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Application of Iron Activated Persulfate for Disinfection in Water Treatment

A Thesis submitted in partial satisfaction
of the requirements for the degree of

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by

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Dedication

I dedicate this to my son, Nathan Dawit. After having you, life becomes about living beyond myself; about being bigger and better.

ABSTRACT OF THE THESIS

Application of Iron Activated Persulfate for Disinfection in Water Treatment

by

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Master of Science, Graduate Program in Chemical and Environmental Engineering
University of California, Riverside, August 2014
Dr. Haizhou Liu, Chairperson

Disinfection is the final step in wastewater treatment processes that plays a vital role in protecting water resources from pathogenic microorganisms. Currently chlorine is the most widely used disinfectant. However, the generation of the disinfection byproducts (DBPs) is a big concern. Ultraviolet (UV) disinfection systems have also been adopted for wastewater treatment due to advantages over chlorination including reducing DBP formation, no odor, and shorter contact time. Alternatively, ozone is used as a more effective disinfectant than chlorine in destroying bacteria and viruses, but there is also concern on DBP formation such as bromate. In recent years, there is a growing interest in the application of other strong but short-lived chemical oxidants as disinfectants such as hydroxyl radical ($HO^{\bullet}$). These highly oxidative radical species have been employed for water reuse applications to destruct chemically recalcitrant micro-pollutants.

This research was conducted to develop an alternative disinfection technology that has less DBP formation concerns and is economically feasible. Specifically, the disinfection efficacy of sulfate radical ($SO_4^{\bullet-}$) was investigated. $SO_4^{\bullet-}$ is a very strong oxidant and generated from persulfate ($S_2O_8^{2-}$) by using ferrous iron (Fe^{2+}) as an activator.

This study is focused on the efficacy of $SO_4^{\bullet-}$ in promoting *E. coli* die-off rate as a function of exposure time. Hydroxylamine, a common reducing agent was introduced in the persulfate/iron system to prevent the rapid oxidation of Fe^{2+} to Fe^{3+} and accelerate the generation of $SO_4^{\bullet-}$. It is found that $SO_4^{\bullet-}$ gave a high bacteria log removal in three hours. The disinfection kinetics of $SO_4^{\bullet-}$ has a very short induction time, which is an advantage over other radical species such as $HO^{\bullet}$. The introduction of hydroxylamine enhanced the efficacy of persulfate disinfection by one natural log removal. In addition, higher dosage of persulfate and ferrous ion led to an enhanced $SO_4^{\bullet-}$ generation and an increasing bacteria viability loss.

This system can be implemented as alternative disinfection mechanism for both wastewater and drinking water applications in the future. The final byproduct of this system, which is mostly sulfate, is not toxic to the environment and human beings. The main drawback of this technology was formation of sludge from the oxidized Fe^{2+}. However, the application of hydroxylamine will ease the problem for large scale wastewater treatment applications.

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1- Introduction

1.1 Disinfection in water treatment

Disinfection is a crucial step in water treatment processes as it destructs pathogenic micro-organisms [1,2]. According to the United Nations Millennium development goal report, access to safe drinking water has improved over the last decades in almost every part of the world, but approximately one billion people still lack access of safe water and over 2.5 billion lack access to adequate sanitation [3]. A water system contaminated with pathogenic microorganisms from wastewater will have severe repercussions and more importantly, it will jeopardize public health [4]. A wide variety of disinfection technologies have been developed to prevent the situation and provide safe water to the public. Generally disinfection technology is designed based on a number of factors. An ideal disinfectant is the one that should be available in large quantities and economically feasible. It should also be effective at ambient temperature and different pH conditions. An effective disinfectant should be toxic to microorganisms and non-toxic to humans and other animals [1-6].

1.2 Typical disinfectants in water treatment

Typical disinfectants in wastewater treatment includes chlorine (Cl_2), chlorine dioxide (ClO_2), chloramine (NH_2Cl), ozone (O_3) and UV. Chlorine is the most widely used disinfectant of pathogenic microorganism in water and wastewater. It destroys target organisms by oxidation of cellular materials [5]. Chlorine can be applied as chlorine gas, hypochlorite solutions, and other chlorine compounds in solid or liquid form [1, 5,6].

However, its reaction with organic constituents in wastewater will produce toxic disinfection byproducts (DBPs) [7], which is a major drawback. Residual chlorine in treated wastewater effluent is also toxic to aquatic life [8]. Because of an increasing concern over these undesirable byproducts, alternative disinfection technologies have to be developed.

Ozone is an alternative effective disinfectant because of its high redox potential. For example, it has been applied for capability of odor control and removal of soluble refractory organics [7] in advanced wastewater treatment, in lieu of carbon adsorption processes. Ozone is effective in disinfecting pathogens in drinking water [1,6,7,9], but at low dosage, it may not effectively inactivate viruses, bacteria and spores [10]. A supplementary benefit of using ozone for disinfection is the elevated dissolved O_2 concentration after application, which may omit the need for re-aeration of the effluent to meet required dissolved oxygen water-quality standards [11]. However, ozone is extremely irritating and possibly toxic, so off-gases from the contactor must be destroyed in order to prevent worker exposure [12 -13].

UV is another disinfection method which is highly effective against a wide variety of pathogens, including chlorine-resistant organisms such as cryptosporidium and giardia [14] and less concerns on DBP formation [15]. UV disinfection has a shorter contact time compared to chlorine and ozone (approximately 20 to 30 seconds with low pressure lamp) [1, 15]. Apart from these promising features of using UV for disinfection, its relative high cost of operation and power consumption is a big hindrance.

Chloramine is most commonly used as a secondary disinfectant to provide residual protection as the water travels from the treatment plant to consumers in the distribution system. Chloramine (NH_2Cl) is formed by the reaction of free chlorine with ammonia in a process called chloramination (equation 1) [16].

$$HOCl + NH_3 \rightarrow NH_2Cl + H_2 \quad (1)$$

NH_2Cl is effective in killing bacteria, viruses and cryptosporidium. However, it takes much longer time to act than chlorine [17]. The reaction of NH_2Cl with natural organic matter (NOM) present in water to form potentially harmful DBPs is another drawback, but the DBP formation potential from chloramine is much less compared to chlorine [18].

Chlorine dioxide (ClO_2) is a disinfectant as effective as chlorine against bacteria, viruses and fungi, and more effective than chlorine for the inactivation of giardia and cryptosporidium [19]. One advantage of using ClO_2 for disinfection is, it produce fewer halogenated byproducts than chlorine [20]. The dosage of ClO_2 is limited by the formation of toxic chlorite (ClO_2^-) and chlorate (ClO_3^-) byproducts [6,21]. ClO_2 is less stable than other chlorine species [1, 10,20,22]. The advantages and disadvantages of the typical disinfectants in water treatment are summarized in table 1.1.

Table 1.1 Comparison of most commonly used disinfectants in water treatment. Advantages and disadvantages [1,5,7,15,15,19,22]

Disinfectant	Chlorine	Chlorine dioxide	Ozone	UV
Advantages	• Effective and well established disinfection technology. • Chlorine residual can be monitored and maintained. • Oxidizes sulfides. • Reliable and effective against a wide spectrum of microorganism. • Relatively inexpensive.	• Effective disinfectant • No effect of pH on disinfection ability unlike chlorine. • oxidize sulfides. • provide residuals. • More effective than chlorine in inactivating most viruses and spores.	• More effective than chlorine in destroying viruses and bacteria. • requires short contact time. • No harmful residuals need to be removed after ozonation. • oxidize sulfides.	• Most effective in disinfecting bacteria and viruses. • No residual toxicity • Improved safety than chemical disinfectants. • requires very little contact time.
Disadvantages	•Hazardous and toxic DPBs • requires a relatively long contact time • Storage, shipping and handling pose safety risks. • Certain types of microorganism have shown resistance to low dose chlorine. • Chloride content of the wastewater is increased.	• Decomposes in sunlight •Unstable, must be produced onsite. • Can lead to formation of odors. • Oxidizes a variety of organic compounds • TDS level of effluent is increased.	•ozone is extremely irritating and possibly toxic. • No residual effect. • Relatively expensive and energy intensive. • Safety concern • Less effective at low dosage. • Off-gas requires treatment.	•No disinfection residual • Energy intensive. • No immediate measure to determine disinfection efficacy. • Hydraulic design of UV system required. • No standardize mechanism measures, calibrates or certifies how well equipment woks before and after disinfection.

