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Controlled Release Chemical Oxidation: Sodium Persulfate Encapsulated in PVAc Polymer

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Biographical Sketch

Mosarrat Samiha Kabir was born on June 15, 1992 in Dhaka, Bangladesh. She is currently a Master of Science degree candidate in Civil, Architectural and Environmental Engineering with a concentration in Environmental Engineering at North Carolina A&T State University. She received her Bachelor of Science in Civil Engineering in 2015. Her diverse educational background and research experience have provided her with an understanding of sustainable environmental stewardship. Following the completion of the master's degree program, Mosarrat will pursue a career as an Environmental Engineer to provide potable and sustainable water resources to people, both domestically and internationally.

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Abstract

In this study, sodium persulfate was encapsulated in polyvinyl acetate (PVAc) polymer to investigate the potential of activated persulfate to remediate total coliform and E. coli bacteria from contaminated water through a control release system. Controlled release structures were produced with the polymer and persulfate melted to form pellets at two different baking times. CRP structures containing 60 weight % sodium persulfates blended with 40 weight % polyvinyl acetate (PS- PVAc) were baked for 4 minutes and 10 minutes at 120ºC. The kinetics release of sodium persulfate was studied in a water system and in sand columns. Experimental results showed that for a baking time of 4 minutes, the pellets appear to release the oxidant at a higher rate than the pellets baked for 10 minutes in water. The average total percent release of sodium persulfate from the 10-minute baked (high-bake time) 60%PS-40%PVAC pellets in water was (95.95 ± 1.4)%, which was lower when compared to the 4-minute baked (low bake time) pellets which were at (99.57± 0.4) %. For soil column, the average percent release of sodium persulfate from 4-minute pellets was (82.69± 4.58) % whereas 10-minute pellet released (17.87± 3.54) % for the same experimental time frame.

For the second phase of the study, pellets consisting of 20% PS-80%PVAC were investigated. Controlled release pellets were made with catalysts. Controlled release Fe, base, and $KMnO_4$ were produced and combined in a batch reactor with the encapsulated persulfate pellets. Additionally, heat was evaluated as a potential catalyst in the studies. The goal for this portion of the study was to observe if controlled release persulfate remediation could be enhanced with controlled release catalysts that would activate the persulfate in solution for bacteria remediation. The catalysts of heat and controlled release Fe^{2+}, $NaHCO_3$ or $KMnO_4$ were studied in water for 72 hours. Among all the catalyst only $KMnO_4$ showed potential of bacteria

inactivation. The controlled release system with Fe^{2+} activated persulfate required 9 hours to achieve complete bacteria remediation. Controlled release persulfate activated with base required 6 hours and the controlled release system with $KMnO_4$ activated persulfate required 3 hours for bacteria inactivation. Controlled release persulfate activated with heat completed coliform inactivation within 15 hours. Experiment results show that while only persulfate (non-activated) completed the disinfection in 30 hours, persulfate activated in CRP system were able achieved complete coliform remediation by half of that treatment time.

CHAPTER 1

Introduction

1.1 Background

Water-related diseases are one of the major health problems globally. According to the world health organization (WHO), 80% of the global disease burden in the year are waterborne (Khan, Hussain, Saboor, Jamila, & Kim, 2019). In the USA, over 40% of drinking water used for domestic purposes is sourced from aquifers, which are susceptible to both chemical and biological contamination (WHO, 2002). Groundwater contamination can result from a variety of human activities including industrial uses of chemicals, leached from landfill, fertilizer in agriculture, leaking of underground septic and storage tank system.

With the progress in the field of Environmental Engineering, a variety of remediation techniques have been developed to treat organic contaminants in groundwater sources. Remediation technologies for contaminating source control and groundwater plume control comprises two major categories: (1) ex-situ technology and (2) in-situ technology. Over the decades, great interest has been placed on in-situ chemical oxidation (ISCO) for groundwater remediation. ISCO has proven as an effective technique for destroying subsurface contamination. Contaminants evidenced to be amenable to treatment by ISCO include: chlorinated solvents (ethenes and ethanes), benzene, toluene, ethylbenzene, and xylenes (BTEX), methyl tert-butyl ether (MTBE), total petroleum hydrocarbons (TPH), polyaromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), chlorinated benzenes (CBs), phenols; organic pesticides (insecticides and herbicides); and munitions constituents (RDX, TNT, HMX, etc.) (Maupin et al., 2017) (ITRC, 2005). A variety of chemical oxidants that are capable of degrading common contaminants have been employed in this practices, such as permanganate ion (MnO_4^-),

persulfate ($S_2O_8^{2-}$), hydrogen peroxide (H_2O^2), and ozone (O_3) (Mumford, Lamarche, & Thomson, 2004; Thomson, Hood, & Farquhar, 2007).

1.2 Tradition ISCO Method

ISCO has had a long history of development and application. ISCO has been considered as an effective as well as aggressive remediation technology as treatment is commonly implemented over a much shorter time frame (ITRC, 2005). In traditional ISCO, a chemical oxidant is injected into the sub-surface to convert the hazardous contaminants into environmentally non-toxic compound. Some commonly used application techniques in ISCO includes but not limited to the following (ITRC, 2005):

Direct Injection: Oxidants are directly injected into the subsurface in a liquid form through high-pressure injection wells and within a specific volume.

Vertical and Horizontal Well Recirculation: Contaminated groundwater is extracted from several extraction wells, treated with oxidants and then reinjected using different injection wells.

Pump and Treat: contaminated groundwater is pumped out, chemically treated with oxidants in surface and then sequentially reinjected into the surface through the same well it was extracted from.

Soil Mixing: oxidants are mixed to produce a slurry. Introduced the slurry into trenches or galleries for within the subsurface. In low permeability zone, this method can promote significant treatment enhancement.

1.3 Limitations of Traditional ISCO Technology

According to ISCO database, 242 remediation projects, including 46 federal sites, have been used ISCO as cleanup technique (NAVFAC, 2013). However, experiences revealed a

variety of limitations of this technology (Huling & Pivetz, 2006; Krembs, Siegrist, Crimi, Furrer, & Petri, 2010). In situ chemical oxidation (ISCO) cleans contaminants directly "as they lie" by injecting liquid oxidant to the subsurface. While effective oxidants exist, the current delivery method requires multiple re-injections to address contaminant rebounding (return of contaminant levels following treatment). Rebounding leads to increased remediation project cost and an unpredictable timing to clean up. Moreover, oxidant delivery could be difficult due to reactive transport and aquifer heterogeneities. Finally, handling highly reactive oxidants during application may cause serious health and work hazard.

