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Removal of Ciprofloxacin from Water with Chemical Oxidation

Major Qualifying Project completed in partial fulfillment
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Submitted by:

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Abstract

Contamination of water sources with compounds of emerging concern, particularly pharmaceuticals such as ciprofloxacin, is becoming an increasingly large problem. Current water and wastewater treatment facilities are not specifically designed to remove pharmaceuticals. The objective of this project was to study the removal and degradation of ciprofloxacin (CIP) from water through reactions with five oxidative treatments. Reactants included hypochlorite, potassium permanganate, potassium ferrate, persulfate and hydrogen peroxide activated with ferrous oxide (Fenton's reaction). The concentration of CIP remaining after treatment was quantified using a UV spectrophotometer. Results showed that all treatment methods evaluated were capable of removing concentrations of CIP from water. Potassium ferrate, Fenton's reaction and hypochlorite all achieved removal extents above 90%. Persulfate and potassium permanganate did not achieve complete removal with the dosages utilized in this study. All treatment methods achieved greater extents of removal with greater dosages of oxidant.

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Chapter 1: Introduction

The pharmaceutical industry has steadily grown over the past eight years, resulting in an average annual growth rate in the world market of almost 7% and topping out in 2010 with $856 billion in sales (IMS Health, 2011). In addition to the development in the pharmaceutical industry, the global population has grown at a rate of about 1.5% per year (Soubbotina, 2005). With the limited number of potable water sources around the world and the continued population increase, it is necessary to ensure that drinking water will be available, abundant, and safe for years to come.

Recent studies have shown that the development of new pharmaceutical drugs poses a potential threat to potable water sources. The United States Environmental Protection Agency (USEPA) has classified endocrine disrupting compounds (EDCs) as compounds that interfere with the “synthesis, secretion, transport, binding, action, or elimination of natural hormones in the body which are responsible for the maintenance of homeostasis, reproduction, development, and/or behavior”. The presence of EDCs in the environment has been linked to deficiencies in human and wildlife hormone systems, such as the feminization of fish throughout several counties in California and in the United Kingdom (United States Interior Bureau of Reclamation, 2009).

Over the past 30 years scientists have found traces of pharmaceuticals and personal care products (PPCPs), including EDCs, in both ground and surface water sources. Short-term studies have suggested that low concentrations of PPCPs in wastewater have no direct adverse effect on human health. Because pharmaceuticals are relatively new to society, there are not many studies on the long-term effects of small concentrations of PPCPs in the environment on human health. The presence of EDCs, PPCPs, metals and nitrosamines in the environment have been reported to interfere with human and animal hormone systems at sub-nanogram levels (United States Interior Bureau of Reclamation, 2009). Therefore, they have all been grouped together and labeled as compounds of emerging concern or CECs.

CECs are being used with increased frequency. Specifically, in the past ten years the use of pharmaceuticals in the U.S. has more than doubled (Araujo, 2010). This boom, along with analytical technology advances, has led to discoveries of concentrations of CECs in surface and groundwater sources. In a test conducted by the U.S. Geological Survey, approximately 80 percent of U.S. streams and 25 percent of groundwater sources were found to be contaminated with pharmaceuticals. Contaminants enter water sources through various pathways including from wastewater treatment plants, landfills, and agricultural runoff (Fatta, 2007). Most human pharmaceuticals are introduced into sewage water because they are only partially metabolized following ingestion. When a human or an animal is given a drug, anywhere from 50 percent to 90 percent of it is excreted unchanged (U.S. Department of the Interior Bureau of Reclamation, 2009). Veterinary pharmaceuticals also contribute heavily to the contamination of water sources because they are excreted un-metabolized and flow directly into water sources through runoff. A large amount of the remaining active components pass through water treatment systems unchanged and are discharged into waterways.

A study was conducted on the Cilfynydd Wastewater Treatment Plant in Wales, UK to determine the removal of various PPCPs. Using solid-phase extraction and ultra-performance liquid chromatography-electrospray tandem mass spectrometry, it was determined that concentrations of antibacterial drugs, antiepileptic drugs, and H-2 receptor antagonists were reduced minimally, if at all. Anti-inflammatory/analgesic drug and lipid-regulating drug concentrations were reduced by roughly 50% and beta-blocker concentrations were reduced by roughly 75%. Most personal care products were reduced by factors ranging from 2 to 20 (Dinsdale, 2008).

While it is likely that this problem has occurred since the introduction of pharmaceuticals and EDCs, only in recent years have the analytical techniques been available to accurately quantify CECs in water sources. The use of equipment, such as gas and liquid chromatography and mass spectrometry, to identify and quantify individual constituents in water samples has helped scientists determine the extent of the problem (AwwaRF, 2005). Although it is now possible to accurately quantify compounds, even at the micro-scale, many pharmaceuticals have not been tested for their environmental impact. There are currently around 87,000 compounds identified by the EPA that need to be evaluated for adverse effects (AwwaRF, 2005).

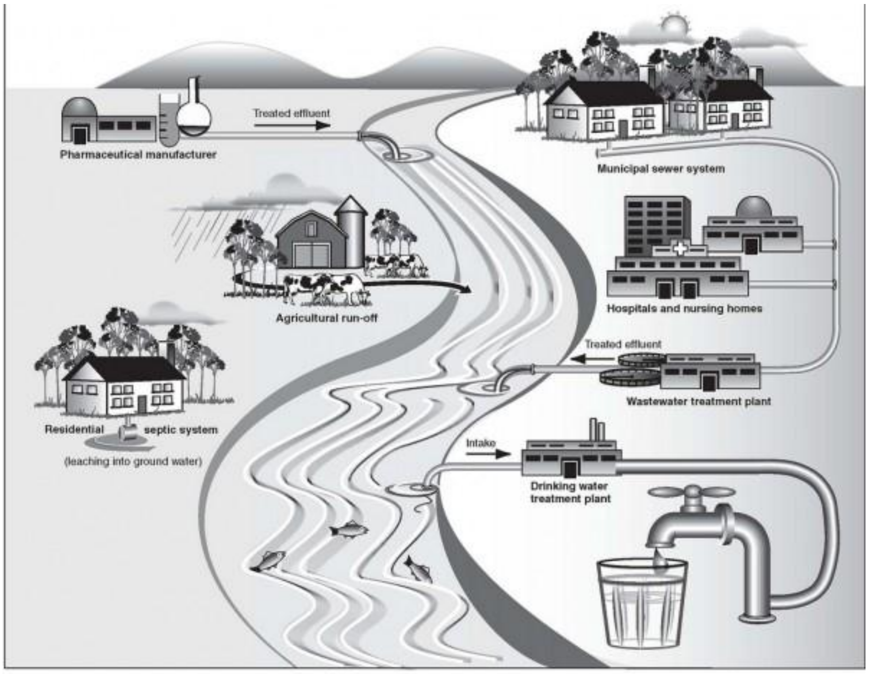
The technology to quantify CECs in water and wastewater has led to research to develop advanced removal methods which could be implemented in water and wastewater treatment plants. Oxidants may be used in these removal processes to decrease the concentrations of CECs to harmless levels. The oxidation processes described in this paper include chlorination, potassium permanganate treatment, potassium ferrate treatment, sodium persulfate treatment, Fenton's oxidation and ozonation.

Chapter 2: Background

This chapter discusses the research that has been conducted related to the presence and risks of Ciprofloxacin (CIP) and other pharmaceutically active compounds (PhACs) in the environment. Studies which have confirmed that PhACs, particularly CIP, are present in the environment are discussed. Ciprofloxacin (CIP) is then introduced and its chemical structure and pharmacokinetics are discussed. Following the introduction of CIP is a description of the environmental and health risks associated with CIP and other PhACs in water supplies. Finally, a discussion of proven removal methods of CIP and other PhACs from water sources is provided.

2.1 Pharmaceuticals and the environment

Pharmaceuticals have been used more frequently over the past decade, with an increase in annual prescriptions from 2 to 3.9 billion between 1999 and 2009 (Braund, 2011). There are several ways in which PhACs can enter the environment. Waste streams from industrial manufacturing that contain PhACs are discharged to air and water resources through regulated and unregulated practices. Veterinary pharmaceuticals utilized in farming activities can be released to the environment through the excretion of fecal matter, urine, or perspiration. The improper disposal of household products releases chemicals directly to wastewater with the intentions of being treated at a waste water treatment plant (WWTP) or domestic septic system. It is estimated that 25 to 33 percent of pharmaceuticals are disposed of improperly and arrive in a landfill or WWTP (Lubliner, 2008).



Source: GAO.

Figure 1: Methods for introduction of PhACs in environmental water (Jain-Cocks, 2011)

Wastewater can be treated in two ways. Septic tanks and filtration beds containing wastewater are commonly used for treatment on site, while wastewater from households and industries can be transported through municipal pipes for treatment at a central location. The treatment of wastewater utilizes two main steps to remove contaminants. Primary treatment targets the removal of sludge and other solid particulates from sewage through physical processes such as screening and filtration. Secondary treatment utilizes bacteria to remove dissolved organics and finer organic particulates from sewage through biological processes such as activated sludge. In some WWTPs, a tertiary step uses advanced treatment methods to remove any constituents which were not targeted through primary or secondary treatment. WWTPs are not designed to treat PhACs and other emerging organic contaminants, thus introducing these chemicals to natural waters (United Nations, 1992).

2.2 Ciprofloxacin

The pharmaceutical antibacterial drug Ciprofloxacin is one such contributor to the contamination of wastewater. Also known as CIP, this drug is an antibiotic used to treat or prevent infections caused by bacteria (PubMed Health, 2011). This antibiotic is from the fluoroquinolone drug class, which works by killing or preventing the growth of bacteria by attacking the enzymes that trigger protein and DNA synthesis. CIP became popular when its capabilities of treating and preventing the symptoms caused by Anthrax were discovered. CIP has now grown to become one of the largest prescribed pharmaceuticals in the United States and Europe (Bhandari, 2008). Figure 2 shows the chemical structure of CIP.

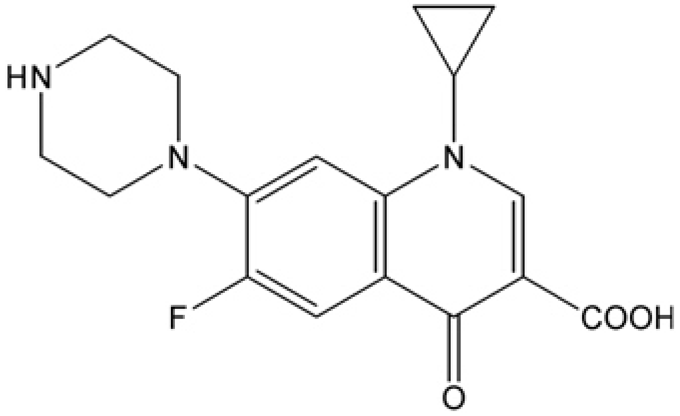


Figure 2: Chemical structure of Ciprofloxacin (U.S. National Library of Medicine, 2011)

The potential risks involved with the presence of Ciprofloxacin in the environment have led to rising concern. The following section contains research evaluating the environmental risks associated with CIP. The goal of this project was to determine feasible methods for the removal of Ciprofloxacin from water to reduce these environmental risks. This goal was accomplished by evaluating the effectiveness of several removal processes.

2.3 Ciprofloxacin in the Environment

2.3.1 Occurrence

With the increase in demand for pharmaceuticals over the past decade, the amount of water contamination from these drugs has also increased. CIP, along with other antibiotics and pharmaceuticals, has been found in many samples of surface water, ground water and even drinking water (Araujo, 2010). Recent technological improvements to detection methods have led to several studies which confirm that concentrations of CIP are present in several countries' environmental waters.

A study performed by the Swiss Federal Institute for Environmental Science and Technology explored the presence of antibiotics, including CIP, in the environment. Their research found detectable levels of CIP in the effluent of wastewater treatment facilities, despite removal of 80-90% of the contaminant during the treatment process. The presence of each contaminant was measured using fluorescence spectroscopy and liquid chromatography. Sewage sludge in wastewater treatment facilities was one component tested for CIP in which concentrations ranged from 1.4 to 2.4 mg/kg of dry matter (Alder, 2003).

A second study performed near Hyderabad, India found concentrations of CIP in the effluent of a wastewater treatment facility and in water samples from wells in six nearby villages. Liquid chromatography–mass spectrometry analytical methods were used to measure the concentrations of the contaminants. Concentrations of more than 1 µg/L were present in several wells and 14 mg/L existed in the facility's effluents. Along with the detection of CIP in the well water and effluent, high concentrations of the contaminant were also found in two nearby lakes (Fick, 2009). In another study conducted in Norway, concentrations of several different hormones and antibiotics were tested in three municipal wastewater treatment facilities. CIP was found to have concentrations 10 times higher than the other drugs tested in the effluent of the facility due to poor removal efficiency (Plosz, 2010).

These studies, along with others, illustrate the frequency with which CIP is present in the environment. Wastewater treatment facilities are inconsistent in their abilities to remove CIP, thus commonly discharging significant amounts of CIP into the environment. The failure to properly remove CIP from wastewater, combined with the small amounts of CIP that leach into the soil through septic systems or improper disposal are causing contamination of ground and surface water in many regions around the world. This occurrence of contamination is important to study because there are associated environmental and health risks, which are described in the following section.

2.3.2 Associated Environmental and Human Risks

The introduction of antibiotics to the modern world has provided illness prevention and treatment to millions of people. However, as more drugs are prescribed there is an increasing concern for their effect on the environment. When drugs are excreted by a consumer or flushed down a drain they enter wastewater streams. If these contaminants are not sufficiently removed during wastewater treatment they can enter drinking water supplies. If an antibiotic such as CIP enters the drinking water supply, humans can unknowingly and continuously ingest small amounts of the drug. One concern with continuous exposure to an antibiotic is bacterial resistance. Bacterial resistance is the ability of a microbe to resist the effects of an antibiotic. With continuous exposure to a specific drug, bacterial DNA can mutate, limiting the effectiveness of the antibiotic. Strains of resistant bacteria have been found in surface and ground waters around the world and possess several harmful qualities (Ahmad, 2009).

An analytical term known as minimum inhibitory concentration (MIC) is used to determine resistance to antibiotics. It is defined as the minimum amount of antibiotic that will inhibit the growth of a bacterium after overnight incubation. The minimum inhibitory concentration for reduced susceptibility is the smallest antibiotic concentration where bacteria can survive. Bacteria that survive between these two MIC concentrations possess intermediate resistance to the antibiotic and those that survive at higher concentrations have a stronger resistance to the drug (Ahmad, 2009).

A study was conducted on the resistance of common bacteria such as fecal coliforms like E. coli and enterococci to Ciprofloxacin. Influent and effluent water samples from wastewater treatment facilities were collected and analyzed for resistance to CIP and other antibiotics. Using several techniques, including the one described above, it was observed that fecal coliforms exhibited intermediate resistance to CIP. Reduced susceptibility to CIP was also found in 3.5% of the total fecal coliforms and 52% of the enterococci in the influent (Ahmad, 2009).

Along with this study, another was conducted looking into the effect of domestic wastewater treatment facilities on bacterial resistance to CIP. The study suggests that nutrient rich environments like sewage and wastewater provide ideal conditions for horizontal gene transfer, allowing bacterial resistance to spread amongst the organisms. This makes wastewater treatment facilities an ideal breeding ground for bacterial resistant organisms. The study highly suggested that research should be conducted to determine treatments to decrease the amount of antibiotics in the effluent of the treatment facility in order to better preserve the environment (Coelho, 2010).

With an increasing number of studies revealing the effects of CIP in water, the argument for removing it becomes stronger. The harmful effects both to the environment and humans described above provide pertinent evidence for its removal. Failure to do so could lead to significantly worse adverse effects than those already prevalent.