1.2 Alternative disinfectants

The idea of developing an alternative disinfection technology is getting attention nowadays in order to minimize the risk of toxic DPB formation and maintain high disinfection efficacy of pathogens compared to traditional disinfectants. In recent year, the application of short-lived radical species in disinfection has gained attention due to their high redox potential and high reactivity. This section discusses the application of hydroxyl radical ($HO^{\bullet}$) and sulfate radical ($SO_4^{\bullet-}$) as alternative disinfectants and the chemical reactions associated with them, respectively.

1.2.1 Chemistry of $HO^{\bullet}$ and $SO_4^{\bullet-}$

Hydroxyl radical ($HO^{\bullet}$) is the most commonly used reactive oxidant for *in situ* chemical oxidation (ISCO) due to its high efficiency of mineralizing organic pollutants [23]. $HO^{\bullet}$ is a very strong oxidant with a redox potential of 1.8-2.7 V [23,31,32,33]. Direct photolysis of hydrogen peroxide (H_2O_2) produces $HO^{\bullet}$ [24]. However, $HO^{\bullet}$ formation in this process is relatively slow because H_2O_2 feebly absorbs solar radiation. Previous studies have shown that the Fenton system (Fe^{2+}/H_2O_2) effectively generates $HO^{\bullet}$ and can oxidize a wide variety of organic pollutants [25]. However, Fenton system has some innate drawbacks that limit its wide spread application, such as the accumulation of ferric oxide sludge caused by the rapid oxidation of Fe^{2+} into Fe^{3+} (equation 2), which causes a slowdown of oxidation rates and requires a separation step [23].

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + HO^{\bullet} \quad (2)$$

Hydroxyl radical is unstable in the subsurface with very short half-life [26]. Previous studies [27] have demonstrated the efficacy of UV/H_2O_2 system for disinfection of *E. coli* bacteria. In this study, disinfection of bacteria cells using the Fenton system was conducted to compare and contrast with iron activated persulfate system. The Fenton system showed a higher induction time (70-90 minutes) for 3-log removal of cells. On the other hand, it takes only 20-30 minutes to observe the effect of sulfate radical on bacteria cell die off-rates. The major drawback of the Fenton system was the accumulation and precipitation of Fe^{3+}, which could further diminish the reaction rate and narrow optimal pH range. This issue can be alleviated by introducing hydroxylamine (NH_2OH) into the system and regenerating Fe^{2+} from Fe^{3+} (equation 3).

$$Fe^{3+} + NH_2OH \rightarrow Fe^{2+} + NH_2O^{\bullet} + H^+ \quad (k_3 = 1 \times 10^{-6} M^{-1} S^{-1})\ [28] \qquad (3)$$

1.2.2 Sulfate radical chemistry

Persulfate is one of the strongest oxidants and has the higher oxidation potential of 2.12 V than the hydrogen peroxide anion H_2O_2 (E^o = 1.76V) [29]. Persulfate react directly with many organic contaminants by exchanging electrons in a process known as direct oxidation (equation 3) [30].

$$S_2O_8^{2-} + 2e^- \rightarrow 2SO_4^{2-} \qquad (4)$$

However, reactions of persulfate with organic pollutants (with bacteria in this study) are generally slow at ambient temperature, and activation of persulfate is necessary to accelerate the process to generate a very oxidative radical species, sulfate free radical ($SO_4^{\bullet-}$). The sulfate radical is a stronger oxidant with a redox potential of 2.6 V. Persulfate

can be activated by heat (equation 5), UV light and transition metals including Fe^{2+}, Mn^{2+}, Co^{2+}, Ag^{1+}, Ce^{2+}, Ni^{2+} and V^{3+} (equation 6) [39].

$$S_2O_8^{2-} + heat\ /UV \rightarrow 2SO_4^{\bullet-} \quad [31] \tag{5}$$

$$S_2O_8^{2-} + Me^{n+} \rightarrow SO_4^{\bullet-} + Me^{(n+1)} + 2SO_4^{2-} \quad [37] \tag{6}$$

Ferrous iron (Fe^{2+}) is selected for persulfate activation in this study due to its non-toxic nature, cost effectiveness and high reactivity. When mixed with persulfate, Fe^{2+} donates electrons and initiates the generation of $SO_4^{\bullet-}$ through a series of chain reactions [37].

$$Fe^{2+} + S_2O_8^{2-} \rightarrow Fe^{3+} + SO_4^{\bullet-} + SO_4^{2-} \quad (k_7 = 2.7 \times 10^1 M^{-1}S^{-1})\ [35] \tag{7}$$

$$SO_4^{\bullet-} + Fe^{2+} \rightarrow Fe^{3+} + SO_4^{2+} \quad (k_8 = 3 \times 10^8\ M^{-1}S^{-1})[31] \tag{8}$$

$$2SO_4^{\bullet-} \rightarrow S_2O_8^{2-} \quad (k_9 = 3.1 \times 10^8\ M^{-1}S^{-1})[32] \tag{9}$$

$$SO_4^{\bullet-} + H_2O \rightarrow SO_4^{2-} + H^+ + HO^{\bullet} \quad (k_{10} = 2 \times 10^{-3}\ M^{-1}S^{-1})[35] \tag{10}$$

$$SO_4^{\bullet-} + HO^{\bullet} \rightarrow HSO_5^- \quad (k_{11} = 1.5 \times 10^{-37}\ M^{-1}S^{-1})[30] \tag{11}$$

1.3 Environmental applications of activated persulfate

In recent years, activated persulfate oxidation is emerging as a robust technology to destroy a wide range of organic contaminants [33]. One efficient way of using activated persulfate for remediation of contaminated ground water or soil is through *in situ* chemical oxidation "ISCO" [33,34]. If sufficient amount of iron minerals are present in the subsurface, injecting persulfate will result in reaction between iron and persulfate for the generation of sulfate radical (equation 7). Persulfate offers some advantages over other oxidants because it is a solid at ambient temperature with the ease of storage and transport, high stability, high aqueous solubility and relatively low cost. Apart from the comparable redox potential of sulfate radical (2.5-3.1 V) with that of hydroxyl radical (1.9-2.7 V), $SO_4^{\bullet-}$ is more efficient to degrade some refractory organic contaminants for its selective oxidation capacity. The list of redox potentials of reactive radical species is summarized in table 1.2.

Table 1.2 Redox potential of reactive species of radicals and oxidants.

Redox potential of some reactive species		
Reactive species		Redox Potential (V)
Persulfate	$S_2O_8^{2-}$	+2.1 [35,2931]
Sulfate Radical	$SO_4^{\bullet-}$	+ 2.5-3.1 [35]
Hydrogen Peroxide	H_2O_2	+ 1.8 [37]
Hydroxyl radical	$HO^{\bullet}$	+ 1.9-2.7 [29,32,33]
Monopersulfate	HSO_5^-	+1.4 [29]

2. Research Motivation and Objectives

2.1 Research Motivation

A wide range of disinfectants has been implemented in water treatment industry in the past decades, including Cl_2 , O_3 and UV. However, the toxic disinfection byproducts (DBPs) and energy intensiveness are the major drawbacks of these mechanisms. Previous studies [27] showed that hydroxyl radical produced from hydrogen peroxide in combination with UV has the potential as an alternative disinfectant. In recent years, the application of $SO_4^{\bullet-}$ in oxidative water treatment and groundwater remediation has gained increasing attention, due to the high oxidative potential of sulfate free radical and the reactivity with a wide spectrum of pollutants. Persulfate is solid at ambient temperature with the ease of storage and transport, has aqueous solubility and relatively low cost. Upon activation, persulfate can produce a highly reactive oxidative species, sulfate radical ($SO_4^{\bullet-}$).The stability of persulfate at ambient temperature and neutral pH is additional benefit of using this system, notwithstanding no previous research has been conducted as a potential disinfectant. This is what brought about the extensive work and results that are described further in this thesis study.

2.2 Research Objective

The overarching objective of this research study was to investigate an alternative disinfection technology for drinking and wastewater treatment. *E. coli* bacteria cells (0157:H7) were exposed to an iron activated persulfate system for three hours and the viability has been assessed. Secondly, a comprehensive study was carried out to examine the impacts of solution pH, dosage of Fe^{2+} and $S_2O_8^{2-}$, and the presence of reductants on the efficacy of $SO_4^{\bullet-}$ disinfection. Thirdly, the performance of $SO_4^{\bullet-}$ on bactericidal disinfection was compared to $OH^{\bullet}$ radical disinfection under the same chemical condition.