1.4 A Novel Approach to Improve Traditional ISCO Technology

An innovative Controlled Release Polymer System (CRPS) was developed as a novel technology to achieve a sustainable oxidant delivery to overcome rebounding issues with a single application, increasing efficacy and lowering overall project costs (US patent #8519061). By encapsulating oxidants in biodegradable polymer, CRP pellets are made which can prevent direct exposure of the chemical, thus mitigates the health hazard of workers while handling. Figure 1 demonstrates the technique discussed where controlled release pellets are usually placed within wells, and as contaminated groundwater flows, it is continuously treated with the oxidant that is released from the pellets.

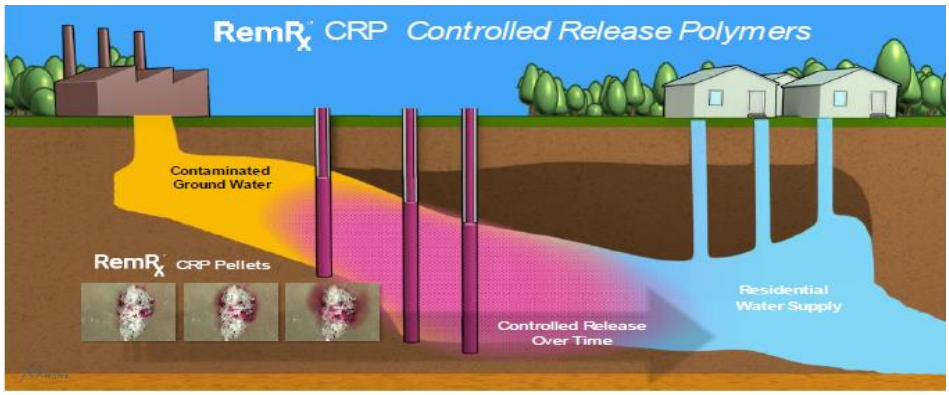


Figure 1. CRP Release Diagram (Source: AxNano)

1.5 Strategic Partnership

North Carolina Agricultural and Technical State University research team has partnered with two small business institution AxNano and Institute for Advanced Learning and Research (IALR), to work on the National Science Foundation (NSF) Small Business Technology Transfer Research (STTR) grant as well as the National Institute of Environmental Health Sciences (NIEHS) in order to assess the commercialization feasibility of a newly developed controlled release chemical oxidation technology (US patent #8519061).

1.6 Persulfate as an ISCO Treatment Oxidant

Persulfate ($S_2O8_2^-$) is one of the recent developments in oxidants used for ISCO. Persulfate effectively treats a broad variety of contaminants, such as chlorinated solvents (ethanes, ethanes, and methanes), BTEX, MTBE, 1,4-dioxane, PCBs and PAHs (e.g., naphthalene, phenanthrene, and pyrene), and energetic compounds such as trinitrotoluene (TNT) (ITRC, 2005). Sodium persulfate, the most suitable persulfate salt for ISCO has a solubility of approximately 40% in water and results in a clear solution. High reactivity and the ability to producing innocuous byproducts, make persulfate an excellent choice for environmental applications to treat contaminated groundwater. In aqueous solution, persulfate salts dissociate to form the persulfate anion ($S_2O8_2^-$), which is a strong oxidant.

$$Na_2S_2O_8 \quad \rightarrow \quad S_2O8_2^- + 2Na^+$$

By adding various catalyst can dramatically increases the oxidative strength of persulfate by producing sulfate free radicals (SO_4^-). Activation of persulfate can be achieved at elevated temperatures (35 to 40 ˚C), by strongly alkaline conditions (pH upwards of 10 to 12), with ferrous iron (Fe^{2+}), by photo (ultraviolet [UV]) activation under alkaline conditions, or by combining with other oxidants. Other ions that can be used as activators include the ions of

silver, copper, manganese, cerium, and cobalt. Each of these activators reacts with persulfate to form the sulfate radical based on the following equation:

$$S_2O_8^{2-} + \text{Activator} \quad \rightarrow \quad \cdot SO_4^- + \cdot SO_4^- \text{ (or) } SO_4^{2-}$$

Persulfate-driven oxidation by SO_4^- is more promising because the sulfate anion has a greater oxidation potential (2.6 V) than the persulfate anion (2.1 V) and has the capability to degrade a wider range of environmental contaminants at a faster rate (Block, Brown, & Robinson, 2004).

1.7 Research Objectives

In this study, the goal is to understand the release behavior of the novel approach of controlled released biodegradable pellets (sodium persulfate encapsulated in PVAc) in different media as well as activating persulfate in a complete control release system (CRPS) to evaluate the capacity of coliform inactivation. It was hypothesized that elevated temperature, Fe^{2+}, $NaHCO_3$, and $KMnO_4$ would activate the persulfate and accelerate the remediation of coliforms while all the activators and persulfate were applied in CRPS.

Consequently, the main objectives of this study can be described as follows:

1. Evaluate the variation in release behavior of controlled release sodium persulfate-PVAc pellets, baked for different time.
2. Measure the release concentration of catalysts (Fe^{2+}, $NaHCO_3$, and $KMnO_4$) that is released from controlled release pellets with which will initiate the production of sulfate radicals ($\bullet SO_4^-$) from persulfate.
3. Bacterial inactivation study to determine the significant difference in persulfate activation with different control release catalyst, which will be translated from the efficiency of coliform bacteria removal from contaminated water samples.

1.8 Thesis Outline

This thesis presents a total of five chapters. Chapter 2 provides a literature review about the existing knowledge about control release of chemicals along with different studies that have been performed using sodium persulfate as an oxidant as well as the use of sodium persulfate in the newly controlled release technology. Chapter 3 provides the material and experimental procedures that have been conducted for this thesis. Chapter 4 provides a detailed overview of the experimental outcomes and modeling results obtained for control release polymer system. Finally, chapter 5 will describe conclusions regarding bacteria inactivation by control release sodium persulfate and suggestions for future research.