2.4 Oxidative water treatment methods

Chemical oxidation is a process by which an organic compound is degraded by an oxidizing agent. Oxidation techniques have application in water treatment because of their ability to oxidize organics to inactive intermediates or CO_2, H_2O, and salts. The mechanism by which this occurs is called a "redox" couple because an oxidation reaction is coupled with a reduction reaction. In a redox couple, oxidation is the loss of electrons from one reactant, while another reactant is reduced, thereby gaining those electrons. Within water treatment, the oxidizing compound reacts with the contaminants to produce less harmful compounds. Another technique used in water treatment is advanced oxidation in which hydroxyl radicals are formed. Hydroxyl radicals are the strongest oxidizers and forming them through advanced oxidation processes, AOP, is highly effective. Hydroxyl radicals can be formed several ways including photocatalysis and electrolysis.

There are many oxidizing agents that are able to degrade organic compounds found in water but the reaction by-products must also be considered. Chemical oxidant by-products must be either non-toxic or easily removed from water sources. Several of the most common oxidizing agents are listed below along with their oxidizing potential.

Table 1: Oxidation Potential of Common Chemical Oxidants (Graham, 2005)

Oxidizing Species	Oxidation Potential (Volts)
Hydroxyl Radical	2.8
Activated Persulfate	2.6
Ferrate (VI)	2.2
Ozone	2.07
Persulfate	2.01
Hydrogen Peroxide	1.77
Perhydroxyl Radical	1.7
Permanganate	1.69
Chlorine	1.38

2.4.1 Chlorine:

Perhaps the most commonly used method for disinfection of water and wastewater in the United States is chlorination (U.S. EPA, 1999). Chlorine is available in all three phases; gas, liquid, and solid with the latter two in the hypochlorite form. The most common aqueous hypochlorite solution is sodium hypochlorite, NaOCl. When added to water, the following reaction occurs:

$$NaOCl + H_2O \rightarrow HOCl + Na^+ + OH^- \tag{1}$$

Commonly referred to as liquid bleach, sodium hypochlorite is a clear, moderately yellow solution of varying concentrations of chlorine with a distinctive odor. Its stability is dependent on the time and temperature of storage, any impurities in solution, and exposure to light. According to White (1992), besides being an effective disinfectant for wastewater, chlorine also serves other helpful purposes such as improved coagulation by activated silica, taste and odor control, and prevention of algal growth due to its strong oxidizing powers (U.S. EPA, 1999).

Research reveals the effectiveness of chlorine as a disinfectant for inactivating pathogens. According to Haas and Engelbrecht (1980), chlorination causes an immediate decrease in oxygen utilization in both Escherichia coli and Candida parapsilosis as well as damage to their cell walls and membranes (U.S. EPA, 1999). Compared to other oxidative techniques such as ozone however, chlorine is incapable of deactivating protozoa. Experimentation revealed lower Ct-values (Concentration*time) for chlorine than for ozone, indicating that less protozoa were inactivated.

Dodd et al. (2005) conducted research to determine the oxidation reaction pathway that occurs when aqueous chlorine is added to a CIP solution. The aliphatic amino groups in CIP's piperazine ring are reactive with chlorine (Huang, 2002). HOCl reacts very rapidly at CIP's secondary N(4) amine, forming a chloramine intermediate that spontaneously decays in aqueous solutions by concerted piperazine fragmentation. Experimentation by Huang et al. found that CIP reacts readily with chlorine.

Below are both the advantages and disadvantages of using chlorine (U.S. EPA, 1999).

Advantages of chlorine, NaOCl:

- is easily measured and controlled
- economical
- proven successful in improving water treatment operations

Disadvantages of chorine, NaOCl:

- produces undesirable DBPs (disinfection by products)
- degradation over time and with exposure to light
- corrosive
- less effective at a high pH
- high doses can cause taste and odor problems

2.4.2 Potassium Permanganate:

Unlike chlorine, potassium permanganate ($KMnO_4$) primarily uses its oxidizing potential to control taste and odors, and remove color as opposed to sterilization because it is a poor disinfectant. Under alkaline conditions, the oxidation half-reaction is as follows:

$$MnO_4^- + 2H_2O + 3e^- \Rightarrow MnO_2 + 4OH^- \qquad (2)$$

Potassium permanganate is a dark purple/black crystalline solid that, when added to water, makes a solution of a pink or purple color. It is a reactive and fast acting oxidizer that can cause eye injury and irritate the skin if not used with care. Oxidation in water yields fast reaction rates and is dependent on temperature, pH and dosages. Cleasby et al. (1964) found that pH is the major factor affecting oxidation with potassium permanganate and that the lower the pH, the more effective the oxidation.

Research has been conducted to determine the effectiveness of potassium permanganate as a disinfectant against pathogens. According to Banerjea (1950), only high dosages of about 20 mg/L and a 24-hour contact time proved to deactivate the studied pathogens. To inactivate the polio virus, a dose of 50 mg/L of potassium permanganate and a contact time of 2 hours was required (U.S. EPA, 1999). Further, a comparison between potassium permanganate and chlorine dioxide as a disinfectant of protozoa was measured using log inactivation (Au, 2004). Log inactivation is a useful and effective way to express the number or percent of microorganisms inactivated through a disinfection process. The higher the number, the greater the percentage of microorganisms removed. It was found that disinfection of Cryptosporidium showed log inactivation of 0.3 using potassium permanganate compared to 2.0 using chlorine dioxide despite the use of twenty times more potassium permanganate. This shows that potassium permanganate has far less disinfecting abilities than other oxidants.

Hu et al. (2011) investigated the reaction products and pathways of CIP oxidized by $KMnO_4$. Using mass spectrometry, they identified 12 oxidation products with oxidation of the tertiary aromatic and secondary aliphatic amine groups on the piperazine ring and the cyclopropyl group which are evident in the figure below.

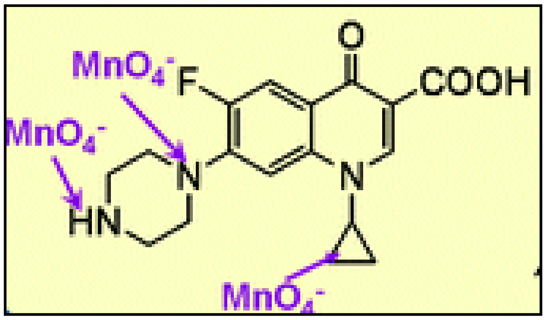


Figure 3: Oxidation of CF with Permanganate
(Hu, 2011)

Results of the study suggest that using permanganate to eliminate pharmaceutical activity in organic-rich matrices is plausible despite its lower reactivity compared to ozone and free chlorine (Hu, 2011).

Below are some of the advantages and disadvantages of using potassium permanganate (U.S. EPA, 1999).

Advantages of potassium permanganate, $KMnO_4$

- oxidizes odor and taste-causing compounds
- is easy to store and transport
- has little impact on other treatment processes at the water treatment facility
- controls the formation of DBPs

Disadvantages of potassium permanganate, $KMnO_4$

- requires longer contact time
- gives water a pink color
- toxic and irritates both the skin and mucous membranes

2.4.3 Ferrate:

Another technology that has applications in water and wastewater treatment is the use of ferrate, Fe(VI). A common form of ferrate used in water treatment is potassium ferrate, K_2FeO_4, and is the most easily produced form of Fe (VI) . Potassium ferrate is a black-purple salt and is stable when isolated from moisture. Ferrate is a strong oxidant, particularly under acidic conditions and has a greater oxidizing potential than manganese (Jiang, 2002). Not only does Fe (VI) have the ability to oxidize and disinfect water sources, it can also be used as a coagulant, helping to reduce turbidity in wastewater (Jiangyong et al., 2005).

Research has been done to determine whether or not ferrate is a viable alternative to more traditional oxidation techniques (Jiangyong et al., 2005). Jiangyong et al. have shown ferrate is able to kill 99.9% of total coliforms, although the required dosage is dependent on the initial number of coliforms. Results of the study also indicate ferrate is more successful than chlorine at treating spore forming bacteria and is capable of inactivating viruses.

In another study, the ability of ferrate to degrade CIP was analyzed. Ferrate is particularly reactive with compounds that contain electron rich moieties, an amine in the case of CIP (Gunten et al., 2009). Gunten et al. showed that a dosage of 2 mg/L Fe (VI) yielded >95% removal of pharmaceuticals containing a phenolic-moiety, while 5 mg/L of Fe (VI) only yielded >85% removal of compounds containing an amine or olefin moiety such as CIP. This indicates that while oxidation using ferrate is successful for CIP, a higher dosage of ferrate is necessary for complete removal.

Several advantages and disadvantages of ferrate are identified below:

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

2.5 Advanced Oxidation Processes

2.5.1 Peroxides:

Hydrogen peroxide is another compound with strong oxidative abilities. It is the simplest peroxide, having the chemical formula H_2O_2 (Goi et al., 2009). Hydrogen peroxide can be used as a bleach or disinfectant, and has applications in water treatment. The disinfection occurs through the oxidation of hydrogen peroxide to highly reactive hydroxyl radicals.

$$H_2O_2 \rightarrow OH^- + OH^\bullet \qquad (3)$$

The degradation into a radical can occur without a catalyst slowly; however, in the presence of catalysts, the reaction happens more rapidly, occurring within minutes. Hydrogen peroxide catalysts range from metals, such as iron or silver, to ozone or ultraviolet light (Gurol, 1994). The hydroxyl radical will react with organic compounds, such as pharmaceuticals, to produce lower-weight, inactive by-products. The dosage of hydrogen peroxide is important, as it affects the speed at which the reaction occurs (Feng, 2003). Lower dosages of H_2O_2 may not generate enough hydroxyl radicals, while dosages above the optimal amount will result in scavenging of radicals. Both scenarios result in an overall decrease in degradation.

2.5.2 Fenton reaction:

One of the most common catalysts used in hydrogen peroxide oxidation is iron (II), or ferrous iron. The use of iron (II) as a catalyst is called Fenton's Oxidation (Gurol, 1994). The addition of the iron causes the hydrogen peroxide to rapidly degrade to the intermediate hydroxyl radical, which reacts with organic compounds with a second-order rate constant ranging from 10^7-10^{10} $M^{-1}s^{-1}$. While there is some dispute about the mechanism by which the Fenton reaction occurs, one widely accepted mechanism is as follows:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH^\bullet \tag{4}$$

$$OH^\bullet + H_2O_2 \rightarrow HO_2^\bullet + H_2O \tag{5}$$

$$Fe^{3+} + HO_2^\bullet \rightarrow Fe^{2+} + H^+ + O_2 \tag{6}$$

$$Fe^{2+} + HO_2^\bullet \rightarrow Fe^{3+} + HO_2^- \tag{7}$$

$$Fe^{2+} + OH^\bullet \rightarrow Fe^{3+} + OH^- \tag{8}$$

Equations 2-6: Fenton Reaction Equations (Chemizmu, 2009)

The Fenton reaction, like all peroxide reactions, is dependent on the concentration of hydrogen peroxide, the ratio of Fe^{2+} to H_2O_2, pH and reaction time. The Fenton reaction is also sensitive to UV radiation (Guo, 2009). Using UV radiation to enhance the Fenton reaction is called the photo-Fenton reaction and is more effective because Fe^{3+} is reduced to Fe^{2+} forming $OH^\bullet$ in the process and Fe^{3+} forms iron-organic complexes which then create organic radicals through UV radiation. This can be seen in the equation below:

$$Fe^{3+} + H_2O + hv \rightarrow Fe^{2+} + OH^\bullet + H^+ \tag{9}$$

$$Fe(OOC - R)^{2+} + hv \rightarrow Fe^{2+} + R^\bullet + CO_2 \tag{10}$$

Equations 7-8: photo-Fenton Reaction (Guo, 2009)

Guo (2009) studied the effectiveness of both the Fenton and photo-Fenton reactions on the degradation of CIP over a range of pHs, temperatures and H_2O_2 and iron dosages. The experiment used 15 mg/L samples of CIP in distilled water for both the Fenton and photo-Fenton reactions while in the photo-Fenton reaction, a 6W UV bulb with a 365 nm wavelength was used as the radiation source. The degradation was observed using a Lambda 17 UV/Vis spectrophotometer with the absorbance wavelength set to 271 nm.

The best results for the photo-Fenton reaction were achieved using a pH of 4, although degradation was still possible in the pH range of 3-5 with no appreciable degradation observed at pH 6 (Guo, 2009). The optimal molar ratio of $[H_2O_2]/[CIP]$ was determined to be 128 and the degradation efficiency increased with increasing amounts of Fe (II). However, too much H_2O_2 had an inhibitory effect on degradation. Finally, at a higher temperature, the degradation occurred more efficiently. The study shows that a very high extent (>90%) of CIP degradation is possible using the Fenton reaction, particularly if UV radiation is used as well.

2.5.3 Persulfate:

Widely used for cleaning swimming pools, bleaching hair, and initiating polymerization reactions, persulfate is a strong oxidant. Out of all the persulfate salts, the sodium form is the most commonly used for environmental purposes. Sodium persulfate ($Na_2S_2O_8$) is a white crystalline solid. It is a highly reactive oxidant but is more stable than other disinfectants such as hydrogen peroxide and ozone. If applied correctly, sodium persulfate can destroy many organic contaminants. It has potential for use for in degrading organic compounds found in contaminated soil and groundwater (Block et al., 2004). The standard oxidation reduction reaction is below.

$$S_2O_8^{2-} + 2H^+ + 2e^- \rightarrow 2HSO_4^- \tag{11}$$

In the presence of a catalyst, persulfate can form sulfate free radicals, resulting in advanced oxidation using persulfate. Sulfate free radicals are molecular fragments that have an unpaired electron causing them to be highly reactive and a strong oxidizing agent. The radical generation and reactions follow (where RH represents an organic compound and $R^{\bullet}$ represents an oxidized organic compound):

Initiation: $$NaS_2O_8 + initiator \rightarrow 2SO_4^{\bullet -} + Na \tag{12}$$

Propagation: $$2SO_4^{\bullet -} + H_2O \rightarrow OH^{\bullet -} + \mathrm{HSO}_4^{-} \tag{13}$$

Termination: $$SO_4^{\bullet -} + RH \rightarrow R^{\bullet} + HSO_4^{-} \tag{14}$$

$$OH^{\bullet -} + RH \rightarrow R^{\bullet} + H_2O \tag{15}$$

(Cronk, 2008)

There are numerous methods that can be used in order to activate sodium persulfate. They include hydrogen peroxide, ferrous or chelated iron, alkaline conditions, and heat. Selection of the proper activation method is dependent upon the contaminant of concern, as well as the conditions surrounding the oxidation. The most aggressive means of activation is the use of a high pH or addition of hydrogen peroxide. These activation methods can cause corrosion and damage to utilities and metal objects. In addition, hydrogen peroxide reacts very aggressively in the subsurface of groundwater. Therefore, unless care is taken to control the reaction by adequately venting the off-gas produced by the reaction, peroxide will come to the surface. Iron activation is not recommended to be used against gasoline and diesel range organics, vinyl chloride, methylene chloride, carbon tetrachloride, TCA or DCA despite its effectiveness on some hydrocarbons. Lastly, heat activation is capable of decomposing a wide range of contaminants in aqueous systems; however, it is very costly due to the complexity of obtaining and generating a heat source (Cronk, 2008).

