Ferrate Oxidation of Ciprofloxacin in Water

Major Qualifying Project completed in partial fulfillment
Of the Bachelor of Science Degree at
Worcester Polytechnic Institute, Worcester, MA

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Abstract

The concentration of pharmaceutical drugs in water supplies around the world continues to grow due to a lack of awareness and financial constraints. This study sought to explore methods to reduce the concentration of pharmaceutical antibiotics in water sources. Based on previous research, reactions between ciprofloxacin (CIP) and potassium ferrate were examined. Quantitative data was collected through a variety of experiments to determine kinetics, extent of reaction and the effects of pH. Overall this study demonstrated the feasibility of utilizing potassium ferrate to oxidize ciprofloxacin and highlighted areas for future research.

Acknowledgements

We would like to thank our faculty advisor John A. Bergendahl for his support and guidance throughout our project.

MQP Capstone Design Statement

In accordance with the Major Qualifying Project requirements, the design goal of this project was to produce a water treatment process that could ultimately be applied in a real world scenario for addressing contaminated water. This project aimed to design a treatment process for ciprofloxacin removal that could be installed with reasonable feasibility in the many, already established, wastewater treatment facilities in the United States. The design was based on the Upper Blackstone Wastewater Treatment Facility. Considerations in this design included minimizing or eliminating down time of the facility during installation of the process, the economic practicality, and assuring that the new process would not interfere with the existing machinery and equipment at the treatment facility. The design involved treatment of the final wastewater effluent produced by the plant. This was cycled through a plug flow reactor that filled a clarification basin. The effluent leaving the basin underwent filtration and was then discharged to the Blackstone River.

Executive Summary

Purpose

This report explored the possible implementation of potassium ferrate (K_2FeO_4) as a chemical agent to react with the antibiotic ciprofloxacin (CIP) to effectively remove the antibiotic from water. With the gathered experimental data, a practical treatment process was designed for the Upper Blackstone Wastewater Treatment Facility taking into account the current average daily flow and design of the plant.

Methods and Results

Various methods of analysis were employed to determine the optimum conditions to drive the reaction between CIP and potassium ferrate to completion. To determine the extent of the CIP degradation in the reaction, multiple solutions of CIP and ferrate with varying molar ratios were mixed in reagent grade water and allowed to react for 24 hours. These prepared samples were then measured in a spectrophotometer to determine the absorbance and in turn the removal of CIP. It was determined that the ratios that were most effective in CIP removal were 1:10 and above, producing higher than 90% removal of CIP. Time trials were conducted in order to determine the rate law constants for the overall reaction between CIP and potassium ferrate. Using an initial concentration of 10 mg/L in water and a molar ratio of 1:1 potassium ferrate to CIP, several solutions were prepared and mixed. The solutions were allowed to mix from times ranging from 15 seconds to 1 hour and the find CIP concentration measured in a spectrophotometer. Based on the results, the reaction reaches the equilibrium phase after only 30 minutes when the ratio of ferrate to CIP is 1:1. The effect of pH on the reaction was studied through experimentation as well. Solutions of 1:10 CIP: Ferrate had an initial concentration of 10 mg/L CIP in water. After each solution was combined, the pH was adjusted using small amounts of concentrated NaOH and HCl until the desired pH was reached. The results from experimentation show a clear bell curve with a maximum removal of CIP occurring at slightly below a pH of 8. This was the pH used throughout experimentation.

Conclusion

Through the experiments performed in this study several conclusions have been reached on the most effective use of potassium ferrate to remove CIP from water. The ideal conditions for the maximum and most efficient removal of CIP from water were found to be with a pH of 8, and a molar ratio of 15:1 potassium ferrate to CIP. It was also found that the necessary time for the reaction to take place after mixing was only a half hour for a 1:1 ratio, any higher ratios were unusable due to the reaction occurring too quickly. Based on the findings of this study, it is advisable to continue study of ferrate as an oxidation reagent in removal of antibiotics, as well as to find the most cost efficient way to introduce it into wastewater treatment plants.

Recommendations

Based on the results the following recommendations have been prescribed:

- Further research into the precipitate formed from the CIP-Ferrate reaction to determine particle size and settling velocity to further optimize removal via settling.
- Exploration of the most effective wastewater treatment processes (e.g. filtration, settling) for the removal of the precipitate should be established.
- Cost efficiency of the process should be analyzed, including insight into whether bulk treatment or multi-stage treatment is more effective.
- Analysis of a pilot-scale test water treatment plant, using realistic levels of CIP to determine effectiveness on a larger scale.

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Chapter 1: Introduction

Pharmaceutical drugs have proven to be a triumph for modern medicine, but with this great advancement unintended and unforeseen consequences have emerged. Around the world water constituent studies are revealing that with more frequency and in greater concentrations antibiotics are present in wastewater and even drinking water sources. Antibiotics often contaminate water supplies due to municipal wastewater discharges. Humans can only partially metabolize antimicrobial medicine and as a result these pharmaceuticals, that enter sewage, can contaminate water supplies. Humans also contribute to this form of pollution with pharmaceutical plants that produce industrial wastewater that carry these same antibiotics that are discharged into rivers and other surface water bodies. Filtration does not provide effective removal of antibiotics from water so safe alternative methods are needed in lieu of it.

Ciprofloxacin (CIP) is a common antibiotic used to prevent and treat bacterial infections. Like many other antibiotics, elevated levels of CIP have been found in water supplies in different regions of the world. In India tadpoles and zebra fish with habitats downstream of a pharmaceutical processing plant have experienced adverse effects in their early stages of development as one study shows (Lubick, 2009). Not only does CIP affect wildlife but it also contributes to antibiotic resistant strains of bacteria in contaminated water. According to one study CIP experienced 0% biodegradation after 40 days in water thus displaying further a need for chemical treatment (Lubick, 2009). These risks pose a challenge to the scientific community to provide a solution that will provide safe water for humans and wildlife.

There have been several studies on the interaction between CIP and ferrate performed within the last five years. These studies have repeatedly addressed the use of ferrate as an oxidant for multiple contaminants present in wastewater. Preliminary research regarding the mechanism of the reaction, effects of pH, effects of concentration, as well as some introductory kinetics calculations can be readily found (Jiang, 2012; Jia-Qian 2012; Lee, 2009). One product of this research has been the manufacturing of small scale ferrate production units that are able to be wheeled directly into a waste water treatment facilities; however these units are expensive to operate (FTT, 2009). These studies have advanced the base of knowledge of the CIP-ferrate oxidation process; however there are still gaps in research that need to be addressed in order for wide scale ferrate oxidation of CIP in sewage treatment facilities to become common.

Several factors contributing to resistance against ferrate oxidation treatment becoming common practice are the cost of ferrate and the numerous physical and chemical properties of the reaction are still unknown. Data regarding the efficiency of ferrate under various constraints such as pH, temperature, pressure and concentration are bountiful but not in regards to CIP. In-depth kinetic analyses have been rigorously done with respect to a slew of other contaminants but little with respect to CIP. The reason these aspects are so important to the advancement of use of ferrate in water treatment is due to their effects on overall costs of the process. Provided the proper research into each one of these factors, the ideal environment for use of ferrate can be found and cost effective processes can be developed.

Our project sought to fill these gaps in research by investigating means to use ferrate more efficiently. Our research will also determine the maximum efficiency and kinetics of ferrate in its oxidation reaction with CIP, by analyzing the effects of pH and concentration. This data will allow optimization of CIP precipitation with minimization of ferrate expenses in modern wastewater treatment. To determine a feasible real world application of ferrate treatment, a retrofit design based on the current Upper Blackstone Wastewater Treatment Facility was constructed to explore specific aspects and challenges of implementation. The goal of this project was to conduct experimental research and produce a design to further the field of study of ferrate oxidation of CIP.

Chapter 2: Background

This Chapter will explore wastewater treatment, the environmental impacts of pharmaceuticals and the reaction between ciprofloxacin and potassium ferrate. First the current state of wastewater treatment will be briefed to expose the current gaps in treatment processes. Then the effect of pharmaceutical drugs and ciprofloxacin have on the environment will be discussed to demonstrate the importance of the development of treatment methods for such drugs. The properties of CIP and ferrate will then be discussed to understand how the oxidation reaction between these two substances functions.

2.1 Wastewater and Treatment Plants

Wastewater is the culmination of consumed water and storm water from a wide variety of sources. Wastewater comes from the domestic, industrial, agricultural and commercial use of water and also produced from natural rain events that result in storm water runoff. Because of human influences, wastewater generally requires some form of treatment before it is released to recharge surface water bodies and the ground water table. Treatment is required because the water has been contaminated by domestic production of human waste, nutrient pollution from agriculture along with many other pollutant sources.

Contaminants in wastewater can be categorized into three subsets: physical, chemical, and microbial. Physical contaminants include soils and other particulate matter that contribute to water turbidity. Heavy metals like lead and cadmium fall under the chemical category in terms of water contaminants. Microbial agents found in wastewater include a wide range of pathogens that can cause disease when they come into contact with humans. With large amounts of potentially hazardous wastewater being produced, sewage treatment plants (STP) are needed to treat this water for various contaminants.

Sewage treatment plants are designed to remove harmful contaminants and to regulate other biologically important water characteristics like biological oxygen demand and dissolved oxygen. STPs are outlined with four general processes: preliminary screening, primary treatment, secondary treatment and tertiary treatment. The four stages of treatment are designed to produce a safe effluent by removal of unwanted physical, chemical, and microbial contaminants.

2.1.1 Preliminary screening

The primary goal of preliminary screening is to stop large floating debris from entering the sewage treatment plant. Often times, rivers and wastewater contain objects ranging in size from small rags to timber logs. Screening these objects serves the purpose of preventing pumps from getting damaged and avoiding the obstruction of hydraulic flow in pipes and open channels (Viessman *et al.*, 2009). A popular piece of machinery for preliminary screening is the water-intake screen or mechanical bar screen. The screens typically range from coarse to fine, where coarse screens have vertical metal bars spaced 2.5 in. and fine screens have bars place together from a distance ranging from $^5/_8$ to 1 $^3/_4$ inches. These screens are mechanically cleaned to prevent buildup of large debris and objects.

There are other design considerations for the most efficient bar screening. To avoid stringy solids from being pulled through bars, the velocity of the wastewater influent is not to exceed 2.5 $^{ft}/s$. Bar screens are often placed in series, from coarse to fine to prevent debris buildup that can greatly reduce hydraulic flow. Additionally, bar screens are typically placed in a hydrologic channel at 22°-45° to the horizontal for ease of mechanical cleaning (Viessman *et al.*, 2009). Sewage treatment plants experiencing an influent with a large number of large objects use shredding devices. Shredders cuts large solids down to smaller sizes that can either be caught and cleaned by mechanical bar screens or removed in primary treatment.

2.1.2 Primary treatment

Primary treatment begins with the use of an aerated grit chamber. Grit chambers use air diffusers within the chamber to create a circular flow pattern in the wastewater causing heavy grit to settle to the bottom of the chamber only leaving light organic matter suspended that will be removed by primary clarification. Figure 1 displays an aerated grit chamber with the addition of a grease skimmer for removing floating debris.

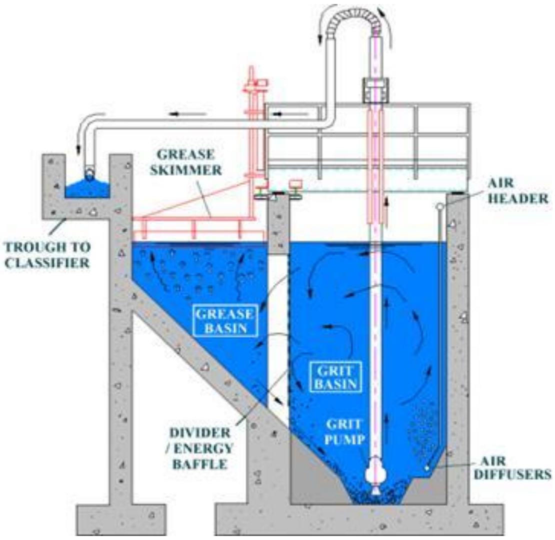


Figure 1. A schematic representation of an aerated grit chamber (Sisk, 2011).