CHAPTER 2

Literature Review

2.1 PVAc a Biodegradable Polymer

Degradable polymers are one of the main interests in research studies aiming to achieve environmentally sustainable structures and inert chemical delivery systems. The use of biodegradable polymers has attracted much attention in recent decades due to the environmental issues involved with commercial plastics (Gan, Yu, Zhong, Liang, & Jing, 1999). Poly (vinyl acetate) (PVAc) and its corresponding polymers poly (vinyl alcohol) (PVA) and poly (vinyl butyral) (PVB) have long been recognized from their discovery. Vinyl ester polymers has a vast number of different applications all around the world.

Biodegradable polymers generally contain a hydrolysable and/or oxidizable linkages along the main chain (Sivalingam, Chattopadhyay, & Madras, 2003). Polymers like poly (vinyl acetate) (PVAc) is known to undergo hydrolysis by side-chain breakage due to their hydrolysable groups in the side chain (Chattopadhyay & Madras, 2003). The optimal temperature for the side-chain hydrolysis of PVAc is 60°C and 65°C (Rieger et al., 2012; Sivalingam et al., 2003). The synthesis route to vinyl ester-based polymers starting from ethylene. The basic monomer for PVAc and its related polymers is VAM. Traditionally, VAM and its related polymers (i.e. ethylene and acetic acid) are produced from fossil resources. There is a proven possibility to substitute the feedstock for these raw materials and switch to ethanol, by producing from renewable resources like corn, sugar cane, or preferably straw and other non-food parts of plants. Though the whole production of PVAc, that mostly based on traditional fossil resources, it could be switched to a renewable, sustainable and CO_2-neutral production process based on bioethanol. vinyl acetate circle can be closed by the important steps of

biodegradation or hydrolysis and biodegradation of vinyl ester-based polymers back to carbon dioxide (Figure 2), then a truly sustainable material circle can be established.

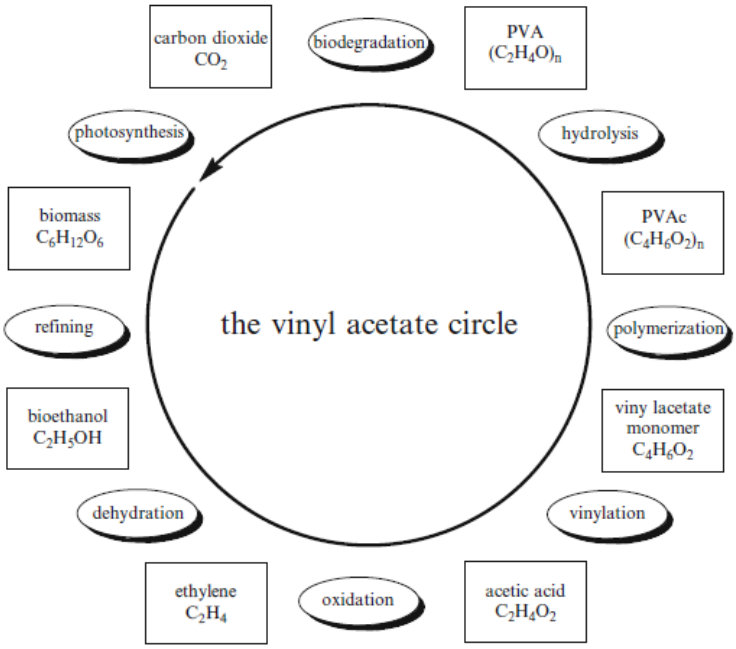


Figure 2. Vision of the "vinyl acetate circle" wholly based on ethanol as a raw material source. (Rieger et al., 2012)

2.2 Control Release Biodegradable Polymer

In 2010, Dr. Luster-Teasley and her research group developed a novel form of control release in- situ chemical oxidation technology. Controlled release biodegradable polymer (CRP) releases chemical oxidants at a controlled or sustained rate to expand the longevity of treatments for soil and water. Their research consists of the encapsulation of a reactive chemical oxidant within a porous, stabilizing polymer. Oxidant ten diffuses via mass transport across the polymer shell (Figure 3) and is also facilitated through hydrolytic erosion of the delivery vehicle (Figure 4) (Luster-Teasley, Onochie, & Shirley, 2010).

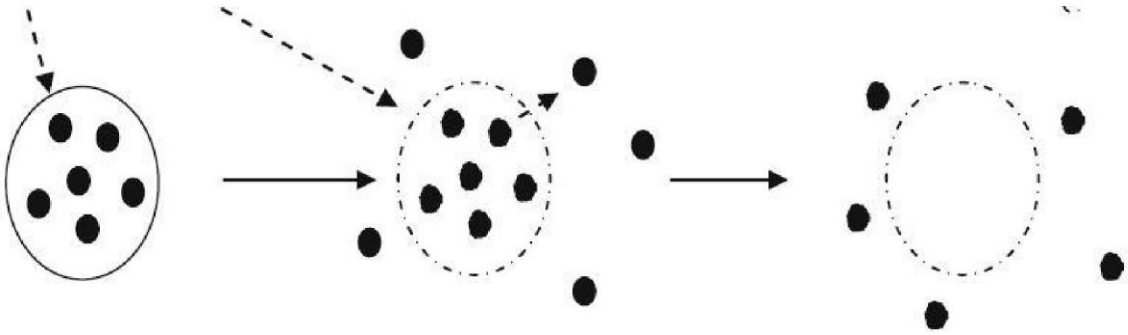


Figure 3. Diagram illustrating the release of the oxidant through the porous polymer surface (Luster-Teasley et al., 2010).