According to Furman et al. (2010), the most commonly used activators for in situ chemical oxidation (ISCO) are chelated iron and base. Chelation is an effective way of maintaining metal activity at neutral and alkaline ground water conditions. It provides protection from hydration and subsequent precipitation under the neutral pH conditions that may be found in the field. Transition metals bound to strong chelating agents make up these chelated metal catalysts. An example is chelated ferric iron (Fe^{3+}) which has been found to have excellent oxidation performance, in addition to ferrous iron (Fe^{2+}) which is the most commonly used and readily available activator for transition metal catalysis (Block et al., 2004).

The reaction equations of ferrous iron with both persulfate and sulfate radicals are as follows:

$$\mathrm{Fe}^{2+} + S_2O_8{}^{2-} \rightarrow Fe^{3+} + SO_4{}^{\bullet -} + SO_4{}^{2-} \tag{16}$$

$$\mathrm{Fe}^{2+} + SO_4{}^{\bullet -} \rightarrow Fe^{3+} + SO_4{}^{2-} \tag{17}$$

(Liu, 2011)

Fe(III)-EDTA was found to be the best performing complex to activate persulfate oxidation of volatile organic compounds (Block et al., 2004).

Where persulfate ISCO takes place, more than half of the activations are base activation. Base-activated persulfate technology has been found to destroy highly chlorinated methanes and ethanes in groundwater and soil systems (Furman, 2010). Research suggests the following reactions occur:

$$2\mathrm{S_2O_8}{}^{2-} + 2H_2O \rightarrow 3SO_4{}^{2-} + SO_4{}^{\bullet -} + O_2{}^{\bullet -} + 4H^+ \tag{18}$$

$$SO_4{}^{\bullet -} + OH^- \rightarrow SO_4{}^{2-} + OH^- \tag{19}$$

(Furman, 2010)

Potassium hydroxide, sodium hydroxide, and lime are bases that can be used to activate persulfate. The buffering capacity (mole ratio of pH modifier to persulfate) is important when creating alkaline-activated persulfate oxidation. The amount of base supply is essential for the alkaline activation of persulfate (Block et al., 2004). If there is not enough base, persulfate will not become activated.

The hydroxyl radical generated by Fenton's chemistry for peroxides has a similar reaction mechanism as the sulfate radical. Comparison of persulfate and activated persulfate oxidation to other oxidant systems has shown persulfates to be more favorable. The sulfate radical travels a greater distance through sub-surfaces in contrast to the hydroxyl radical due to its greater stability. In addition, persulfate is more efficient in organic soils because it has a less affinity towards natural soil organics when compared to permanganate (Block et al., 2004).

2.5.4 Ozone:

Ozone is the triatomic form of oxygen, O_3, and exists as a gas at room temperature. It is a highly unstable molecule because it readily decomposes back to oxygen and as such is a strong oxidant (U.S. EPA, 1999). The oxidizing abilities of ozone are becoming more frequently used in water treatment to decompose organic compounds and pharmaceuticals.

Ozone readily decomposes in water, forming the free radical $OH^{\bullet}$ (Balcioğlu, 2003). The hydroxyl radical is the strongest oxidizer and is highly useful in water treatment because it is nonselective in oxidizing organic compounds. The attack on organic compounds through the hydroxyl radical is one method by which ozone is useful in water treatment. This method, called radical oxidation, occurs in water with a pH at or above 7. The second method by which ozonation occurs is called direct oxidation by ozone and occurs at a pH less than 3. Radical oxidation is generally more effective over a shorter exposure period because the hydroxyl radicals are highly reactive and will attack most functional groups, causing the oxidation to occur extremely quickly.

Ozonation can be improved through the use of hydrogen peroxide as a catalyst (U.S. EPA, 1999). This method, called peroxone, accelerates the ozone decomposition, thus favoring the radical oxidation. The main chemical reaction with the addition of hydrogen peroxide is as follows:

$$O_3 + H_2O_2 \rightarrow 2OH^{\bullet} + 3O_2 \tag{20}$$

2.6 Summary

The occurrence of CIP in both water and soil is a cause for concern due to its contamination of ground and surface water, and potential to develop antibiotic resistant bacterial. WWTPs are ideal breeding grounds for these organisms; therefore, proper removal of antibiotics from the influent of the treatment facility would lower environmental risks. Chemical oxidation is a proven method for water treatment, but optimal methods and conditions have yet to be conclusively determined.

Chapter 3: Methodology

3.1 Sample Preparation

Solutions containing known concentrations of CIP were created using CIP received from LKT Laboratories and purified water (ROpure ST Reserve Osmosis/tank system, Thermo Scientific). The solutions were created by mixing predetermined masses of CIP weighed using a Mettler Toledo (AB104-S) scale with purified water. The solutions were stirred for a minimum of 10 minutes until all CIP was dissolved. The pH of all samples was adjusted to a range of 6.9-7.1 by the drop-wise addition of NaOH or HCl and the use of an Accument Basic AB 15 pH meter.

3.2 Measuring Sample Absorbance

Samples of CIP solutions were analyzed before and after treatment experiments for equilibrium studies and during treatment for time trials to determine the concentration of CIP removed during each trial. The analyses were done using a Varian-Cary 50 Scan UV-visible spectrophotometer and Plastibrand UV-cuvettes to measure absorbance at a wavelength of 270 nm.

3.3 Ciprofloxacin Concentration Standard Curves with Detection Limit

In order to determine unknown concentrations of treated samples, a standard concentration curve was generated using samples of known concentrations at pH 7. Nine solutions of known concentrations, ranging from 20 mg/L to 0.078 mg/L CIP in water, were analyzed with a Varian-Cary 50 Scan UV-visible spectrophotometer to measure absorbance at 270 nm. The absorbance readings were correlated to the known concentrations and graphed to generate a concentration standard curve, thus allowing any concentration within this range to be determined. The limit of detection was also identified using a T test in Microsoft Excel. The T test compares blank samples to samples of a known concentration to determine the concentration at which there is no longer a statistical difference between pure water and CIP samples. The limit of detection was determined to be 0.313 mg/L CIP. The full data for the standard curve can be seen in Appendix A.

3.4 24 Hour Steady State Oxidation Tests

3.4.1 Hypochlorite Oxidation

The first oxidation treatment was conducted using a solution of 20 mg/L CIP with the addition of NaOCl based on a molar ratio. Solutions were created using 100:1, 50:1, 25:1, 17:1, 11:1, 5:1 and 1:1 molar ratios of NaOCl to CIP. The oxidant was added to the CIP solution and the pH altered to 7 through the drop-wise addition of NaOH and HCl. Solutions were then placed in a rotator for 24 hours. After 24 hours, the solutions were removed and each pH was adjusted back to 7. Each sample was then analyzed by the spectrophotometer at 270 nm to determine the final absorbance. The absorbance reading was converted to a final concentration using the concentration standard curve.

Controls were made for each molar ratio using this process, except the 20 mg/L CIP solution was replaced with purified water. These samples were also analyzed by the UV spectrophotometer to determine the absorbance reading of the chlorine.

3.4.2 Potassium Permanganate Oxidation

The oxidation treatment using potassium permanganate was conducted using a solution of 20 mg/L CIP with the addition of K_2MnO_4 based on a molar ratio. Solutions were created using 100:1, 50:1, 25:1, 17:1, 11:1, 5:1 and 1:1 molar ratios of K_2MnO_4 to CIP. The oxidant was added to the CIP solution and the pH altered to 7 through the drop-wise addition of NaOH and HCl. Solutions were then placed in a rotator for 24 hours. After 24 hours, the solutions were removed and each pH was adjusted back to 7 if necessary. Each sample was then analyzed with the spectrophotometer at 270 nm to determine the final absorbance. The absorbance reading was converted to a concentration using the concentration standard curve.

Controls were made for each molar ratio using the same process, except the 20 mg/L CIP solution was replaced with purified water. These samples were also analyzed by the UV spectrophotometer to determine the absorbance reading of the potassium permanganate.

3.4.3 Potassium Ferrate Oxidation

The oxidation treatment using potassium ferrate was conducted using a solution of 20 mg/L CIP with the addition of K_2FeO_4 based on a molar ratio. Solutions were created using 100:1, 50:1, 25:1, 17:1, 11:1, 5:1 and 1:1 molar ratios of K_2FeO_4 to CIP. The oxidant was added to the CIP solution and the pH altered to 7 through the drop-wise addition of NaOH and HCl. Solutions were then placed in a rotator for 24 hours. After 24 hours, the solutions were removed from the rotator, adjusted to pH 7 if necessary and centrifuged for 4 minutes to remove the ferric hydroxide precipitate. Each sample was then analyzed by the spectrophotometer at 270 nm to determine the final absorbance. The absorbance reading was converted to concentration using the concentration standard curve.

Controls were made for each molar ratio using the same process, except the 20 mg/L CIP solution was replaced with purified water. These samples were also centrifuged and analyzed with the UV spectrophotometer to determine the absorbance reading of the potassium ferrate.

3.4.4 Persulfate Oxidation

The oxidation treatment using persulfate was conducted using a solution of 20 mg/L CIP with the addition of $Na_2S_2O_8$ based on a molar ratio. Solutions were created using 100:1, 50:1, 25:1, 17:1, 11:1, 5:1 and 1:1 molar ratios of $Na_2S_2O_8$ to CIP. The oxidant was added to the CIP solution and the pH altered to 7 through the drop-wise addition of NaOH and HCl. Solutions were then placed in a rotator for 24 hours. After 24 hours, the solutions were removed from the rotator and adjusted to pH 7 if necessary. Each sample was then analyzed by the spectrophotometer at 270 nm to determine the final absorbance. The absorbance reading was converted to a concentration using the concentration standard curve.

Controls were made for each molar ratio using the same process, except the 20 mg/L CIP solution was replaced with purified water. These samples were also analyzed by the UV spectrophotometer to determine the absorbance reading of the persulfate.

3.4.5 Fenton's Oxidation

The oxidation treatment using Fenton's reaction was conducted using a solution of 20 mg/L CIP with the addition of H_2O_2 based on a molar ratio. Ferrous iron in the form of ferrous sulfate was used to activate the hydrogen peroxide and was added in a constant ratio of 5 moles ferrous to 1 mol CIP. Solutions were created using 100:1, 50:1, 25:1, 17:1, 11:1, 5:1 and 1:1 molar ratios of H_2O_2 to CIP. The oxidant was added to the CIP solution and the pH altered to pH 7 through the drop-wise addition of NaOH and HCl. Solutions were then placed in a rotator for 24 hours. After 24 hours, the solutions were removed from the rotator, adjusted to pH 7 if necessary and centrifuged for 4 minutes to remove the iron precipitate. Each sample was then analyzed by the spectrophotometer at 270 nm to determine the final absorbance. The absorbance reading was converted to a concentration using the concentration standard curve.

Controls were made for each molar ratio using the same process, except the 20 mg/L CIP solution was replaced with E-Pure water. These samples were also centrifuged and analyzed with the UV spectrophotometer to determine the absorbance reading of the hydrogen peroxide and ferrous iron.

3.5 Time Trial Methodology

3.5.1 Hypochlorite

A molar ratio of 17:1 NaOCl to CIP was chosen to conduct the time trial experiments. The pH of the solution containing 26.4 mL of 20 mg/L CIP solution was adjusted to pH 3.04 at which point the requisite 3.6 mL NaOCl solution was added to the solution, thus bringing the final pH up to 7. The time trial began at this point and the solution was continuously mixed throughout. Aluminum foil was used to prevent degradation from UV rays. After 1 minute, a sample of the CIP and NaOCl solution was taken and analyzed in the UV spectrophotometer. The resulting absorbance reading was recorded. Samples were analyzed at regular intervals for 24 hours.

Another chlorine time trial was conducted using a 5:1 molar ratio of NaOCl to CIP. The methods are the same as the initial chlorine time trial with several exceptions. The initial CIP solution contained 28.4 mL CIP and the pH was adjusted to 3.6 before 1.6 mL

NaOCl was added. The time trial was only conducted for a total of nine hours until equilibrium was reached.

A chlorine time trial was also conducted using a 100:1 molar ratio of NaOCl to CIP. The methods are the same as the initial chlorine time trial with several exceptions. The initial CIP solution contained 30 mL CIP and the pH was adjusted to 2.2 before 23.9 mL NaOCl was added. The time trial was only conducted for 15 minutes until equilibrium was reached.

3.5.2 Persulfate

A molar ratio of 17:1 persulfate to CIP was chosen to conduct the time trial experiments. The pH of the solution containing 25.9 mL of 20 mg/L CIP solution was adjusted to pH 6.98, at which point the requisite 4.1 mL persulfate solution was added to the solution. The time trial began at this point and was continuously mixed throughout. Aluminum foil was used to prevent degradation from UV rays. After 1 minute, a sample of the CIP and persulfate solution was analyzed in the UV spectrophotometer. The resulting absorbance reading was recorded. Samples were analyzed at regular intervals for 21 hours.

3.5.3 Potassium Ferrate

A molar ratio of 17:1 potassium ferrate to CIP was chosen to conduct the time trial experiments. The pH of the solution containing 25.5 mL of 20 mg/L CIP solution was adjusted to pH 3.5 at which point the requisite 4.5 mL potassium ferrate solution was added to the solution, thus bringing the final pH up to 7. As soon as the oxidant was added to the solution, the timer was started and the solution was mixed continuously. Two methods were used to remove the ferrate in order to accurately test the absorbance of the CIP in solution. The first method used a Whatman microfiber glass 25mm syringe filter to remove the ferrate from the solution. After 1 minute, a sample of the CIP and K_2FeO_4 solution was taken and analyzed by the UV spectrophotometer. Samples of the solution and absorbance readings were taken at regular time intervals for 30 minutes. The second method used an Eppendorf centrifuge to separate out the ferrous precipitate from the solution. Once the precipitate was removed from the solution, an absorbance reading was taken 7 minutes after the oxidant was added. Absorbance readings were taken at regular intervals for 30 minutes at which point the solution reached equilibrium.

3.5.4 Fenton's Oxidation

A molar ratio of 17:1 H_2O_2 to CIP was chosen to conduct the time trial experiments. The ratio of Fe(II) was maintained at 5:1 ferrous to CIP. The pH of the solution containing 30 mL of CIP and ferrous solution was adjusted to pH 7 at which point the requisite 0.6 mL of 0.3 mass percent H_2O_2 solution was added, thus bringing the final pH up to 7. As soon as the oxidant was added to the solution, the timer was started and the solution was mixed continuously. Two methods were used to remove the iron precipitate in order to accurately test the absorbance of the CIP in solution. The first method used a Whatman microfiber glass 25mm syringe filter to remove the ferrate from the solution. After 1 minute, a sample of the solution was taken and analyzed by the UV spectrophotometer. Absorbance readings were taken of the sample at regular time intervals for 30 minutes. The second method used an Eppendorf centrifuge to separate out the ferrous precipitate from the solution. Once the ferrous precipitate was separated out of the solution, an absorbance reading was taken 7 minutes after the oxidant was added. Absorbance readings were taken at regular intervals for 15 minutes, at which point the solution reached equilibrium.

Chapter 4: Results and Discussion

The objective of this study was to obtain data for the oxidation reactions of CIP with hypochlorite, potassium permanganate, potassium ferrate, sodium persulfate, and Fenton's reagent. The data were analyzed to compare the extent of each reaction over a fixed period of time and the kinetics of each reaction. The comparative data were used to analyze and form recommendations for potential oxidative treatment methods or further research.

4.1: Degradation over 24 Hours

4.1.1 Hypochlorite

Initial concentrations of CIP in purified water were 20 mg/L in each solution. Controls containing no CIP were prepared for each hypochlorite concentration to determine interference on final absorbance readings. Table 2 displays the resulting concentrations and the extent of removal after 24 hours of various hypochlorite concentration treatments.