Primary settling or primary clarification follows the process of aeration for the additional removal of physical contaminants. The purpose of a clarifier is to settle out solids to the bottom of the clarifier and skim plastics, oils, and grease from the surface of the water (Viessman et al., 2009). Physical contaminants removed through settling include various soils, particles washed off roads and earth by storm water runoff, and microscopic organic matter. Clarifiers are usually rectangular or circular with slanted bottoms that lead to hoppers for sludge collection (Guyer, 2009). Other design considerations for clarification depend upon the peak daily flow rate of the treatment plant and the rate at which the smallest particles settle. Hydraulic loading and settling velocity play a large part in calculating the detention time of settling tanks and overall tank sizing.

2.1.3 Secondary treatment

Secondary treatment focuses on the degradation of organic matter through aerobic biological processes and to continue to settle out solids. A large amount of chemical contaminants in wastewater can have deleterious effects on receiving streams such as an increase in biological oxygen demand (BOD), therefore it is important that these particles be removed from the effluent. In this phase of sewage treatment approximately 85 percent of total suspended solids are removed from wastewater, just as it is mandated in the U.S. Clean Water Act (Meehan, 2007). Aerobic biological processes commonly utilize activated sludge to deconstruct organic material by modes of settling, agitation, and aeration. Activated sludge is comprised of microorganisms such as fungi, protozoa, and aerobic bacteria. These microorganism feed on the organic chemical contaminants thus reducing the organic load of the wastewater. The sludge used in the process is continuously recycled for extended use (Meehan, 2007).

Microorganisms are activated by dissolved oxygen (DO), thus establishing a need to regulate the DO content of wastewater. Because of this need, aeration tanks will be placed before the activate sludge settling tanks in series. An additional design consideration is the management of contents of the activated sludge. Nutrients must be monitored closely to aide in the production of more biomass. A 5:1 ratio of nitrogen to phosphorus is to be observed to obtain optimal production of sludge (Droste, 1997). Optimizing the production of sludge is important for compensating for the portion of the sludge disposed because it contains dead organism that are no longer useful to aerobic biological processes.

2.1.4 Tertiary Treatment

Tertiary treatment is a process that is only used in sewage treatment plants that need to reduce nutrient levels in wastewater before discharge. The first stage of tertiary treatment involves the removal of the nutrients nitrogen and phosphorus. These chemicals can enter wastewater through the use of fertilizer in agriculture (Brusseau *et al.*, 2004). The biological treatment method of anaerobic metabolism has proven to be an effective process of nutrient removal. Like aerobic processes, anaerobic digestion relies on a substrate of sludge containing wide range of microorganisms. The microorganisms work similarly to aerobic processes by consuming nutrients, but instead of consuming oxygen, the microorganisms oxidize ammonia (NH_3) to nitrate (NO_3) (Viessman *et al.*, 2009). Design considerations of anaerobic metabolism include pH, mixing, and temperature.

The second stage of tertiary treatment is disinfection. Disinfection focuses on the inactivation of various microbial contaminants which can also be classified as pathogens. Common pathogens include, but are not limited to bacteria and viruses. Bacteria can enter wastewater through waste excreted by humans and animals. The bacterium Escherichia coli resides in the guts of humans and animals and can be harmful to health, or is used as an indicator organism of other harmful pathogens. Chlorine is the standard disinfectant used in disinfection but ozone and ultraviolet radiation are two other commonly used disinfection methods.

2.2 Pharmaceuticals in Wastewater

Although it is a growing concern, treatment of antibiotics and other pharmaceutical drugs in wastewater is not standard practice in the United States. The consequence of antibiotics in water is antimicrobial resistance or AMR. AMR occurs when bacteria that are not killed by antimicrobial drugs survive, reproduce and pass on their drug resistant properties. This results in bacterial strains that can’t be treated by conventional antimicrobials (Acar, 2012).

Although the problem is not wide spread, the effects of AMR already being felt. It’s estimated that every year 150,000 deaths are caused by the development of 440,000 new cases of multidrug-resistant tuberculosis (WHO, 2012). Figure 2 provides a world map displaying where drug resistance forms of tuberculosis are most prevalent.

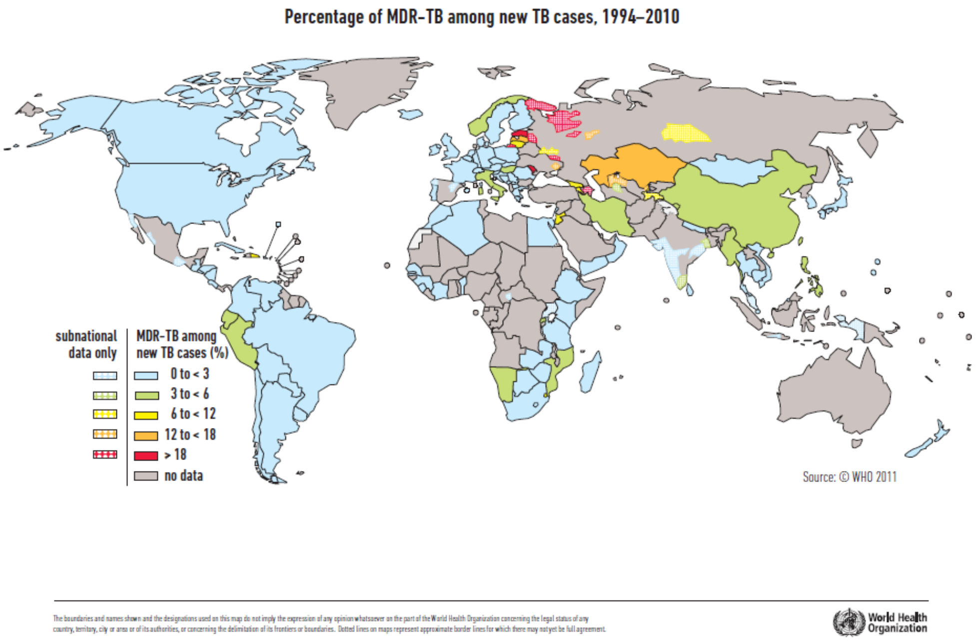


Figure 2. World distribution of new multidrug-resistant tuberculosis (WHO, 2012).

In countries where malaria is prevalent, it’s been found that the effectiveness of early generation antimalarial drugs is reducing as the microbes that cause the disease develop resistant strains. Wastewater treatment plants are a breeding ground for bacterial reproduction. During primary settling, a large basin of water with no chemical agents allows bacteria to multiply in the presence of antibiotics. Here a possible microcosm for accelerated production of AMRs is found.

The general presence of pharmaceutical drugs in water is possibly a direct threat to human health as well. In India, where water regulations are less stringent, rivers and lakes have some of the highest levels of pharmaceutical drugs ever recorded. The high levels are due to the booming pharmaceutical industry in India. Essentially rivers, lakes, and streams are being polluted from the effluent of pharmaceutical processing plants. Studies on these water sources have shown adverse effects on the early development of zebra fish and tadpoles (Lubick, 2009). Ciprofloxacin is a commonly used antibiotic in developing countries for medically treating bloody diarrhea caused by Shigella organisms. Because of ciprofloxacin levels in water, drug resistant strains are forming and are in turn reducing the options available for the safe and effective treatment of shigellosis (WHO, 2012). From these developments, it is clear that research regarding removal of CIP along with other pharmaceutical drugs from wastewater is needed.

2.3 Ciprofloxacin

Ciprofloxacin is a widely used antibiotic in usage today. The empirical formula for CIP is $C_{17}H_{18}FN_3O_3$•HCL•H_2O and it has a chemical structure shown in Figure 3.

This is not in fact the pure chemical of Ciprofloxacin but instead the monohydrochloride monohydrate salt for CIP used as an antibiotic in solution.

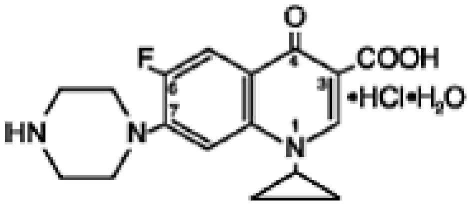


Figure 3. Chemical Stucture of Ciprofloxacin (Jaing *et al.*, 2012)

Ciprofloxacin belongs to a group of drugs generally known as flouroquinolones, or FQs. It is considered a broad spectrum antibiotic due to how effective FQs are when treating gram-positive and gram-negative strains of bacteria. CIP is only effective in use for treatment of gram-negative bacteria in addition to a gram-negative activator. (Davis *et al.*, 1996) Some examples of infections that are widely treated with CIP are anthrax, bacterial sexually transmitted diseases like gonorrhea, serious skin or bone infections as well as gastrointestinal infections. In some serious cases CIP can be used to treat urinary tract infections caused by E-coli. While CIP can be used in the treatment of Staphylococcus epidermis of the skin or throat, this is only used in cases of patients with mixed bacterial infections due to Staphylococcus' rapid ability to develop a resistance to CIP and other similar antibiotics (Hoiby, 1997)

The phenomenon of a bacterial strain developing a resistance to an antibiotic is not uncommon. This resistance is built up over time, only when a bacterial strain survives contact with an antibiotic will it be able to build a resistance to the drug (Hoiby, 1997). One way that bacteria manage to adapt is called a biofilm, an extracellular polymer that bacteria have a tendency to adhere to. This biofilm restricts diffusion of antibiotics into the bacteria (Hoyle, 1991). This biofilm forces doctors to prescribe higher doses of antibiotics in order to effectively kill off the bacteria. This over prescription of antibiotics in general has slowly begun to effect more than the people being prescribed the drugs, but the general population as well. This is a more of an issue due to the way that humans process antibiotics. Most antibiotics prescribed are only partially metabolized by the human body. The rest of them are excreted and are flushed into the sewage system (Al-Ahmad, 1999).

A study performed in Switzerland found that in regards to CIP "Individual concentrations in raw sewage and in final wastewater effluents ranged from 255 to 568 ng/L" (Golet, 2002). This concentration may seem small, possibly insignificant even; however this is not the case. Since FQs are being found in surface waters as well, this information means that waste water treatment is not effectively removing these substances. In the same study concentrations of CIP were found in the Glatt River at below 19 mg/L (Golet, 2002). These antibiotics are seeping into water sources outside the control of treatment plants, creating more possible issues than can be foreseen.

At this point there is not a large amount of information in regards to the negative effects that these small doses of CIP in drinking water and other sources could have on the human body. There are many known negative side effects of CIP including some cases of tendon damage, from tendonitis to full tendon rupture, as well as more common effects such as nausea, dizziness, confusion, headache and others (WebMD, 2009). There have also been some preliminary studies to analyze the effect of CIP on adult human cartilage. The study showed that minor cases of necrosis of the cartilage could be seen after some long term cases of FQ treatment for bacterial infections like anthrax (Menschik, 1997).

2.4 Ferrate

Iron is a member of the transition metals which allows free exchange of electrons and greater potential to form oxidation states. Iron's most common oxidation states are +3 or +2, however oxidation states up to +8 can be achieved. These high oxidation states are called oxyanions, and are generally unstable, with the notable exception of Ferrate (VI). Ferrate is a tetrahedral molecule known in the chemical world as the anion $[FeO_4]^{-2}$, or Iron (VI) but is most commonly used in the form of Potassium Ferrate (K_2FeO_4). Ferrate's oxidation state is +6 which indicates that only two of eight possible electrons occupy its outer shell. Ferrate's high oxidation state allows it to maintain unique physical and chemical properties.