3. Material and Methods

3.1 Materials

All chemicals used for solution preparation in this study were reagent grade. Sodium persulfate (Acros Organics; 99 % by mass) was used to prepare stock persulfate solutions. Ferrous ion was derived from iron (II) sulfate hepta hydrate (Sigma Aldrich; >99%). Potassium iodide (Across Organics; 99%) and sodium bicarbonate (Fisher Scientific; 99%) was used for color development of colorimetric persulfate concentration measurement. Hydroxylamine hydrochloride (Fisher Scientific; 99.9%) was used to accelerate the transformation of Fe^{3+} particles into Fe^{2+}. Phenol (Sigma Aldrich; >99%) was used as a probe compound to measure steady state $SO_4^{\bullet-}$ and $OH^{\bullet}$ concentrations. Sodium hydroxide (Fisher Scientific; 98.8%) and perchloric acid (Fisher Scientific; 70% by volume) were used for pH adjustments. Potassium chloride (Fisher Scientific; 99.9%) was utilized to adjust ionic strength. Difco ^{TM} LB Broth, miller (Fisher Scientific) were used as a growth media for the bacteria.

3.2 Persulfate activation experiment

3.2.1 Persulfate measurement

Persulfate activation is done using ferrous iron (Fe^{2+}). Hydroxylamine (NH_2OH), a common reducing agent was used to reduce ferric iron (Fe^{3+}) particles back to Fe^{2+}. Stock solutions of 100 mM potassium persulfate, iron (II) sulfate hepta hydrate, NH_2OH and phenol was prepared and a specific aliquot was diluted in the batch reaction vessel to

achieve an initial concentration of 3, 2,1 or 0.5 mM, corresponding to 1:1, 1:2 or 2:1 mole ratio of persulfate versus the activator and phenol, the probe compound. Persulfate concentration is quantified by colorimetric method. 100 µM of sample is withdrawn every 15 minutes and mixed with potassium iodide/sodium bicarbonate and keep in darkness for 10-15 minutes for color development. Horiba Aqualog UV spectroscopy was used to measure the absorbance of the samples at 352 nM wavelength. A corresponding calibration curve of lower concentrations of persulfate was constructed for each experiment to quantify the exact persulfate concentrations.

3.2.2 Quantification of sulfate radical generation

Steady state sulfate radical concentrations [$(SO_4^{\bullet-})_{ss}$] were determined by using phenol as a probe. 0.5 and 1 mM of phenol was introduced into 3 mM of persulfate/iron and Fenton systems in the presence of hydroxylamine (all in 1:1 molar ratio). The pHs of both systems were adjusted to 7 using 0.1, 0.5 and 1 mM of perchloric acid ($HClO_4$) and sodium hydroxide (NaOH). All experiments were conducted in batch reactors in triplicates for three hours. Samples (1.9 mL) were taken every 15 minutes and mixed with methanol (0.1 mL) to quench sulfate radical in a 2 mL HPLC vial (Fisher Scientific). Samples were analyzed on an Agilent 1200 series high performance liquid chromatography (HPLC) equipped with a diode array detector. C-13 HPLC column (Agilent Technologies) was used with 40% of acetonitrile and 60 % of 10 mM formic acid at a flow rate of 0.75 mL/min and a detection wavelength of 254 nm. As shown in Figure 4.2 and equation 11, phenol was oxidized by sulfate and hydroxyl radicals.

The degradation of phenol was modeled as a pseudo-first order reaction with respect to phenol. The pseudo-first order rate constant, $k_{obs,}$ was determined by plotting log of normalized phenol concentration versus reaction time. Steady state sulfate radical concentration [$(SO_4^{\bullet-})_{ss}$] was quantified from this pseudo-first order rate constant, $k_{obs,}$ through normalization with the rate constant for phenol reaction with $SO_4^{\bullet-}$ ($k_{phenol} = 8.8x10^{-9}$ $m^{-1}s^{-1}$) [37].

3.3 Bacterial Experiment

3.3.1 Cell preparation and culture

E. coli 0157:H7, a pathogenic strain of *Escherichia coli* bacteria was investigated as the model microorganism. Cells were selected from a fresh agar petri-dish which is prepared from a stock culture. The selected *E. coli* cells were inoculated into a 5 mL of autoclaved LB broth in 37 ^{o} C for 12-14 hours. This preculture was then used to inoculate a 300 mL LB broth (1:100 v/v). From the growth curve characteristics (Figure 1), this strain of *E. coli* cells reach mid-exponential phase in 3-4 hrs. The culture in 300 mL LB broth was incubated in 37 ^{o} C for 3-4 hrs. Cells were harvested by centrifugation for 15 min at 4 ^{o} C and 3700 x g to separate cells from the LB growth media. After the centrifugation, the growth media was removed and 10 mL of 5 mM potassium chloride (KCl) was added and the suspension was mixed using a vortex before a second centrifugation for additional 15 min at 4 ^{o}C and 3700 G. The washing steps including pouring off, adding electrolyte (KCl), and vortexing consecutively for three times. After the final washing cycle, 5 mL of 5 mM KCl was added to the pellet creating the stock

solution to be used for further experiment.

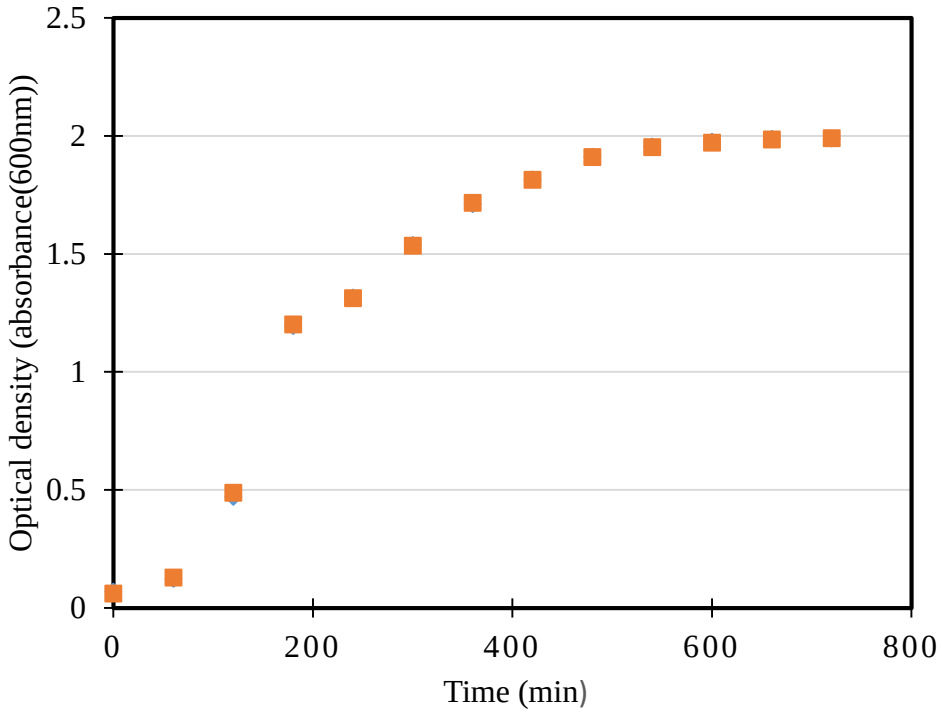


Figure 3.1 Growth curve of *E. coli* 0157:H7

3.3.2 Disinfection experiment

The concentration of each cell stock solution was quantified through a cell counting chamber and a light microscope (Micromaster, Fisher Scientific). For this study, initial cell concentration were adjusted to approximately 1.5 x 10^{8} cells/mL.

3.3.3 Quantification of bacterial viability

Cell viability was quantified via a viability assay [36], that determines the number of cells which have not had their membranes compromised by the disinfection method. 5 µL of sample was withdrawn from the experiment every 15 minutes and mixed with 10 µL of Live/Dead dye (L-13152; Molecular probes, Eugen, OR) on microscope slide (Fisher Scientific). Samples were kept in darkness for fifteen minutes for color development. 40x magnification of the florescent microscope were used for counting. Live bacteria were counted as those which florescence green. Dead bacteria cells were counted as those which florescence red. Bacteria cells with a florescent color of orange or red were counted as dead. Cell viability was calculated by adding the real live and real dead bacteria and then by computing the natural logarithm of the ratio of real live cells to real total cells [27].