Table 2: Hypochlorite Molar Ratio Comparison

Molar Ratio Cl:CIP	Concentration of CIP After 24 Hours	Extent of Removal of CIP (%)
1	19.99	0.061
5	4.298	78.5
11	2.816	85.9
17	2.374	88.1
25	1.739	91.3
50	1.608	92
100	0.6623	96.7

The resulting concentration of CIP after 24 hours of treatment with hypochlorite was also plotted against the molar ratio of chlorine to CIP. Figure 4 shows this relationship.

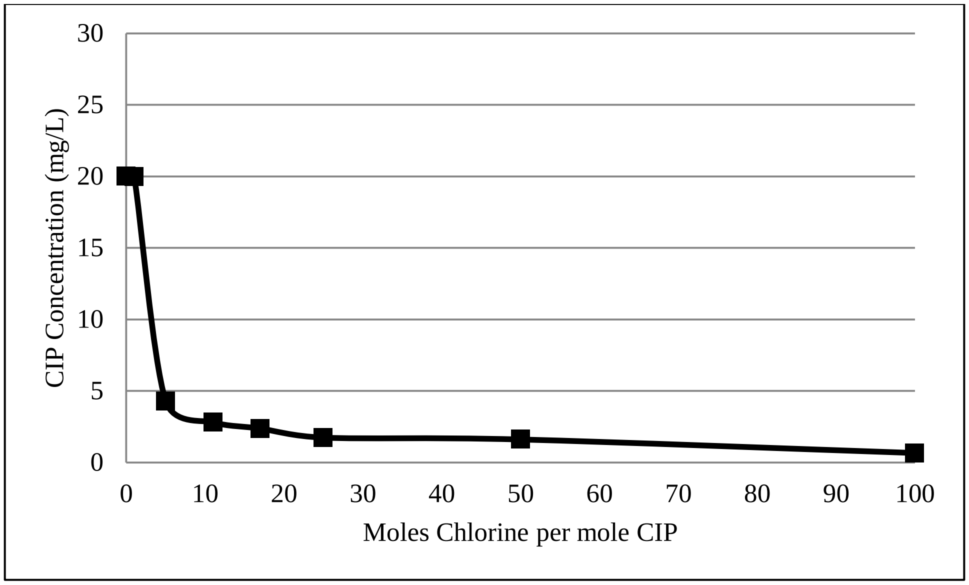


Figure 4: Hypochlorite Concentration and Corresponding CIP Concentration after 24 hours

The results show insignificant removal with a 1:1 molar ratio of chlorine to CIP. However, significant removal of 75% or higher was achievable with chlorine concentrated more than 5 moles per mole of CIP. With 100 moles of chlorine per mole of CIP almost complete degradation of CIP occurred. The general trend shows that as the concentration of chlorine increased, the degradation of CIP increased. When compared to the resulting concentration of a 1:1 molar ratio of chlorine to CIP, the 5:1 molar ratio of chlorine to CIP had greater than five times the amount of degradation. The removal achieved using molar ratios higher than 5:1 was not proportional to the increase in molar ratio.

The results from this experiment were compared to literature documenting previous experiments of the oxidation of ciprofloxacin using hypochlorite. Both the literature and the experimental results from this study suggest that hypochlorite readily oxidizes CIP. In a study by Anderson et al. (2012), a moderate concentration of the chlorine dioxide, 20 mg/L, was found to remove 90-100% of the CIP contaminant. This is comparable to the results of this study which showed a 91% reduction in CIP with a molar ratio of 25:1 hypochlorite to contaminant (Anderson, 2012).

Another study done by Huber et al. (2005) researched degradation of pharmaceuticals using chlorine dioxide. The study tested several pharmaceuticals and found that chlorine dioxide oxidized only 4 out of the 9 drugs tested. Using chlorine dioxide doses of 0.95 and 11.5 mg/L with a contact time of 30 minutes, the study found that macrolide and sulfonamide antibiotics as well as estrogens and phenazones were oxidized and sufficiently removed from the water. However, chlorine was not able to oxidize five pharmaceuticals: bezafibrate, carbamazepine, diazepam, ibuprofen, and iopromide. Chlorination can be highly useful in water treatment facilities, but as the study by Huber et al. shows, it is not capable of oxidizing all organics and further treatment may be required (Huber, 2005).

4.1.2 Potassium Permanganate

Initial concentrations of CIP in E-pure water were 20 mg/L in each solution. Controls containing no CIP were prepared for each potassium permanganate concentration to determine interference on final absorbance readings. Table 3 displays the resulting concentrations and the extent of removal after 24 hours of various potassium permanganate concentration treatments.

Table 3: $KMnO_4$ Molar Ratio Comparison

Molar Ratio $KMnO_4$:CIP	Concentration of CIP After 24 Hours	Extent of Removal of CIP (%)
1	24.84	-24.2
5	17.68	11.6
11	15.49	22.6
17	16.55	17.2
25	15.44	22.8
50	11.51	42.4
100	8.161	59.2

The resulting concentration of CIP after 24 hours of treatment with potassium permanganate was also plotted against the molar ratio of potassium permanganate to CIP. Figure 5 shows this relationship.

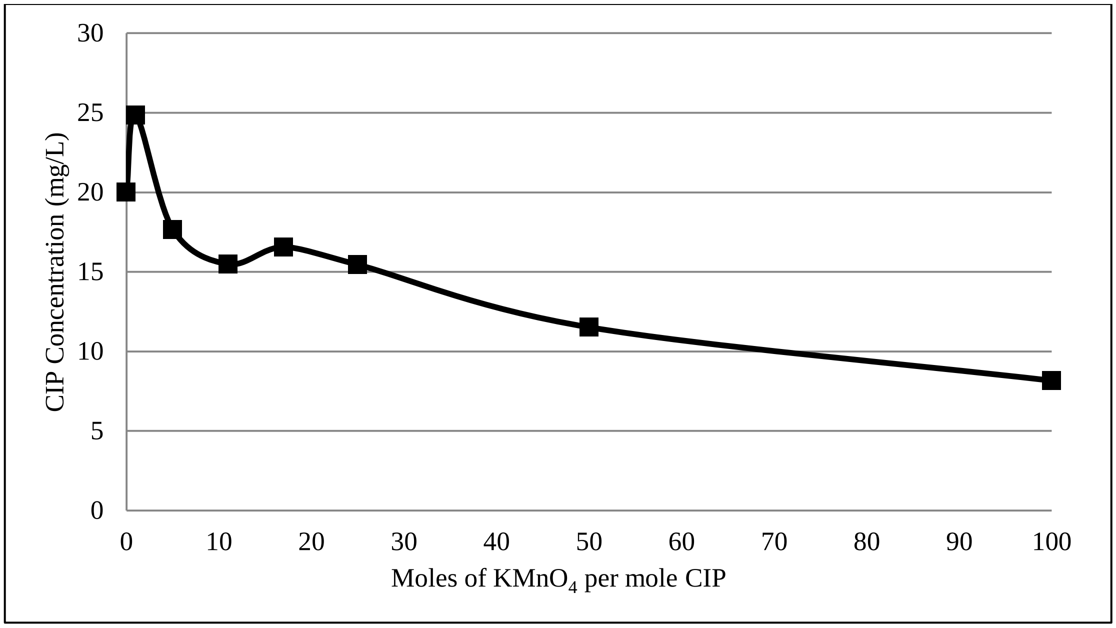


Figure 5: Potassium Permanganate Concentration and Corresponding CIP Concentration after 24 hours

With potassium permanganate treatment, a 50:1 and 100:1 molar ratio of oxidant to CIP were the only concentrations capable of removing over 40% of the initial CIP. With a 1:1 molar ratio of potassium permanganate to CIP, the resulting concentration of CIP was almost 25 mg/L. Controls of potassium permanganate in E-pure water without any CIP were tested after mixing for 24 hours and the resulting absorbance values were subtracted. Despite subtracting the absorbance readings of the E-pure water and oxidant solution, the concentration of the 1:1 potassium permanganate to CIP solution was above the initial value. This may indicate that a side reaction occurred between potassium permanganate and CIP during treatment, causing interference and a spike in absorbance readings. It is inconclusive what the cause of the interference was in the 1:1 molar ratio sample, and it is also undetermined if the same interferences were present in higher molar ratio samples. However, the solutions with a molar ratio of 5:1 or higher produced results showing some increased extent of removal.

Most literature on potassium permanganate in wastewater treatment studies the oxidants ability to deodorize or eliminate color. However, one study done by Hu et al. looked into the oxidation of three different antibiotics, including ciprofloxacin, using potassium permanganate. The experiment by Hu et al. used an excess of potassium permanganate to study the effects on ciprofloxacin and two other antibiotics. The results showed noticeable reactivity of all three antibiotics with potassium permanganate. It is also evident in the study that increasing the dosage of oxidant yields greater removal which supports the results of this study (Hu et al., 2010).

4.1.3 Potassium Ferrate

Initial concentrations of CIP in E-pure water were 20 mg/L in each solution. Controls containing no CIP were prepared for each potassium ferrate concentration to determine interference on final absorbance readings. After 24 hours of mixing, a precipitate formed in the solution. To avoid absorbance interference, the samples were centrifuged before analysis by the UV spectrometer. Table 4 displays the resulting concentrations and the extent of removal after 24 hours of various potassium ferrate concentration treatments.

Table 4: Potassium Ferrate Molar Ratio Comparison

Molar Ratio Ferrate:CIP	Concentration of CIP After 24 Hours	Extent of Removal of CIP (%)
1	13.13	34.3
5	5.669	71.7
11	2.713	86.4
17	1.031	94.8
25	1.515	92.4
50	1.016	94.9
100	0.6643	96.7

The resulting concentration of CIP after 24 hours of treatment with potassium ferrate was also plotted against the molar ratio of chlorine to CIP. Figure 6 shows this relationship.

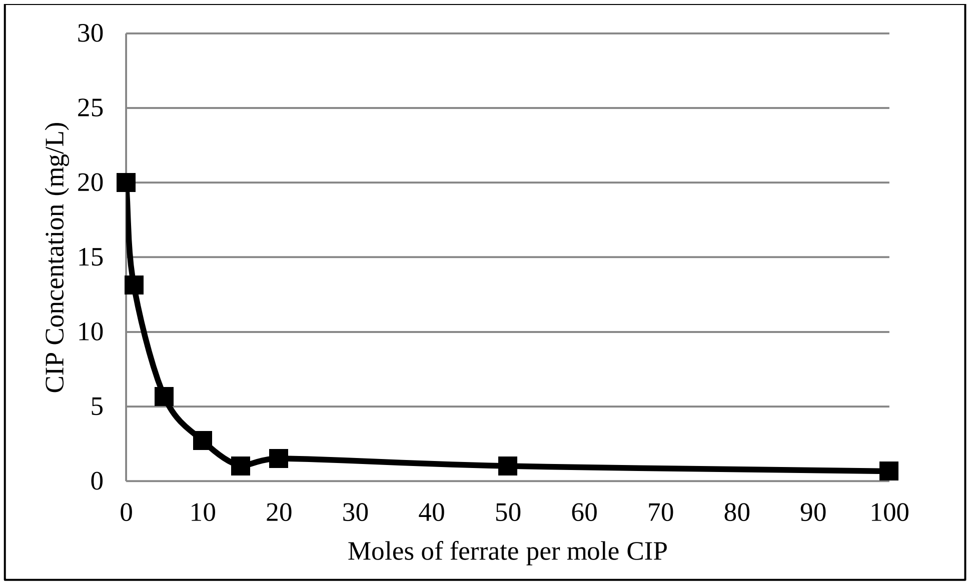


Figure 6: Potassium Ferrate Concentration and Corresponding CIP Concentration after 24 hours

Potassium ferrate treatment was shown to be effective in removing CIP from E-pure water. Samples with a molar ratio higher than 17:1 moles of potassium ferrate to CIP had extents of removal greater than 90%. The results show that there was not a significant difference between the 17:1 molar ratio and the 100:1 molar ratio with a range in concentration of 0.8507 mg/L. The least amount of degradation was 34.3% which was achieved using a 1:1 molar ratio solution.

A study by Jiang et al. investigated the removal of CIP by potassium ferrate. Beginning with solutions containing 10 mg/L CIP in deionized water, Jiang et al. tested potassium ferrate removal using concentrated doses of 1, 3, 5, 7, 9, 10, 15, and 20 ([K_2FeO_4]/[CIP]). Once the appropriate potassium ferrate was added to the CIP solution, a wastewater treatment system was simulated through three steps: fast mixing for 1 minute at 400 rpm; slow mixing for 20 minutes at 45 rpm; followed by sedimentation for one hour. Samples were then analyzed, and results from the experiment showed that the average extent of removal ranged from 60-69%, with the general trend indicating an increase in removal as the dose of potassium ferrate was increased (Jiang et al., 2011). The study by Jiang et al. resulted in extents of removal less than those achieved in this study at similar molar ratios of potassium ferrate to CIP. The variance between the results of the study by

Jiang et al. and this experiment could be attributed to the differences in methods, treatment time and initial CIP concentration. However, both studies clearly indicate that removal of CIP from water is possible using potassium ferrate as a treatment method, with increased removal possible using higher dosages of oxidant.

4.1.4 Persulfate

Initial concentrations of CIP in purified water were 20 mg/L in each solution. Controls containing no CIP were prepared for each persulfate concentration to determine interference on final absorbance readings. Table 5 displays the resulting concentrations and the extent of removal after 24 hours of various persulfate concentration treatments.

Table 5: Persulfate Molar Ratio Comparison

Molar Ratio Persulfate:CIP	Concentration of CIP After 24 Hours	Extent of Removal of CIP (%)
1	17.88	10.6
5	17.28	13.6
11	16.33	18.4
17	15.16	24.2
25	14.6	27
50	12.14	39.3
100	8.185	59.1

The resulting concentration of CIP after 24 hours of treatment with persulfate was also plotted against the molar ratio of persulfate to CIP. Figure 7 shows this relationship.

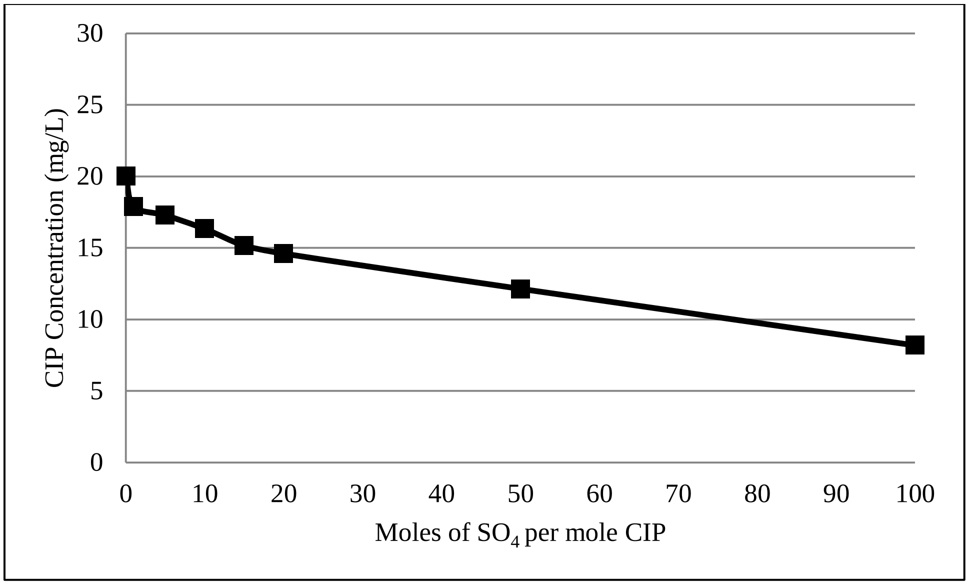


Figure 7: Persulfate Concentration and Corresponding CIP Concentration after 24 hours

Persulfate oxidation resulted in a steady decrease in CIP concentration as the molar ratio of CIP to persulfate was increased; however, the overall oxidation was not significant. A 100:1 molar ratio was the only concentration capable of a removal extent greater than 50% of the initial concentration. The overall range for resulting concentrations using persulfate was less than 10 mg/L. This suggests that a large increase in the molar ratio of CIP to persulfate would be needed to achieve a greater removal extent. An almost linear correlation resulted between the molar ratio of persulfate to CIP and the resulting CIP concentration. After formatting a line of best fit through the data points collected and obtaining an R^2 value of 0.9689, the corresponding equation for that line was:

$$y = -0.0941x + 17.212 \tag{21}$$

Table 6 predicts the molar concentrations of persulfate to CIP needed to reduce initial CIP concentrations to selected extents using the above best fit line.