Often scientists find that Ferrate's most frustrating property is its relative stability and reactivity at certain pHs. In particular Ferrate is extremely unstable in acidic solutions as the "Fe (VI) ion reduces rapidly and exothermally to Fe (III) and oxygen in strong acids"(Sharma, 2002), although it is relatively stable compared to other high oxidation state iron molecules. In fact pH governs both Ferrate's reaction rate and oxidation reaction potential. As pH changes so does the "reduction potential varying from +2.2 V to +0.7 V in acidic and basic solutions, respectively" (Sharma, 2002). The reason Ferrate is more stable in basic solutions is due to its reaction mechanism with water.

$$4K_2FeO_4 + 10H_2O \rightarrow 4Fe\,(OH)_3 + 3O_2\uparrow + 8KOH$$

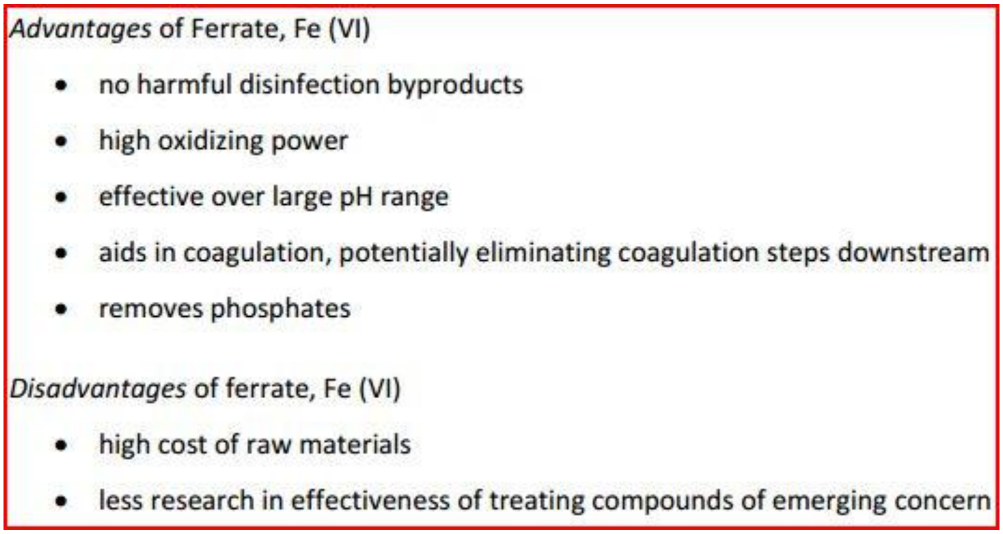
A product of Ferrate's reaction with water is potassium hydroxide, which readily dissociates into both a K^+ cation and a OH^- anion. Le Chatelier's principle explains that the higher concentration of OH^- present the less likely potassium ferrate is to react with water and create potassium hydroxide. Ferrate's stability is so dependent on pH that it has been "observed that the FeO_4^{2-} ion is an order of magnitude more stable in 10 M KOH than in 5 M KOH. In 10 M KOH, the stability of K_2FeO_4 is increased by an order of magnitude, from hours to weeks" (Sharma, 2002).

Ferrate's most sought property is its ability to act as a potent oxidizing compound. Ferrate (VI) "is perhaps the most powerful oxidizing compound that can be utilized in normal applications, with an oxidation potential of 2.2 volts under acid conditions. This potential can be compared to ozone (O_3) that has an oxidation potential of 2.04 volts…" (FTT, 2006). The oxidation potential if a chemical described above is "a gauge of their ability to gain or donate electrons in a chemical reaction; the higher the redox potential, the more powerful the reaction" (FTT, 2011). However Ferrate is not an exceptional oxidizing agent under normal circumstances. Specifically when "under acidic conditions, the redox potential of ferrate (VI) ions is greater than ozone and is the strongest of all the oxidants/disinfectants…" (Jiang *et al.*, 2002). The ability to act as an oxidant or disinfectant has made Ferrate as popular choice for research and waste water treatment.

Through research Ferrate has proven to be a widely successful oxidizer and disinfectant for waste water treatment. Its extreme oxidizing ability allows it to deactivate bacteria and viruses while neutralizing harmful compounds. In terms of bacteria “Ferrate (VI) has sufficient disinfection capability to kill *Escherichia coli* (*E. coli*). At pH 8.2 and a dose of 6 mg/l as Fe, the *E. coli* percentage kill was 99.9% when the contact time was 7 min” (Jiang *et al.*, 2002). Ferrate’s ability to disinfect extends beyond E.coli. Ferrate is “able to kill 99.9% of total coliforms” (Jiangyong, *et al.*, 2005), “is more successful than chlorine at treating spore forming bacteria and is capable of inactivating viruses” (Hannmann *et al.*, 2012).

Ferrate possesses other qualities aside from its ability to kill bacteria that make it ideal for waste water treatment. In fact Ferrates’ most valuable attribute is that its byproducts, when undergoing oxidation reactions, further oxidizes, disinfects and coagulates unwanted bacteria and chemicals. When Ferrate undergoes a reaction “Ferrate (VI) ions will be reduced to Fe (III) ions or ferric hydroxide, and this simultaneously generates a coagulant in a single dosing and mixing unit process” (Jiang *et al.*, 2002). This coagulant (Ferric hydroxide) is even “suitable for removal of metals, non-metals, radionuclides, and humic acids” (Sharma, 2008). The benefit of a compound used for water treatment, which as it reacts produces molecules to further precipitate and neutralize components, is valuable. Ferrate can save money and positively impact the environment because this “dual-function chemical reagent offers significant advantages in terms of a more simplified and cheaper process and of avoiding the formation of reaction by-products of toxicological concern” (Jiang *et al.*, 2002).

While there are many pros about using Ferrate for waste water treatment such as its byproducts dual functionality and its extreme oxidizing/disinfecting properties, there are also several cons.



Advantages of Ferrate, Fe (VI)

- no harmful disinfection byproducts
- high oxidizing power
- effective over large pH range
- aids in coagulation, potentially eliminating coagulation steps downstream
- removes phosphates

Disadvantages of ferrate, Fe (VI)

- high cost of raw materials
- less research in effectiveness of treating compounds of emerging concern

(Hannmann *et al.*, 2012)

The largest con, Ferrates low stability, requires specific environmental conditions to maintain feasible amounts, which is costly to transport and store. Many treatment facilities have tried off site production of Ferrate and failed because "at over $20/lb, Ferrate has been too expensive for bulk industrial use" (FTT, 2011). One company called Ferrate Treatment Technologies has eliminated this problem by producing Ferrate on site. In fact "synthesizing Ferrate on-site eliminates product handling and transport and reduces the traditional cost of manufacturing a Ferrate product by over 90%"(FTT, 2011) which sufficiently reduces the cost of Ferrate to feasible levels. This revolutionary concept and design has allowed a plethora of commercial and industrial facilities utilize Ferrate for their processes.

Chapter 3: Methodology

3.1 General

Stock solutions of 250 mg CIP/L purified water and 250 mg potassium ferrate/L purified water were prepared and used for the duration of the project. Stock solutions of CIP were used no later than two weeks after creation while solutions with potassium ferrate were used within thirty minutes. Solutions of potassium ferrate left unused for more than a few hours were found to precipitate ferrous flocs, which could skew absorption readings, and were therefore disposed. Purified water was produced with a water purification system from Thermo Scientific.

3.2 Calibration Curves

Calibration curves relating concentrations of CIP and Ferrate to light absorption in a UV-vis Varian cary50 spectrophotometer were created to allow for the interpretation of data in later experiments.

Solutions of CIP with concentrations ranging from 0-25 mg CIP/L purified water were prepared from the stock solution and pipetted into individual vials. Each vial was put into the UV spectrophotometer operating at a wavelength of 280 nm and tested twice for light absorbance. The average of the two runs for each concentration was used for graphical representation.

Solutions of potassium ferrate acquired from Aldrich Chemicals with concentrations ranging from 0-500 mg potassium ferrate/L purified water were prepared from the stock solution and pipetted into individual vials. Each vial was inserted into the UV-vis spectrophotometer operating at a wavelength of 280 nm and tested twice for absorbance. The average of the two runs was used for graphical representation.

3.3 pH Adjustment Effect on Degradation

Solutions of 1:10 molar ratio of CIP: potassium ferrate were prepared with an initial concentration of 10 mg CIP/L purified water. A clean pH probe was inserted into the solution after thoroughly mixing with a glass rod. The pH of the solution was adjusted to the desired value (2,4,6,8,10 or 12) using 0.1 M/L H_2SO_4 and 0.1 M/L NaOH solutions. After each solution was adjusted to the desired pH, it was pipetted into a vial, sealed and continuously agitated for 24 hours using an end-over-end agitator. After 24 hours each vial was filtered through a clean .22 μm pore size filter to remove any ferrous flocs or other precipitants that may have formed. Then each solution was pipetted into new vials for UV spectroscopy. Each vial was inserted into the spectrophotometer operating at a wavelength of 280 nm and tested twice for light absorbance. The average of the two runs was used for graphical representation.

3.4 Degradation Over 24 Hours

Solutions of 10 mg CIP/L purified water with concentrations of potassium ferrate varying from 1:1 – 1:50 molar ratio of CIP: potassium ferrate were prepared. After thorough mixing with a glass rod, each solution was pipetted into a vial, sealed and continuously agitated for 24 hours using the end-over-end agitator. After 24 hours each vial was filtered through a clean .22 μm pore size filter to remove any ferrous flocks or other precipitant that may have formed. Then each solution was pipetted into new vials for a UV spectroscopy analysis. Each vial was inserted into the spectrophotometer operating at a wavelength of 280 nm and tested twice for absorbance. The average of the two runs was used for graphical representation.

3.5 Kinetics Time Trial

Solutions of 1:1 molar ratio of CIP: potassium ferrate were prepared with an initial concentration of 10 mg CIP/L purified water. These solutions were measured for absorbance at time intervals 0, 1, 2,3,4,5,10,20,30 and 60 minutes after mixing. Each solution was continuously mixed using either a glass rod or an agitator. Solutions being tested for absorption under 20 minutes were mixed by hand while those over 20 minutes were mixed by the agitator. Solutions that were mixed longer than 5 minutes were filtered through a clean .22 μm pore size filter to remove any ferrous flocks or other precipitant that may have formed. Each solution was then inserted into the spectrophotometer operating at a wavelength of 280 nm and tested twice for absorbance. The average of the two runs was used for graphical representation.

Chapter 4: Results and Discussion

The objective of this study was to analyze the oxidation reaction between CIP and potassium ferrate, including extent of reaction, kinetics of the reaction, and ideal pH for removal of CIP from water. The data found were compared with previous findings on different advanced oxidation processes, such as peroxides, persulfate, and the Fenton reaction. The comparisons were used in order to analyze and create recommendations for the treatment of CIP using ferrate and potential future research.

4.1 Calibration Curves

Calibration curves were established for both CIP and potassium ferrate using a UV spectrometer at a wavelength of 280 nm for use as detection of effectiveness of treatment. The two curves can be seen below in Figure 4 and Figure 5.