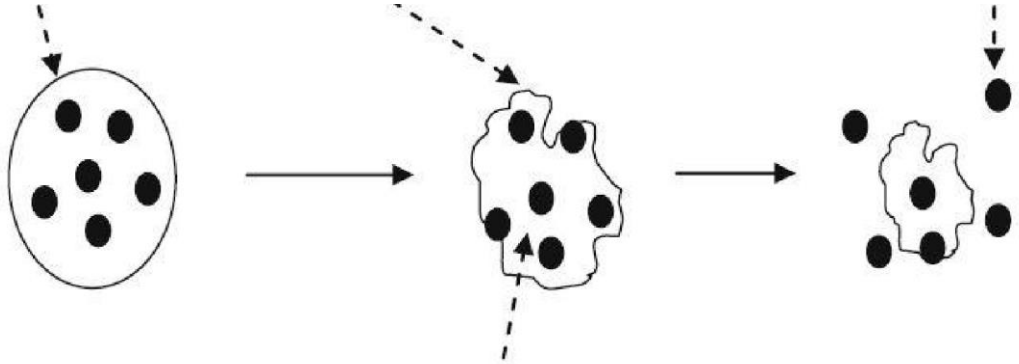


Figure 4. Diagram illustrating the release of the oxidant due to polymer matrix hydrolysis (Luster-Teasley et al., 2010)

U.S. patent (Patent #8,519,061) describes the formation procedure of CRP structure. The Luster-Teasley research group has created and investigated several versions of this CRP for ISCO remediation including potassium permanganate distributed thorough poly-(ε-caprolactone) (PCL), potassium peroxymonosulfate distributed thorough PCL. Potassium Permanganate embed in Polyvinyl Acetate (PVAc) and Polyethylene Oxide (PEO). In this thesis, combination of sodium persulfate with Potassium Permanganate will be produced and their potential in ISCO treatment will be investigated.

2.3 Persulfate Activation Process

Persulfate ($S_2O_8^{2-}$) is a relatively new oxidant used for ISCO and has become a widely popular oxidant (Huling & Pivetz, 2006) due to the promising application results (R. J. Watts, Teel, A.L. , 2006). Three different types of persulfate salt of different solubility are commercially available (Table 1). For ISCO applications, the solubility of potassium persulfate is very low where highly soluble ammonium persulfate generates ammonium while injecting, and ammonium is regulated in groundwater. On the other hand, sodium persulfate has a solubility of approximately 40% in water and produces a clear solution. In addition, this highly reactive salt produces innocuous byproducts, all of these makes it an excellent choice for environmental applications to treat contaminated groundwater (NAVFAC, 2015).

Table 1

Solubility of different persulfate salt (NAVFAC, 2015)

Persulfate salt	Solubility (25oc)
Ammonium persulfate	46%
Sodium persulfate 40%	40%
Potassium persulfate	6%

Persulfate poses a complex reaction chemistry. Persulfate ion ($S_2O_8^{2-}$) is a strong oxidant (E. =2.1 V) that under certain circumstances can generate free sulfate radicals (SO) (•-E. = 2.6 V). A range of catalysts (heat, high pH, ferrous iron, ultraviolet light, hydrogen peroxide, and transition metals) can activate the persulfate ion and generate the sulfate radical ($SO_4^{\bullet-}$) and other reactive intermediates (Tsitonaki et al., 2010).

2.3.1 Heat activation of persulfate. Heat-activation of persulfate has been studied intensively to oxidize recalcitrant toxic contaminants. Heat can excite persulfate to produce sulfate radical and can enhance the oxidation of contaminants significantly.

$$S_2O_8^{2-} + \text{heat} \rightarrow 2SO_4^{-\bullet}$$

Huang et al. (Huang, Couttenye, & Hoag, 2002) listed that the heat-activated persulfate could effectively oxidize 59 volatile organic compounds, including benzene, ethyl benzene, xylene, toluene, and chlorinated solvents. Huang et al. (Huang, Hoag, Chheda, Woody, & Dobbs, 2002) observed the degradation of methyl tert-butyl ether (MTBE) and reported that the degraded occurred in a pseudo first- order manner and with increase in temperature (20°C to 50°C) , the pseudo-first-order rate constant increased accordingly where an increase in pH resulted in a decrease in the rate constant. Temperature elevation between 30°C to 70°C could also increase the oxidation of chlorinated ethenes including tetrachloroethylene TCE, PCE, 1,1,1-trichloroethane, cis-dichloroethylene (DCE), and trans-DCE (Waldemer, Tratnyek, Johnson, & Nurmi, 2007).

2.3.2 Iron activation of persulfate. Iron-activated persulfate technology has attracted increasing interest over the last few years. Fe (0) and Fe (2+) are the most commonly used persulfate activators because of their natural abundance in porous media and benign nature. It is reported that Fe^{2+} is one of the strongest species that can activate persulfate to generate $SO_4^{\bullet-}$ which can enhance the efficiency of the pollutant degradation (Anipsitakis & Dionysiou, 2004)(Eq.1). However, a high dose of iron can promote $SO_4^{\bullet-}$ scavenging (Eq.1) and reduce the overall degradation rate and efficiency; thus, it is essential to optimize the iron dosing to achieve effective activation without excess scavenging (Rajib, Assumaning, Chang, & Addai, 2017; Tsitonaki et al., 2010).

$$Fe^{2+} + S_2O_8^{2-} \rightarrow 2SO_4^{-\bullet} + Fe^{3+} \quad (1)$$

$$SO_4^{-\bullet} + Fe^{2+} \rightarrow Fe^{3+} + SO_4^{2-} \quad (2)$$

Liang et al. reported Fe^{2+} activated persulfate could significantly increase the oxidative degradation of TCE when sequential addition of Fe^{2+} in small increment was applied. Besides, thiosulfate ($S_2O_3^{-}$) addition to the Fe^{2+}-persulfate system could also improve the oxidation of TCE by converting Fe^{3+} to Fe^{2+} (C. Liang, Bruell, Marley, & Sperry, 2004). Sulfate radicals generated from activation of persulfate with ferrous ion can also effectively destructed 2-chlorobiphenyl, chlorophenols and MTBE (Addai, Chang, Assumaning, & Rajib, 2016; Tsitonaki, Mosbæk, & Bjerg, 2006).

