lower sludge volumes than jar test 1. One interpretation is that jar test

2 had a more compact sludge volume. A different interpretation could imply that fewer

solids settled. Table 4-3 shows the analytical results.

Table 4-3. Jar Test 2 Analytical Results

Jar	Coagulant	Dosage, mg/L	pH	Alkalinity, mg/L	TSS, mg/L	VSS, mg/L	COD, mg/L	Total P, mg/L	TKN, mg/L	NH$_3$-N, mg/L
Raw	none	0	7.4	2600	1147	717	1631	243	745	590
Cont.	none	0	7.4	2300	613	383	1134	214	720	580
2	Alum+Floc	200	7.7	2300	273	253	888	232	-	600
3	Alum+Floc	400	7.6	2400	487	290	807	204	660	590
4	Alum+Floc	600	7.6	2500	327	177	798	212	750	590
5	Alum+Floc	800	7.6	2400	280	190	657	200	750	590
6	Alum+Floc	1000	7.6	2200	500	210	714	170	830	580

Table 4-3 shows the analytical results using alum and an anionic flocculant.

BOD$_5$ data are not included because quality control checks were not met. However,

BOD$_5$ concentrations could be estimated at less than 300 mg/L. Chemical treatment did not have a significant effect on ammonia levels. For 400 mg/L, we do see a slight decrease in TKN concentration with 50% removal of organic nitrogen achieved. In general, phosphorous levels appear relatively unaffected. A slight increase in pH occurs; however, temperature in the laboratory fluctuates and may have affected this parameter. The chemical treatment was not responsible. The following figures show solids and organic removal compared to chemical dosage.

Table 4-3 and Figures 4-6 through 4-8 (see appendix) show that increase in dosage does not correlate with increased solids and organic removal. Too much coagulant may have been added. Another possibility is that floaters in the jar test may have entered into the drawn supernatants. The best dosages appeared to be the 200, 600, and 800 mg/L. This conclusion results because the best TSS, VSS, and COD removal percentages occurred in three different dosages. The dosages respectively achieved 76, 71, and 76 percent removal of TSS. The dosages achieved 65, 75, and 74 percent removal of VSS, while also achieving 46, 51, and 60 percent removal of COD respectively.

4.4 Alum and PolyDADMAC Blend with Anionic Flocculant Results- Jar Test 3

The third coagulation experiment consisted of varying percentages of an alum and PolyDADMAC blend with a constant 4 mg/L of anionic flocculant. The dosage of the combined chemicals remained constant at 300 mg/L. Percentages of alum to PolyDADMAC ranged from 95-5 to 75-25. For example, the 95-5 ratio represents a chemical treatment with 275 mg/L of alum and 15 mg/L of polyDADMAC. Three hundred mg/L was chosen due to the previous jar test results. A higher dosage may

provoke the formation of floaters, while a lesser dose may not provide adequate solids

and organic removal. Visual assessment showed floaters were present in each jar. Visual

clarity improved when compared to the previous two jar tests. This was the first test

where the paddle wheel on the jartester was visual after treatment. Both the clarity and

the sludge volume after thirty minutes of settling increased as the ratio of PolyDADMAC

to alum increased. In other words, treatment improved with an increase in

polyDADMAC dosage and a decrease in alum dosage. Figure 4-9 shows the sludge

volume after thirty minutes of settling, while Table 4-4 shows the analytical results.
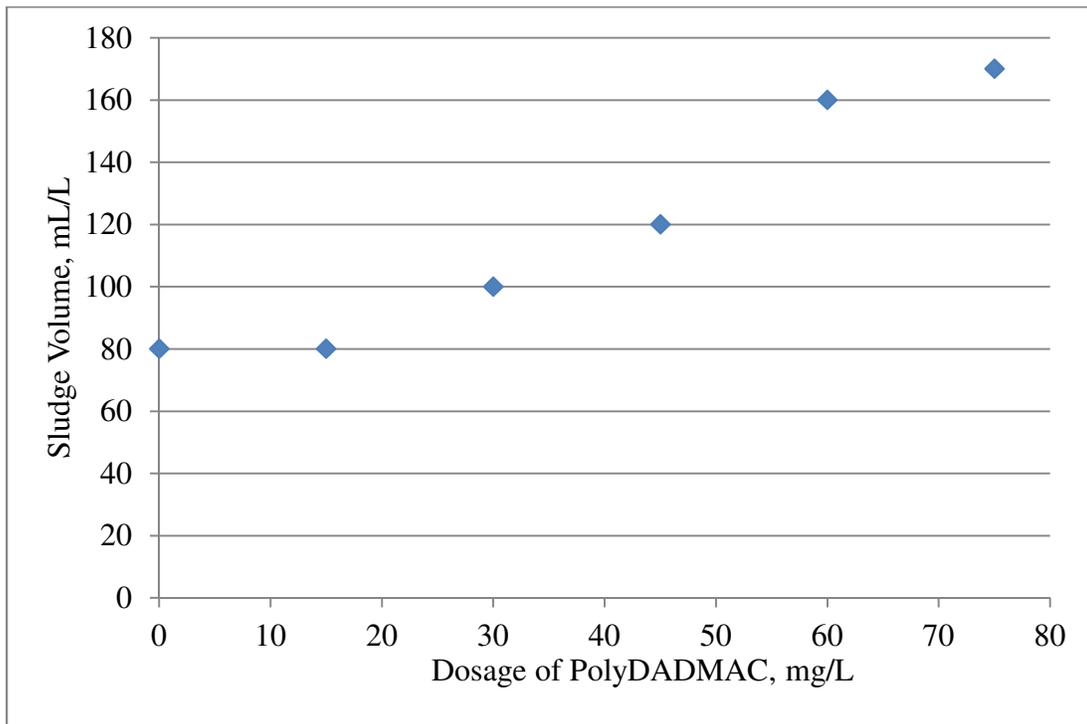

Figure 4-9. Sludge Volume after 30 Minutes of Settling for Blend and Flocculant
Treatment

Table 4-4. Jar Test 3 Analytical Results

Jar	Coagulant	Ratio	pH	Alkalinity, mg/L	TSS, mg/L	VSS, mg/L	COD, mg/L	Total P, mg/L	TKN, mg/L	NH$_3$-N, mg/L
Raw	none	0	7.4	2600	1147	717	1631	>360	745	590
Cont.	none	0	7.4	2300	613	383	1134	>360	720	580
2	Blend+Floc	95-5	7.3	2500	407	250	915	360	835	580
3	Blend+Floc	90-10	7.3	2600	473	297	894	>360	980	560
4	Blend+Floc	85-15	7.3	2600	253	90	600	>360	730	550
5	Blend+Floc	80-20	7.3	2600	170	60	432	>360	750	580
6	Blend+Floc	75-25	7.3	2600	140	23	360	>360	730	630

