Ferric Chloride in Wastewater Treatment

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The Use of Ferric Chloride for Phosphorus Removal in Wastewater Treatment

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Abstract

Wastewater Treatment Facilities have been built to remove biological and chemical waste from water as it is used. These facilities maintain a healthy environment for organisms as well as people because it removes potentially harmful material and kills pathogens that would easily spread through cities. Phosphorus is a compound of interest because a high concentration of it at discharge will eventually lead to eutrophication and hypoxia in local waterways. For these reasons, the Environmental Protection Agency has reduced the allowable concentration of phosphorus in effluent from 1.0 ppm to 0.1 ppm. Ferric chloride is used in wastewater treatment facilities to precipitate phosphorus to remove it from the system. The question is whether ferric chloride can continue to remove phosphorus at a steady rate or will it reach a point at which it is no longer effective? I hypothesize that at the facility level the ferric chloride will have a significant effect on the amount of phosphorus in the effluent as it is discharged into the lake. In the lab I hypothesize that as more ferric chloride is added to a standardized solution more phosphorus will be precipitated out. Ferric chloride has a significant effect on the removal phosphorus at facility levels because as more ferric chloride is added into the effluent the phosphorus is precipitated out of the effluent and the final concentration of phosphorus is less than 1.0 ppm. In the lab, phosphorus concentrations at one ppm behave as expected with more phosphorus precipitated at greater doses of ferric chloride. At greater initial phosphorus levels, it seems to be less effective and precipitates less phosphorus as ferric chloride doses increase.

Introduction

Wastewater treatment is important for keeping the ecosystem healthy because it removes biological and chemical wastes from the wastewater before it enters receiving water. An important part of wastewater treatment is the removal of phosphorus before the effluent leaves the Treatment Facility. Phosphorus is a main focus for treatment facilities because it is a pollutant if found in high concentrations in waterways, and the Environmental Protection Agency (EPA) as of 2010 requires WWTF to maintain a monthly phosphorus concentration below
0.1 parts per million (ppm) whereas the previous level was 1.0 ppm. Phosphorus is currently removed most commonly through the use of a chemical compound called ferric chloride which precipitates out the phosphorus into non-soluble forms that is unable to be used by plants and microorganisms. Research is needed to determine whether ferric chloride can be used to maintain a concentration of less than 0.1 ppm or if systems must be update with membranes to meet these new regulations (Citulski et al 2009).

Phosphorus is naturally occurring within the ecosystem and wastewater systems. In natural ecosystems phosphorus is most commonly found in stone where it is slowly released into the ecosystem through a process called weathering. Weathering is the break down of rocks, soil, and minerals by the planet’s atmosphere. Phosphorus is important for growth because it is required to produce adenosine tri-phosphate (ATP) which is the main source of energy in all organisms. Phosphorus is thus a limiting factor for growth of plants and animals because of its typically low availability in the ecosystem (Vanni 2002). As phosphorus is released into the ecosystem, it is readily taken up by plants and used to grow; animals can then obtain the phosphates by devouring the plants and other animals that have ingested the phosphates; the materials are broken down and can be used as energy. As the plants and animals approach the end of their life cycle they die and microorganisms slowly release the nutrients stored in the organisms back into the ecosystem through decomposition.

Humans have disrupted this natural phosphorus cycle by increasing the rate at which phosphorus enter the ecosystem because it is found in common household products such as dish soap and detergents as well as drinking water, fertilizers, and many other products (Herried 2007). Phosphates are used in dishwashing detergents because they easily break down grease and remove stains. The benefit of its optimal ability to remove stains very well is offset by the fact that detergents enter the wastewater system and pose a great problem. Fertilizer is another common source of phosphorus. It is used commercially in agriculture and golf courses; additionally it is used around the household most commonly to maintain green lawns. This means that activities such as taking
showers, washing dishes, laundry, as well as the passive occurrence of runoff all will lead to additional phosphorus in the sewers and the wastewater systems which then must be removed before it enters the receiving waters (Oram 2005).