Table 6: Predicted molar concentrations of persulfate to CIP required for greater removal

Extent of Removal (%)	**Resulting CIP Concentration (mg/L)**	**Molar Concentration of Persulfate:CIP Needed**
70	6	119
80	4	140
90	2	162

Using sodium persulfate as an oxidant in water treatment is a largely untested process. As such, there is little research on removal extents of CIP or other pharmaceuticals using persulfate oxidation. Relative comparisons have not yet been made for the use of persulfate to remove CIP from water.

4.1.5 Fenton's Oxidation

Initial concentrations of CIP in purified water were 20 mg/L in each solution. Controls containing no CIP were prepared while varying the hydrogen peroxide concentration and keeping the Fe(II) concentration at a constant ratio of 5:1. However for the controls of this experiment, no precipitate formed after 24 hours, resulting in absorbance readings greater than that of the original CIP solution. It is possible no precipitate formed because without the CIP in solution, no oxidation occurred and the iron remained in solution as ferrous sulfate. Therefore, the control absorbance readings were not deducted from the CIP/oxidant solutions. Within the CIP/oxidant solutions, a precipitate did form and the samples were centrifuged to avoid absorbance interference before analysis by the UV spectrophotometer. Table 7 displays the resulting concentrations and the extent of removal after 24 hours of various reactant doses.

Table 7: H_2O_2 Molar Ratio Comparison using 5:1 ratio of ferrous to CIP

Molar Ratio H_2O_2:CIP	**Concentration of CIP After 24 Hours**	**Extent of Removal of CIP (%)**
1	10.74	46.3
2	1.96	90.2
3	0.91	95.5
4	2.71	86.5
5	1.17	94.1
11	1.02	94.9
17	1.68	91.6
25	0.83	95.8
50	0.86	95.7
100	1.44	92.8

The resulting concentration of CIP after 24 hours of treatment with Fenton's oxidation was also plotted against the molar ratio of H_2O_2 to CIP. Figure 8 shows this relationship.

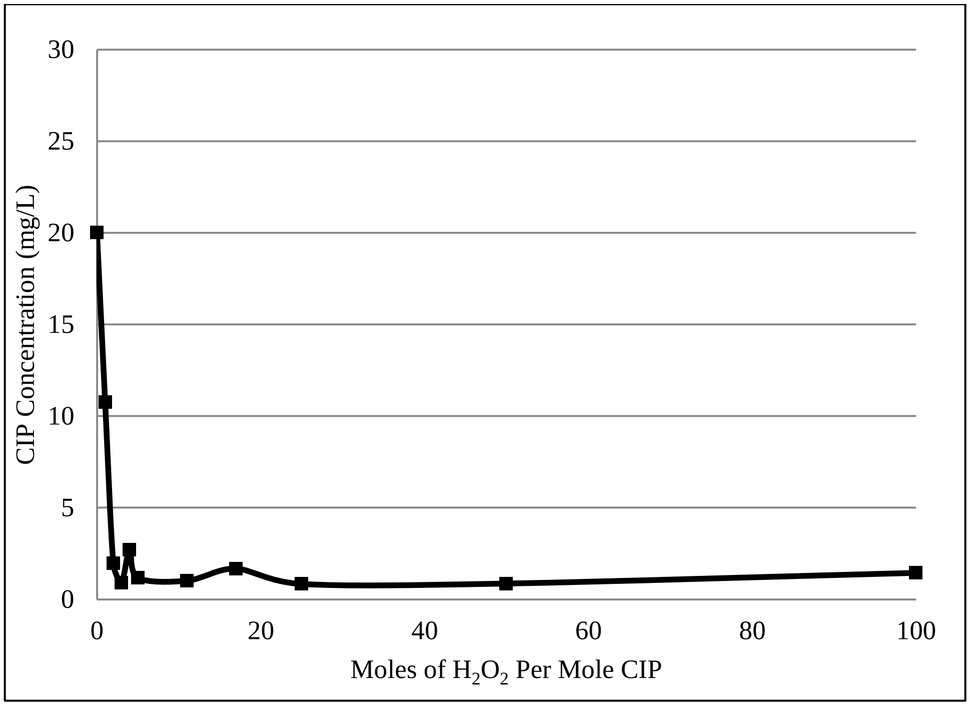


Figure 8: Fenton's Oxidation: Hydrogen Peroxide Concentration and Corresponding CIP Concentration after 24 hours (using 5:1 ferrous to CIP)

Similar to potassium ferrate treatment, each molar ratio of hydrogen peroxide to CIP reduced CIP concentrations below 15 mg/L. While a molar ratio of 1:1 did not remove more than 50% of the initial CIP, every molar ratio tested which was greater than 1:1 had a rate of removal higher than 85%. The greatest extent of removal was 95.8% and occurred with a 25:1 ratio. The 100:1 and 50:1 ratio solutions resulted in similar removals, although there was a slight increase in the final concentration as compared to the 25:1 molar ratio. The increase was approximately 0.6 mg/L, which could have been a result of error in the spectrophotometer or due to an increase in interference from the excess oxidant. While there may be slight experimental error in the results, the data show that it is possible to get over 85% removal of CIP with a molar ratio of only 2:1 hydrogen peroxide to CIP. These results show that Fenton's oxidation is a viable option for the removal of CIP from water.

To further supplement the study of Fenton's oxidation as a potential treatment method for CIP, the experiment was conducted using a set molar ratio of 1.4:1 Fe (II) to CIP. The concentrations of hydrogen peroxide were varied as before and all controls were prepared and analyzed similarly. Table 8 displays the resulting concentrations and the extent of removal after 24 hours of various hydrogen peroxide concentration treatments.

Table 8: H_2O_2 Molar Ratio Comparison using 1.4:1 Ratio of Fe (II) to CIP

Molar Ratio H_2O_2:CIP	**Concentration of CIP After 24 Hours**	**Extent of Removal of CIP (%)**
1	14.14	29.2
5	9.766	51.0
11	6.918	65.4
17	6.816	66.0
25	7.935	60.4
50	2.543	87.1
100	4.273	78.4

The resulting concentration of CIP after 24 hours of treatment with Fenton's oxidation was also plotted against the molar ratio of H_2O_2 to CIP. Figure 9 shows this relationship.

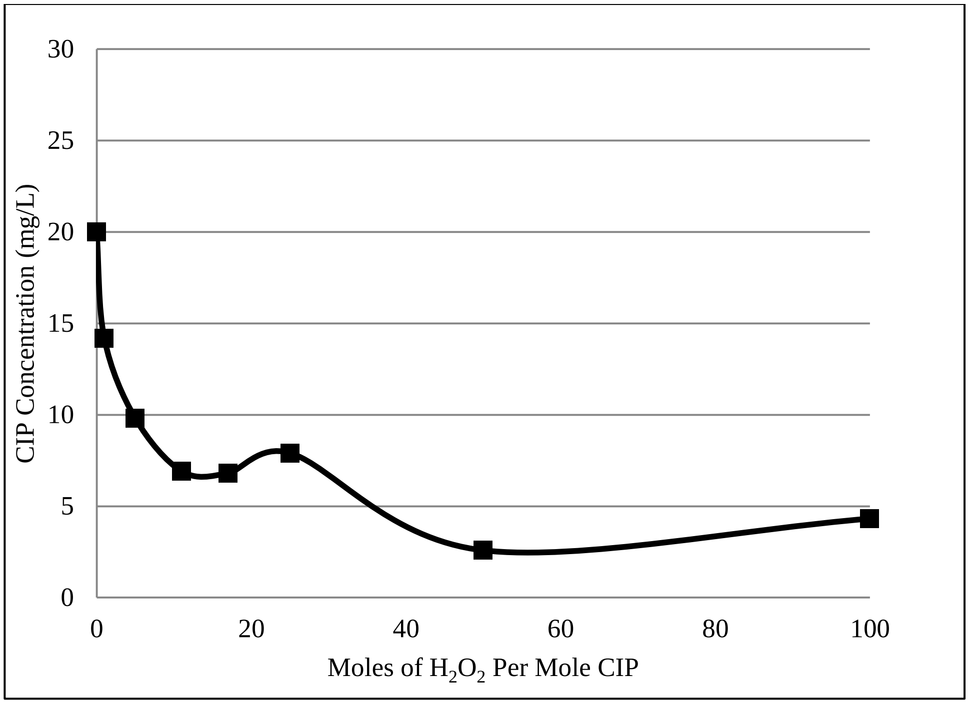


Figure 9: Fenton's Oxidation: Hydrogen Peroxide Concentration and Corresponding CIP Concentration after 24 hours (using 1.4:1 ferrous to CIP)

Using a molar ratio of 1.4:1 Fe (II) to CIP the overall removal extent is decreased. The maximum removal was 87% which was achieved using a 50:1 molar ratio of H_2O_2 to CIP. When comparing a 1.4:1 ratio of Fe (II) to CIP to that of the 5:1 molar ratio, more hydrogen peroxide is required to achieve removal extents greater than 85%. The additional iron serves as a catalyst to more quickly generate hydroxyl radicals which results in greater removal. Again, there is some variability in the results of this study, evident in the slight peak at 25 on the x-axis and the increase at 100 on the x-axis. These fluctuations can likely be attributed to variability in the spectrophotometer readings or in an incomplete removal of the iron precipitate. However, despite the experimental error, the results indicated that using a lower ratio of ferrous iron to as a catalyst had a deleterious effect on the overall removal of CIP from water.

These results are comparable to those achieved in a study conducted by Guo et al. in 2008. Their research showed the photo-Fenton reaction is capable of the total degradation of CIP using a molar ratio of 128:1 H_2O_2 to CIP in 60 minutes. The study also showed that by increasing the amount of ferrous ions in the solution, greater removal was possible. Despite the addition of UV light to enhance the reaction, the results of the study by Guo et al. are comparable to those in this experiment. Both studies achieved a very high removal extent of CIP from water and showed that increases in both the moles of H_2O_2 and Fe(II) increase the removal extent of CIP (Guo et al., 2008).

Furthermore, a study by Chaudhuri and Elmolla in 2009 investigated the ability of Fenton's oxidation to degrade three different antibiotics in water: amoxicillin, ampicillin and cloxacillin. Their results conclude that Fenton's oxidation is capable of complete removal of each antibiotic in two minutes using a molar ratio of 1:3:0.3, antibiotic:H_2O_2:Fe(II). The results of the study by Chaudhuri and Elmolla compare well to those determined in this experiment. Both studies showed that a ratio of 3:1 H_2O_2 to antibiotic is sufficient for near complete removal of the antibiotic. While there are differences in each of the three studies, it is clear that total removal of CIP as well as other antibiotics is possible using Fenton's oxidation (Chaudhuri and Elmolla, 2009).

4.2 Kinetic Time Trials

Time trials were conducted to determine the rate law constants for the reaction between NaOCl and CIP. Three time trials were conducted using 20 mg/L CIP in water with the oxidant NaOCl in a 17:1 molar ratio with CIP. Samples of the solution were analyzed in the UV spectrometer at 1 minute and subsequent regular intervals and the absorbance determined. A concentration was determined for each time interval using the standard curve. The time trial was conducted over 24 hours and the results of CIP concentration verses time are shown below.

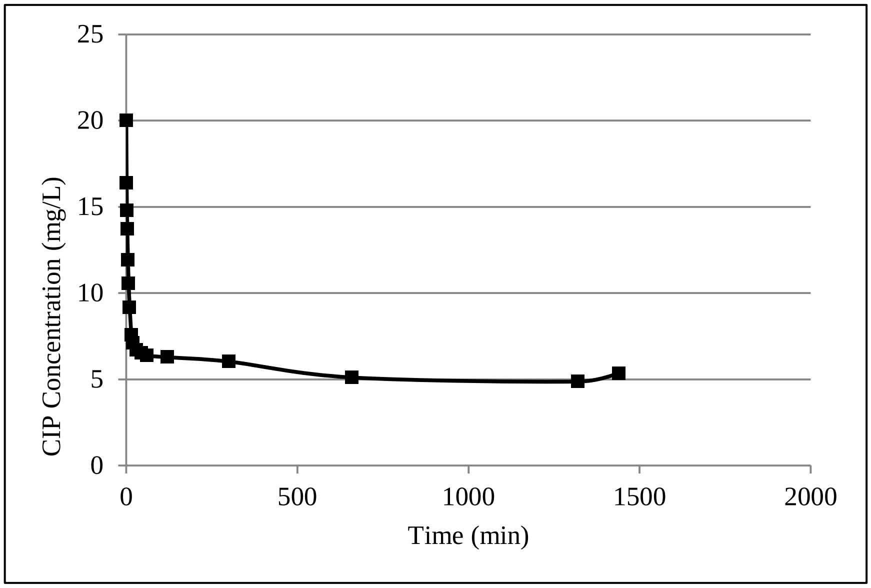


Figure 10: CIP Concentration at Various Treatment Time Intervals with a 17:1 molar ratio of hypochlorite to CIP

While the time trials were conducted over a 24 hour period as seen in figure 10, 90% of the initial CIP was removed within 30 minutes. Shown below is the data collected from the first 30 minutes of the 24 hour time trial which was used to calculate the rate law constants and reaction order.

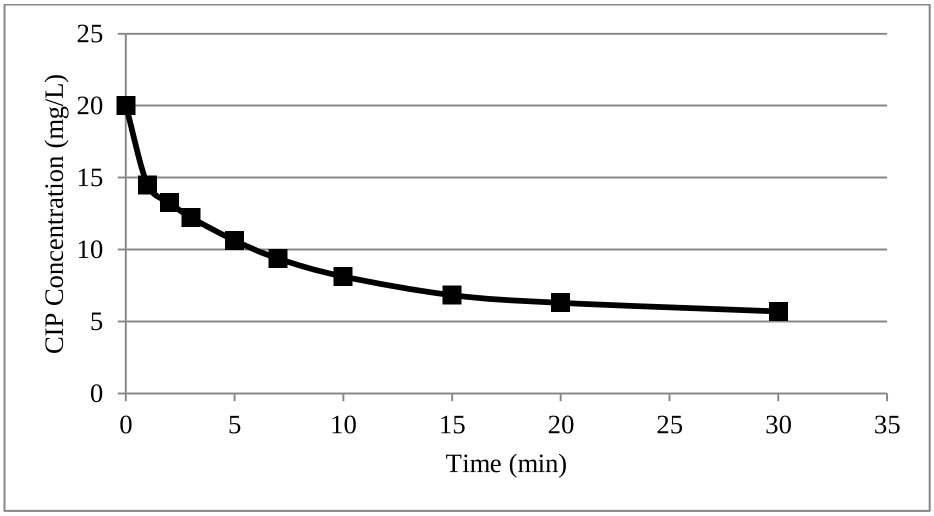


Figure 11: CIP Concentration through first 30 Minutes of Treatment with a 17:1 molar ratio of hypochlorite to CIP

The rate constant for a first order reaction is determined by the concentration of one reactant in solution with a characteristic rate constant as shown in the equation below.