Figure 4-9 shows that the clearest supernatant, also achieved the greatest sludge volume after settling. The 170 mL/L value is less than the 320 mg/L dosage during Jar Test 1. This leads to a conclusion that the floc has better settling characteristics for this treatment when compared to the alum treatment. The sludge is denser for this treatment. Table 4-4 shows the analytical results using an alum and polyDADMAC blend and an anionic flocculant. The ratios in Table 4-5 represent the alum to polyDADMAC ratio in each 300 mg/L dosage. BOD$_5$ data are not included in this table because quality control checks were not met. Average blank depletion was 0.7 mg/L. However, BOD$_5$ concentrations could be estimated at less than 120 mg/L due to the dilution factor that was used. Phosphorous concentrations were underestimated for this experiment. This result and previous phosphorous findings reveal that phosphorous concentrations can fluctuate greatly from sample to sample. Chemical addition had no effect on organic nitrogen or ammonia during this experiment. The following figures show solids and organic removal compared to polyDADMAC dosage.

Figures 4-10 through 4-12 (see appendix) show that the chemical blend and flocculant combination experiment achieved the best organic removal compared to the previous two jar tests. The dosage that achieved the best removal percentage contained 225 mg/L of alum, 75 mg/L of PolyDADMAC, and 4 mg/L of anionic flocculant. This treatment achieved 88% TSS, 97% VSS, and 78% COD removal. This jar also contained the clearest supernatant thus far. Increases in polyDADMAC dosage correlates with COD removal. This is also true for TSS and VSS with the exception of the 90-10 ratio. This might imply that the treatment was less effective, or that floaters entered into the drawn supernatant.

Another point of analysis can come from supernatant concentrations. Most of the analysis in this project is in terms of percentage removal. This is often the chosen method in scientific literature. However, it is important to note that the 75/25 blend also achieved lower TSS, VSS, and COD concentrations than the previous two jar tests. These concentrations are 140, 23, and 360 mg/L respectively.

4.5 Ferric Chloride Results- Jar Test 4

The fourth coagulation experiment was conducted using different dosages of ferric chloride. No flocculant was added. Chosen dosages were similar to that of the jar test 1 experiment. This design allowed a comparison of the two coagulants. Visual observation showed the 40 mg/L dosage did not have an impact on the wastewater. For dosages above 40 mg/L, cloudiness was evident in all the supernatants. This cloudiness did decrease with each dosage increase. Suspended particles also decreased as dosage increased. Thirty minute sludge volume is shown in Figure 4-13, while analytical results are shown in Table 4-5.
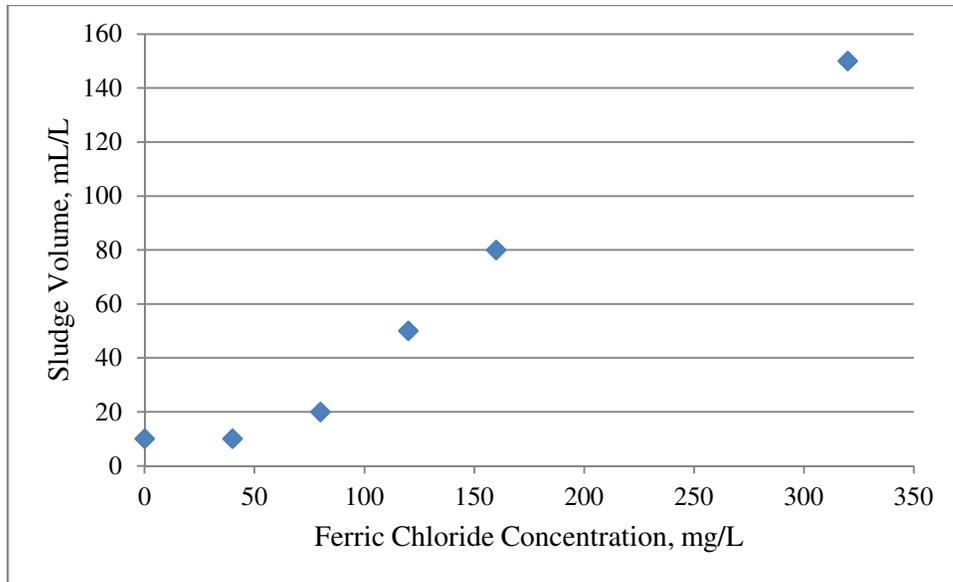
Figure 4-13. Sludge Volume after 30 Minutes of Settling for FeCl₃Treatment

Table 4-5. Jar Test 4 Analytical Results

Jar	Coag.	Dosage, mg/L	pH	Alk., mg/L	TSS, mg/L	VSS, mg/L	BOD₅, mg/L	COD, mg/L	Total P, mg/L	TKN, mg/L	NH₃-N, mg/L
Raw	none	0	7.7	2300	1050	620	81	1233	476	800	590
Cont.	none	0	7.7	2200	500	240	48	944	>480	790	580
2	FeCl₃	40	7.7	2300	420	207	69	876	>480	790	570
3	FeCl₃	80	7.8	2300	390	290	104	808	>480	830	540
4	FeCl₃	120	7.8	2200	307	193	96	780	381	780	400
5	FeCl₃	160	7.8	2300	253	193	56	-	390	820	540
6	FeCl₃	320	7.9	2300	113	93	91	648	438	820	400

Table 4-5 shows BOD₅ data could be calculated for the first time. A correction factor was used to estimate the data as quality control checks were not met. Average blank deletion was 0.8 mg/L. Phosphorous concentrations showed continued variation. However, it could be concluded that some phosphorous removal occurred for dosages 120, 160, and 320 mg/L. Similar to the previous experiments, chemical treatment did not achieve significant nitrogen removal. The following figures show solids and organic removal compared to ferric chloride dosage.

Figures 4-14 through 4-16 (see appendix) show that the 320 mg/L dosage performed the best. This dosage achieved 89% TSS, 85% VSS, and 47% COD removal. The 89% TSS removal is the highest removal percentage of any treatment seen thus far. The treatment also achieved the lowest TSS concentration thus far, at 113mg/L. An error occurred during the COD test for the 160 mg/L dosage. However, the rest of the COD data show an increase in dosage enhances COD removal.