The removal of phosphorus before it enters the receiving waters is important because of the impact it has on the ecosystem. When excess nutrients enter an ecosystem they can cause nutrient-loading which in turn leads to eutrophication (Richter 2003). Eutrophication is a process which occurs when there is an overabundance of nutrients which in turn causes rapid growth in phytoplankton, algae, and other microorganisms (Muir 2009). With phosphorus being a common limiting factor for growth in the environment, an excessive amount of phosphorus will lead to increased algae growth (El-Bestawy et al. 2005); just one pound of phosphorus can support over five-hundred pounds of algae (Herried 2007). These algae blooms have undesirable consequences such as reducing the amount of light that penetrates into the water, which in turn reduces the productivity of bottom-rooted plants (Herried 2007). Decreased plant productivity means decreased oxygen levels because the plants cannot photosynthesize as efficiently. Without the ability to photosynthesize plants will begin to die and as they decompose the microbes will use the dissolved oxygen that is present in the water to assist in the decomposition process (Muir 2009). Not only do the bottom-rooted plants decompose, but the excess growth and competition of algae at the surface will lead to more organic material settling onto the bed of the lake that will also decompose slowly creating an anoxic environment that is toxic to fish and other organisms which require dissolved oxygen to breathe (Herried 2007). Hypoxic conditions in aquatic ecosystems are being discovered more commonly as nutrient loading from runoff and effluent rise (EPA 2004).

In 2008 there were more than 245,000 square kilometers of Marine Ecosystems rated as “Dead Zones” (Diaz and Rosenberg 2008). These dead zones are areas of hypoxia, where dissolved oxygen (DO) levels are less than 2 mL of oxygen per L of water (Dodson 2005). Dead zones are amplified by stratification where water mixing is slowed and areas of extremely low DO levels
Stratification is then followed by a seasonal change allowing hypoxic waters to mix with oxygenated water, which dilutes the overall oxygen content and results in a low DO level for the entire system (Dodson 2005). If this condition occurs on a frequent basis, the water will soon approach anoxic conditions where there is an absence of oxygen and only anaerobic bacteria, which require no oxygen, can survive (Diaz and Rosenberg 2008). The most cost effective and appropriate method for controlling the level and extent of eutrophication is prevention through wastewater treatment (El-bestawy et al. 2005).

Anthropogenic phosphorus loading is reduced through the effective use of Wastewater Treatment Facilities. These facilities use three methods to remove phosphorus: ferric chloride or ferrous chloride is used to precipitate out the phosphorus into a non-soluble form that algae cannot readily use, aerobic bacteria are cultured in the aeration tanks to aid in the removal of organics and phosphorus, and finally anaerobic bacteria remove phosphorus in their fermentation process (Lenntech 2009). Another alternative to remove phosphorus is through the use of a membrane filtration system. These systems not only remove phosphorus suspended in the effluent, but also phosphorus that dissolved in the effluent as well. These membranes can achieve concentrations of less than 0.1 ppm and can bring concentrations of phosphorus as low as 0.008 ppm (Strom 2006). In Kenosha, Wisconsin the Wastewater Treatment Facility is located directly on the lakefront on the Southside of the city. The effluent is then discharged just offshore into the lake. For this reason, the KWWTF utilizes the use of ferric chloride to remove phosphorus at the Kenosha Wastewater Treatment Facilities because the bacteria and algae can only use phosphorus so quickly while ferric chloride can precipitate the phosphorus out chemically with little time lag.

Wastewater Treatment Facilities (WWTF) are an important part of what keeps the environment and our society healthy (Brooks 1905). Water that enters the WWTF is known as influent and as it exits the facility it is known as effluent. The influent is contaminated with organic and inorganic wastes, which are
removed through the treatment process so the effluent that enters the receiving waters is free from major contaminants (USGS 2010). The development of WWTF has also toadied in the control of waterborne diseases such as typhoid, cholera, E. coli, dysentery, and salmonella. These waterborne illnesses became a major health hazard as populations began to increase in cities (Richter 2003).