The rate equation was written for a batch process, which was the type of process used to obtain the data in this study.

$$\text{Rate of degradation:} = -\frac{d[A]}{dt} = k[A] \tag{22}$$

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 equation 23:

$$\ln[A] = -kt + \ln[A]_0 \tag{23}$$

In order to determine if the rate was first order, the natural log of the concentration of CIP verses time was plotted, which gave a trend line with a slope of -k. Using first order kinetics, the rate law constant was determined to be 0.0376/min (R^2=0.8183).

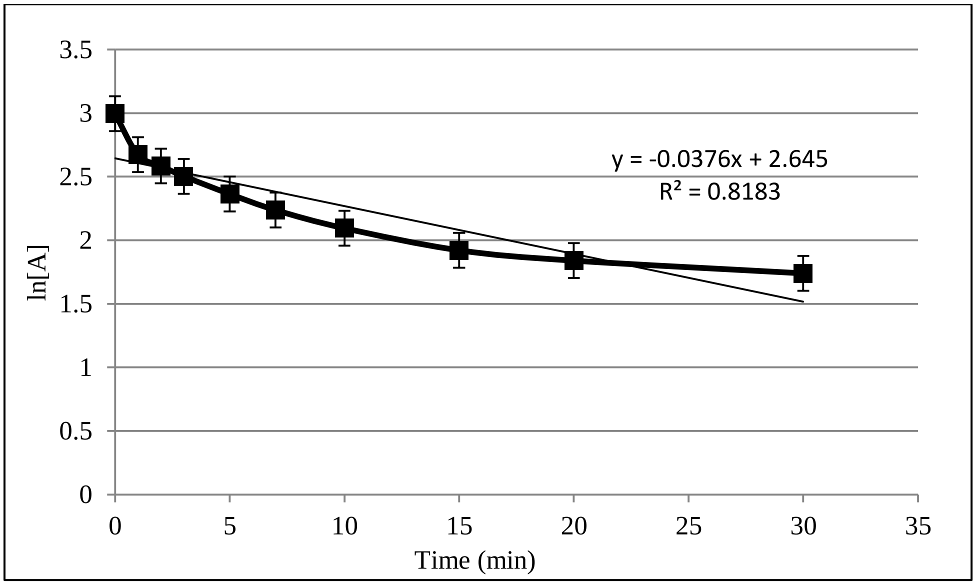


Figure 12: 17:1 ratio first order hypochlorite oxidation kinetics

The linear correlation was not as accurate in predicting the relationship as was expected for the reaction. Most oxidation reactions taking place in water and wastewater treatment can be considered pseudo-first order when the oxidant is present in excess. For this reason, the reaction was also examined as a second order reaction.

A second order rate equation for a batch process is shown below:

$$\text{Rate of degradation:} = -\frac{d[A]}{dt} = k[A][B] \tag{24}$$

The reaction rate is written in terms of both concentration of CIP and hypochlorite; however, it was not possible to measure the changing concentration of hypochlorite. To determine the rate law constant, the inverse of the concentration verses time was plotted with the slope of the trend line equal to k. Using second order kinetics, the rate law constant is equal to 0.0041 (R^2=0.9216) as is shown in figure 13.

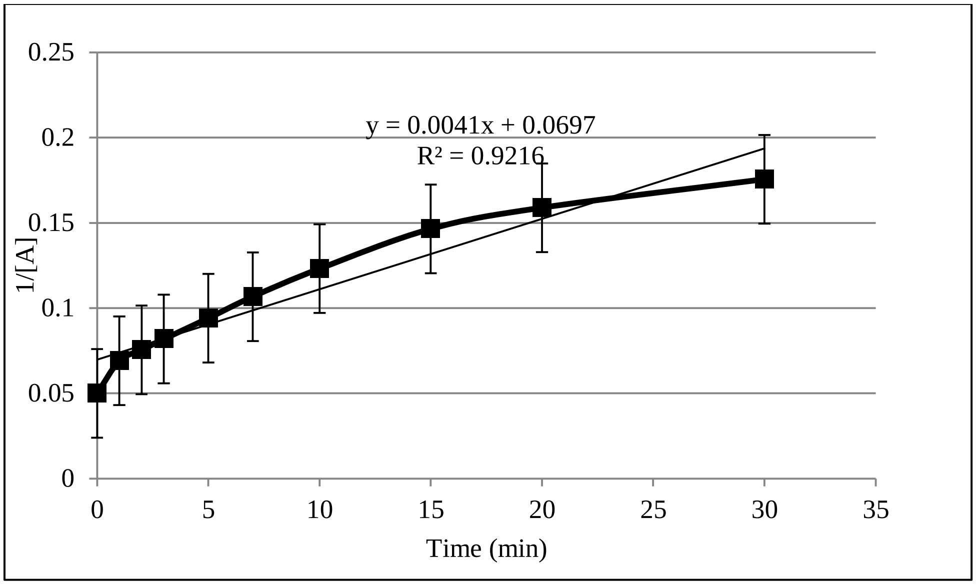


Figure 13: 17:1 ratio second order hypochlorite oxidation kinetics

The results of the kinetics study for a 17:1 molar ratio indicate that the degradation of CIP by hypochlorite more likely occurs by a second order reaction because there is a stronger linear correlation (R^2) using a second order kinetic analysis. Using the rate constants generated from the first and second order kinetics, as well as the rate laws, a model of CIP removal was generated to determine how closely the theoretical predictions match the experimental results. The figure is shown below.

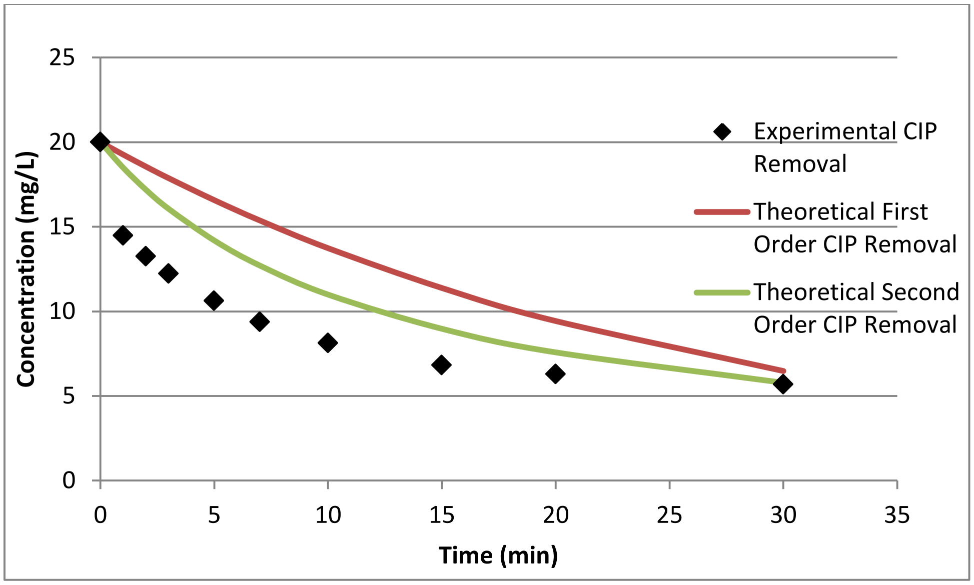


Figure 14: Experimental CIP removal using 17:1 (hypochlorite to CIP) molar ratio compared with theoretical removal based on first and second order rate models

Figure 14 shows that the rate constant determined using second order kinetics better models the experimental data for CIP removal. This was unexpected because, as was previously mentioned, the hypochlorite was added in excess. Generally, when one reactant is present in excess, it is possible to consider the reaction zero order in terms of that reactant, thereby making the reaction a pseudo-first order reaction. However, neither model fits the data with high accuracy. Although the second order model fits more closely to the data, the order of the reaction is still not conclusive.

In order to more conclusively determine whether the reaction is first or second order, time trials were conducted using 5:1 and 100:1 molar ratios of NaOCl to CIP. The overall degradation of CIP was similar for both the 17:1 and 5:1 molar ratios; although the degradation of CIP with a 5:1 molar ratio was slower, not reaching 90% degradation until after 90 minutes of treatment. The results of the time trial can be seen below.

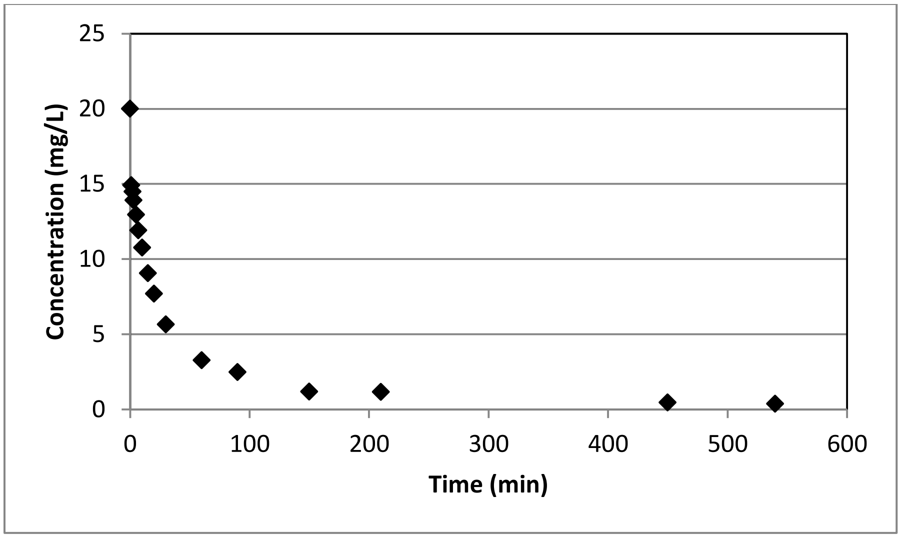


Figure 15: CIP Concentration after various treatment time intervals with a 5:1 molar ratio of hypochlorite to CIP

The kinetic analysis was conducted using the data from the first 90 minutes of the reaction, the time interval which encompassed over 90% of the total oxidation. The results of the 5:1 molar ratio time trial support the results of the 17:1 molar ratio time trial. When plotted, a second order reaction again fits the data more closely, as evidenced by an R^2 value above 0.99. However, both first and second order reactions appear plausible. When comparing the rate constants generated from the 17:1 and 5:1 second order plots, the two values are nearly identical. This gives further support to the likelihood that the reaction is occurring as a second order reaction. The results of both the first and second order kinetic data for a 5:1 ratio can be seen below in figures 16 and 17, respectively.

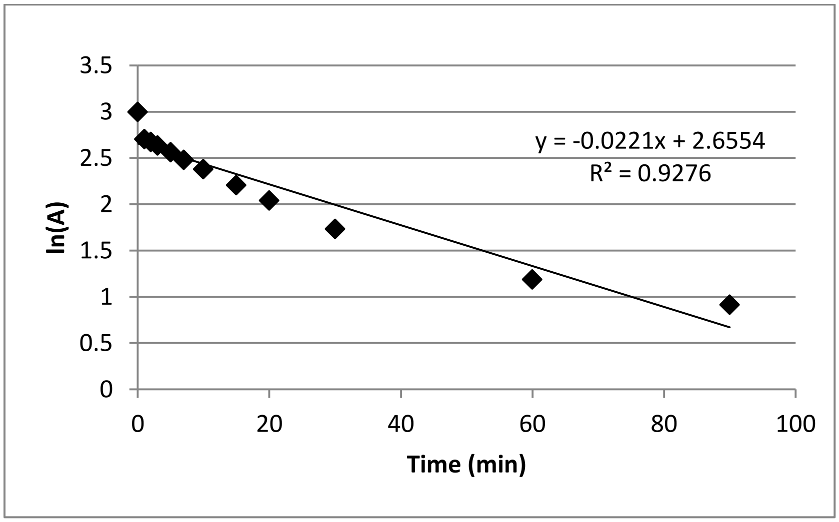


Figure 16: 5:1 ratio first order hypochlorite kinetics

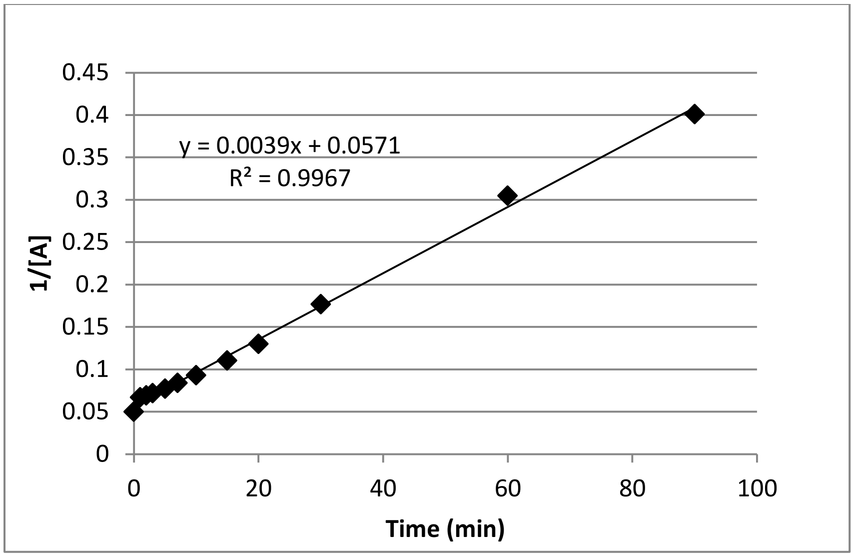


Figure 17: 5:1 ratio second order hypochlorite kinetics.

To more clearly compare the results of the kinetic analysis, the rate constants generated from both the first and second order kinetics and the rate laws were used to plot the theoretical removal of CIP. The results of these theoretical models can be seen in figure 18.

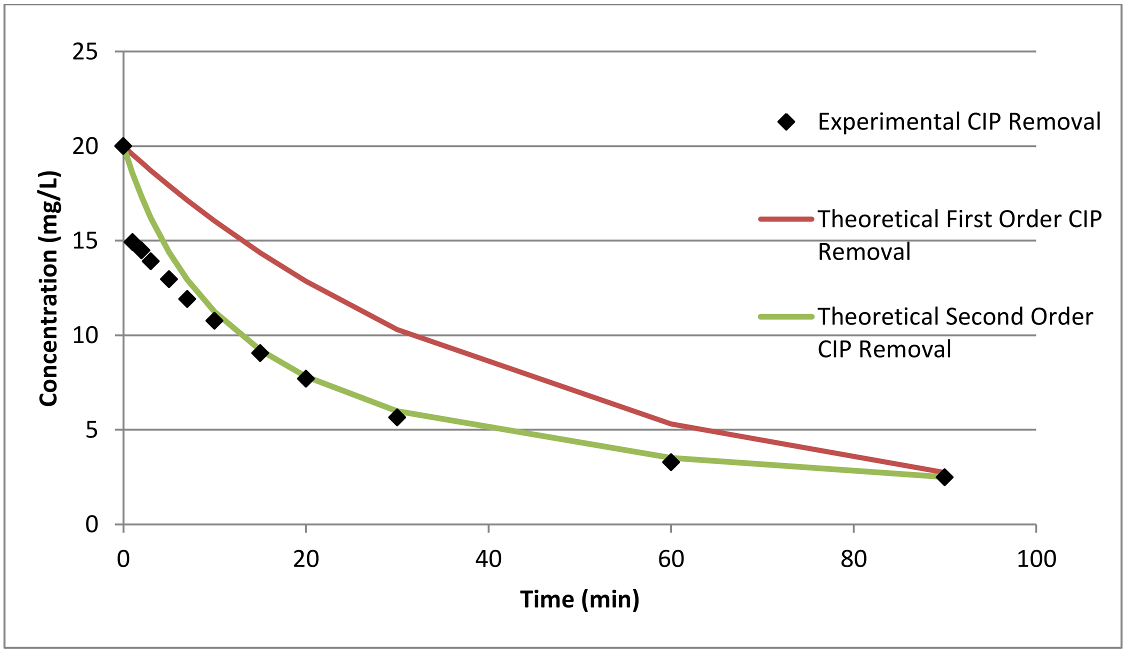


Figure 18: Experimental CIP removal using 5:1 (hypochlorite to CIP) molar ratio compared with theoretical removal based on first and second order rate models

This plot shows graphically how similar the theoretical degradation using a second order rate constant is to the experimental results. The second order kinetics appear to be a very close fit to the observed removal of CIP and generated a more accurate model in both the 17:1 and 5:1 molar ratio experiments.