4.6 Ferric Chloride with an Anionic Flocculant Results- Jar Test 5

The fifth coagulation experiment was conducted using ferric chloride and an anionic flocculant. Chosen dosages were similar to jar test 4 in order to compare ferric chloride treatment with and without an anionic flocculant. The anionic flocculant dosage remained constant at 4 mg/L. Visual observation showed the largest floc formation compared to previous experiments. Additionally, the floc size increased as dosage of ferric chloride increased. Clearest supernatants occurred with the 40 mg/L and 80 mg/L dosage. The paddle wheel could be seen inside the jartester apparatus for both of these jars. This similar clarity occurred in the 75-25 alum and polyDADMAC treatment. Floaters were evident in all dosages except the 320 mg/L jar. In this jar, bubbles were present on the surface. This result possibly indicates too much coagulant was used. Figure 4-17 shows the sludge volume after 30 minutes of settling, while Table 4-6 shows the analytical results.
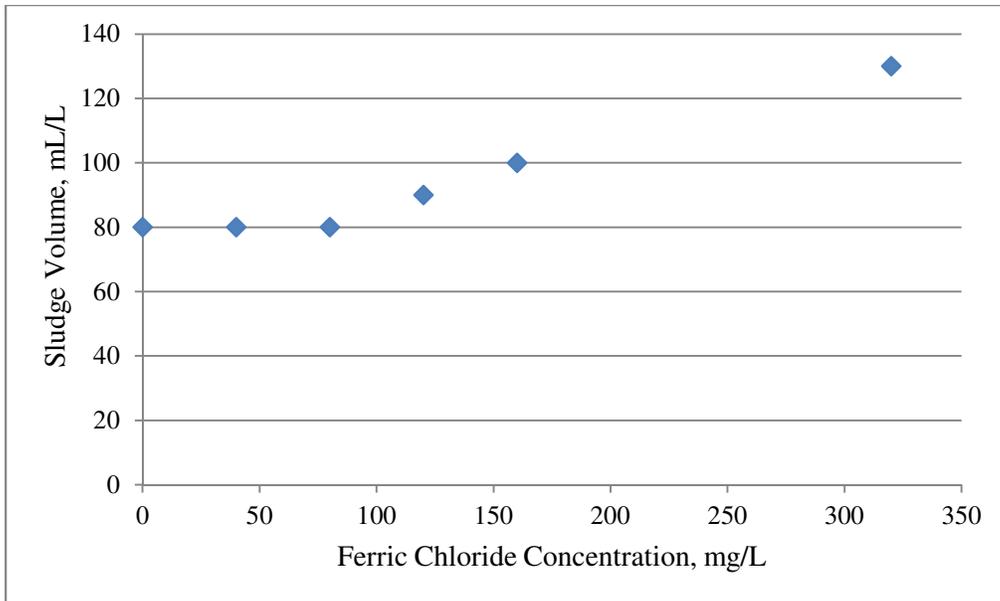
Figure 4-17. Sludge Volume after 30 Minutes of Settling for FeCl$_3$ and Flocculant Treatment

Table 4-6. Jar Test 5 Analytical Results

Jar	Coagulant	Dosage, mg/L	pH	Alk., mg/L	TSS, mg/L	VSS, mg/L	BOD$_5$, mg/L	COD, mg/L	Total P, mg/L	TKN, mg/L	NH$_3$-N, mg/L
Raw	none	0	7.7	2300	873	493	81	1090	243	770	520
Cont.	none	0	7.7	2200	440	329	56	800	214	740	530
2	FeCl$_3$ + Floc	40	7.8	2300	450	250	32	710	278	670	520
3	FeCl$_3$ + Floc	80	7.7	2200	410	220	61	580	210	680	520
4	FeCl$_3$ + Floc	120	7.8	2300	233	167	30	580	191	750	530
5	FeCl$_3$ + Floc	160	7.9	2200	300	167	32	550	198	660	540
6	FeCl$_3$ + Floc	320	7.9	2300	300	180	27	475	156	670	530

Table 4-6 shows the analytical results using ferric chloride and an anionic

flocculant. Concentrations for the raw sample of wastewater are much lower than

previous raw samples. Phosphorous concentrations again continued to vary. However, it

could be concluded that significant phosphorous removal was obtained for higher dosages of coagulant. The BOD_5 test did not clear the quality control check. The average depletion in the blanks was 1.0 mg/L of DO. A correction factor was used to calculate the values above. Chemical treatment did not appear to have an effect on nitrogen. The following figures show solids and organic removal compared to ferric chloride dosage.

Figures 4-18 through 4-20 (see appendix) show that two different treatments perform the best with regards to organics removal. The 120 mg/L dosage achieved 73% TSS, 66% VSS, and 47% COD removal. The 320 mg/L dosage achieved 66% TSS, 64% VSS, and 56% COD removal. The 120 mg/L dosage is a significant decrease in dosage to obtain over 70% removal of TSS. In general, this coagulation experiment showed less removal of solids and organics than the previous experiments. One factor that may have influenced this is the lower concentration of organics in the raw sample. Higher percentages of removal could be more difficult to obtain in a wastewater with lower concentrations of organics.

4.7 Influent Treatment with Alum and PolyDADMAC Blend Results- Jar Test 6

Chemical treatment of the Maxson WWTP raw influent was also examined. The alum and polyDADMAC blend was used as the coagulant because it typically performed the best on the anaerobic supernatant. Collection and jar test procedure was similar to that of the anaerobic lagoon supernatant. Chosen dosages included 50, 100, 150, 200, and 250 mg/L. During this examination no floc formation occurred. No flocculant was added, and no parameters were tested. These results indicate that the coagulated solids

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in the filtrate return stream could have adversely impacted the chemical reactions during coagulation.

4.8 Conclusion

When treating large flows of return streams, finding the minimum yet effective dosage of treatment is very important. For this reason, this study focused on finding a combination of coagulant and flocculant that worked the best with the least amount of chemicals. In general, it appeared that several options worked well in removing organics. Table 4-7 shows a comparison of the best results from each test.