In seventeenth-century colonial America the most popular way to dispose of waste from a privy was through discharge into the yard, street, gutter, or an open channel which would act as a sewer. This technique worked well until population densities increased and the natural process of waste removal in the ecosystem became overloaded and could no longer handle the amount of waste being dumped (Burian et al. 2000). After numerous disease outbreaks, sanitation was given more attention and sewage systems were designed to discharge into a cesspool or vault until the waste leached out or was manually removed (Tarr et al. 1984). There were no real sewer systems until the nineteenth-century.

In the early nineteenth-century most sewage systems were constructed to handle only storm water (Goldman 1997). Water carriage systems were tunnels which were developed to provide a water flow to remove waste and storm water from the cities. This approach cleaned cities but it also contaminated the water supply because the sewage would be discharged directly into the receiving waters without treatment (Tarr et al. 1984). It was not until the early twentieth-century that techniques for sterilizing sewage were introduced. Sterilization techniques first started with the addition of chlorine compounds and finally with the addition of chlorine itself in later years (Armstrong 1976). Even with the new wastewater practices of the early twentieth-century, about 95% of urban population discharged untreated sewage directly into receiving waters. This process continued until the late twentieth-century when the federal government began protecting water quality with the Clean Water Act which would update WWTF (Burian et al. 2000).

Current day WWTF follow a relatively standard procedure for the treatment of wastewater; the following wastewater treatment steps are those followed by the Wastewater Treatment Facility in Kenosha, Wisconsin. The initial
step to treating the effluent is screening; this process removes any material larger than 10 mm, such as wood, rocks, and rags. These materials must be removed because they can clog the pumping system and the wastewater system would become backed up reducing the efficiency of the facility; these materials are sent to a landfill to be disposed (Zafari 2009). After the effluent is screened it enters the primary clarifier where the velocity of the effluent is reduced to allow suspended solids to settle out. These settled particles are then pumped to digesters where anaerobic bacteria are cultured to increase the rate of decomposition. The remaining sludge is then pumped out of the digesters and transported away to be used as a fertilizer, such as milorganite, or disposed of in a landfill (Dukes 2008).

After the larger suspended solids are removed, the effluent leaves the primary clarifier, and flows towards the aeration tanks. Before entering the aeration tanks the effluent is treated with ferric chloride to reduce the concentration of phosphates in the water; these phosphates can originate from soaps, shampoo, and many other household products that are used on a daily basis. The ferric chloride reacts with the phosphates present in the water to form a ferric phosphate (Equation 1, California Water Technologies 2004).

$$\text{Equation 1}$$

$$\text{Fe}^{3+} + H_n\text{PO}_4^{3-n} \leftrightarrow \text{FePO}_4 + n\text{H}^+$$

This ferric hydroxide acts as a coagulant and a flocculent, meaning that it settles out ferric phosphate and other sulfide compounds as well as other suspended solids and microorganisms which digest suspended solids (American Chemistry Council 2003). In the aeration tank, air is pumped into the tank by blowers to promote aerobic digestion and also to reduce odors. Aerobic microorganisms, involving rotifers, nematodes, pseudomonas, aerobacter, zoogloea and many others (Gerardi 2006), digest smaller suspended solids that failed to settle out in the primary clarifier because they were too small (Dukes 2010). As the water passes through the aeration tank, it enters the secondary
clarifier, where clumps of bacteria (called floc) and other particles settle out, and the resulting sludge is then pumped into digesters for disposal. In the final step of treatment, the wastewater slowly trickles out of the final clarifier and then is chlorinated to kill pathogens before it enters the receiving waters (Engineering 2008).

The Kenosha Wastewater Treatment Facility (KWWTF), located in southeast Wisconsin, uses chlorine to kill pathogens; other facilities such as the Gurnee WWTF located in Northern Illinois use ultraviolet light to damage the DNA of the microbes essentially killing them. There are advantages and disadvantages to each approach. UV light must physically reach the bacteria therefore turbid water would cause a loss of efficiency in the treatment. Another disadvantage to UV in wastewater is the fact that microbes in water can withstand more ultraviolet irradiation than in the air, which will require a greater exposure time to the UV light to kill the bacteria, whereas chlorine is pumped into the system and allowed to mix. UV light has the advantage of preventing unwanted chemical reactions because it uses no chemicals, whereas chlorine has the possibility of forming chloramines and chlorophenols. Another disadvantage of chlorine is the fact that storage is dangerous along with the possibility of operator injuries. There is, however, a major advantage to using chlorine over UV which is the fact that chlorine can continue to disinfect even after it leaves the plant which is one reason why its use is continued in treatment systems (Mone 2010).