3.4 Analytical methods

Both persulfate and phenol samples were analyzed using potassium iodide colorimetric method and high performance liquid chromatography (HPLC) respectively. Samples without hydroxylamine were first filtered by 0.22 µM 5ml syringe (Fisher Scientific)) driven filter (Fisher Scientific) before analysis. Persulfate was titrated with 50mM potassium iodide and measured by UV-Visible Spectrometer (Aqualog, Horiba Scientific) at 352nm. Phenol was characterized by Agilent High Performance Liquid Chromatograph (HPLC, Agilent Technologies 1200 series). The growth of bacteria was evaluated by measuring the cell density via optical density spectroscopy (Bio-mini DNA/Protein Analyzer, Shimadzu). Once the cell growth reach mid-exponential phase (3-

4 hrs), the concentration was quantified and adjusted via cell counting chamber and light microscope (Micromaster, Fisher Scientific). Bacteria cell viability was quantified using Live/Dead backlight kit (L-13152; Molecular Probes, Eugene, OR) and a florescence microscope (Olympus, Japan).

4. Result and Discussions

4.1 Persulfate activation

Sulfate radical generation was investigated by activating persulfate in the presence of ferrous iron. The rate of persulfate decomposition varied substantially with higher ferrous iron dosage and presence of hydroxylamine promoting the rapid activation. 65% of persulfate was activated in the first 30 minutes of the reaction with 3 mM of ferrous iron with the presence of hydroxylamine as shown in figure 4.1.

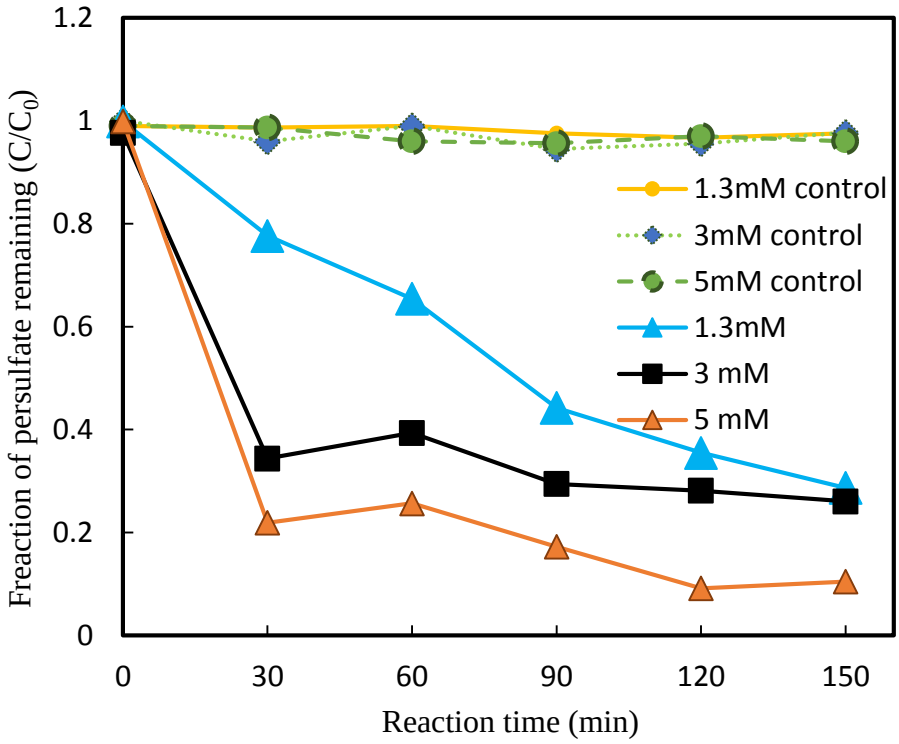


Figure 4.1. Activation of persulfate by ferrous Iron at pH 7. Ratio of persulfate to ferrous Iron is 1:1. Initial persulfate concentrations were 0.5 mM, 1 mM, 2 mM and 3 mM Control experiments were without ferrous iron. Fe^{2+} was 3 mM for all cases. Hydroxylamine [3mM] is used to reduce ferric iron particles pack to Fe^{2+} for more sulfate radical generation.

The generation of sulfate radicals have been demonstrated by using phenol as a probe compound in both persulfate and Fenton systems.

$$SO_4^{\bullet-} + Phenol \rightarrow Phenol\ Oxidized \quad (kp = 8.8 \times 10^9 \quad M^{-1}S^{-1})\ [37] \qquad (11)$$

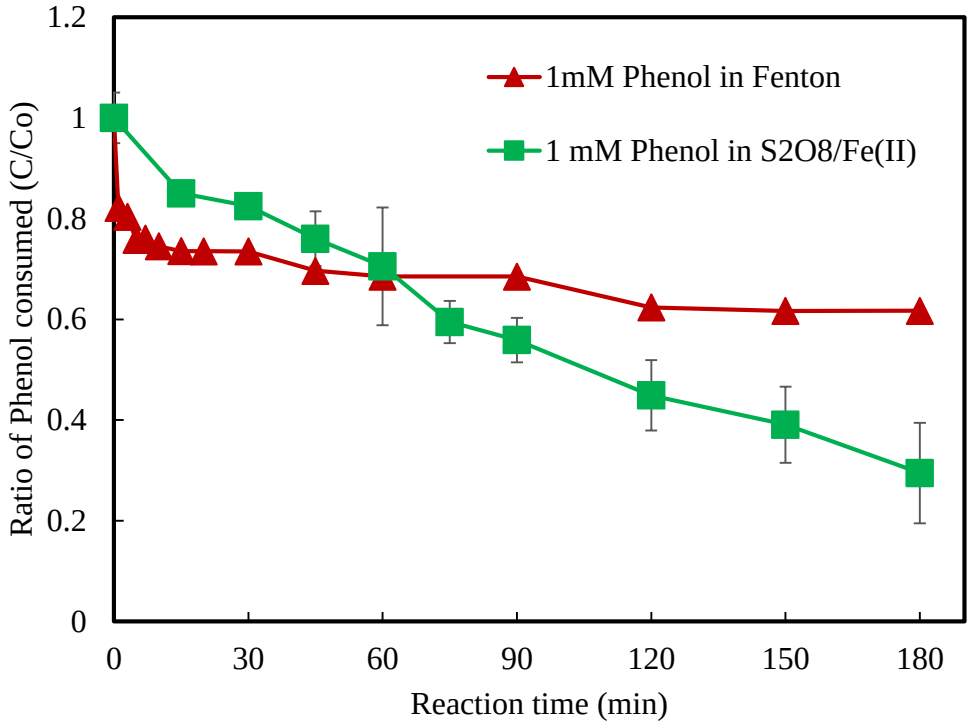


Figure 4.2. Degradation of Phenol in persulfate/iron and Fenton systems. Conditions, 3mM of Persulfate, iron, NH_2OH and hydrogen peroxide at pH=7. Phenol concentrations are o.5 and 1 mM

4.2 *E. coli* disinfection by $SO_4^{\bullet-}$

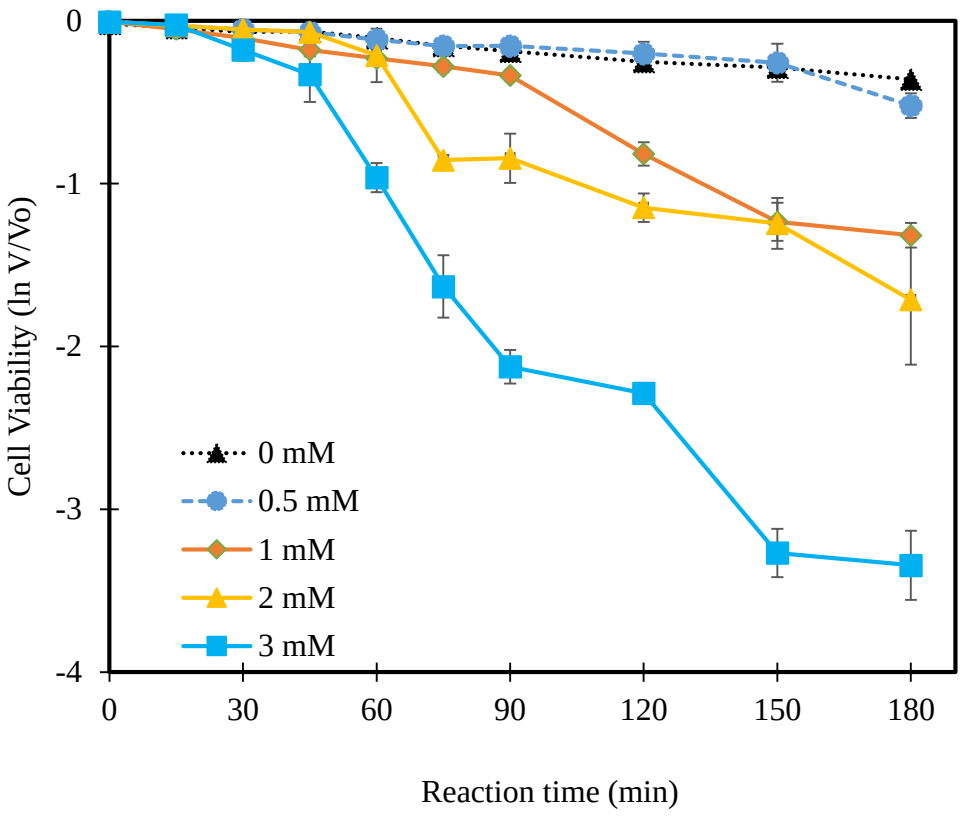
It has been observed that sulfate radical has a potential of disinfecting bacteria cells. The efficacy is determined by reactant dosage and pH of the system. At high persulfate and ferrous iron dosage (3 mM/L) and with the presence of the reducing agent hydroxylamine,