Treatment	Coagulant Dosage, mg/L	Flocculant Dosage, mg/L	TSS, Percentage Removal	VSS, Percentage Removal	COD, Percentage Removal
Alum	320	0	77	79	53
Alum + Floc	200	4	76	65	46
Blend + Floc	300	4	88	97	78
Ferric Chloride	320	0	89	85	47
Ferric Chloride +Floc	120	4	73	66	47
Ferric Chloride +Floc	320	4	66	63	56

Table 4-7. Organics Removal Comparison on Anaerobic Lagoon Supernatant

Table 4-7 shows that the ferric chloride treatment achieved the highest removal percentage of TSS, while the alum and polyDADMAC 75/25 blend achieved the greatest VSS and COD removal. The 320 mg/L of ferric chloride also achieved the lowest TSS concentration at 113mg/L. The 75/25 blend achieved the clearest supernatant, and the lowest concentrations of VSS and COD at 23 and 360 mg/L, respectively. This treatment also achieved the second lowest TSS concentration at 140 mg/L. In general, this treatment performed the best and is considered the best coagulant for this specific sludge return stream.

When sludge return stream flow is high, it is always important to consider the cost of chemicals. If a WWTP was considering the cheapest option of treatment, the 120 mg/L dosage of the ferric chloride and 4 mg/L of an anionic flocculant could be the best option because it uses the least amount of chemicals.

During these experiments, raw samples of supernatant were collected on a weekly basis. Pollutant concentrations in these samples varied from sample to sample. Percentages of removal would vary considerably considering the raw sample characteristics varied considerably. Because sludge return stream samples were obtained at different times, identical sludge stream samples could not be achieved. This introduced some variability in the treatment schemes evaluated during this study. However, the results obtained in this research are useful in spite of the raw sludge stream variability with time.

This experimental design was catered towards organics and solids removal. It is important to note that a different design could have achieved better nutrient removal with coagulation. Varying chemicals, dosage, pH, and temperature could have improved coagulation performance. Regardless of this, some phosphorous was removed. The most precise results for phosphorous occurred from jar test 2 and jar test 5. For both of these tests, some phosphorous was removed. The best removal percentage was 36 percent by the 320 mg/L dosage of ferric chloride with 4 mg/L of flocculant. Organic nitrogen removal percentages varied. However, two treatments achieved 50 percent removal, the 40 mg/L of alum and the 400 mg/L of alum with 4 mg/L of flocculant. Also, the 160 mg/L of ferric chloride with 4 mg/L of flocculant accomplished a 44 percent removal.

The coagulation had no effect on ammonia; however the readings were imperative to the testing in order to calculate organic nitrogen concentrations.

The influent treatment jar test had interesting results. During this jar test, no floc particles were formed. This resulted because the coagulant dosage was too high, or the cationic emulsion polymer used to treat the filtrate adversely affected the chemical reactions needed to form floc particles.

When considering chemical treatment of return streams, it is important to comment on the limitations of the process. The first is the high cost of chemicals, construction, and sludge handling and disposal. The second limitation is that chemical residuals are left in the supernatants. The effect of these residuals on aquatic ecosystems and on the microorganisms in biological treatment need to be further examined.

4.9 Recommendations

After obtaining the results from this study, further research is needed to continue exploring chemical addition to reduce organics in return streams. The author poses the following ideas for continued research:

1. To test a broader range of return streams that include but are not limited to: aerobic digester supernatant, dewatering filtrate where polymers are not used, and overland return streams that allow for drainage of surface disposal sites.

2. To test different streams during different seasons and document flow during rainy periods vs. dry periods.

3. To test a broader range of chemicals, blends, and flocculants because streams vary considerably.

4. To attempt different dosages and coagulants that treat return streams after they have combined with influent streams.

As effluent limits become more stringent in the future, more WWTPs will need to consider treatment of their return streams. In order to find the best and cheapest option, chemical treatment needs to be considered.