Previous research with the Kenosha Wastewater Treatment Facility has resulted in beneficial results because it was determined that the use of ferrous chloride as a precipitating agent was costly due to the fact that it required an oxidation step to promote precipitation with the phosphates. This oxidation step was required to convert Fe$^{2+}$ form to Fe$^{3+}$. This oxidation step meant that the facility had to run extra blowers to force enough air into the system to keep the aerobic microbe levels from decreasing which would result in a partial treatment process (California Water Technologies 2004). The constant use of extra blowers was costing the Kenosha facility more money than other local plants so for these
reasons, the KWWTF decided it would be more beneficial to switch to ferric chloride as the precipitating agent which does not require an oxidation step and can be pumped directly into the Facility.

The Environmental Protection Agency (EPA) currently requires WWTF to have an average effluent final phosphorus concentration below 0.1 ppm/month as previously stated. The KWWTF has yet to receive notice on when the new goals must be met, but this will require the KWWTF to optimize the use of ferric chloride in the treatment system or it will require the KWWTF to update their phosphorus removal methods through the use of tertiary treatments such as membrane filtration (Citulski et al 2009). Although the Kenosha facility is not yet required to meet the 0.1 ppm requirements, it wishes to do research to discover an efficient and inexpensive way to meet regulations.

Ferric chloride is currently the compound of choice to reduce the concentration of phosphorus; it is delivered in an aqueous phase before aeration to precipitate out phosphorus so it is no longer useable by algae. The ferric chloride dissolves, allowing the ferric cation to react with the phosphate anion forming an insoluble ferric phosphate salt that settles out into the sludge and is disposed of in a landfill, although one notable issue with using ferric chloride is the fact that the efficiency of coagulation begins to fall as the concentration of phosphorus decreases. To aid in the coagulation of the ferric phosphate, lime is added in order to raise the pH. The chloride anion reacts with the hydrogen cation to produce hydrochloric acid as a bi-product (Lenntech 2009).

The process of removing phosphorus through the use of ferric chloride has yet to be optimized for efficiency; therefore by analyzing the influent flow in million gallons daily (MGD), the current amount of ferric chloride added daily and the resulting effluent phosphorus concentration, the correlation between ferric chloride addition and phosphorus reduction can be analyzed. For these current conditions, I hypothesize that there should be a significant correlation between the amount of ferric chloride added and the final phosphorus concentration. The other approach to optimizing ferric chloride efficiency is to determine the relationship with phosphorus reduction on a small scale in the laboratory (ideal
I hypothesize that under ideal conditions the phosphorus should react in a linear fashion with the ferric chloride in the effluent. Thus, as more ferric chloride is added, more phosphorus will be removed.

**Methods**

*Study Site*

The Kenosha Wastewater Treatment Facility, located at 7835 Third Avenue in Kenosha, Wisconsin, was chosen as the site of study because of easy access and the availability of data. The data used was of easy access because the plant is required by the Environmental Protection Agency to keep records of what occurs in the facility. The construction of this treatment facility began in 1938 and was put into service in 1940. The KWWTF facility provides wastewater services to over 110,000 people in the greater Kenosha Metropolitan area and is located on lakefront of Lake Michigan. This allows for easy discharge of effluent directly into Lake Michigan. This facility averages 25 million gallons of sewage daily (MGD) and has a capacity of 72 MGD.

This facility follows the basic wastewater treatment steps by first removing larger material in a bar screen. From the bar screen, the effluent moves to the primary clarifier and then to an aerator where it is treated with ferric chloride. After aeration, the effluent enters the secondary clarifier after which it is treated with chlorine and released into Lake Michigan. An aerial photograph of the site can be seen in Figure 1.
Figure 1: Map of Kenosha Wastewater Treatment Facility
Image obtained from Google Earth. The image displays the set-up of the treatment steps: Blue represents the primary clarifier, yellow represents the aeration, red represents secondary clarifiers, and green represents area of chlorination.