a 3.5 log removal of bacteria cells have been observed. Generally higher pH and persulfate/iron concentration give rise to higher disinfection potential (Figure 4.3a)

4.2.1 Effect of persulfate dosage on disinfection

Persulfate concentration highly affected the disinfection efficiency in this system as higher persulfate concentration leads to more sulfate radical generation. Fig 4.2a showed that 3mM persulfate gave a higher log removal than lower concentrations at neutral pH

A)



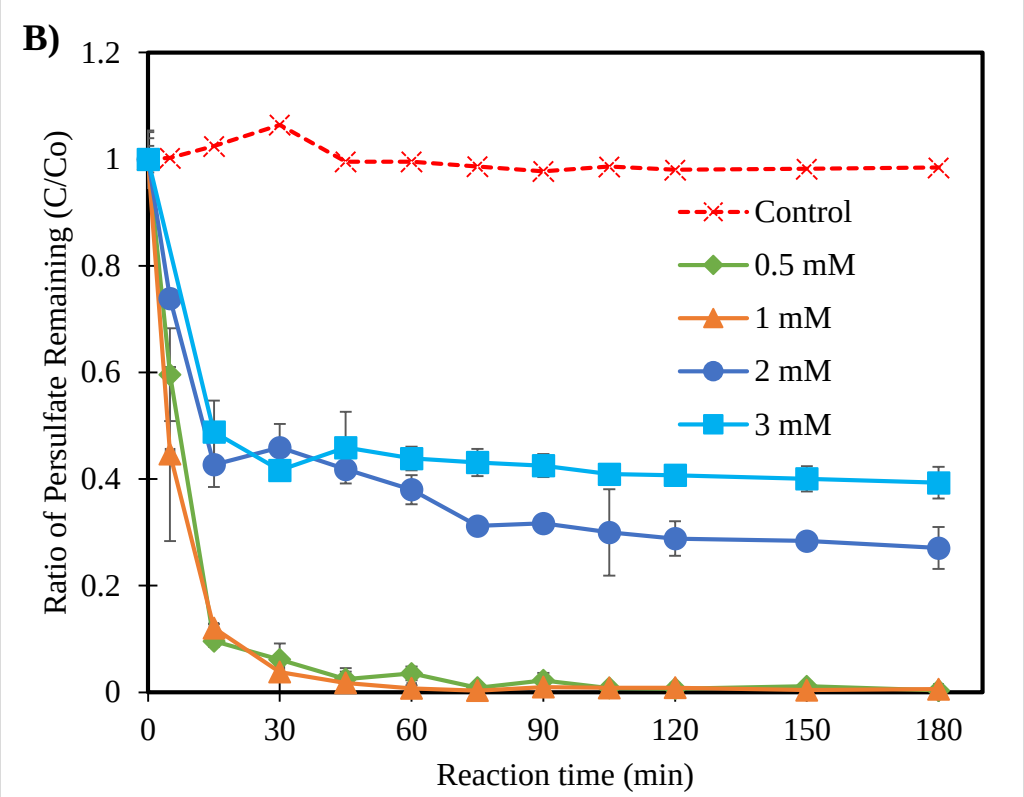
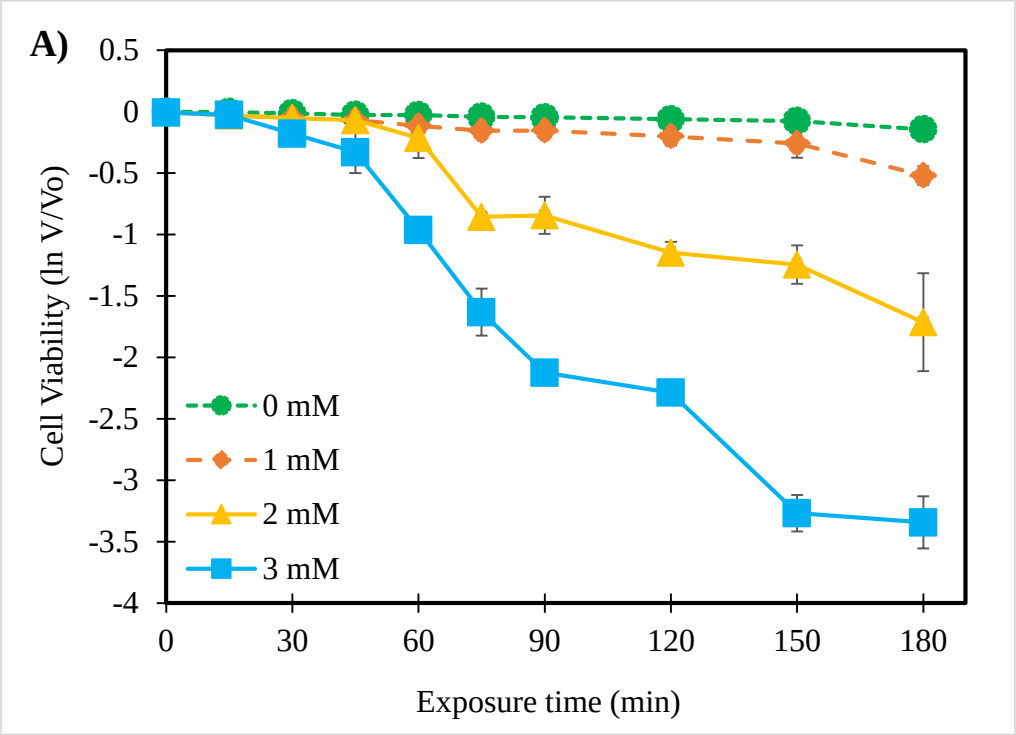


Figure 4.3. Effect of persulfate concentration on disinfection efficacy. Condition, Fe^{2+} and hydroxylamine are kept at 3mm and pH at 7 while Persulfate concentration is varied at 0, 0.5,1, 2 and 3mM. A) Impact of persulfate dosage on cell viability (B) Persulfate activation by ferrous iron at pH 7 and with the presence of hydroxylamine. Conditions, 3 mM of iron and NH_2OH 0, 0.5, 1, 2 and 3 mM of persulfate.

4.2.2 Effect of Fe^{2+} dosage on disinfection

Since Fe^{2+} iron is the reagent that initiates sulfate radical generation, higher concentration leads to higher sulfate radical generation. Figure 4.4b demonstrates this hypothesis. 3mM of ferrous iron showed the highest cell disinfection whereas lower concentrations of Fe^{2+}

lacked the potential to generate enough radical species for effective disinfection.