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APPENDIX

This appendix includes TSS, VSS, and COD removal percentages achieved for every treatment.
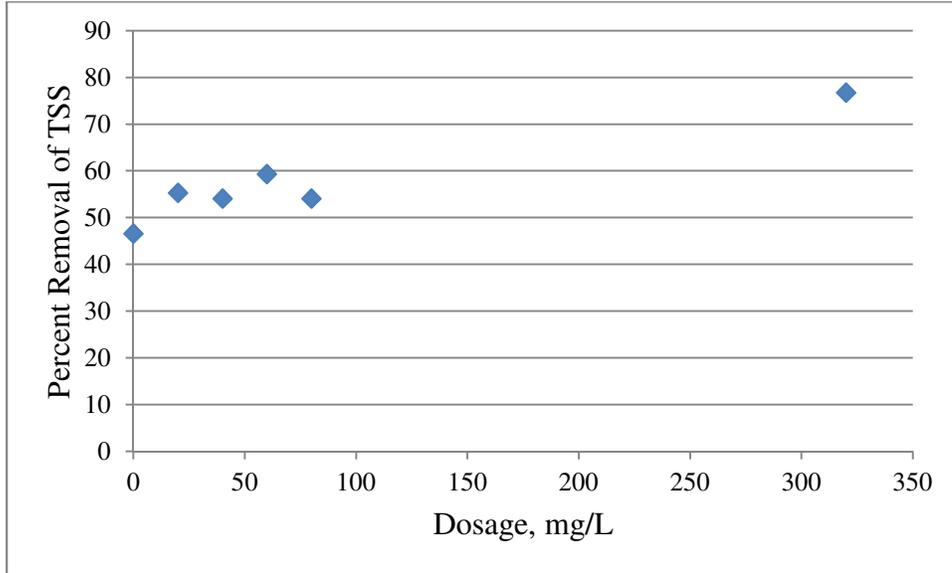
Figure 4-2. Removal Percentage of TSS for Alum Treatment
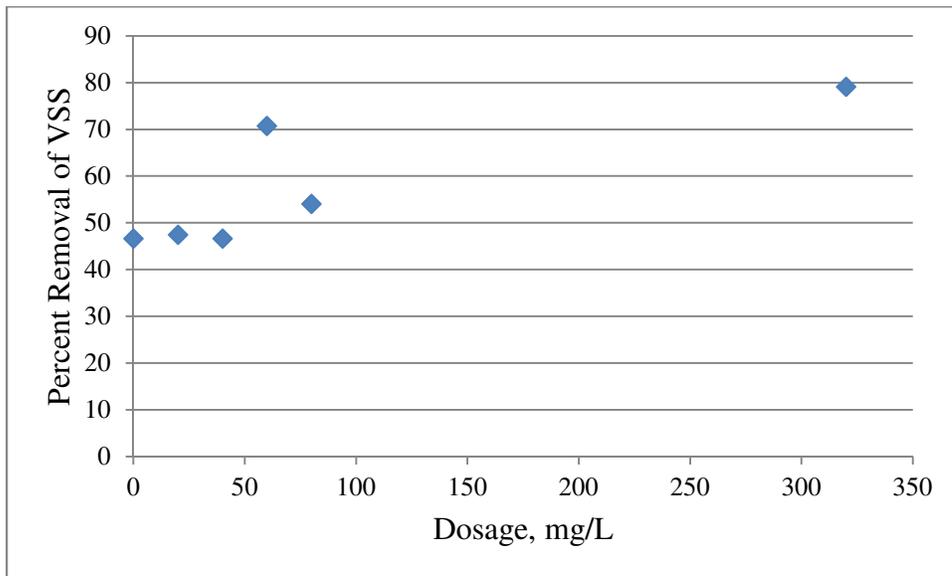
Figure 4-3. Removal Percentage of VSS for Alum Treatment
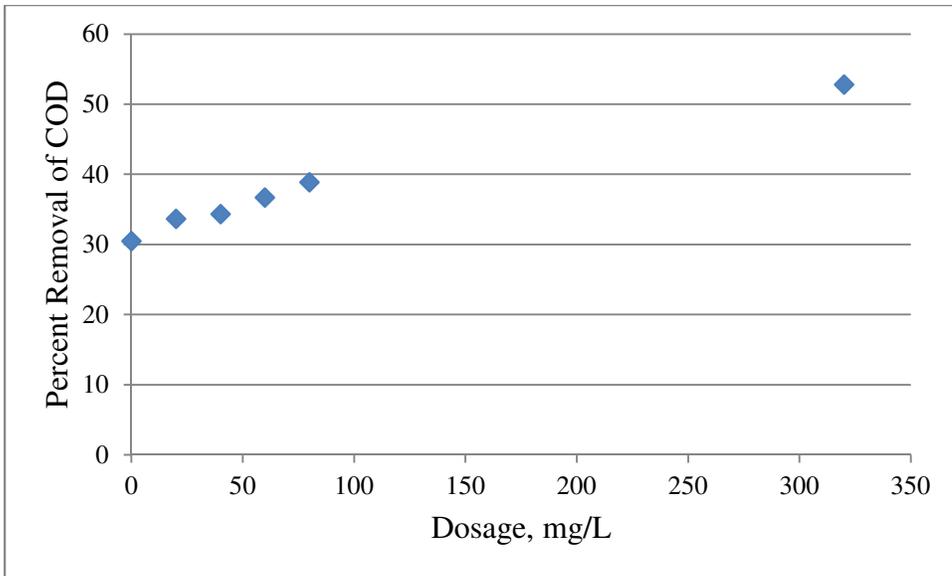
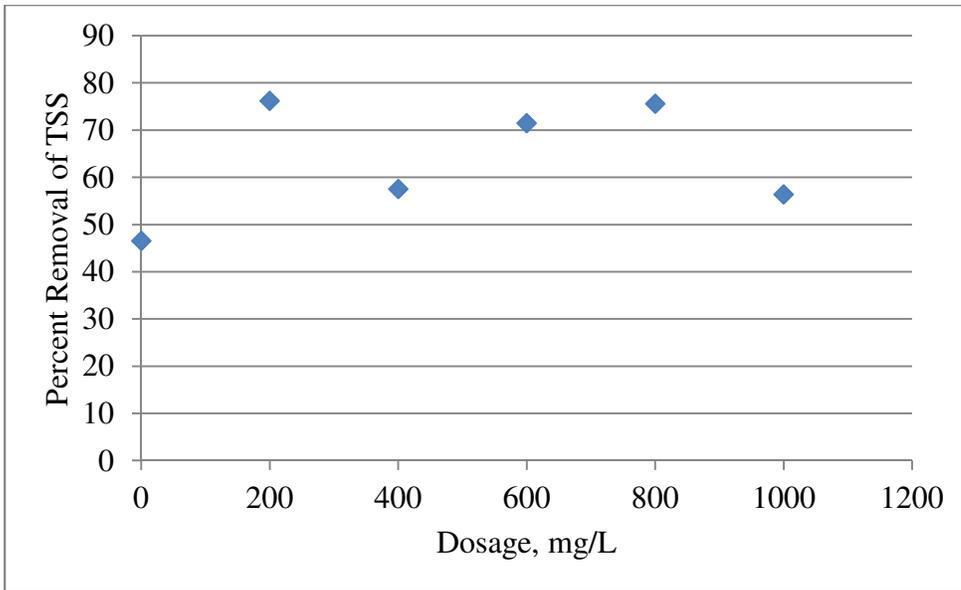Figure 4-4. Removal Percentage of COD for Alum Treatment

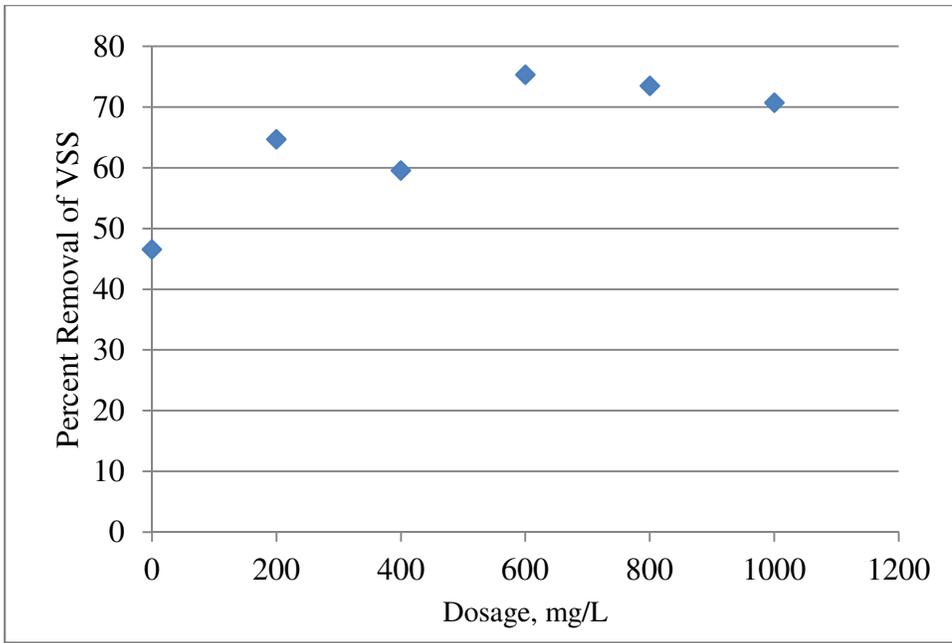Figure 4-6. Removal Percentage of TSS for Alum and Flocculant Treatment