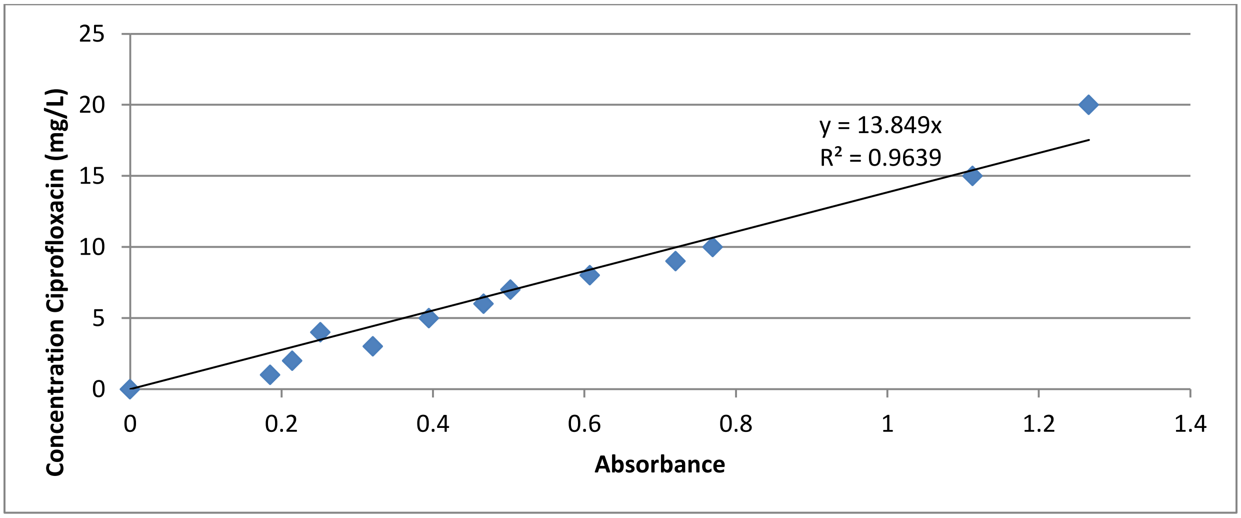


Figure 4. Calibration Curve of CIP at 280 nm

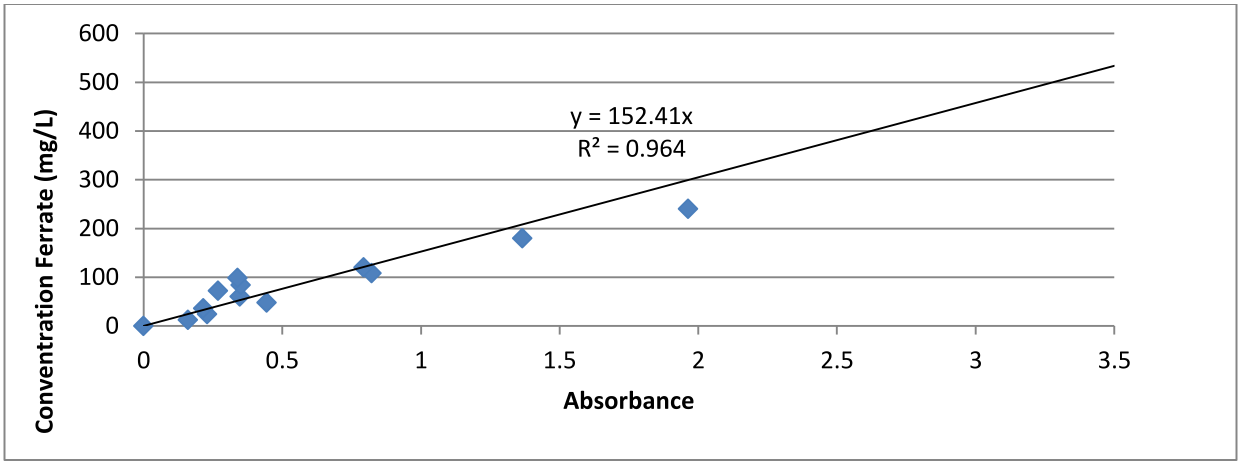


Figure 5. Calibration curve of ferrate at 280 nm

. Both of the calibration curves were determined to be an accurate form of detecting concentrations of CIP up to 17.5 mg/L and concentrations of ferrate up to 500 mg/L both with R^2 values above 0.96. These curves were used in order to determine the concentrations of CIP during both the extent, pH, and kinetics experiments.

4.2 pH Adjustment Effect on Degradation

Solutions of 1:10 CIP: Ferrate had an initial concentration of 10 mg/L CIP in water. After each solution was combined the pH was adjusted using small amounts of concentrated NaOH and HCL until the desired pH was reached. The ferrate standard curve was used in order to determine the total interference on the absorbance readings following the same methodology for removing CIP over. The values where then plotted comparing pH and final concentration of CIP. Figure 6 shows this comparison.

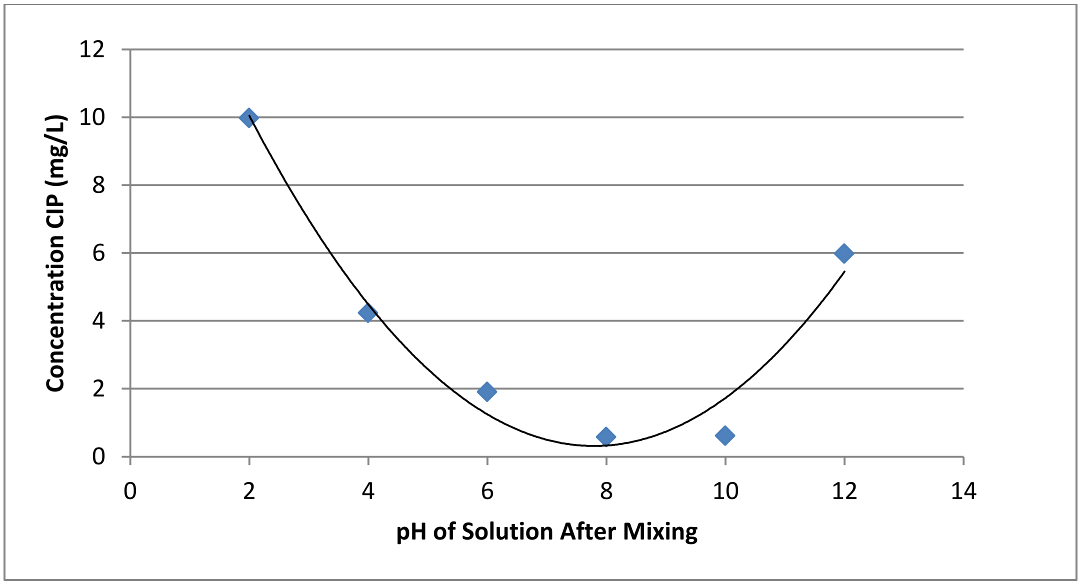


Figure 6. Concentration of CIP after 24 hours at different known values of pH with a molar ratio of CIP:Ferrate of 1:10 and an initial concentration of 10 mg/L CIP in water.

The data shows variations of treatment with maximum removal of CIP occurring between a pH of 8-10. Reports of ideal pH for reactions with CIP include ranges from 4-7, or 6-10, however no truly specific pH or range has been found for the reaction with potassium ferrate. In the medical field the maximum solubility level for CIP in urine is cited as a pH of 7.3 (Emedexpert, 2012). Using this value as a reference a pH level of a little under 8 was found to be a reasonable value for experimentation. This pH level was kept constant throughout the rest of experimentation for the study, within reasonable levels of error.

4.3 Degradation in 24 hours

Initial concentrations of CIP in purified water were 10 mg/L in each solution. The ferrate standard curve was used in order to determine the interference on the final absorbance readings. After a full 24 hours of mixing, a precipitate formed in the solution. To remove the precipitate each sample was filtered through a .22 μm pore size filter in order to avoid interference of the absorbance readings. Table 1 shows the numerical values of the concentration as well as the extent of removal of CIP.

Table 1: Comparison of Ferrate: CIP Ratio and Extent

Molar Ratio Ferrate:CIP	Concentration of CIP After 24 hours	Extent of Removal of CIP (%)
1	5.17	48
2	4.37	56
3	3.94	60
4	3.29	67
5	3.14	68
6	2.48	75
7	1.84	81
8	1.07	89
9	1.40	85
10	0.758	92
15	0.404	95
20	0.127	98
25	0.480	95
50	0.226	97

The final concentration of CIP after 24 hours of treatment with specified molar ratios of potassium ferrate was also plotted graphically. Figure 7 shows this relationship.

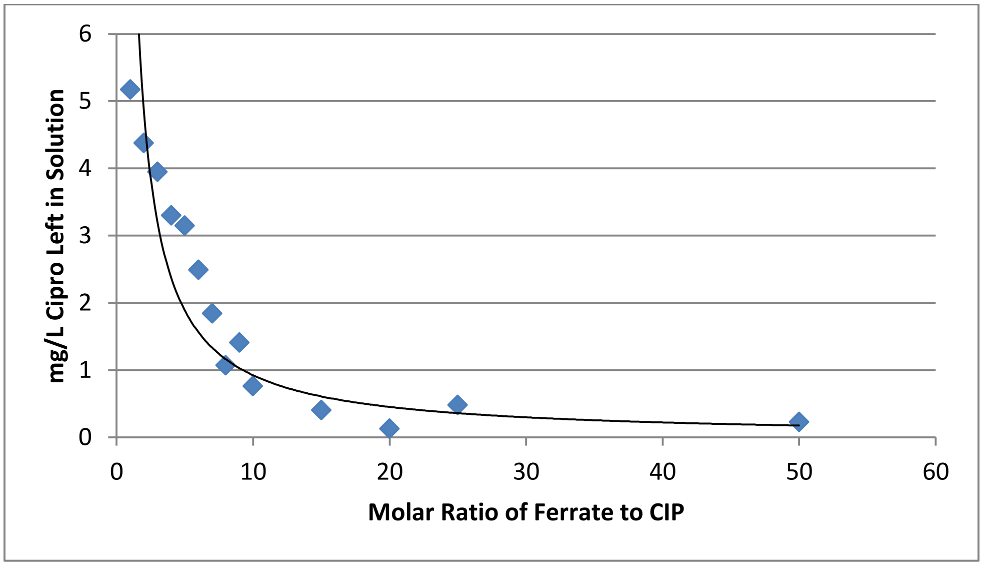


Figure 7. Degradation of 10 mg/L Ciprofloxacin over a 24 hour period, using Ferrate Oxidation at Various Molar Ratios.

This data shows that potassium ferrate treatment is an effective method for the removal of CIP from purified water. Solutions with molar ratios of 15:1 moles ferrate to CIP had an extent of removal of 95%. Increasing the ratio past the 15:1 ratio did not significantly increase the removal of CIP from water, ranging in concentrations that are close to equal or half the value of the 15:1 ratio. The smallest percent of degradation was found to be about 48% which was achieved using a 1:1 molar ratio solution.

A study by Jiang *et al.* (2011) tested molar ratios of ferrate to CIP of 1, 3, 5, 7, 9, 10, 15, and 20. After the solutions were made they were run through three different steps to simulate a water treatment system. First the solutions were mixed vigorously for 1 minute at 400 rpm, second a slower mixing at 45 rpm for 20 minutes followed by a sedimentation step for one hour.

The solutions were then analyzed to determine the total degradation of the system. The study found that the extent of removal ranged from 60-69%, with a trend of increasing removal with increasing doses of potassium ferrate (Jiang *et al.*, 2011). While the study by Jiang et al. resulted in extents of removal only $^{2}/_{3}$rds the effectiveness of this study, there are clear differences between the two processes of water treatment. While the initial concentration of CIP in water was the same, the mixing time was increased to a full 24 hour cycle, and filtration was used to increase accuracy of data, opposed to settling.

A second study performed by Hannmann *et al.* used techniques similar to those in this study. Hannmann *et al.* used an initial concentration of 20 mg/L CIP in water and used solutions of 1, 5, 7, 11, 17, 25, 50, and 100 ([Ferrate]/[CIP]). The solutions were mixed for 24 hours and then a centrifuge was used in order to induce sedimentation. The study performed by Hannmann *et al.* found that at molar ratios of 17:1 and higher had extents of removal greater than 90% (Hannmann *et al.*, 2012). These values are much closer to the ones found in this study and provide increased support to the effectiveness of ferrate for use in the treatment of waste water. Minor differences between this study and the one performed by Hannmann *et al.* could be a result of different initial concentrations of CIP as well as the use of a centrifuge for removal of precipitant compared to a filter. Both studies results show just how effective potassium ferrate can be as an oxidation reagent, allowing for the total removal of CIP as well as the possibility for use with other antibiotic contaminants.

4.4 Kinetics Time Trials

Time trials were conducted in order to determine the rate law constants for the overall reaction between CIP and potassium ferrate. Using an initial concentration of 10 mg/L in water and a molar ratio of 1:1 potassium ferrate to CIP, several solutions were made and mixed.

Samples were removed from mixing from 1 minute to 1 hour after initial mixing and filtered through the same filters used for degradation. A ratio of 1:1 was chosen in order to increase the accuracy of readings as less precipitate would be created and less interference would occur, as well as allowing the reaction to be slow enough to be able to be analyzed. A concentration for each interval was determined using the CIP standard curve and ferrate standard curve to correct for interference. The time trial conducted over an hour is shown in Figure 8 below.