Current Conditions
Wastewater data was obtained directly from the Kenosha Wastewater Treatment Facility; this data consisted of daily flow, initial phosphorus, final phosphorus, and daily pickled liquor (ferric chloride) pumped into the system for the months of July 2010 and August 2010. Daily flow, amount of ferric chloride added and effluent phosphorus was measured on a daily basis and influent phosphorus was measured weekly. These data show what is currently occurring at the facility and are the same data that the EPA uses to determine the efficiency and effectiveness of the plant. Analysis of the data consisted of comparing the average amount of ferric chloride added daily to the behavior of
phosphorus in the effluent after ferric chloride is added. Influent phosphorus concentration was measured only once a week; therefore, daily flow, final phosphorus, and the amount of ferric chloride added was averaged for the week. Table 1 shows the original data after it was simplified into samples; the phosphorus in the primary settling tank (Primary Phosphorus) was not used and therefore left blank.

Table 1: Simplified version of the original data taken from the WWTF used to create Figure 2.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Influent MGD</th>
<th>Influent Phosphorus mg/L</th>
<th>Primary Phosphorus mg/L</th>
<th>Effluent Phosphorus mg/L</th>
<th>Pickled Liquor Gal</th>
<th>Initial PO4-Effluent PO4</th>
<th>Pickled Liquor L</th>
<th>Influent MLD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample 1</td>
<td>18.343</td>
<td>3.95</td>
<td></td>
<td>1.20</td>
<td>327</td>
<td>2.75</td>
<td>1239.344</td>
<td>69.437</td>
</tr>
<tr>
<td>Sample 2</td>
<td>26.232</td>
<td>2.96</td>
<td></td>
<td>0.81</td>
<td>329</td>
<td>2.15</td>
<td>1245.400</td>
<td>99.298</td>
</tr>
<tr>
<td>Sample 3</td>
<td>20.703</td>
<td>2.85</td>
<td></td>
<td>0.82</td>
<td>331</td>
<td>2.03</td>
<td>1251.890</td>
<td>78.371</td>
</tr>
<tr>
<td>Sample 4</td>
<td>39.376</td>
<td>1.68</td>
<td></td>
<td>0.53</td>
<td>390</td>
<td>1.15</td>
<td>1476.851</td>
<td>149.055</td>
</tr>
<tr>
<td>Sample 5</td>
<td>25.793</td>
<td>2.210</td>
<td></td>
<td>0.35</td>
<td>401</td>
<td>1.86</td>
<td>1519.032</td>
<td>97.639</td>
</tr>
<tr>
<td>Sample 6</td>
<td>21.219</td>
<td>4.070</td>
<td></td>
<td>0.45</td>
<td>401</td>
<td>3.62</td>
<td>1516.869</td>
<td>80.323</td>
</tr>
<tr>
<td>Sample 7</td>
<td>20.897</td>
<td>3.050</td>
<td></td>
<td>0.39</td>
<td>402</td>
<td>2.66</td>
<td>1522.817</td>
<td>79.105</td>
</tr>
<tr>
<td>Sample 8</td>
<td>18.134</td>
<td>3.330</td>
<td></td>
<td>0.44</td>
<td>400</td>
<td>2.89</td>
<td>1513.083</td>
<td>68.645</td>
</tr>
<tr>
<td>Sample 9</td>
<td>17.026</td>
<td>3.300</td>
<td></td>
<td>0.40</td>
<td>401</td>
<td>2.90</td>
<td>1516.869</td>
<td>64.449</td>
</tr>
</tbody>
</table>

The ferric chloride then had to be converted from gallons to liters because the concentration of phosphorus is in ppm or mg/L. After conversion, the amount of ferric chloride and final phosphorus a regression was performed to see the behavior of phosphorus with relation to ferric chloride. This behavior was then scaled down for the laboratory and lab samples were analyzed under ideal conditions.