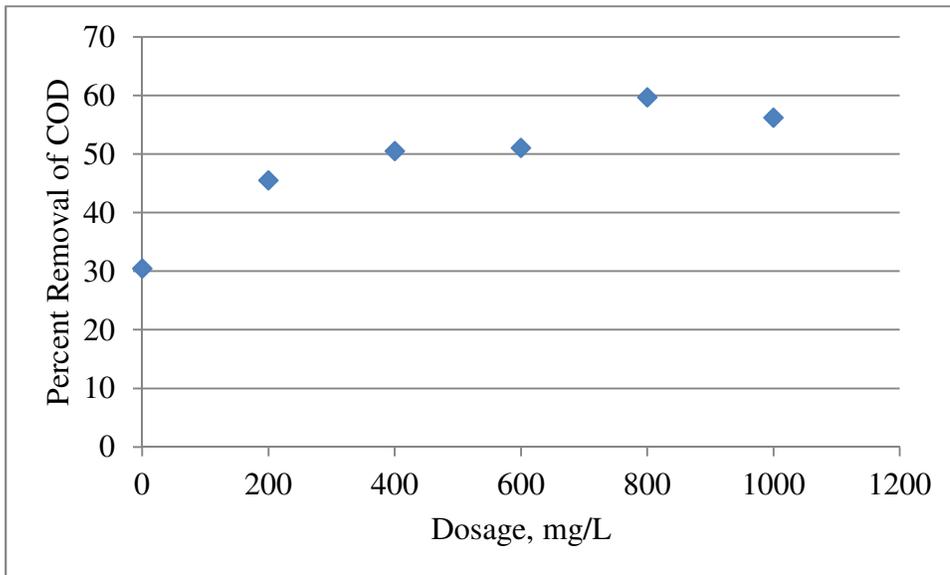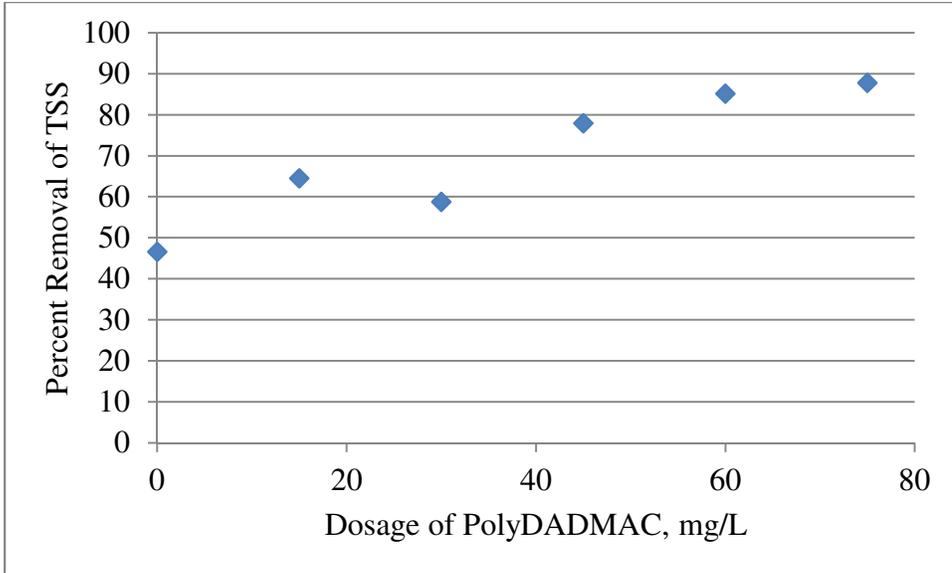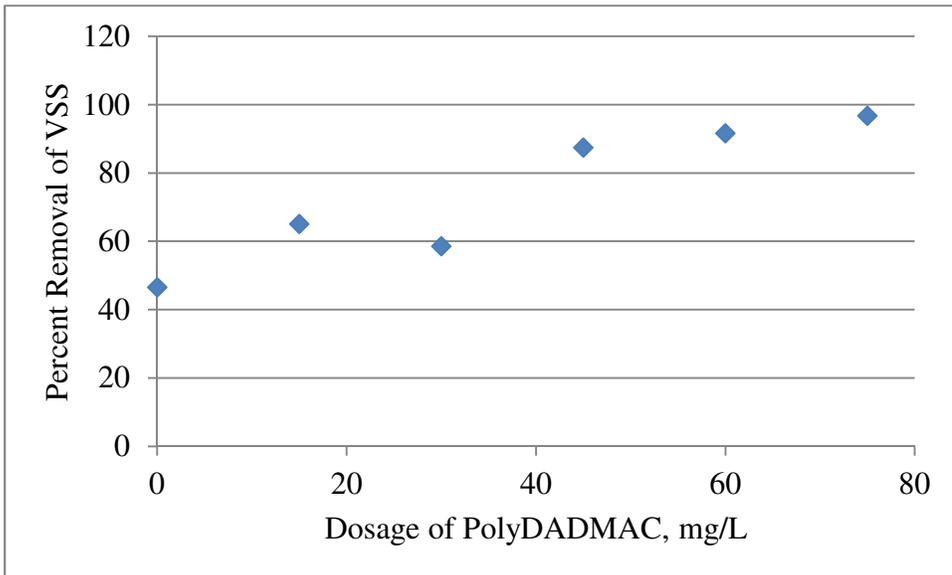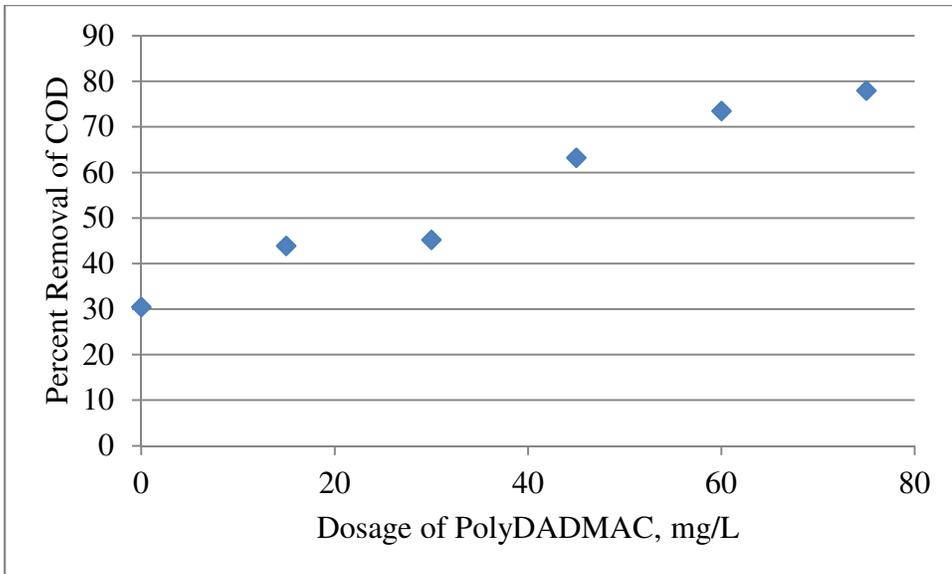