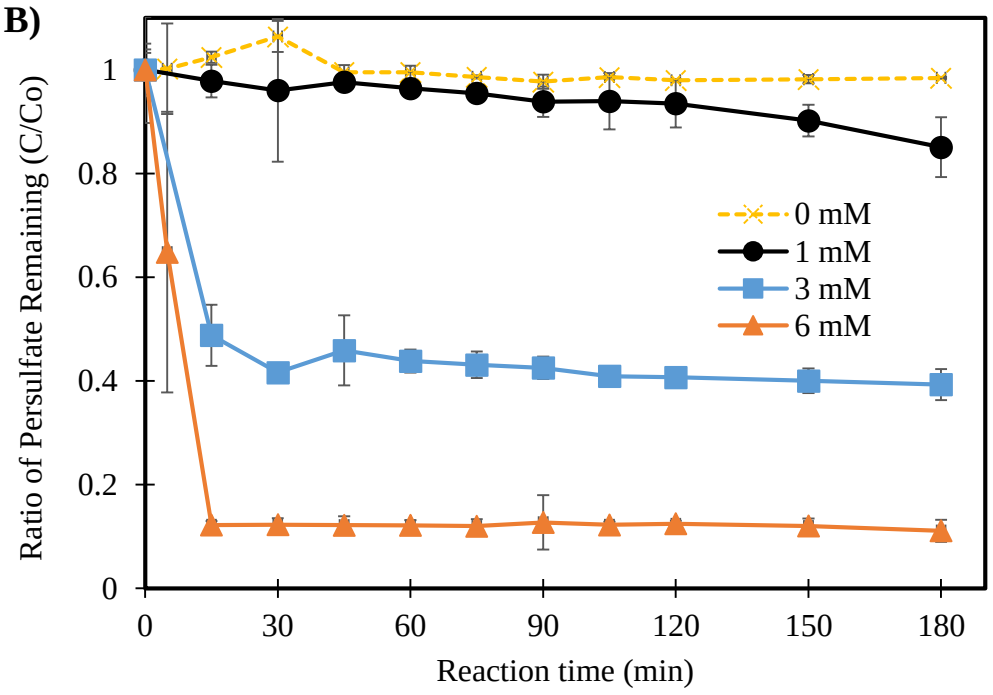


Figure 4.4. Effect of Fe^{2+} concentration_on disinfection efficacy. Condition, PS and hydroxylamine are kept at 3mm and pH at 7 while Fe^{2+} concentration is varied at 0, 1, 2 and 3mM.A) Changing viability in cell population in the presence of different Fe^{2+}dosage. Data are presented as the natural log of cell viability normalized by initial viability versus the reaction time B) Effect of Fe^{2+} dosage on persulfate activation.

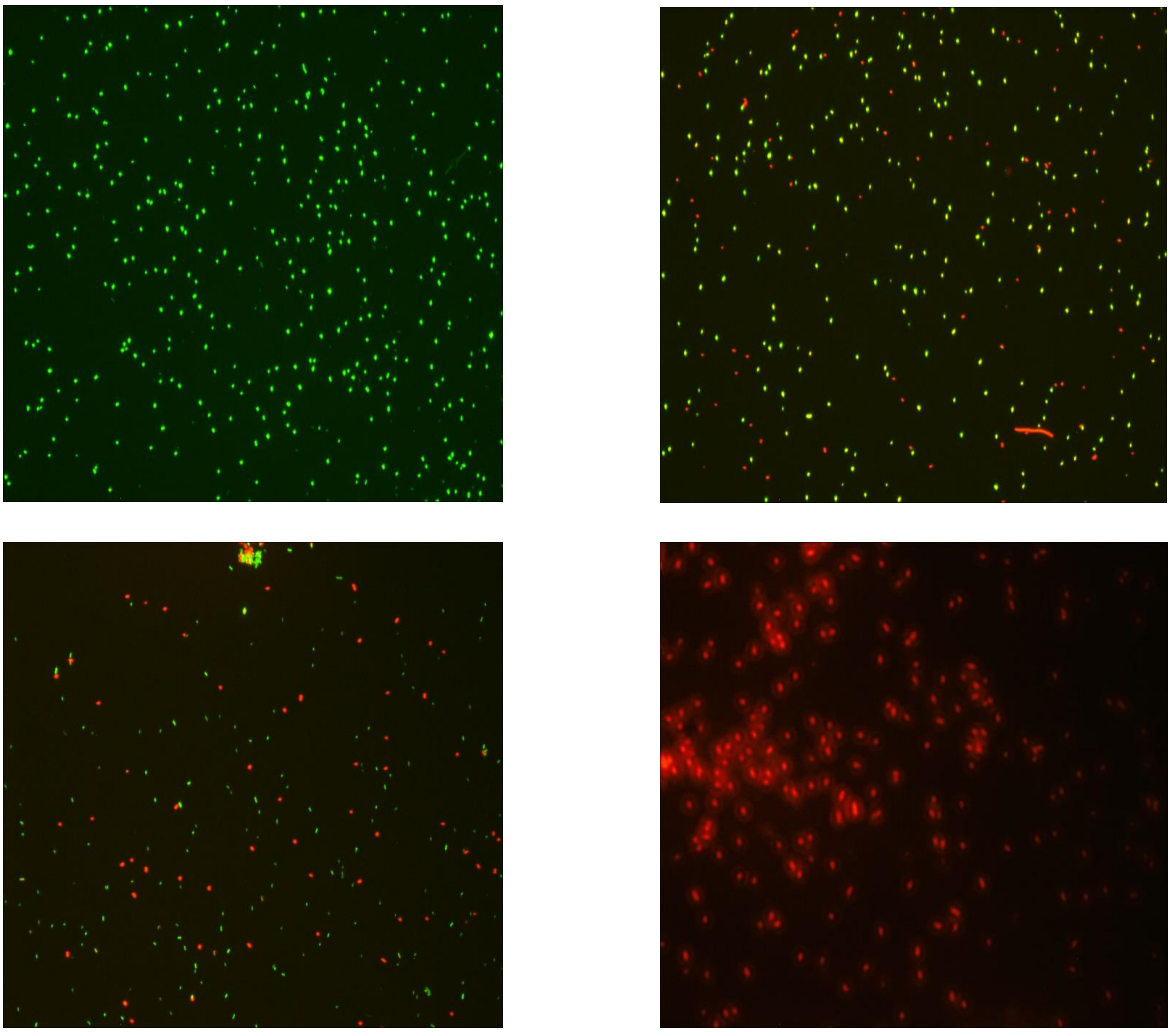
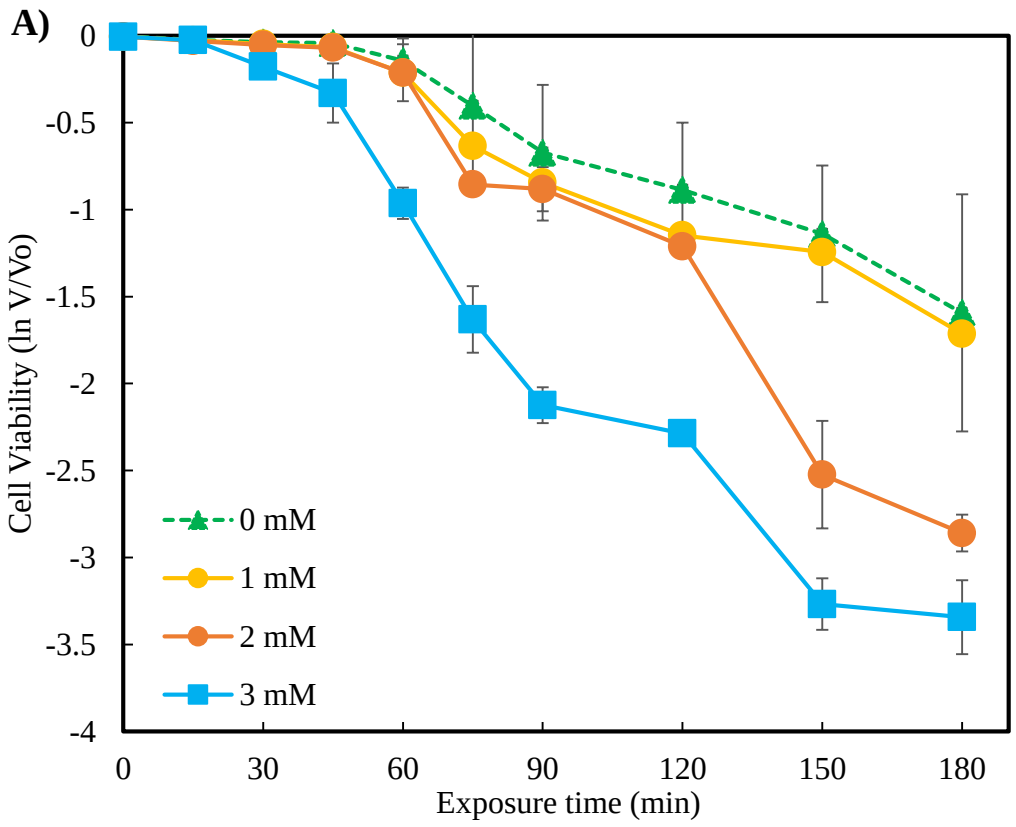


Figure 4.5. Bacteria cell pictures captured during the initial, middle and end of disinfection from the florescent camera microscope in activated persulfate system at pH 7. Experimental conditions are [3mM] of persulfate, [3mM] of ferrous iron and [3mM] of hydroxylamine. The cells in in green are alive whereas the red cells are dead bacteria.