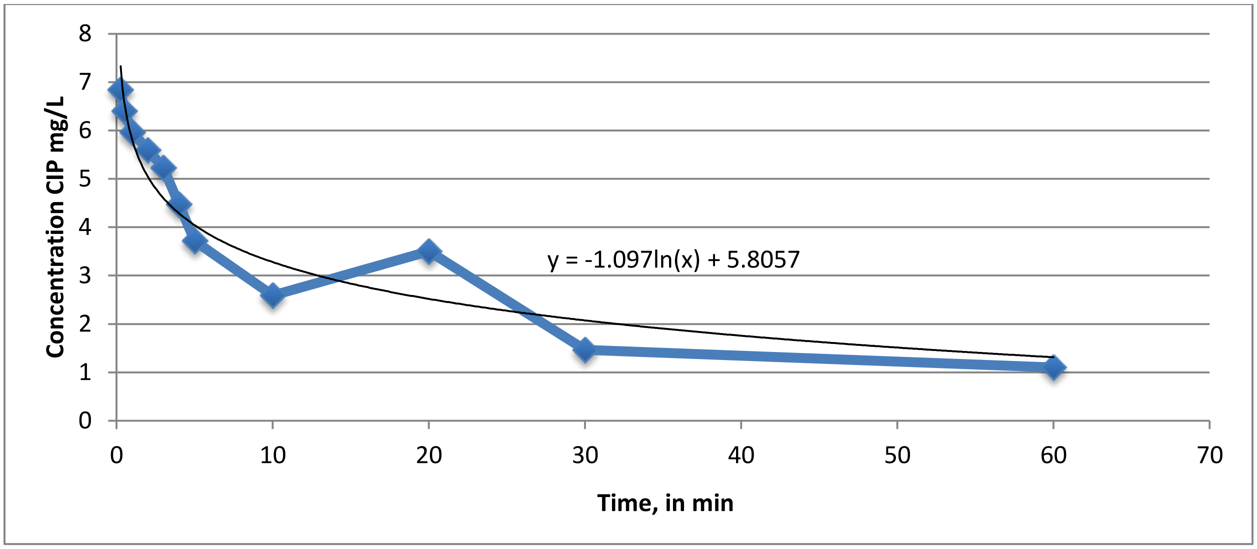


Figure 8. Time trial of 10:1 Ratio Ferrate to CIP over 1 Hour with an Initial Concentration of 10 mg/L

From this data it was determined that using a 10:1 ratio that almost 90% degradation was achieved. This shows some significant potential for use in an industrial setting. If a ferrate treatment process was inserted into any waste water treatment process it would only need approximately one hour in order to achieve significant removal of CIP out of water. In order to determine the rate constant for a first order, or second order reaction the concentration of one reactant in solution is used to determine a specified rate constant for the reaction. The rate equation for a first order batch process is shown below.

$$\text{Rate of degradation: } = -\frac{dA}{dt} = k\,[A]$$

Where [A] = Concentration of CIP (mg/L)

t = time (min)

k = rate constant (1/min)

The integrated form of the rate equation is shown in the equation below:

$$\ln[A] = -kt + \ln[A]_0$$

For second order reactions the integrated rate equation can be seen in the equation below:

$$\frac{1}{[A]_t} = kt + \frac{1}{[A]_o}$$

Using these equations the natural log of the concentration of CIP vs time in the time trial was determined and plotted. A linear trend line was used to determine the value for –k. Analysis of the first order kinetics data found that the rate constant for the reaction k=0.0303 min^{-1} (R^2=.8374). The plot of ln X vs time can be seen in Figure 9 below.

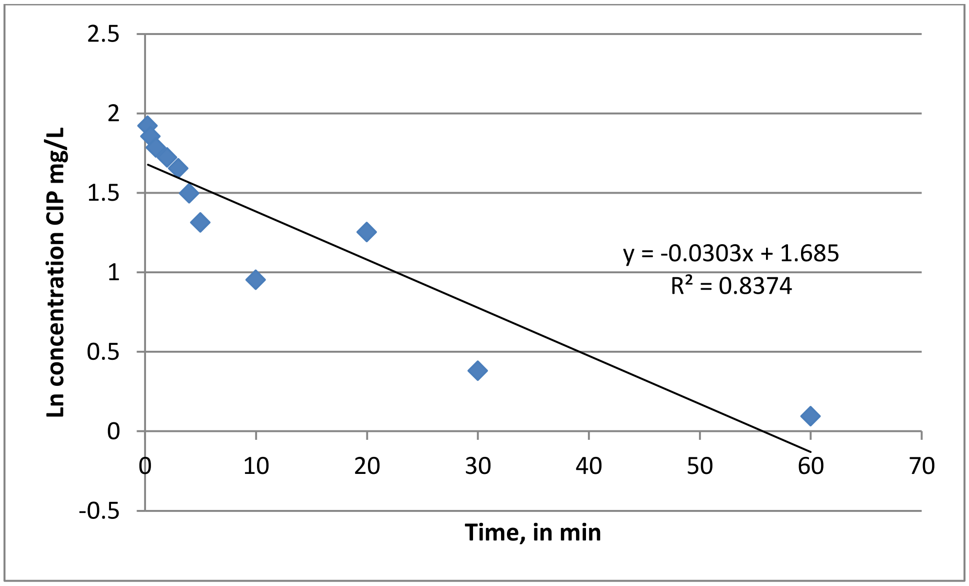


Figure 9. Plot of Ln Concentration of CIP vs. Time at a 1:10 Molar Ratio of 10:1 Ferrate: CIP and an initial concentration of 10 mg/L

It can be clearly seen in Figure 10 that a simple first order reaction is not the best model for the reaction between CIP and ferrate with an R^2 value of .8374. This is interesting considering most oxidation reactions can be modeled using a first order reaction. A possible explanation for this difference could be that it is a pseudo-first order reaction that takes place after an initial mixing step. This hypothesis can be seen in the same plot as before, but split into two separate parts as seen in Figure below.

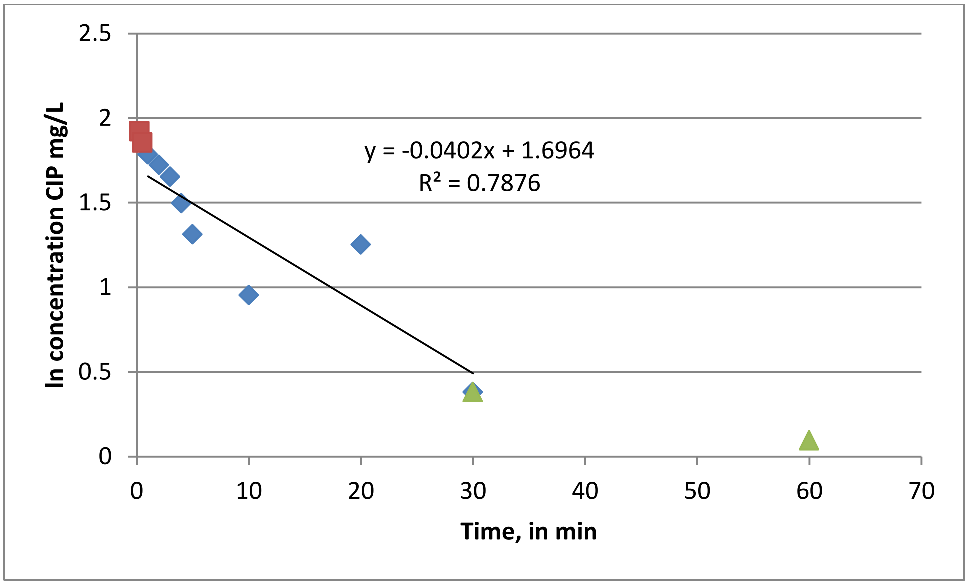


Figure 10. Plot of Ln CIP vs. Time with a split between initial mixing phase and the first order rate reaction with a final equilibrium phase.

It can be seen that the value of k for the system increases to 0.0402 min^{-1} in this case; however the correlation between the linear trend and the data is lower with a R^2 value of 0.7876. This correlation led to the conclusion that this system does not fit either the first order or the pseudo-first order style reaction and that other kinetics rates would have to be analyzed.

A pseudo-second order reaction was analyzed by plotting a graph of 1/Concentration of CIP vs. Time and by fitting a linear graph to the data. The plot of this analysis can be seen in Figure 11 below.

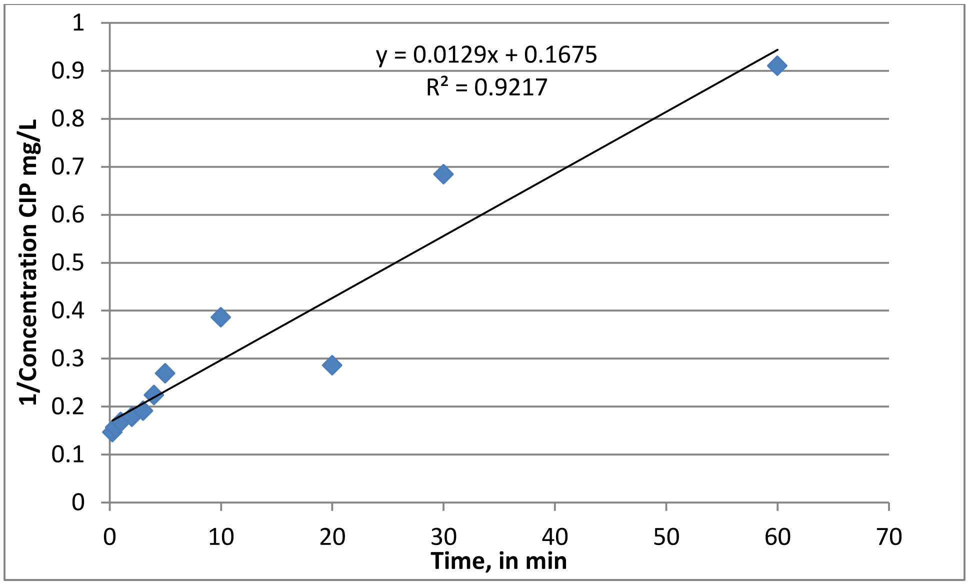


Figure 11. Plot of 1/Concentration CIP with an initial concentration of 10 mg/L CIP in water and a molar ratio of 10:1 Ferrate: CIP.

It can be seen that the pseudo-second order reaction correlation has a rate constant of .0129 $M^{-1}min^{-1}$ and a R^2 value of .9217. This correlation shows that a pseudo-second order reaction fits the data found much better. This is interesting because most oxidizing agents would be expected to follow a first order reaction. This difference in reaction could be caused by the degradation of ferrate into ferric iron. Another possibility is that the byproducts of the reaction between CIP and ferrate react again with CIP as well. This explains why this reaction follows a second order reaction rather than a first order reaction dynamic.

A second order reaction also has some benefits for use in an industrial setting. The main characteristic of a second order reaction is that it has reacts very quickly at the initial start time of mixing and tapers off exponentially over time. This would allow for a water treatment plant to determine the shortest amount of time needed for the reaction to remove as much CIP as necessary.

4.5 Comparison to other Oxidants

The graph below, taken from Hannmann *et al.*, shows a comparison between several different oxidants' extent using different molar ratios of solution. Each solution had an initial concentration of 20mg/L CIP in water.

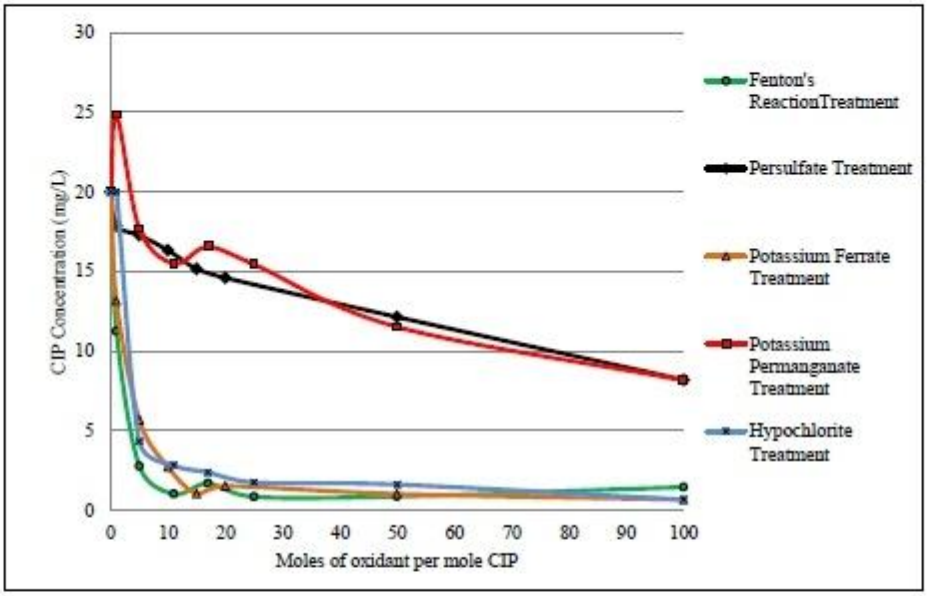


Figure 12. Comparison of extent (Hannmann et al., 2012)

In comparison to different oxidation reagents potassium ferrate is among the best at removing CIP from water. The molar ratio needed for a significant decrease in concentration of CIP is only about 10, and it removes more than most other reagents. Compared to the Hannmann *et al.* study the concentration and methods of analysis used was different in this study, and it also produced higher levels of removal. Without further information on different reagents under the same conditions as this study a conclusive comparison cannot be performed, however several hypotheses can be created. First it can be hypothesized that the effectiveness of ferrate in the removal of CIP is going to be higher than almost any other oxidant. Due to the second order kinetics of ferrate it can also be hypothesized that the reaction between ferrate and CIP will take place much quicker than that of most other oxidants as well. Finally the pH of the ferrate reaction can be considered to be different, and in some ways more ideal then other oxidants.