2.3.3 Alkaline activation of persulfate. Alkaline activation is one of the newest catalysts used to excite persulfate. Mixing persulfate with KOH or NaOH to result in a solution with pH near 11, alkaline activation can be achieved. Block et al.(Block et al., 2004) reported complete degradation of several recalcitrant compounds in bench scale study. However, alkaline activation is potentially one of the least efficient approaches due to the very fast decomposition of persulfate under alkaline conditions (Ahmed, Karr, Rouphail, Chun, & Tanvir, 2019; Crimi & Taylor, 2007). Moreover, for in situ applications, overcoming the base neutralizing capacity of the soil may require large amounts of base, which could result in environmental and economic complications (Tsitonaki et al., 2010). In the field, alkaline activation has displayed swing results. In one case (FMC, 2007), a near complete elimination of the targeted chlorinated ethenes was achieved but in another field application, the mixing of sodium persulfate with KOH resulted in the formation of the less soluble potassium persulfate, which precipitated in the mixing tank, causing reduced delivery of oxidant to the contaminated zone (Smith, Barnes, Janes, & Patterson, 2006).

2.4 Control Release Sodium Persulfate

The development of slow-release chemical oxidants for subsurface remediation is an emerging technology. While the development and testing of slow-release permanganate has been investigated for years (Christenson, 2011; Kang, Hua, & Rao, 2004; Ross, Murdoch, Freedman, & Siegrist, 2005; B. Yuan, Chen, & Fu, 2012) the investigation on the potential of slow-release persulfate for contaminant first initiated science 2011. In 2011, Liang and his research team have prepared a slow-release persulfate cement cube (4 x 6 x 7 cm) from a mixture of persulfate (sodium or potassium), cement, sand, and water (S. Liang, Kao, Kuo, & Chen, 2011). They kept the ratio of the amount of ingredients variable according to the designed persulfate release rate and treatment target. Column experiments was conducted to evaluate the efficacy of the cubes in removing benzene and MTBE. To activate persulfate, Fe (2+) was their choice. Activated persulfate cube was able to oxidize 86–92% MTBE and 95–99% of the benzene. Success of persulfate-releasing barrier indicates slow-release persulfate as a means of treating petroleum contaminated groundwater.

In 2012, slow-release persulfate-paraffin candles were developed to treat BTEX-contaminated groundwater (Kambhu, Comfort, Chokejaroenrat, & Sakulthaew, 2012). By heating and mixing $Na_2S_2O_8$ with paraffin in a 2.25 to 1 ratio (w/w) laboratory-scale candles were prepared. Cylindrical mold was used to produced candles of 2.38 cm long and either 0.71 or 1.27 cm in diameter. Activator candles consisted $FeSO_4$ or zerovalent iron (ZVI) and wax. At laboratory scale tests, activated persulfate was able to transform all the BTEX compounds. These results highly as well supported support as a technology for treating BTEX-contaminated groundwater. Inspired by the success of persulfate-paraffin + ZVI candle in remediating BTEX, the same technology was used to achieve a sustainable degradation treatment for 1,4-dioxane

(Kambhu, Gren, Tang, Comfort, & Harris, 2017) and 100% removal of dioxane was accomplished by this technology. With the objective to quantify the efficacy of slow-release persulfate candle to treat organic contaminants in a long-term and controlled manner, a two-dimensional flow tank experiment was done for treating Methyl Orange. In the tank, 90% removal was observed within 120 hours (Chokejaroenrat et al., 2015; Kabir, Appiah Assumaning, & Chang, 2019).

2.5 Oxidative Bacterial Inactivation

Fecal coliforms are a common class of bacteria that live in large numbers in the intestines of man and warm- and cold-blooded animals. Fecal coliform by themselves are not usually pathogenic; they are indicator organisms, which means they may indicate the existence of other pathogenic bacteria in the sample. The presence of fecal coliform bacteria in aquatic environments indicates that the water has been contaminated with the fecal material and there could be a potential chance that the source water may have been contaminated by pathogens or disease producing bacteria or viruses which can also exist in fecal material. (Toothman, Cahoon, & Mallin, 2009) mentioned that they are used to indicate the potential presence of pathogenic microorganisms from fecal origin and sewage in water resources.

Escherichia coli (E. coli) is a gram-negative fecal coliform bacterium. Although naturally existing in the body, some E. coli strains can cause intestinal illness. Based on virulence mechanism, strains are divided into groups. These mechanism groups comprise enteropathogenic E.coli (EPEC), enterotoxigenic E. coli (ETEC), and enterohemorrhagic E. coli (EHEC)(Percival & Cutting, 2010). An egregious Escherichia coli is O157:H7 of the EHEC virulence type. It has been a worldwide threat to public health and has been implicated in many outbreaks' fatal

hemorrhagic colitis(Perna et al., 2001). More than 75,000 cases of O157:H7 infection has been estimated to occur annually in the United States(Mead et al., 1999).

Bacterial contamination of rivers and streams originates from fecal material of both livestock and wildlife and wastewater effluents (Gallagher, 2012). Coliform may be introduced into groundwater through the infiltration of lake water and poorly installed sewage systems is a more likely source of contamination (Fong et al., 2007). manure-based biofertilizer from livestock and liquid swine manure application in field can also cause E. coli infiltration into shallow aquifers, which are more susceptible to biological contamination than those at further depths(Samarajeewa et al., 2012).

In recent years activated persulfate has attracted increasing interests in in water treatment, because of their promising results in degrading a wide range of intractable micro-contaminants as well as different biohazard (Anipsitakis, Tufano, & Dionysiou, 2008; S. Yuan, Liao, & Alshawabkeh, 2013). The bacterial envelope is composed of outer membrane, peptidoglycan layer, and cytoplasmic membrane which always worked as the first target of being in contact to reactive oxygen species (ROS) attack (Xia et al., 2016). Upon activation of persulfate, sulfate radicals are generated which undergo degradation of hazardous contamination in aqueous atmosphere and further produces reactive oxygen species (Ahmad et al., 2015; Ahmed, Rouphail, & Tanvir, 2018). Sulfate, hydroxyl, peroxide and super oxide are some known ROS generates in activated persulfate system (Xu, Zhao, Li, Liu, & Dong, 2014). Ahn et al. (2013)(Ahn, Peterson, Righter, Miles, & Tratnyek, 2013) combined zero valent iron (ZVI) with persulfate for activation and disinfected ballast water and concluded that the marine phytoplankton could be entirely inactivated and mineralized without formation of harmful byproducts. Michael-Kordatou et al. (2015a) (Michael-Kordatou et al., 2015) evidence that the UVC/Persulfate system can result in

rapid and complete degradation of erythromycin (ERY) and ERY-resistant Escherichia coli inactivation in secondary treated wastewater, thus produces a final treated effluent with lower phytotoxicity (<10%) compared to the untreated wastewater. Xi et al (Xia et al., 2016) introduced a natural occurring magnetic pyrrhotite (NP) as alternative catalyst to activate persulfate (PS) to control microbial water contaminants. The E. coli K-12 inactivation kinetics observed in NP/PS system also exhibited successful E. coli K-12 activation in authentic water matrices like surface water and effluent of secondary wastewater.