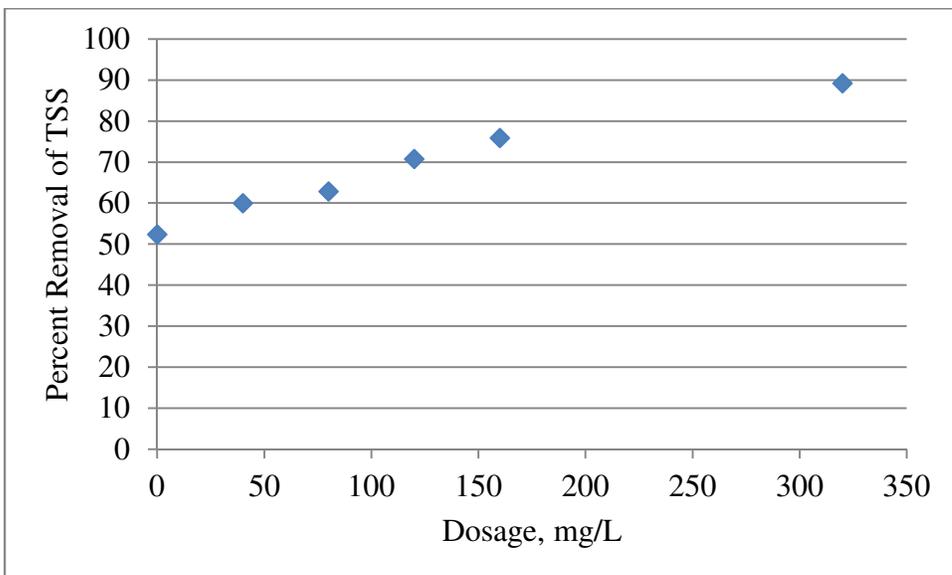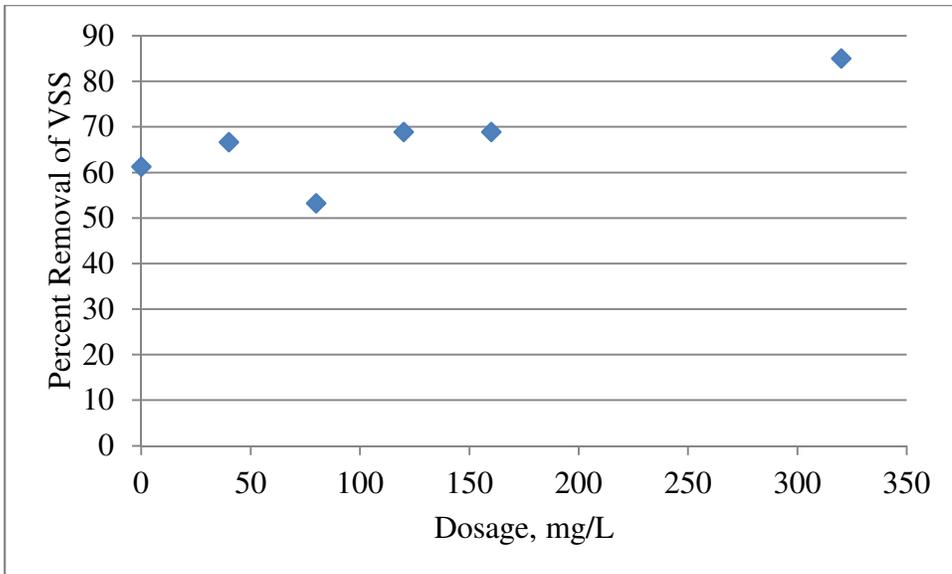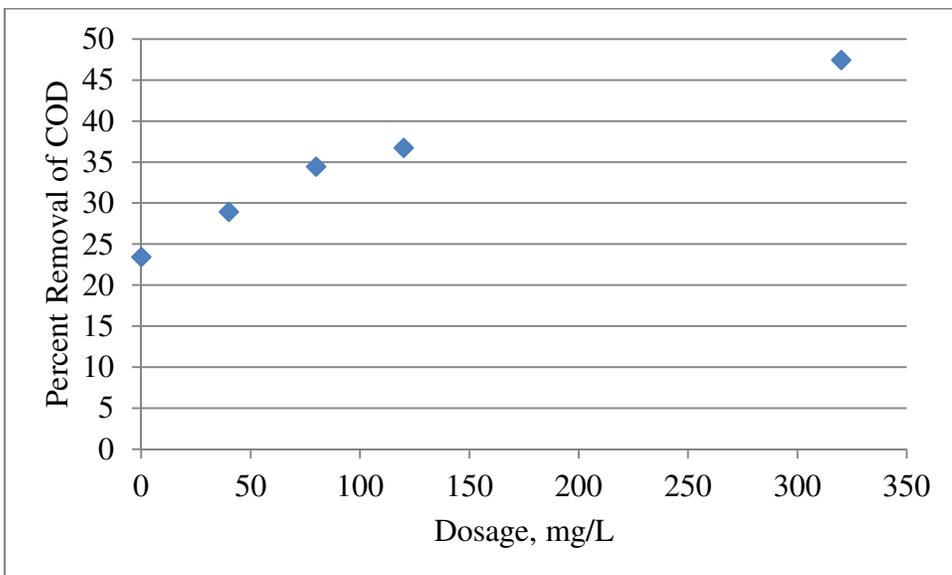Figure 4-7. Removal Percentage of VSS for Alum and Flocculant Treatment