Chapter 5: Design

It has been recognized that wastewater treatment facilities that serve municipalities are well established in the United States therefore it has been deemed prudent to offer a retrofit design where minimal changes are made to the current plant for simplicity and economic factors. The treatment plant selected for the design was Upper Blackstone Wastewater Treatment Facility located in Millbury, MA. The treatment plant experiences a daily average flow of 25 MGD. The basic outline of treatment processes for the facility in displayed in the figure 13 below.

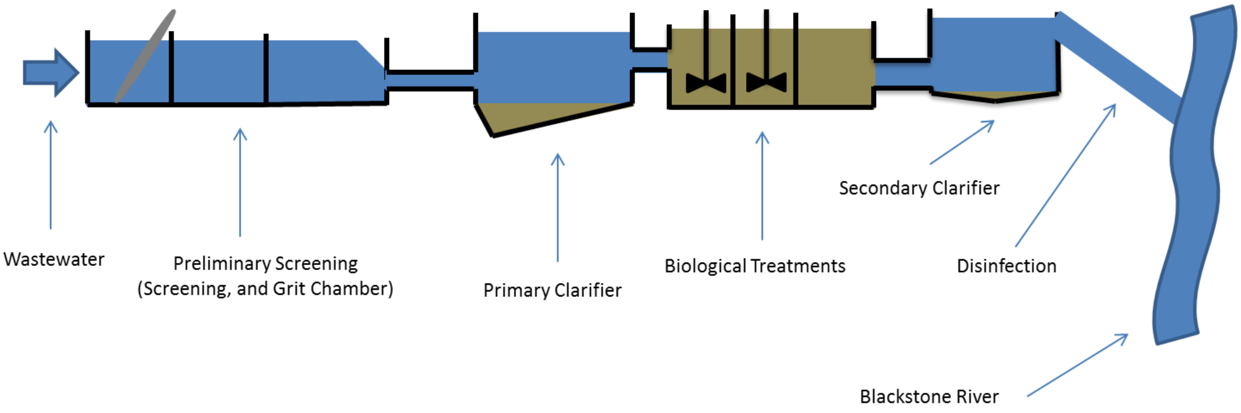


Figure 13. Upper Blackstone Wastewater Facility treatment processes.

The design for the implementation of ciprofloxacin removal involves the use of a clarifier designed to accommodate half of the daily average flow which is 25 MGD. The principle of this design is to take approximately half of the average amount of water processed (12.5 MGD) by the treatment plant and direct it towards a clarifier constructed separate from the rest of the facility's treatment processes to undergo treatment for removal of CIP.

For dosing the wastewater with ferrate, the use of a Ferrator has been recommended. A Ferrator is a self-containing ferrate reactor that operates on-site at the wastewater treatment facility and produces its own ferrate (FTT, 2011). The Ferrator allows for a simple retrofitting installation where plumbing simply needs to be run to and from the reactor. At the junction of the ferrator and the treated wastewater influent a sensor valve would be put in place to monitor the ratio of ferrate to CIP. The lab data collected concluded that the reaction was most effective with a molar ration of 10:1 ferrate to CIP. This ratio will be maintained by the sensor valve controlling to flow of ferrate from the Ferrator.

Following the sensor valve would be a plug flow reactor (PFR) to allow mixing in the wastewater to increase the contact of CIP and ferrate. The PFR will run into the settling tank designed for this process. The settling tank will allow sufficient time for the precipitate formed in the oxidation of CIP to settle to the bottom of the tank. The resulting effluent will be processed through a multimedia filter to remove any remaining particulates from clarification. The processed effluent will then be discharged to the Blackstone River. Figure 14 displays the proposed design.

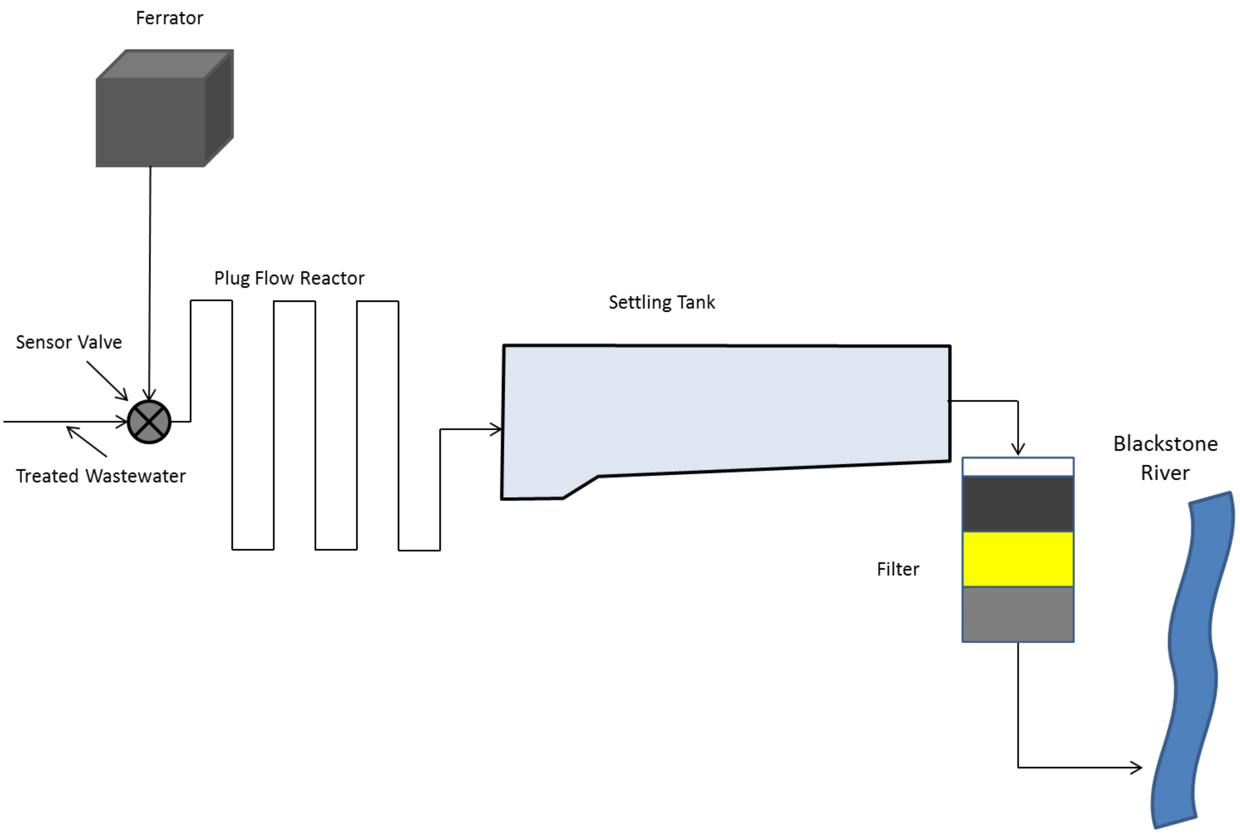


Figure 14. Proposed design for Upper Blackstone Treatment Facility

Figure 14. Proposed design for Upper Blackstone Treatment Facility

When considering the size of the settling tank, the focus was to have a rectangular tank large enough to handle half of the daily flow and to provide enough time for the oxidation reaction to near completion. These provisions would allow the resulting flocs to settle out. The equation below was used to solve for a feasible hydraulic residence time (HRT). The Water Environment Federation (2010) recommends that rectangular clarifiers be constructed to have a length of 15-90 m, a width ranging for 3-24 m, and a depth from 3-4.9 m. Following these guide lines, a tank with the dimension 60x15x3.2 m was designed. Using the equation below the HRT was calculated.

$$t_R = \frac{V}{Q}$$

$$t_R = \frac{60m \times 15m \times 3.2m}{1.25E7\ \frac{Gal}{Day}} \times \frac{264.172\ Gal}{1\ m^3} \times \frac{24\ hrs}{1\ day} = 1.46\ Hours$$

In this equation t_R is residence time, V is volume, a Q is volumetric flow rate per unit time. With this design an HRT of 1.46 hours was achieved. This is theorized to be an acceptable sizing because from the experimental data it was determined that a half hour was needed for the reaction to reach near completion. This leaves about an hour of residence time for the flocs to settle. Figure 16 shows the proposed tank design.

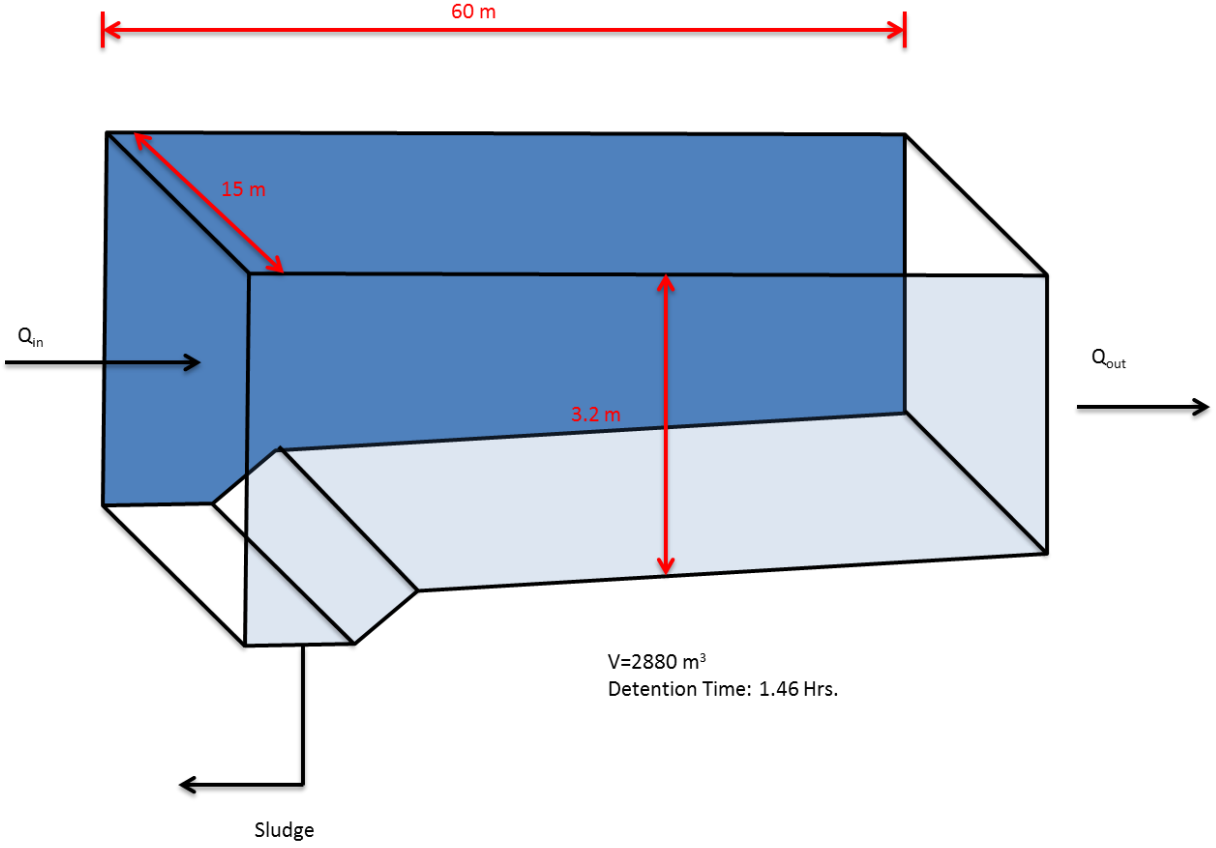


Figure 15. Proposed dimensions for tank sizing.