CHAPTER 3

Methodology

3.1 Introduction

The purpose of this investigation was to: (1) assess the concentration of sodium persulfate, released from the controlled release polymers (CRP) produced by encapsulating oxidant in polyvinyl acetate (PVAc) polymers (2) assess the activation of persulfate in the presence of different catalysts like heat, iron, base and other oxidants and to compare the disinfection efficiency of catalyst activated persulfate. These were accomplished by carrying out a series of laboratory experiments. The preliminary oxidant release study was used to determine the effect of baking temperature of pellets on persulfate release behavior in water and soil. Finally, a bacterial inactivation study was conducted to determine the potential of different CRP catalysts to activate the persulfate and thus variance in removal of coliform bacteria from contaminated water sample.

3.2 Materials

The study oxidant in this thesis is Sodium Persulfate (PS). To produce a control release matrix, SP is encapsulated in polymer Polyvinyl Acetate (PVAc)**.** After studying the release performance, persulfate activation studies were done by introducing the controlled release polymers to heat, ferrous sulfate, a salt of iron along with a solid (Sodium Bicarbonate) and liquid (Sodium Hydroxide) base to for remediation of bacteria.

3.2.1 Sodium Persulfate ($Na_2S_2O_8$). Persulfate is a strong oxidizing agent. Due to diverse reactivity, persulfate became popular in many industrial processes, such as metal surface oxidation, polymerization, and organic chemical manufacturing (R. J. Watts & Teel, 2006). Persulfate usually occurs in the form of sodium, ammonium or potassium salts. The most

preferred form used in ISCO is sodium persulfate, as it has the highest water solubility and the most benign residual products (Huling & Pivetz, 2006). Sodium persulfate is an inorganic compound is a salt peroxydisulfuric acid.

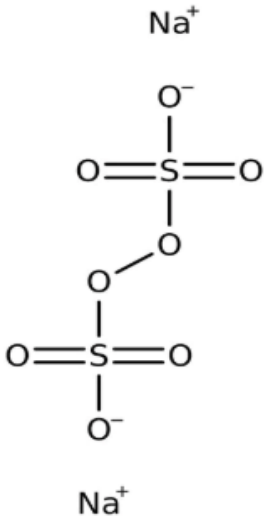


Figure 5. Structure of Sodium Persulfate

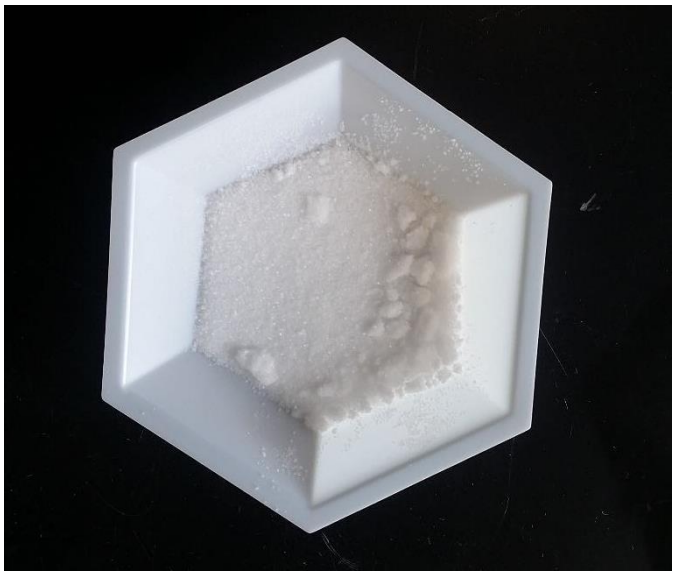


Figure 6. Sodium Persulfate used as oxidant in Control Release polymer pellet

The sodium persulfate used in this study was acquired from Thermo Fisher Scientifics. The form of the salt was in white crystalline powder and the molecular weight was 238.092 g/mole.

3.2.2 Polyvinyl Acetate (PVAc). Polyvinyl acetate is a biodegradable polymer. PVAc can degrade naturally by fungi, algae, yeast, lichen and some other bacteria. PVAc is also referred as thermo plastic. Its thermal stability is lower than 40 °C, and its stability is not that strong against solvent action. The water-resistance of the polymer is low and has a heavy creep. A glass transition temperature between 28°C and 32 °C makes PVAc an excellent non-structural adhesive for room temperature applications (Zeng, 2013). The following figure 7 demonstrates vinyl acetate monomer and polyvinyl acetate structures:

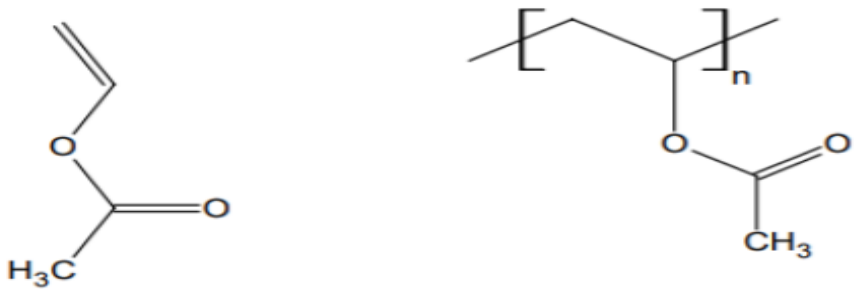


Figure 7. Vinyl Acetate (Left) and Polyvinyl Acetate (Right)

Controlled release pellets were produced using PVAc which was purchased from Acros Organics a band of Thermos fisher Scientific. The molecular formula on the label was $C_4H_6O_2$ and Molecular weight was 86.09 g/mol. The physical form of the available PVAc was in beads shape. To ease the encapsulation of oxidant inside the polymer, the beads were crushed into power with a small-scale grinding machine.