Figure 4-8. Removal Percentage of COD for Alum and Flocculant Treatment

Figure 4-10. Removal Percentage of TSS for Blend and Flocculant Treatment

Figure 4-11. Removal Percentage of VSS for Blend and Flocculant Treatment

Figure 4-12. Removal Percentage of COD for Blend and Flocculant Treatment

Figure 4-14. Removal Percentage of TSS for FeCl$_3$ Treatment

Figure 4-15. Removal Percentage of VSS for FeCl$_3$Treatment

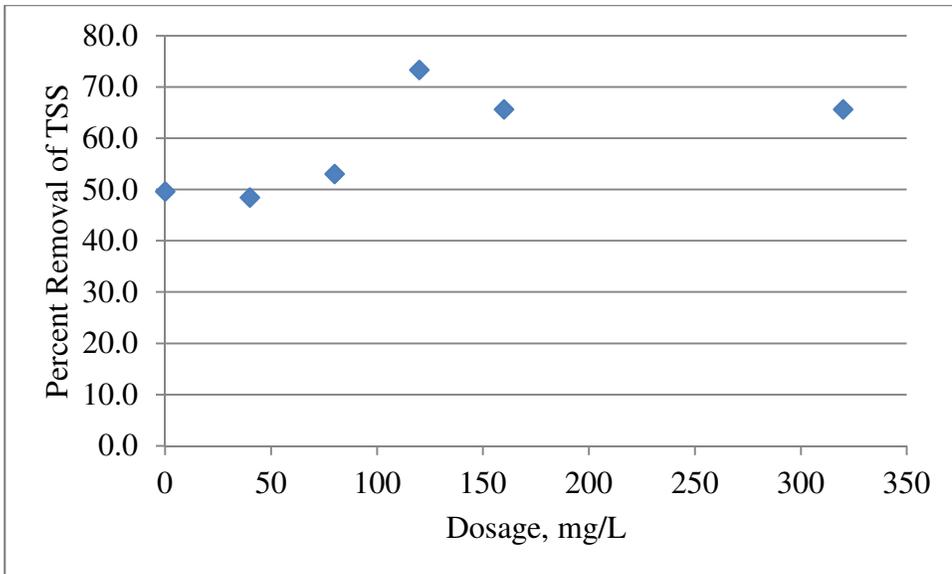Figure 4-16. Removal Percentage of COD for FeCl$_3$Treatment

Figure 4-18. Removal Percentage of TSS for $FeCl_3$ and Flocculant Treatment

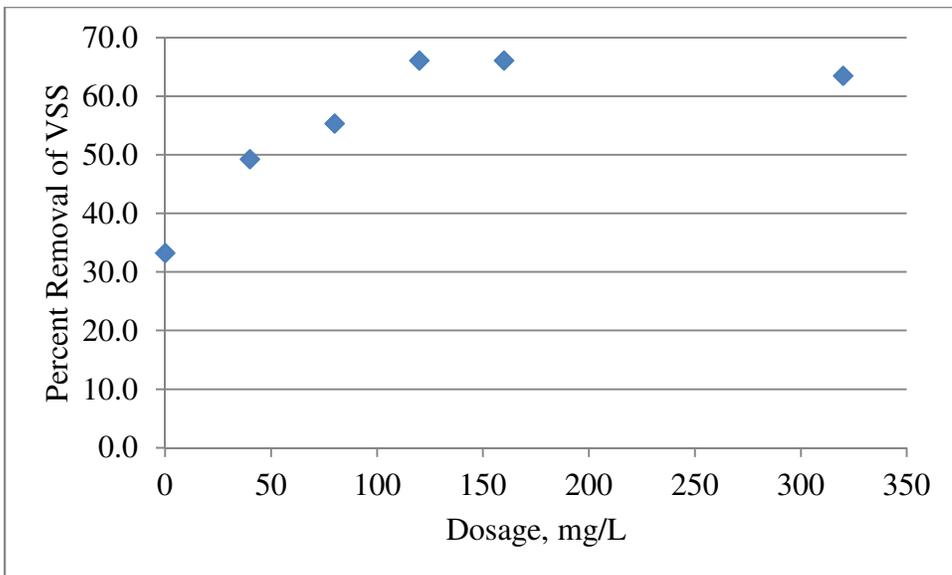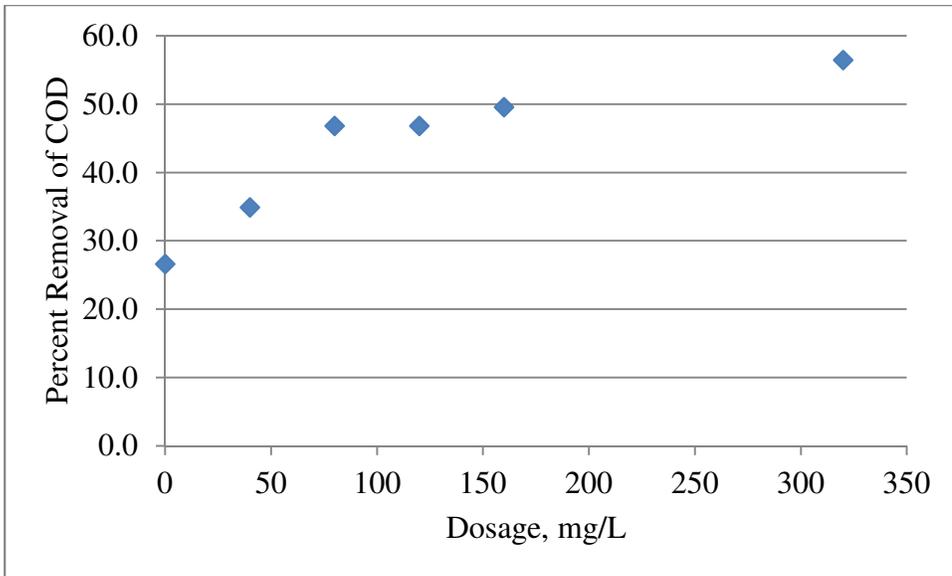Figure 4-19. Removal Percentage of VSS for $FeCl_3$ and Flocculant Treatment

Figure 4-20. Removal Percentage of COD for FeCl$_3$ and Flocculant Treatment