**Ideal Conditions**

Three different concentrations of phosphorus were needed for analysis; the starting phosphorus concentrations used were one ppm, two ppm, and four ppm of phosphorus, the phosphorus solution was created from Potassium Phosphate Tribasic. One ppm was tested to determine how effectively ferric chloride can precipitate phosphorus to below 0.1 ppm. Two and four ppm of
phosphorus were tested to examine the normal levels of phosphorus present in the wastewater system. After the solutions were prepared, ferric chloride was added at three different amounts; 95 µL, 105 µL, and 115 µL and preserved with ten drops of HCl (See Appendix 1 for further explanation).

These twelve samples were then brought to the Wastewater Treatment Plant to be tested. For a visual on how the samples were divided see figure X.

The first step was to add digestives to all the samples to reduce all the phosphates in the samples to orthophosphates to be measured by the spectrophotometer. Approximately 0.5 mL of sulfuric acid was added to oxidize the sample; 0.4 g of ammonium persulfate was added as the oxidizing agent. The samples then placed into an autoclave for three hours which provided heat and pressure for digestion. The samples were then removed from the autoclave and phenolphthalein was added to test for acidity. The acid in the tube was neutralized with NaOH, which caused the samples to turn a faint pink color.

Testing for phosphorus was done with the “Ascorbic Acid Method.” Reagents in this method have to be mixed together in the correct order and on the same day of testing because the solution is unstable. This method is from Standard Methods, 19th Edition, by the EPA and is method 4500-P E. The ammonium molybdate and potassium tartrate react with the orthophosphate creating an antimony-phospho-molybdate complex. This complex was then turned blue by ascorbic acid; the intensity of the blue reveals the amount of orthophosphates. The samples can be placed in 4 mL cuvettes and placed inside the spectrophotometer (Genoesysiovis 800 nanolengths). The same
process was then repeated twice more but instead of using the samples with 95 µL of ferric chloride the samples containing 105 µL and 115 µL of ferric chloride were used.

Results

Current Conditions

A significant relationship between the amount of ferric chloride added and the final concentration of phosphorus was found in the large-scale wastewater sampling, having a p-value of 0.001 (Figure 3). When there is a lower dosage of ferric chloride pumped into the effluent, there is a greater final concentration of phosphorus in the effluent. If the trend continues normally, it would take approximately 1,653 L of ferric chloride to reduce the phosphorus concentration to 0.1 mg/L. It is important to note that the actual amount of ferric chloride would need to be greater than 1,653 L because as phosphorus concentrations drop it is more difficult to precipitate out the remaining phosphorus.

![Figure 3: Concentration of Phosphorus Post Ferric Chloride in Waste Treatment Facility](image)

As the amount of ferric introduced into the effluent is increased there is a visible drop in the final concentration of phosphorus. The lowest amount of ferric chloride added to the effluent is approximately 1250 L per day and that dosage
results in an average level of phosphorus in the effluent under 1.00 ppm. When the dose is increased to 1520 L per day, the average concentration is reduced to 0.40 ppm. There is a 60 percent reduction in phosphorus concentration by increasing the dose of ferric by about 250 L per day.

*Ideal Conditions*

In the lab under ideal conditions, additions of 95 µL, 105 µL, and 115 µL of ferric chloride, reduced the final concentration of phosphorus in standardized phosphorus solutions. At a higher initial phosphorus concentration, the amount of phosphorus removed decreases as the amount of ferric is increased whereas at a lower initial phosphorus concentration the higher dose of ferric reduces the final concentration more. At the 2.00 ppm level, there is little to no reduction of the phosphate levels between 115 µL and 105 µL. At 4.00 ppm, the final concentration shows that there was not the same reduction in phosphates experienced at 1.00 ppm (Figure 4).

The ferric chloride reacted in a linear fashion only at the 1.00 ppm initial level because the final concentration of phosphorus after adding ferric chloride was lower (Figure 4). However, it seems that at greater initial phosphorus concentrations phosphorus does not decrease at a steady rate, the intersection of the slopes in Figure 4 clearly shows that at a higher initial concentration ferric has a lower rate of removal.
In Figure 5 it can be seen that the phosphorus does not follow the trend that was hypothesized. The line lowest on the graph at 1.00 ppm has a negative slope meaning that at higher amounts of ferric chloride there is a smaller concentration of phosphorus remaining. From the 95 µL to the 115 µL there is a visible decrease at one ppm initial phosphorus, but by comparing 95 µL and 115 µL at two and four ppm it can be seen that at 115 µL less of the phosphates were precipitated out. As the initial concentrations of phosphorus increases the slope begins to turn positive meaning that the ferric chloride is not removing phosphorus at the same rate as at lower levels of ferric chloride.