The 100:1 molar ratio time trial was inconclusive. It appears that the reaction occurred much more quickly than the 17:1 molar ratio, indicating a faster rate. In fact, because the reaction happened so quickly it was not possible to gather enough samples to accurately determine kinetics. The results of the time trial are shown below.

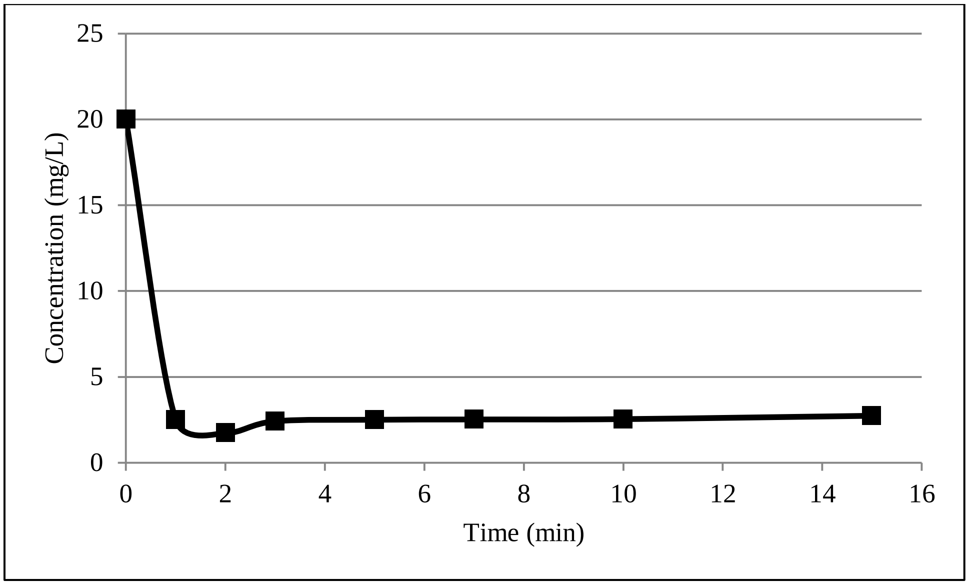


Figure 19: CIP Concentration after various treatment time intervals with a 100:1 molar ratio of hypochlorite to CIP

Overall, it appears that the oxidation of CIP by NaOCl was a second order reaction; however, further studies would need to be conducted to conclusively determine the reaction order and rate constants. Without analyzing the changes in concentration of chlorine throughout the time trial, it is not possible to accurately determine a second order rate law. It is possible that several molecules of NaOCl are required to degrade one molecule of CIP and thus the final concentrations of chlorine and CIP are equal. The preliminary conclusion that the reaction is second order could be further substantiated by studying the change in concentration of both NaOCl and CIP over time.

Time trials were conducted for potassium ferrate, persulfate and Fenton's oxidation using a 17:1 molar ratio of oxidant to CIP. It was not possible to determine a reaction order or rate constant for any of these oxidants because the reactions occurred too quickly. The results of these time trials can be found in Appendix D.

4.3 Comparison of Oxidants

The graph below compares the different oxidation methods and their effectiveness in removing CIP over a 24-hour period. As the plot indicates, all solutions began with 20 mg/L of CIP.

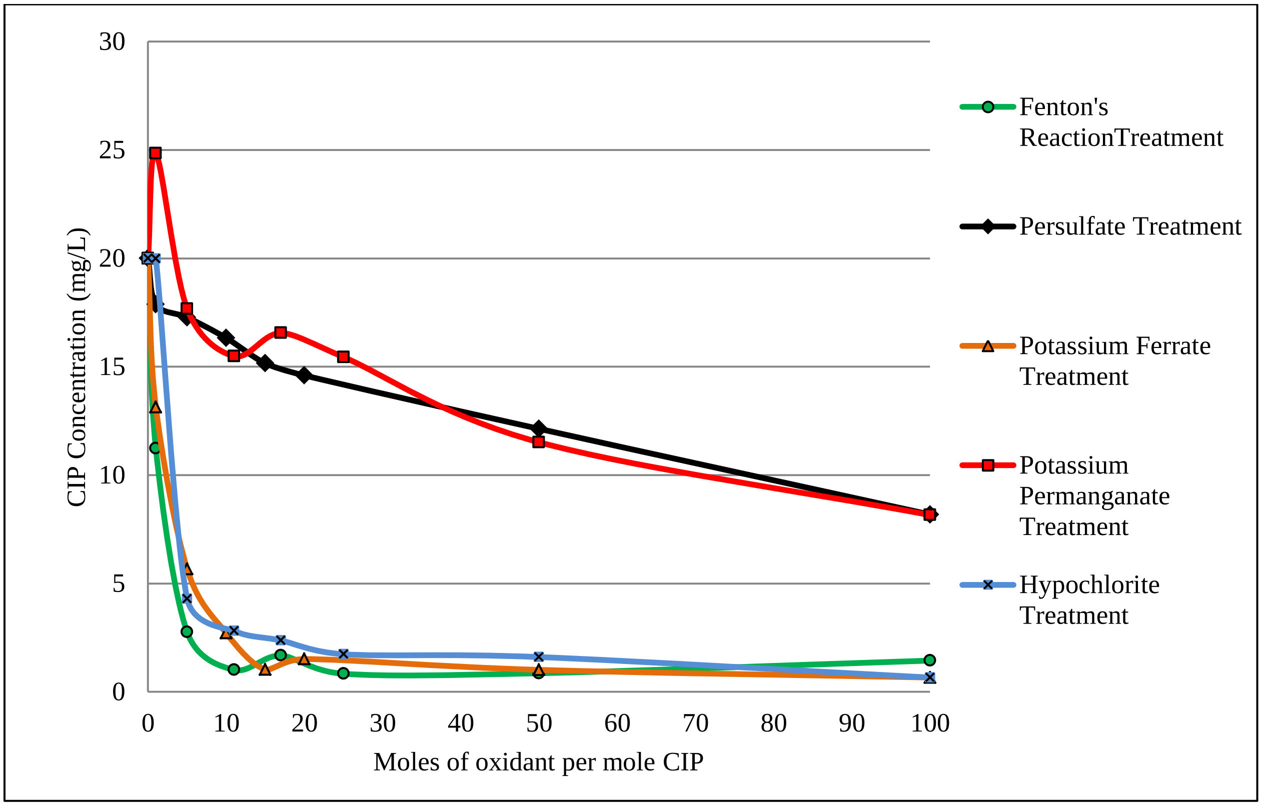


Figure 20: Comparison of CIP concentration after 24 hours of treatment with each oxidant

Ferrous iron, potassium ferrate, and chorine treatment all decreased the concentration of CIP drastically using only a 10:1 molar ratio of oxidant to CIP and all resulted in a final concentration of less than 2 mg/L. Unexpectedly, Fenton's oxidation peaked at a 17:1 molar ratio with a CIP concentration of about 2 mg/L before leveling out at about 1.5 mg/L. Comparatively, potassium ferrate dipped at the same molar ratio before maintaining a constant concentration of CIP of about 1 mg/L. Evident from the plot, the most inconsistent of all the oxidants was potassium permanganate. However, the peak in CIP concentration on the potassium permanganate curve could be a result of experimental or analytical error. The concentration of CIP sharply peaked at a 1:1 molar ratio, decreased and then peaked once more at a 17:1 molar ratio before showing a continued decline. Persulfate was perhaps the most gradual treatment, decreasing in a nearly linear fashion. Use of persulfate and potassium permanganate both reached a final concentration of 8 mg/L. However final CIP concentrations never leveled off, indicating higher molar ratios could produce greater CIP removal.

Chapter 5: Conclusions and Recommendations

All oxidation methods evaluated in this study are potentially successful methods for removing CIP from water; however, some are more effective than others. The treatment of CIP in water using Fenton's oxidation achieved a significant removal extent. Removal of over 90% of the CIP was achieved in 24 hours of treatment using all molar ratios greater than 4:1 hydrogen peroxide to CIP and a 5:1 molar ratio of Fe(II) to CIP. Oxidation using potassium ferrate was also highly successful and achieved over 90% removal over 24 hours of treatment using molar ratios of 17, 25, 50 and 100:1 ferrate to CIP. Some treatment facilities may find potassium ferrate is easier to use because the oxidation requires only one additive instead of the two required for Fenton's oxidation. Both treatment techniques are viable options to use in water treatment facilities to degrade organic contaminants and have applications as a flocculent. However, due to the addition of iron, a settling step is necessary after oxidation to remove the iron precipitate. Chlorine oxidation was also very effective and achieved over 90% removal after 24 hours of treatment using ratios of 25, 50 and 100:1 NaOCl to CIP. Although this oxidation technique required a higher molar ratio, it may be easier to implement chlorine oxidation due to its frequent use in existing water treatment plants.

A study conducted by Roma et al. (2011) investigated the removal of CIP by UV and UV combined with hydrogen peroxide oxidation. All samples for the oxidation experiments in this research project were concealed from any outside sources of UV light to isolate the compound from further degradation. Complete oxidation was achieved after 60 minutes using UV treatment at 254 nm, at which point Roma et al. were able to degrade a CIP solution at pH 7 by 94.6% (Roma et al., 2011). This percentage increased slightly to 97.5% and the residence time decreased to 30 minutes when a 50:1 molar ratio of H_2O_2 to CIP was added. Several oxidants used in this study were able to achieve similar results.

In this work, using a molar ratio of 100:1 NaOCl to CIP, 89% removal was achieved after 10 minutes of treatment and 96.7% was removed after 24 hours. Comparatively, using a 17:1 NaOCl to CIP ratio resulted in 71% removal within 30 minutes and 83% removal within 24 hours. The results of the hypochlorite tests indicate that chlorination is a viable option for use in CIP removal. However, hypochlorite doses greater than 100:1 NaOCl to CIP would be required to achieve similar results to the 50:1 molar ratio UV/H_2O_2 oxidation studied by Roma et al.

Using solutions of 50:1 and 100:1 potassium ferrate to CIP with 24 hours of treatment, removal extents of 94.9% and 97.6% were achieved, respectively. A time trial was conducted using a 17:1 ratio of potassium ferrate to CIP, resulting in the removal of 88% of CIP within ten minutes and 88.6% after 30 minutes, indicating all significant removal occurred within ten minutes. This oxidation technique is comparable to UV/H_2O_2 in both extent of removal and residence time. Similar removal extents (over 90%) are possible using 17:1 and 25:1 molar ratios of potassium ferrate to CIP and 88% oxidation occurs within 30 minutes with a 17:1 molar ratio.

Fenton's oxidation also achieved substantial removal of CIP in water. Several ratios of hydrogen peroxide to CIP, including 5, 11, 25 and 50:1, used with a 5:1 ratio of Fe(II) to CIP, achieved greater than 94% removal. While lower doses of hydrogen peroxide were able to achieve removal extents greater than those observed by Roma et al. using UV/H_2O_2, the process requires increased residence time. Only 44% removal was achieved after 15 min using a 17:1 ratio of H_2O_2 to CIP, whereas after 10 minutes Roma et al. saw 89.6% removal of CIP using UV/H_2O_2.

Further research must be conducted before definitive treatment suggestions can be made. Neither potassium permanganate nor persulfate achieved removal extents greater than 60%; however, further studies could use higher doses of each oxidant to determine if greater removal is achievable. Furthermore, kinetic studies of potassium ferrate and Fenton's oxidation could be conducted using molar ratios which yielded the greatest removal extents in order to compare the corresponding reaction rates, rate constants and required residence times. The comparison of reaction rates and residence times would allow the process efficiencies to be compared and a treatment process to be recommended more definitively.

Before a treatment process is determined or implemented, a more thorough analysis is recommended. It would be useful to study the effect of mixtures of antibiotics in the same solution to test for the selectivity of treatment. An oxidant which requires a higher dosage or residence time but is able to oxidize many compounds may be more useful for a water or wastewater treatment facility. An analysis of the energy and environmental considerations involved with these treatment methods would also supplement the study. Essential parameters to consider would be the removal and disposal of oxidants or byproducts following treatment, further treatment steps required and storage the of chemicals. Finally, a complete economic analysis of each treatment process should be conducted to ensure there is balance between the effectiveness, efficiency and economics in the chosen treatment process.

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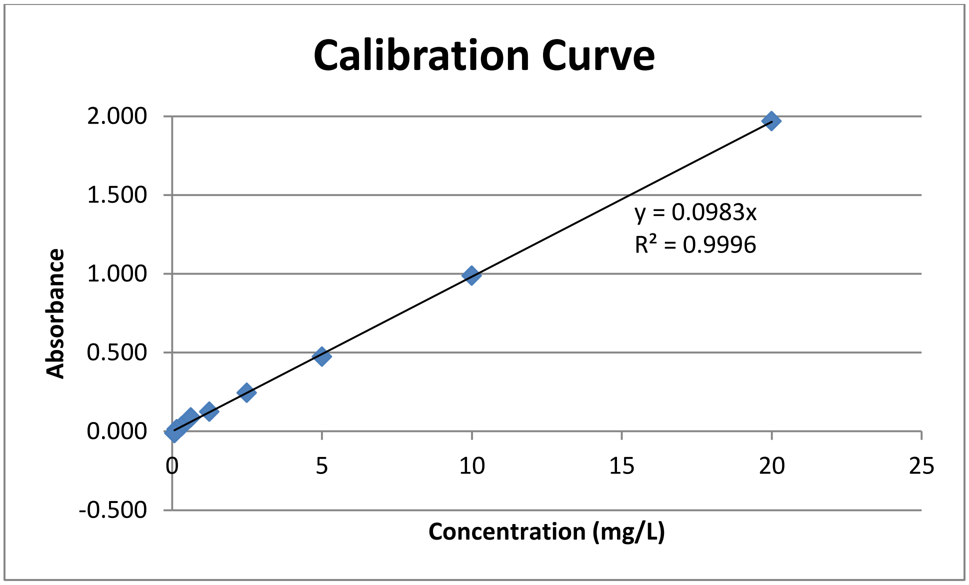
Appendix

Appendix A: Calibration Curve

Measured concentration of CIP (mg/L)	pH	Absorbance
20	7.07	1.968
10	7.02	0.986
5	6.98	0.474
2.5	6.92	0.243
1.25	6.97	0.124
0.625	7.07	0.088
0.313	7.04	0.031
0.156	7.00	0.012
0.078	6.90	-0.013



Appendix B: Raw Data

Chlorine:

Initial Concentration (mg/L)	Cl:CIP Molar Ratio	pH	ABS	Final Concentration (mg/L)	Interference (ABS)	Adjusted Final Concentration (mg/L)	Δ Conc.	% CIP Removed
20	N/A	6.940	1.801	18.321		18.321		
N/A	5 mg/L Cl	7.080	0.162	1.647		1.647		
20	1	6.930	1.986	20.198	0.021	19.988	0.012	0.061
20	5	6.940	0.467	4.755	0.045	4.298	15.702	78.510
20	11	6.940	0.345	3.514	0.069	2.816	17.184	85.921
20	17	6.960	0.336	3.418	0.103	2.374	17.626	88.128
20	25	6.920	0.333	3.386	0.162	1.739	18.261	91.307
20	50	6.980	0.392	3.987	0.234	1.608	18.392	91.958
20	100	6.910	0.461	4.691	0.396	0.662	19.338	96.689

Potassium Permanganate:

Initial Concentration (mg/L)	$KMnO_4$:CIP Molar Ratio	pH	ABS	Final Concentration (mg/L)	Interference (ABS)	Adjusted Final Concentration (mg/L)	Δ Conc.	% CIP Removed
20	N/A	7.040	1.707	17.362		17.362		
N/A	5 mg/L Cl	7.040	0.971	9.881		9.881		
20	1	6.920	2.528	25.718	0.086	24.842	-4.842	-24.212
20	5	6.970	2.007	20.412	0.269	17.677	2.323	11.617
20	11	7.060	2.020	20.547	0.497	15.490	4.510	22.548
20	17	6.940	2.599	26.439	0.971	16.558	3.442	17.208
20	25	7.050	2.490	25.330	0.971	15.449	4.551	22.757
20	50	6.930	2.575	26.196	1.443	11.519	8.481	42.406
20	100	7.080	2.861	29.107	2.059	8.161	11.839	59.196

Potassium Ferrate:

Initial Concentration (mg/L)	Ferrate:CIP Molar Ratio	pH	ABS	Final Concentration (mg/L)	Interference (ABS)	Adjusted Final Concentration (mg/L)	Δ Conc.	% CIP Removed
20	N/A	7.050	1.775	17.064		17.064		
N/A	5 mg/L Cl	6.930	0.177	0.615		0.615		
20	1	7.090	1.354	13.772	0.063	13.133	6.867	34.334
20	5	6.930	0.615	6.258	0.058	5.669	14.331	71.653
20	11	6.930	0.319	3.246	0.052	2.713	17.287	86.434
20	17	7.080	0.162	1.646	0.061	1.031	18.969	94.847
20	25	7.060	0.221	2.252	0.073	1.515	18.485	92.426
20	50	7.100	0.159	1.621	0.059	1.017	18.983	94.914
20	100	6.930	0.139	1.410	0.073	0.664	19.336	96.679

Persulfate:

Initial Concentration (mg/L)	Persulfate:CIP Molar Ratio	pH	ABS	Final Concentration (mg/L)	Interference (ABS)	Adjusted Final Concentration (mg/L)	Δ Conc.	% CIP Removed
20	N/A	7.030	1.855	18.120		17.064		
N/A	5 mg/L Cl	6.900	0.056	0.659		0.615		
20	1	6.950	1.789	18.195	0.031	17.879	2.121	10.605
20	5	6.960	1.763	17.933	0.064	17.279	2.721	13.606
20	11	7.010	1.623	16.514	0.018	16.328	3.672	18.362
20	17	6.950	1.545	15.721	0.056	15.157	4.843	24.217
20	25	7.050	1.491	15.165	0.056	14.600	5.400	26.999
20	50	6.940	1.229	12.498	0.035	12.138	7.862	39.308
20	100	7.100	0.859	8.738	0.054	8.185	11.815	59.074

Fenton’s Oxidation:

Using a 5:1 molar ratio of ferrous oxide:CIP

Initial Concentration (mg/L)	H_2O_2:CIP Molar Ratio	pH	ABS	Final Concentration (mg/L)	Interference (ABS)	Adjusted Final Concentration (mg/L)	Δ Conc.	% CIP Removed
20	No H_2O_2 or ferrous	7.070	1.855	18.874		18.874		
20	5 mg/L H_2O_2 (no ferrous)	7.070	1.769	17.992		17.992		
N/A	5 mg/L H_2O_2 w/ ferrous	7.050	1.770	18.006		18.006		
20	1	6.950	1.104	11.229	1.615	-5.204	8.771	43.856
20	2	7.010	0.152	1.548	N/A	N/A	18.452	92.258
20	3	7.030	0.159	1.620	N/A	N/A	18.380	91.902
20	4	6.990	0.158	1.604	N/A	N/A	18.396	91.979
20	5	6.910	0.115	1.174	1.711	-16.233	18.826	94.130
20	11	6.970	0.100	1.018	1.770	-16.988	18.982	94.908
20	17	6.940	0.165	1.678	1.805	-16.683	18.322	91.612
20	25	7.080	0.082	0.838	0.068	0.149	19.162	95.809
20	50	6.950	0.085	0.862	1.797	-17.420	19.138	95.692
20	100	6.970	0.142	1.445	0.088	0.546	18.555	92.777

Using a 1.4:1 molar ratio of ferrous oxide:CIP

Initial Concentration (mg/L)	H_2O_2:CIP Molar Ratio	pH	ABS	Final Concentration (mg/L)	Interference (ABS)	Adjusted Final Concentration (mg/L)	Δ Conc.	% CIP Removed
20	No H_2O_2 or ferrous	7.070	1.855	18.874		18.874		
20	5 mg/L H_2O_2 (no ferrous)	7.070	1.769	17.992		17.992		
N/A	5 mg/L H_2O_2 w/ ferrous	7.050	0.145	1.475		1.475		
20	1	7.070	1.393	14.167	0.191	12.224	5.833	29.166
20	5	6.960	0.964	9.810	0.177	8.007	10.190	50.951
20	11	7.040	0.680	6.915	0.145	5.439	13.085	65.427
20	17	7.020	0.669	6.803	0.183	4.945	13.197	65.987
20	25	7.070	0.778	7.910	0.166	6.226	12.090	60.448
20	50	7.040	0.254	2.586	0.141	1.155	17.414	87.070
20	100	7.030	0.425	4.321	0.213	2.156	15.679	78.393

Appendix C: Ratio Comparisons

1:1 Ratio		
Oxidant	**Concentration of CIP After 24 Hours**	**Extent of Removal of CIP (%)**
Hypochlorite	19.99	0.061
Potassium Permanganate	24.84	-24.2
Sodium Ferrate	13.13	34.3
Persulfate	17.88	10.6
Fenton’s Oxidation	12.22	38.9

5:1 Ratio		
Oxidant	**Concentration of CIP After 24 Hours**	**Extent of Removal of CIP (%)**
Hypochlorite	4.3	78.5
Potassium Permanganate	17.68	11.6
Sodium Ferrate	5.67	71.7
Persulfate	17.28	13.6
Fenton’s Oxidation	8	60

11:1 Ratio		
Oxidant	**Concentration of CIP After 24 Hours**	**Extent of Removal of CIP (%)**
Hypochlorite	2.374	88.1
Potassium Permanganate	16.55	17.2
Sodium Ferrate	1.031	94.8
Persulfate	15.16	24.2
Fenton’s Oxidation	4.945	75.3

17:1 Ratio		
Oxidant	**Concentration of CIP After 24 Hours**	**Extent of Removal of CIP (%)**
Hypochlorite	2.816	85.9
Potassium Permanganate	15.49	22.6
Sodium Ferrate	2.713	86.4
Persulfate	16.33	18.4
Fenton’s Oxidation	5.439	72.8

25:1 Ratio		
Oxidant	**Concentration of CIP After 24 Hours**	**Extent of Removal of CIP (%)**
Hypochlorite	1.739	91.3
Potassium Permanganate	15.44	22.8
Sodium Ferrate	1.515	92.4
Persulfate	14.6	27
Fenton’s Oxidation	6.226	68.9

50:1 Ratio		
Oxidant	**Concentration of CIP After 24 Hours**	**Extent of Removal of CIP (%)**
Hypochlorite	1.608	92
Potassium Permanganate	11.51	42.4
Sodium Ferrate	1.016	94.9
Persulfate	12.14	39.3
Fenton’s Oxidation	1.155	94.2

100:1 Ratio		
Oxidant	**Concentration of CIP After 24 Hours**	**Extent of Removal of CIP (%)**
Hypochlorite	0.6623	96.7
Potassium Permanganate	8.161	59.2
Sodium Ferrate	0.6642	96.7
Persulfate	8.185	59.1
Fenton’s Oxidation	2.156	89.2

Appendix D: Time Trials

5:1 Chlorine:CIP

Time (minutes)	ABS	Conc. (mg/L)	Adjusted Conc. (mg/L)	ln(A)	1/A
0		20	20	2.996	0.050
1	1.863	18.951	14.923	2.703	0.067
2	1.820	18.514	14.485	2.673	0.069
3	1.764	17.948	13.920	2.633	0.072
5	1.670	16.991	12.962	2.562	0.077
7	1.568	15.949	11.921	2.478	0.084
10	1.455	14.798	10.769	2.377	0.093
15	1.287	13.092	9.063	2.204	0.110
20	1.153	11.730	7.702	2.042	0.130
30	0.952	9.687	5.658	1.733	0.177
60	0.719	7.309	3.281	1.188	0.305
90	0.641	6.522	2.493	0.914	0.401
150	0.514	5.228	1.199	0.182	0.834
210	0.510	5.192	1.164	0.152	0.859
450	0.442	4.493	0.465	-0.766	2.151
540	0.434	4.416	0.388	-0.948	2.580

17: 1 Chlorine:CIP—Trial 1

Time (minutes)	ABS	Conc. (mg/L)	Adjusted Conc. (mg/L)	ln (A)	1/A
0		20	20	2.99573	0.05
1	1.613	16.405	15.361	2.732	0.065
2	1.456	14.808	13.764	2.622	0.073
3	1.350	13.728	12.685	2.540	0.079
5	1.170	11.899	10.856	2.385	0.092
7	1.038	10.559	9.515	2.253	0.105
10	0.902	9.174	8.130	2.096	0.123
15	0.745	7.578	6.534	1.877	0.153
20	0.698	7.101	6.057	1.801	0.165
30	0.658	6.689	5.645	1.731	0.177
45	0.641	6.521	5.477	1.701	0.183
60	0.627	6.376	5.333	1.674	0.188
120	0.618	6.284	5.240	1.656	0.191
300	0.593	6.032	4.988	1.607	0.200
660	0.502	5.109	4.065	1.402	0.246
1320	0.479	4.874	3.830	1.343	0.261

17:1 Chlorine:CIP—Trial 2

Time (minutes)	ABS	Conc. (mg/L)	Adjusted Conc. (mg/L)	ln (A)	1/A
0		20	20	2.99573	0.05
1	1.437	14.621	13.577	2.608	0.068
2	1.349	13.723	12.680	2.540	0.073
3	1.220	12.406	11.362	2.430	0.081
5	1.074	10.923	9.879	2.290	0.092
7	0.954	9.704	8.660	2.159	0.103
10	0.838	8.523	7.479	2.012	0.117
15	0.736	7.489	6.446	1.863	0.134
20	0.689	7.012	5.968	1.786	0.143
30	0.652	6.633	5.589	1.721	0.151
80	0.603	6.130	5.086	1.627	0.163
180	0.535	5.444	4.400	1.482	0.184
280	0.494	5.022	3.979	1.381	0.199
320	0.493	5.019	3.976	1.380	0.199
440	0.430	4.374	3.331	1.203	0.229
560	0.454	4.615	3.572	1.273	0.217
680	0.438	4.453	3.409	1.226	0.225
1320	0.437	4.440	3.397	1.223	0.225
1440	0.462	4.697	3.653	1.296	0.213

17:1 Chlorine:CIP—Trial 3

Time (minutes)	ABS	Conc. (mg/L)	Adjusted Conc. (mg/L)	ln (A)	1/A
0		20	20	2.99573	0.05
1	1.530	15.566	14.522	2.676	0.064
2	1.413	14.371	13.328	2.590	0.070
3	1.343	13.666	12.623	2.535	0.073
5	1.199	12.201	11.158	2.412	0.082
7	1.079	10.977	9.933	2.296	0.091
10	0.964	9.805	8.761	2.170	0.102
15	0.840	8.549	7.506	2.016	0.117
20	0.777	7.899	6.856	1.925	0.127
30	0.678	6.895	5.851	1.767	0.145
60	0.630	6.408	5.364	1.680	0.156
90	0.631	6.423	5.379	1.683	0.156
120	0.587	5.968	4.925	1.594	0.168
210	0.562	5.718	4.674	1.542	0.175
330	0.497	5.057	4.013	1.390	0.198
750	0.458	4.658	3.614	1.285	0.215
1350	0.426	4.338	3.294	1.192	0.231
1440	0.377	3.837	2.793	1.027	0.261
1485	0.419	4.261	3.218	1.169	0.235

100:1 Chlorine:CIP

Time (minutes)	ABS	Conc. (mg/L)	Adjusted Conc. (mg/L)	ln (A)	1/A
0		20	20	2.99573	0.05
1	0.608	6.185	2.157	0.769	0.464
2	0.458	4.663	0.635	-0.455	1.575
3	0.593	6.033	2.004	0.695	0.499
5	0.601	6.118	2.090	0.737	0.479
7	0.603	6.136	2.108	0.746	0.474
10	0.612	6.224	2.195	0.786	0.456
15	0.646	6.571	2.542	0.933	0.393

17:1 Persulfate:CIP—Trial 1

Time (minutes)	ABS	Conc. (mg/L)
0		20
1	1.598	16.255
2	1.656	16.847
3	1.648	16.762
5	1.613	16.405
7	1.619	16.474
10	1.618	16.457
15	1.602	16.292
20	1.606	16.337
30	1.585	16.122
60	1.583	16.102
100	1.598	16.254
190	1.610	16.375
310	1.617	16.454
730	1.678	17.073
1270	1.740	17.697

17:1 Persulfate:CIP—Trial 2

Time (minutes)	ABS	Conc. (mg/L)
0		20
1	1.631	16.594
2	1.647	16.752
3	1.635	16.635
5	1.639	16.670
7	1.648	16.767
10	1.627	16.553
15	1.632	16.605
20	1.615	16.431
30	1.532	15.585
50	1.629	16.570
90	1.633	16.613
180	1.664	16.925
300	1.719	17.487
720	2.067	21.030
1260	2.806	28.545

17:1 Potassium Ferrate:CIP—Trial 1

Time (minutes)	ABS	Conc. (mg/L)
0		20
2	1.818	18.493
3	1.579	16.061
4	1.192	12.128
6	0.273	2.772
9	0.247	2.512
10	0.236	2.398
12	0.227	2.312
15	0.232	2.360
17	0.234	2.384
20	0.221	2.251
30	0.224	2.279

17:1 Potassium Ferrate:CIP—Trial 2

Time (minutes)	**ABS**	**Conc. (mg/L)**
0		20
2	0.202	2.055
3	0.215	2.184
5	0.186	1.891
15	0.362	3.683
20	0.274	2.789
30	0.276	2.803

17:1 Potassium Ferrate:CIP—Trial 3

Time (minutes)	**ABS**	**Conc. (mg/L)**
0		20
12	0.243	2.475
25	0.244	2.485

17:1 H_2O_2:CIP—Trial 1 (Filtered)

Time (minutes)	**ABS**	**Conc. (mg/L)**
0		20
1	0.708	7.203
2	0.875	8.899
3	0.698	7.103
5	0.799	8.128
7	0.842	8.565
10	0.728	7.407
15	0.705	7.169

17:1 H_2O_2:CIP—Trial 2 (Centrifuged)

Time (minutes)	**ABS**	**Conc. (mg/L)**
0		20
7	1.086	11.045
10	1.059	10.777
13	1.066	10.839
15	1.058	10.759