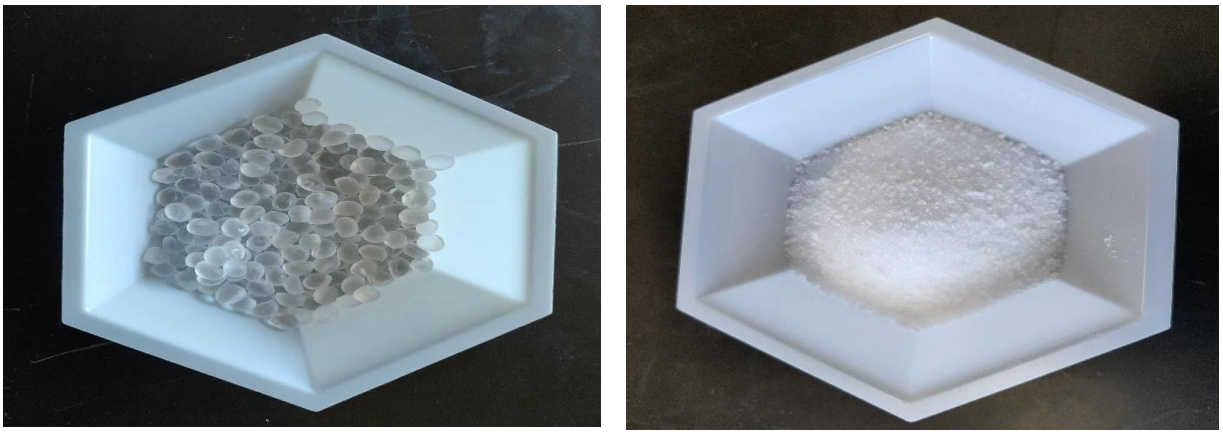


Figure 8. PVAc in beads and grinded from

3.2.3 Methylene Blue ($C_{16}H_{18}ClN_3S$). Methylene blue (MB) is a popular dye and has several applications in different other domains. MB is commonly used in bacteriologic stain as an indicator. Methylene blue (MB) can be easily degraded in thermally activated persulfate systems (Ghauch, Tuqan, Kibbi, & Geryes, 2012). The discoloration kinetics of MB was measured by spectrophotometric method to determine the concentration of SP in any solution.

The MB that was used in this study was purchased by Sigma- Aldrich. The molecular weight of the Methylene Blue was 319.85 g/mole. The reagent compound was a consisting of dark green crystalline powder, having a bronze-like luster. In aqueous media it gives different shades of blue solution according to the concentration of MB.

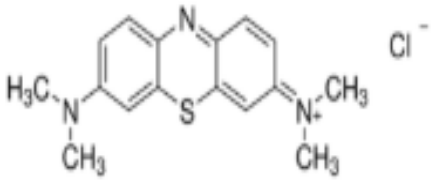


Figure 9. The structure of Methylene blue

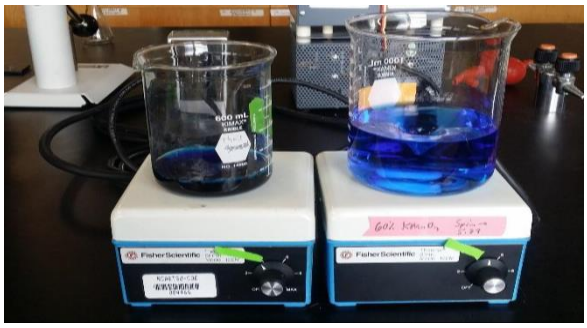


Figure 10. Methylene blue solution of different concentrations

3.2.4 Potassium Permanganate ($KMnO_4$). Potassium permanganate ($KMnO_4$) is strong chemical oxidant that has been extensively used for the treatment of contaminated groundwater as well as wastewater. Potassium permanganate has a significant reduction potential, stability, predictable chemistry as well as the ability to produce nontoxic by-products. In this study, potassium permanganate is being used as an activator for sodium persulfate. $KMnO_4$ is susceptible to reacting with natural organic matter and forming byproducts of manganese dioxide (MnO_2) which can be considered to be a potential catalyst for sodium persulfate to generate free radicals which is particularly important for remediation application (Conrad, Glass, & Peplinski, 2002; Jo, Do, & Kong, 2014) . Potassium Permanganate was procured from Fisher Scientific. This dark purplish colored crystalline solid has a molecular weight of 158 g/mole.

Figure 11. Potassium Permanganate ($KMnO_4$) used as a Control Release activator

3.2.5 Ferrous Sulfate Heptahydrate ($FeSO_4.7H_2O$). Ferrous Sulfate Heptahydrate is common salt of iron which is also known as Green Vitriol. This greenish crystalline solid loses its seven waters of hydration at 90ºC. Because of its low cost, little toxicity and commercially availability, iron salt is widely used in water treatment (Deng et al., 2014).

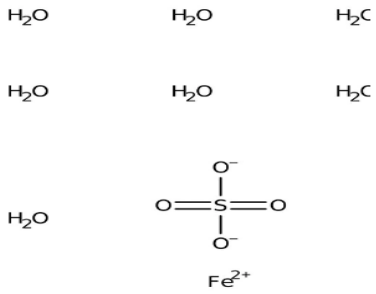


Figure 12. Chemical Structure of Ferrous Sulfate Heptahydrate

In this study, Ferrous sulfate was encapsulated in PVAc to use a as a catalyst in CRP system and Fe2+ has the potential to activate the study oxidant. Ferrous Sulfate was purchased from fisher Scientific. The material was available in crystalline form. The Molecular weight was 278.01 g/mol. The ratio of Fe2+ to SP applied for inactivation of bacteria was 1:1.

3.2.6 Sodium Bicarbonate ($NaHCO_3$). To incorporate a control release base activation of Sodium persulfate, Sodium Bicarbonate was captured inside a PVAc pellets. Sodium

Bicarbonate ($NaHCO_3$) is commonly known as baking soda and has a molecular weight of 84 g/mole. The $NaHCO_3$ that was available in the laboratory was in white crystalline form.