Figure 5: Phosphorus Reaction to Ferric Chloride in Ideal Settings
The three lines represent three different initial concentrations of phosphorus. At a lower initial concentration phosphorus is more easily precipitated than at a greater initial concentration.

Discussion

Current Conditions

After examination of effluent data obtained from the Wastewater Treatment Facility, ferric chloride has a significant effect on the final concentration of phosphorus in effluent; this can be seen by the negative slope (Figure 3). As more ferric chloride is added into the effluent the final phosphorus concentration drops a significant amount (p-value = 0.001). This small p-value supports the hypothesis of ferric chloride having a significant effect on the final concentration of phosphorus in the effluent. So as more ferric is introduced into the system, the phosphorus concentration in the effluent should continue to decrease until the phosphorus is almost zero. While the plant uses upwards of 1500 L of ferric chloride daily, they only reach a final concentration of about .40 ppm of phosphorus in the effluent (Figure 3). The wastewater treatment facility has no issue maintaining a level of phosphorus under 1 ppm in the effluent, but it may have more difficulty when the new regulations (stating that the facility will have to maintain a level of phosphorus less than 0.1 ppm) take effect. At 1500 L of ferric chloride added and reaching only 0.4 ppm, the rate at which phosphorus is removed is inefficient at current conditions.

Ideal Conditions

The second hypothesis was that as more ferric chloride was introduced into the phosphorus samples, more phosphorus would be precipitated out resulting in an overall lower final concentration. This hypothesis was not supported because the slope for 95 µL and the slope for 105 µL intersect (Figure 4). This intersection shows that at a higher dose of ferric chloride, the amount of phosphorus that is precipitated out is reduced. The solutions that were prepared in the lab contains only de-ionized water, phosphorus, and ferric chloride allowing
the solution to become highly acidic because there is no introduction of any base into the system, the WWTF uses lime to assist in the control of the pH to keep it around 7.0. If the solution reaches a pH of less than two or greater than nine, the precipitated phosphorus will disassociate from the ferric releasing the phosphorus back into the solution (General Chemical 2008).

The experimental design for the ideal conditions could have been improved by doing more replicates instead of limiting to three of each sample (Figure 2). Samples sizes were limited to what the WWTF could analyze with their own samples on a weekly basis. An increased number of samples would give a better result on whether there is actually less phosphorus precipitated out at greater initial concentrations (Figure 5).

To determine whether the waste water facility experiences the same issue, testing on the pilot plant will have to be done. The pilot plant is a scaled down version of the treatment facility which undergoes the same processes as the facility. The effluent is extracted just after grit removal and enters a tub where primary settling, aeration, and ferric chloride takes place. As it moves from the aeration tank, it proceeds into a drum that is similar to the secondary clarifier where the velocity of the water is reduced to allow settling of any other suspended solids before it is discharged back into the facility as treated. Samples of the effluent can then be taken after the secondary clarifier and phosphorus concentrations can be analyzed to determine the effects of increased ferric chloride. This is the next step because if the pilot plant experiences the same conditions, then adjusting the way ferric chloride is introduced into the system may have better results.

**Further Discussion**

The chemical means of ferric chloride can efficiently maintain a final phosphorus concentration below 1.0 ppm but the Environmental Protection Agency’s new regulations, which state phosphorus concentrations must be less than 0.1 ppm, will require the plant to update it their methods. After analyzing the data, it seems that it would be difficult to use only ferric chloride to reach a final
phosphorus concentration of 0.1 ppm because as phosphorus is precipitated out in the system ferric chloride becomes inefficient (Lenntech 2009). For this reason, the Waste Water Treatment Facility should utilize a membrane filtration system to assist in the process of removing phosphorus from the effluent. The use of a physical system to assist in the removal of phosphorus would be more efficient than introducing an increased amount of ferric chloride into the effluent until the final phosphorus concentration drops below 0.1 ppm.