The design of the PFR is designated as a concrete, rectangular open flow channel. With the use of Manning's equations the hydraulic properties of the PFR can be determined. First the daily flow rate of this process was converted from 12.5 MGD to 0.547 m/s to comply with the units of the Manning equation. A design velocity of 5 m^3/s for channel from was selected to promote mixing and to not overload the clarifier. With this value it was possible to determine the cross sectional area of the channel. The equation below describes the process to calculate the area and dimensions of the channel.

$$Q = A \times V$$

$$0.547m^3/s = A \times 5m/s$$

$$A = 0.111m^2$$

Here, Q is the flow rate, A is the cross-sectional area of the channel, and V is the velocity. Through simple algebra the width and depth of the channel were determined to be 0.37m and 0.30m respectively. Next Manning's equation for velocity was employed to solve for the slope of the channel.

$$V = \frac{k_M}{n} \times R_h^{\frac{2}{3}} \times S_0^{\frac{1}{2}}$$

In this equation kM is a unit conversion factor ($1.00m^{1/3}/s$), n is Manning's coefficient of channel roughness (0.013 for concrete), R_h is the hydraulic radius (0.12 m) and S_o is the bottom sloped of the channel. That following calculation is shown below.

$$5\frac{m}{s} = \frac{1.00\frac{\frac{1}{3}}{s}}{0.013} \times 0.12m^{\frac{2}{3}} \times S_0^{\frac{1}{2}}$$

$$S_O = 0.073\frac{m}{m}$$

With these design considerations calculated a proper channel for this application can be constructed. The aim of this PFR is to provide a conduit leading to the clarifier that will catalyze the reaction between CIP and ferrate.

Chapter 6: Conclusions and Recommendations

While almost any oxidation method can be useful for the removal of CIP from waste water, the purpose of this study was to determine the overall effectiveness of potassium ferrate as well as the ideal conditions for maximum efficiency. There have been several studies on different treatments of ciprofloxacin including several oxidation reagents, Fenton's oxidation, and even UV light combined with hydrogen peroxide. Potassium Ferrate has also been analyzed for use as an oxidation agent. Despite these past studies the conclusions drawn from these studies were limited and left a complete analysis of the process to be desired. Jaing *et al.* (2012) studied the extent of removal of CIP using potassium ferrate, under specific mixing and settling conditions. In this paper, studies were broadened to include higher molar ratios of reagent to contaminant, an alternative mixing and filtration method meant to remove the maximum amount of precipitant, and research to determine the ideal conditions the reaction should take place in, including pH analysis, and a kinetics rate analysis to determine a general residence time for the reaction.

The findings of this study show that potassium ferrate has significant potential for use as a treatment in waste-water treatment plants. Under laboratory conditions, it was found that at any ratio above 10:1 potassium ferrate to CIP, over 90% removal of CIP occurs. During the kinetics study of a 10:1 ratio Ferrate to CIP it was found that the maximum removal of CIP occurred only after an hour of mixing and that this reaction follows a second order reaction process with a rate constant of .0129 (M^{-1} s^{-1}). It was also determined that the reaction rate increases greatly when the molar ratio is increased however due to increased amounts of precipitate in solution, it was not possible to determine . In a study performed by Hannmann *et al.* (2012) a time "time trial was conducted using a 17:1 ratio potassium ferrate to CIP, resulting in the removal of 88% CIP within ten minutes and 88.6% after 30" (Hannmann *et al.*, 2012). This comparison in differing times between molar ratios implies that with an increase in molar ratio, an increase in rate of reaction occurs as well, however an analysis of the amount of data found during this study makes drawing conclusions from this data inconclusive. The last point that was discovered during this study was the ideal pH level should be between 8-10 for the reaction to reach its maximum extent. pH levels lower than 6 began to severely limit the removal of CIP from water, as well as pH levels more basic than 10. This is beneficial considering that the natural pH of this reaction was found to be around 7.5 for all molar ratios.

Using these findings a preliminary design, based on the Upper Blackstone Wastewater Treatment Facility was developed. A simple injection system of analyzing the amount of CIP in wastewater and then injecting the needed amount of potassium ferrate is proposed. This process should be inserted after the final clarification in order to not allow other contaminants to interact in the reaction. In order to allow for maximum removal of CIP a ratio of 15:1 was used to allow for maximum removal of CIP to be achieved. It should be noted that a 15:1 ratio will be expensive to achieve, and that this study does not include a cost analysis of the process.

There are several more aspects to study in regards to the use of potassium ferrate in water treatment. First a cost analysis should be performed to determine whether the process will be cost effective if implemented into a full scale treatment plant. Primary treatment water from the Blackstone treatment facility should undergo the same experimental procedures stated in the methods section to better understand how CIP in ferrate react in wastewater. Research into a multi-stage treatment process should be analyzed as well, to determine if a ratio of 1:5 applied over three separate mixing and settling phases is equally, or more effective than a bulk treatment process. Research into the effectiveness of potassium ferrate for treatment of different contaminants should be conducted as well providing insight into further uses of ferrate. Studies on the precipitant created through the reaction between CIP and potassium ferrate should be analyzed in detail, including the size of the particle as well as possible side reactions that may occur. This would provide insight into the residence time of the particle as well as interactions that could occur during waste treatment. Finally a large scale economic analysis should be conducted again, taking into account any and all potential combinations of circumstances. It is necessary to provide a balance between the efficiency of the process, the effectiveness of the removal, as well as the economics of the process. In order for this process to be effective it must also be appealing to any waste water facility to use.

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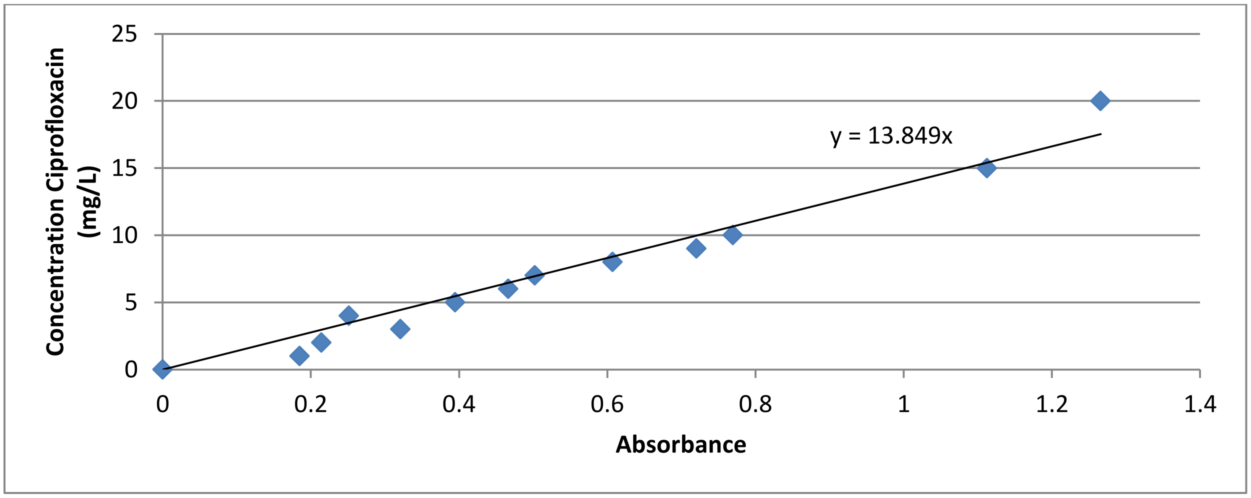
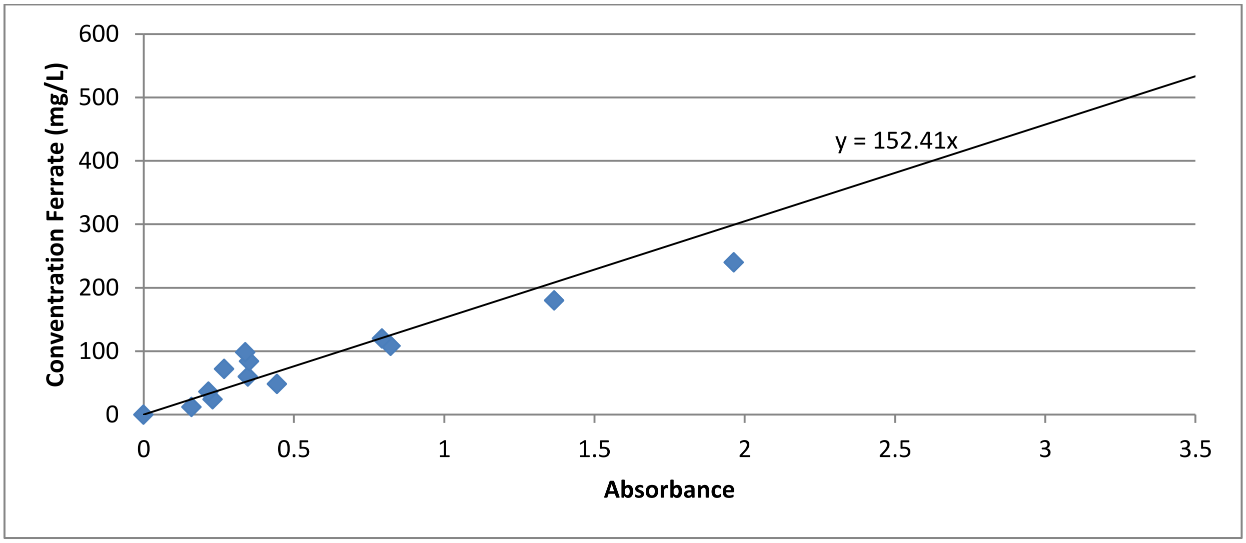
Appendix

Appendix A: Calibration Curves

Measured Concentration CIP	pH	Absorbance
0	7.01	0
1	7.12	0.1849
2	6.95	0.2142
3	7.04	0.3208
4	7.03	0.2513
5	6.96	0.3946
6	6.99	0.4667
7	7.01	0.5022
8	7.03	0.6072
9	7	0.7206
10	6.97	0.7695
15	6.98	1.1127
20	7.02	1.2661

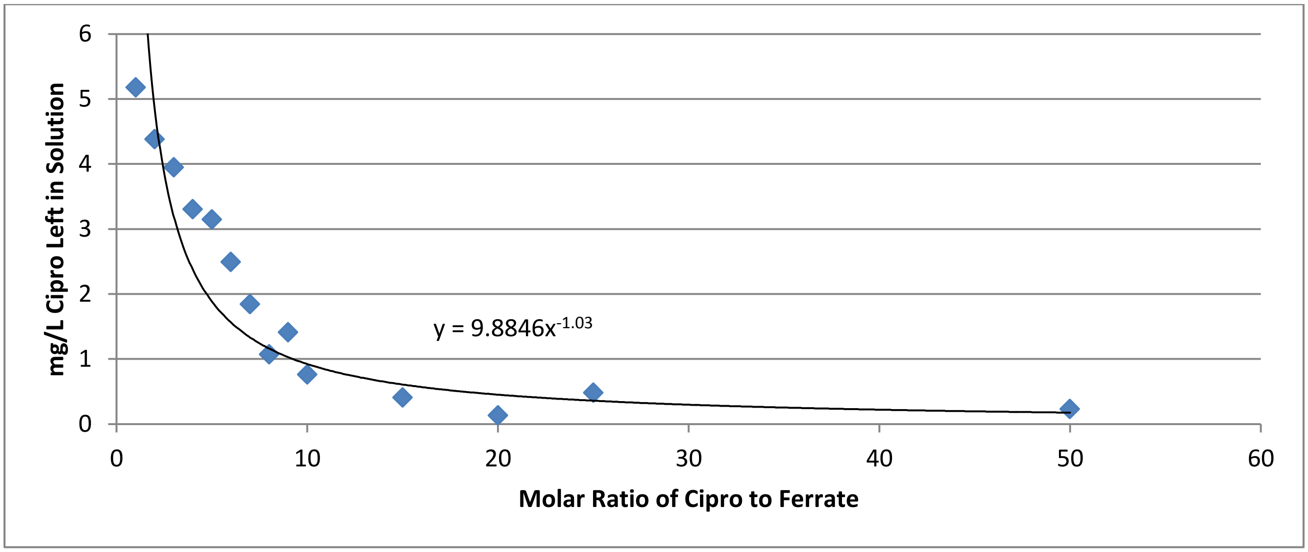


Measured Concentration Ferrate	pH	Absorbance
0	7.01	0
12	7.22	0.1597
24	7.16	0.2297
36	7.3	0.2156
48	7.26	0.4433
60	7.2	0.3472
72	7.14	0.2681
84	7.07	0.3506
98	7.23	0.3386
108	7.25	0.8218
120	7.28	0.7931
180	7.21	1.3661
240	7.26	1.9638
600	7.24	3.678