4.2.3 Effect of hydroxylamine dosage on disinfection

The disinfection efficacy of this system was enhanced by the addition of hydroxylamine (NH_2OH), a reducing reagent to accelerate the transformation of Fe^{3+} particles into Fe^{2+} soluble ions which would enhance the generation of $SO_4^{\bullet-}$. Higher hydroxylamine concentration has higher impact in improving the sulfate radical generation as proved in figure 4.6b.



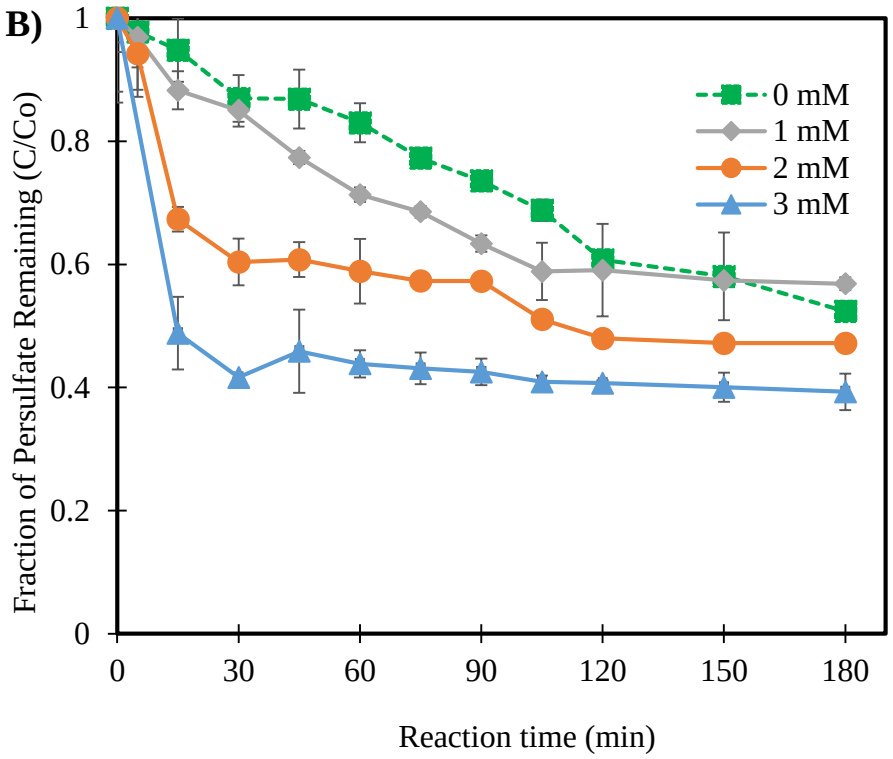


Figure 4.6. Effect of Hydroxylamine concentration on disinfection efficacy. Condition, Fe^{2+} and $S_2O_8^{2-}$ are kept at 3mm and pH at 7 while hydroxylamine concentration is varied at 0,1, 2 and 3mM. A) Changing viability in cell population in the presence of different NH_2OH dosage. Data are presented as the natural log of cell viability normalized by initial viability versus the reaction time. B) Effect of NH_2OH concentration on persulfate activation by ferrous iron.

4.2.4 Effect of pH on iron activated persulfate disinfection

The influence of pH on the disinfection potential of sulfate radical ($SO_4^{\bullet-}$) was investigated. It has been observed that neutral and alkaline pH gave higher induction time and disinfection potentials. At acidic pH, the rate of sulfate radical generation was slower (Figure. 4.7b), and as demonstrated in figure 4.7a, the bacteria die-off rate was slower at acidic pH of 5.0.

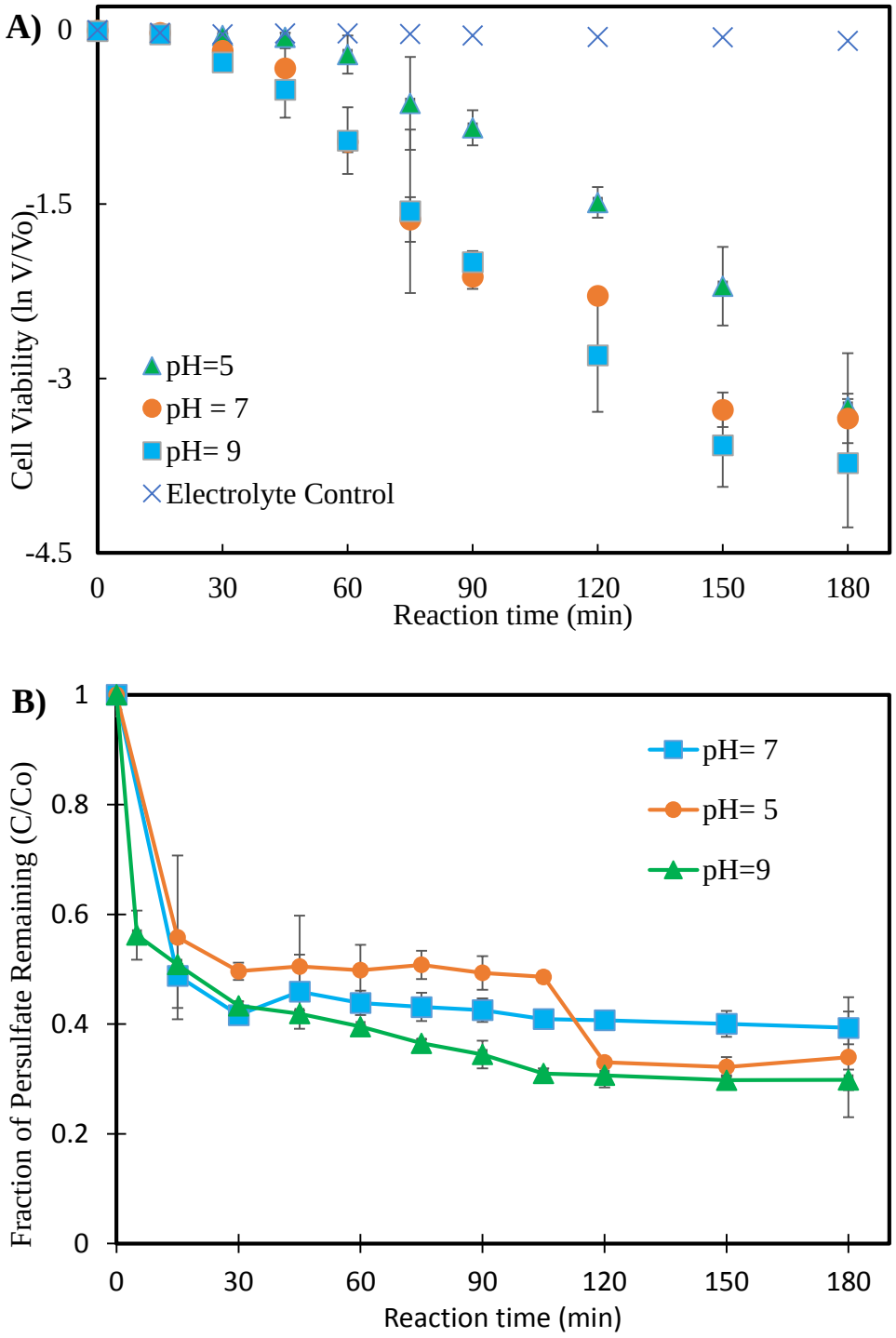
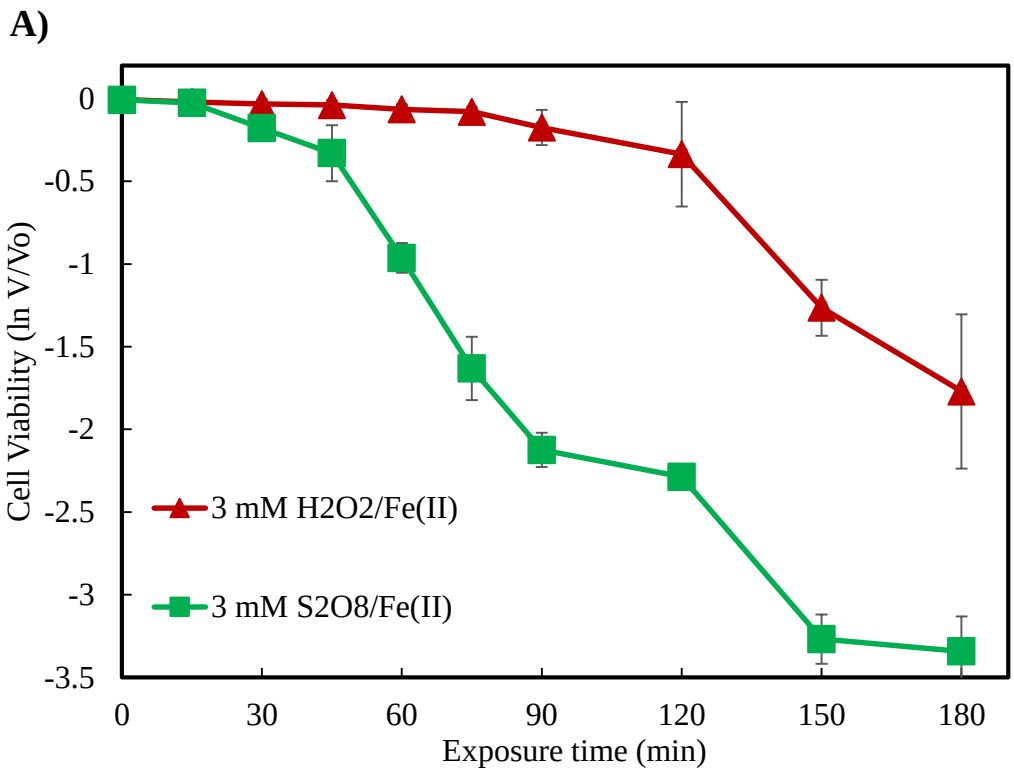