The use of an ultrafiltration (UF) membrane in combination with ferric chloride would reduce the amount of phosphorus in the system more than using just one or the other. Using the UF membrane with ferric chloride will produce better results because a UF membrane will only filter out the materials larger than the more size of the membrane. Therefore there will still be suspended or dissolved solids that will still manage to get through. By introducing ferric chloride into the system before filtration, the size of the particles is increased because the ferric chloride acts like a coagulant increasing the size of the particles to be more easily filtered (Citulski et al 2009).

**Conclusion**

In conclusion, the Wastewater treatment helps maintain a healthy ecosystem by removing potentially harmful materials from the effluent before it re-enters the receiving waters. Phosphorus is a major nutrient for plant growth and can result in algal blooms and a mat of algae on the beach line, for this reason, phosphorus is to be reduced before re-entering the receiving waters. Optimizing the use of ferric chloride can assist in the reduction of phosphates in effluent and save potentially valuable resources but may no longer be able to keep up with the new regulations that the EPA has put out. For this reason, it may be time to update the wastewater treatment plant with a membrane filtration system to assist in the cleaning of the effluent. Combining both membrane filtration and ferric chloride may yield results greater than that which the EPA requires currently.
Works Cited


Strom, Peter. "Technologies to Remove Phosphorus from Wastewater." Rutgers University. Aug. 2006


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**Appendix 1: Analysis of Phosphorus**

*Methods*

Samples of phosphorus were needed at 1.00 ppm, 2.00 ppm, and 4.00 ppm so a 1000 ppm stock solution of $\text{K}_3\text{PO}_4$ was prepared. This solution was prepared by taking the mass of $\text{K}_3\text{PO}_4$ and dividing by the mass of
PO₄$^{3-} \frac{212.27 g}{94.97 g} = 2.24 g$. The resulting 2.24 g can then be added to 1.00 L of de-ionized water to obtain a concentration of 1000 ppm of phosphorus.

The 1000 ppm phosphate solution was then diluted to 100.0 ppm. This was done by using the equation $M_1V_1 = M_2V_2$, where $M_1$ is the initial concentration and $V_1$ is the volume need to create a 100.0 ppm solution and $M_2$ is the final concentration and $V_2$ is the final volume:

$1000 \text{ ppm}(x) = 100.0 \text{ ppm}(1000mL) \rightarrow (x) = 100.0mL$. So 100.0 mL of the 1000 ppm stock solution was added to a 1.00 L Erlenmeyer flask and then filled with de-ionized water to create a 100.0 ppm stock solution and then poured into a 1.00L bottle.

Once the 100 ppm solution was prepared the stock could be diluted down to 50 mL samples at three different concentrations, 1.00 ppm, 2.00 ppm, and 4.00 ppm. To obtain the 1.00, 2.00, and 4.00 ppm testing solutions, the same $M_1V_1 = M_2V_2$ equation was used as before:

$100.0 \text{ ppm}(x) = 1.00 \text{ ppm}(300mL) \rightarrow (x) = 3.00mL$
$100.0 \text{ ppm}(x) = 2.00 \text{ ppm}(300mL) \rightarrow (x) = 6.00mL$
$100.0 \text{ ppm}(x) = 4.00 \text{ ppm}(300mL) \rightarrow (x) = 12.0mL$

The 1 ppm solution was created by pipeting 3.00 mL of the 100.0 ppm solution to a 300.0 mL Erlenmeyer flask. This flask was then filled to the 300.0 mL mark with de-ionized water and then swirled to ensure complete mixing. Then 50.00 mL of this solution was poured into four vials where 95.00 µL of ferric chloride was added with a micro-pipette. The ferric chloride solution used in the WWTF is approximately 39% FeCl₃. Then to preserve the sample, 10 drops of 6.00M HCl was added from an eye dropper to the samples before being sealed. The same steps were used to prepare the 2.00 ppm and 4.00 ppm samples.