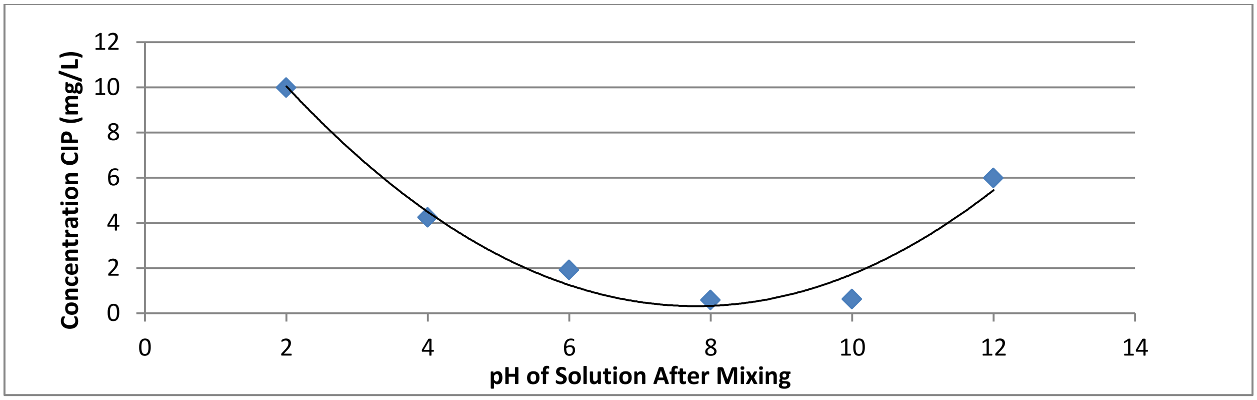
Appendix B: Raw Data

Initial Concentration mg/L	Ferrate:CIP Molar Ratio	pH	ABS	Interference	Adjusted Final Concentration	% CIP Removal
10	1	7.46	0.4522	0.078734991	5.172116908	48.27883092
10	2	7.63	0.4735	0.157469982	4.376699715	56.23300285
10	3	7.55	0.5212	0.236204973	3.946896123	60.53103877
10	4	7.53	0.5532	0.314939965	3.299663231	67.00336769
10	5	7.56	0.6208	0.393674956	3.145454738	68.54545262
10	6	7.47	0.6521	0.472409947	2.488527546	75.11472454
10	7	7.48	0.6842	0.551144938	1.842679554	81.57320446
10	8	7.46	0.7203	0.643002428	1.070494079	89.29505921
10	9	7.5	0.8103	0.70861492	1.408236669	85.91763331
10	10	7.57	0.8421	0.787349911	0.758233977	92.41766023
10	15	7.6	1.2102	1.181024867	0.404046415	95.95953585
10	20	7.46	1.5839	1.574699823	0.127413253	98.72586747
10	25	7.44	2.0031	1.968374779	0.480909592	95.19090408
10	50	7.53	3.9531	3.936749557	0.226437284	97.73562716



Appendix C: pH

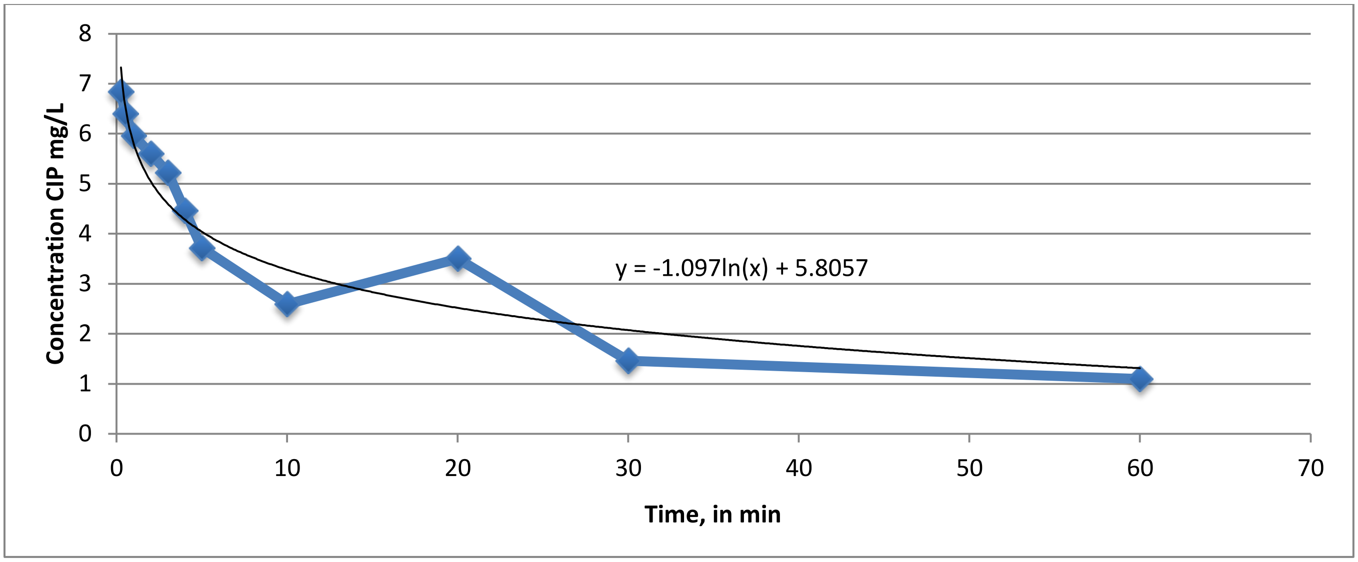
Initial Concentration CIP mg/L	Molar Ratio Ferrate:CIP	pH	ABS	Final Concentration
10	10	12	0.4317	5.9786133
10	10	10	0.0446	0.6176654
10	10	8	0.0419	0.5802731
10	10	6	0.1375	1.9042375
10	10	4	0.3059	4.2364091
10	10	2	0.7206	9.9795894

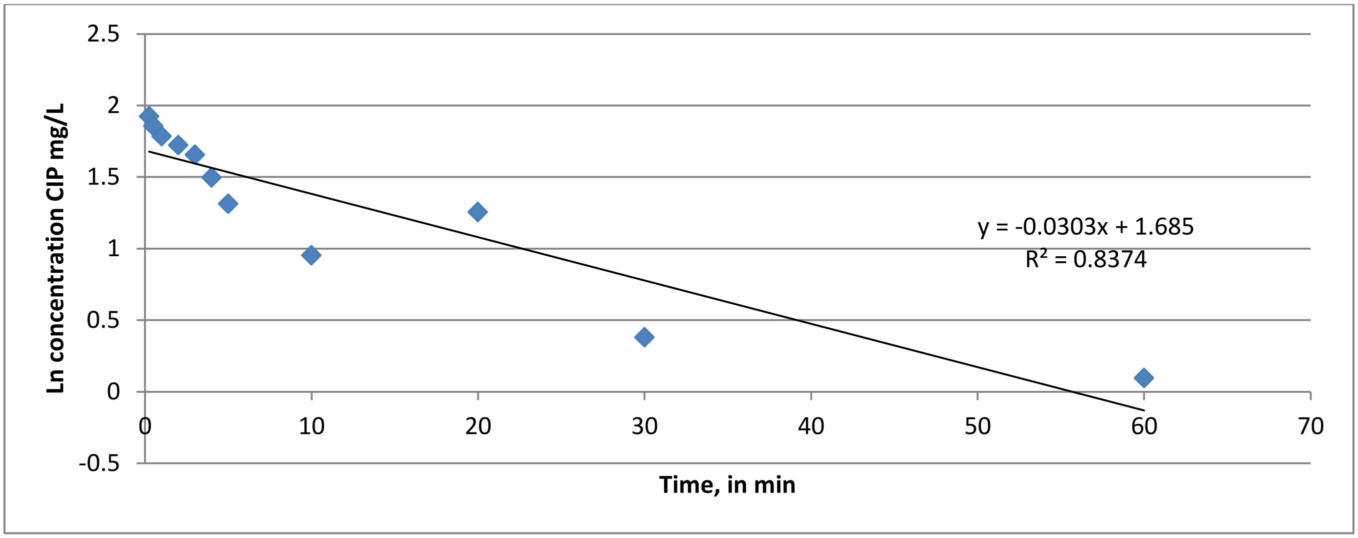


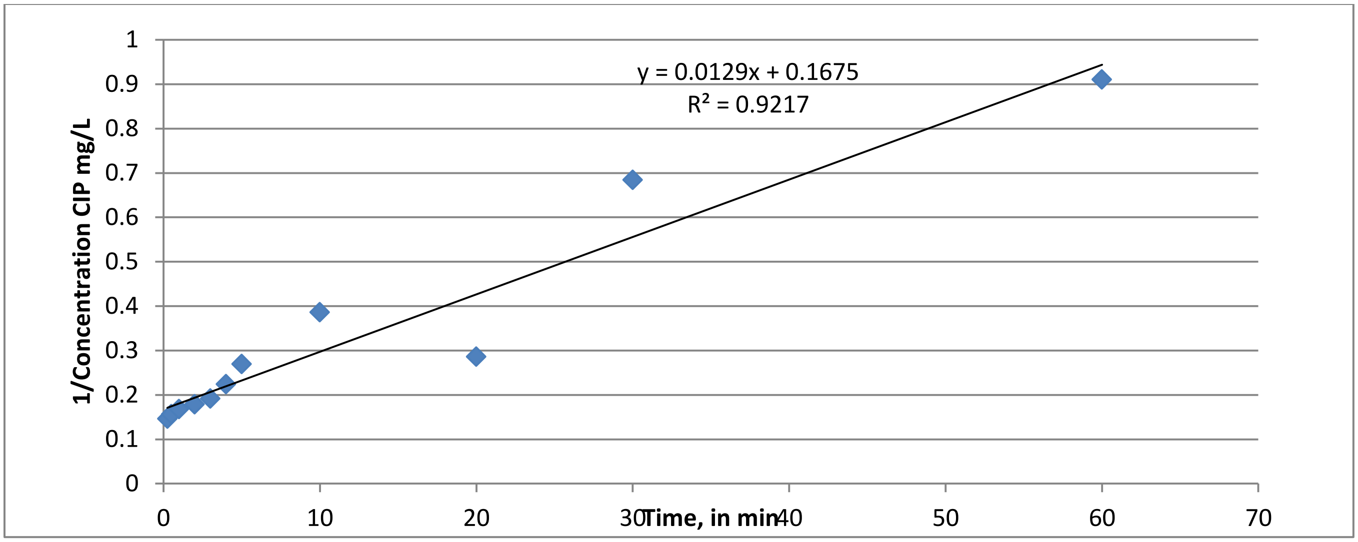
Appendix D: Kinetics Time Trial

Initial Concentration mg/L	Molar Ratio Ferrate:CIP	Time, in Min	Adjusted ABS	Final Concentration	Ln Conc	1/Conc
10	10	0.25	0.49363853	6.8364	1.92226128	0.14627582
10	10	0.5	0.462040581	6.3988	1.85611047	0.1562793
10	10	1	0.430355982	5.96	1.78507048	0.16778523
10	10	2	0.404054444	5.59575	1.72200738	0.17870705
10	10	3	0.377319662	5.2255	1.65355049	0.19136925
10	10	4	0.322463716	4.4658	1.49644837	0.22392404
10	10	5	0.268358726	3.7165	1.31278237	0.26907036
10	10	10	0.187143476	2.59175	0.95233332	0.38583968
10	10	20	0.252725829	3.5	1.25276297	0.28571429

10	10	30	0.10558163	1.4622	0.37994215	0.68390097
10	10	60	0.079316196	1.09845	0.0939001	0.91037371






y = 0.0129x + 0.1675
R² = 0.9217
1/Concentration CIP mg/L
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
10
20
30
40
50
60
70
Time, in min