Figure 4.7 Effect of pH on activated persulfate disinfection of *E. coli* bacteria. Conditions, 3mM of persulfate, ferrous iron and hydroxylamine. Cell concentration was adjusted to 1.5

x 10^{-8}. A) Sulfate radical disinfection at pH 5, 7 and 9.B) Impact of pH on persulfate activation by Fe^{2+}.

4.2.5 Comparison of disinfection efficacy of $SO_4^{\bullet-}$ and $HO^{\bullet}$

In this study the efficacy of sulfate radical was compared with that of hydroxyl radical. A shorter induction time, 30 minutes, was observed in the persulfate system whereas the Fenton system die-off rate started at 75 minutes (figure 4.8a).This indicates an advantage of using $SO_4^{\bullet-}$ mediated system for disinfection over $HO^{\bullet}$.



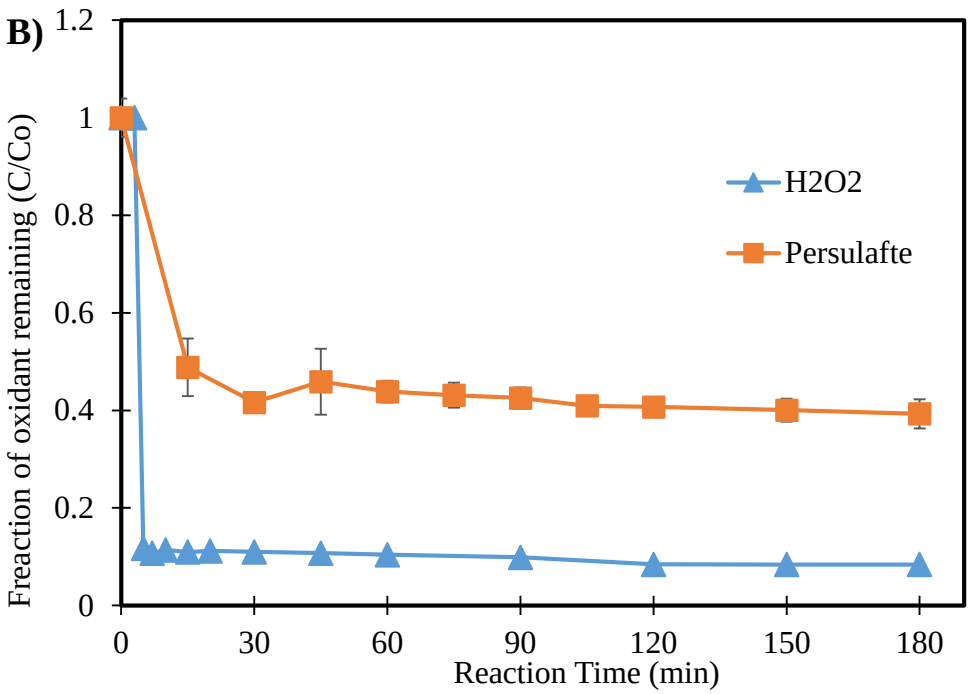


Figure 4.8 A) comparison of iron activated persulfate and hydrogen peroxide disinfection. Conditions, [persulfate] =3mM, [ferrous iron] = 3mM, [hydroxylamine] = 3mM, [hydrogen peroxide] = 3mM at pH=7. B) Activation of persulfate and hydrogen peroxide by ferrous iron. Conditions, 3mM of all chemicals and at neutral pH.

5. Conclusions

This thesis research was conducted to study the efficacy of ferrous iron activated persulfate in disinfecting bacteria for potential wastewater disinfection processes. The variables tested were activation of persulfate to generate sulfate radical ($SO_4^{\bullet-}$), the potential of sulfate radical in disinfecting bacteria, effect of reactant dosage & effect of pH on the overall disinfection potential. *E. coli* bacteria cells were exposed to $SO_4^{\bullet-}$ for three hours. Based on analyses of experimental results, the following conclusions were drawn:

1. Persulfate was activated by ferrous iron (Fe^{2+}) through a series chain of reactions to generate a highly oxidative radical species, the sulfate radical ($SO_4^{\bullet-}$).

2. The effect of pH and reactant dosage were examined. Results showed that higher pH 7 and 9 showed that higher disinfection efficacy was achieved at than acidic pH 5.

3. Both persulfate and ferrous iron dosage have a direct impact on disinfection efficacy. At higher concentration (3 mM) of both, the maximum bacteria die-off rate (3.5 log removal in three hrs) was achieved. As the dosage of both persulfate ($S_2O_8^{2-}$) and ferrous iron (Fe^{2+}) lowered to 2 and 1 mM, the die-off rate became slower. This is because the higher the reactant dosage (persulfate and ferrous iron), the higher the generation of sulfate radical.

4. Hydroxylamine (NH_2OH) can effectively reduce ferric iron (Fe^{3+}) particles generated from the oxidation of Fe^{2+} during persulfate activation, back to Fe^{2+} which enhanced the generation of sulfate radical and the disinfection efficacy.
5. Iron activated persulfate can be an alternative disinfectant for wastewater treatment because of its efficacy against microorganisms with a lower induction time compared to $HO^{\bullet}$ radical generated from Fe^{2+}/H_2O_2 system under the same condition.

6. Future work and Recommendations

An alternative and effective disinfection technology using sulfate radical species against *E. coli* bacteria cells were investigated in this study. However, due to limited time, the following section details are recommended for future research.

- Persulfate activation was tested using ferrous iron (Fe^{2+}). Previous studies [38] showed the activation potential of other transition metals (Mn^{2+}, Ag^{+}, Co^{2+}, Ni^{2+}), heat, UV light and activated carbon [39]. But the disinfection efficacy of using these metals as an activator was not the scope of this MS thesis.. It is recommended disinfection tests be conducted on activated persulfate using these activators.

- *E. coli* is a common test organism and disinfection results correlate to the effects of iron activated persulfate on other pathogenic bacteria strains. However, it is recommended that sulfate radical disinfection tests be conducted on organisms other than bacteria. For instance, effects of sulfate radical disinfection on spore forming organisms and protozoa.

- Previous studies investigated the efficaciousness of persulfate/UV systems for degradation of organic contaminants [2,38]. This combination of UV and persulfate demonstrated higher degradation potential. It is recommended that these UV/persulfate combined system been applied for disinfection of microorganisms as a potential effective alternative disinfection technology.

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