3.2.7 Sodium Hydroxide (NaOH). According to the hypothesis, a complete CRP base activation of PS was not achieved. As $NaHCO_3$ was unsuccessful to raise the pH to a targeted level, Sodium Hydroxide was used to elevate the basic condition of the sample water. Sodium Hydroxide (NaOH) was purchased from fisher Scientific. The molecular formula on the label Molecular weight was 34 g/mol.

3.3 Control Release Pellet Formation

Control release polymer pellets were produced following by using a hand pellet press. This method is commonly referred as ‘cookie method. For baking the pellets, a small oven was used.

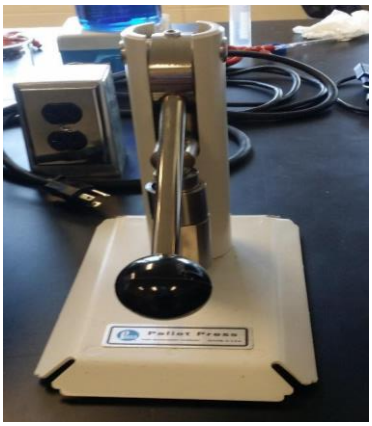


Figure 13. Pellet Press

Figure 14. Baking Oven

The list of pellets used in the study are:

- 60% PS-40% PVAc Pellet baked at 120°C for 4 minutes.
- 60% PS- 40% PVAc Pellet baked at 120°C for 10 minutes.
- 20% PS - 80% PVAc Pellet baked at 120°C of no-bake.

- 25% Fe $SO_4.7H_2O$ - 75% PVAc Pellet of no-bake.
- 20% $NaHCO_3$- 80% PVAc Pellet of no-bake.
- 1% $KMnO_4$- 99% PVAc Pellet of no-bake.

3.4 Kinetics Release of 60% PS- 40% PVAc Baked at 120℃ for 4, and 10 min in Water

To begin producing pellets, the mass of pellets was weighted and recorded for their actual mass after baking to determine the actual mass of PS in pellet. 500 ml of DI water was taken in a glass beaker. The test was done in triplicate. The beakers were kept under a continuous agitation with same size of stir bars. The same spinning speed of stir bar was maintained for each beaker as well. For the experiment, 5 ml of sample solution from each beaker was collected at the time intervals of zero, 0.5, 1, 5, 10, 15, 20, 60, 120, and 180 minutes.

Figure 15. Experimental setup for kinetics release of sodium persulfate in water with agitation

A methylene blue solution of absorbance 3.00 was prepared. The molarity of MB was 20.22 µMole/L. 15 ml of that MB solution was thoroughly mixed with each collected sample (5ml) in a 25ml flask. The absorbance of the mix was measured at 650 nm wavelength using HACH DR3900 UV spectrophotometer. With the aid of a microwave oven, the solution was then microwaved for 40 seconds. As soon as the microwaving was done, the flask was covered with aluminum foil and set into a cold bath to cool down to temperature 4ºC. After cooling, the

absorbance was measured again at the same wavelength. From the delta absorbance of before and after microwaving, the concentration of SP was determined by using the calibration curve of sodium persulfate.

3.5 Release of 60 % SP- 40%PVAc Pellets Baked for 4 and 10 mins at 120̊ C in Soil Column

At first the mass of pellet was measured and recorded. Approximately, 115 grams of sand was taken to fill up a Chromaflex glass soil column. Half of soil mass was poured in the column with a continuous vibration with a shaker to preserve the packing homogeneity. With the help of a tweezer, the pellet was then pleased half-filled soil column. After that the remaining filler was done by the other half of the soil. Cole-Parmer Masterflex Peristaltic Pump was used to initiate flow of a buffer solution through the soil column. The flow rate of the solution was maintained at 10 ml per 45 second. The pH of the buffer solution was 8. For three hours, 18 samples of the effluent solution were collected with a 10 min interval and four samples were collected with a 30 min interval for next two hours. The absorbance of the collected effluents was measured following the same procedure mentioned in the previous experiments.

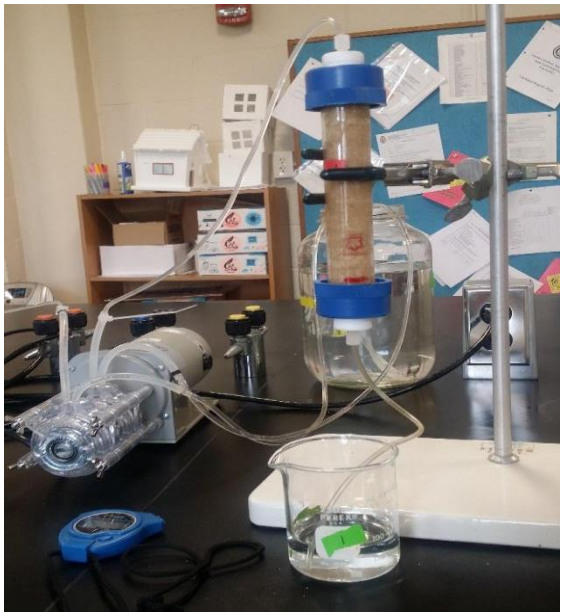


Figure 16. Experimental setup for release of sodium persulfate in soil column

Post- Column: For all the soil column experiments, after the end of each run, post column analysis was done. The pellet was added to 200 ml DI water and analyze the presence of SP with 19.45 μM of MB after 24 Hours.

3.6 Spectrophotometer

The released concentration of sodium persulfate in the sample was measured by the spectrophotometric method. In order to measure the absorbance of the collected samples, a HACH DR3900 UV spectrophotometer was used (Figure 17). The absorbance was measured using a single wavelength of 650 nm which was determined through the calibration curves. The wavelength scan (Figure 19) demonstrated an absorbance peak at 650 nm and thus represented the value to use in order to determine the absorbance of the samples. An aliquot of 10 ml of DI water was used as the control in order to set the reading to zero at the start of each experiment. In case the absorbance exceeds 1.958, a series dilution of the solution sample was performed until an absorbance less than 3.00 was achieved.

Figure 17. HACH DR3900 used for oxidant concentration measurement

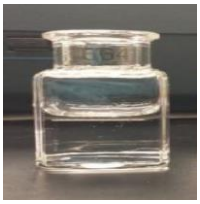


Figure 18. HACH DR3900 used for oxidant concentration measurement

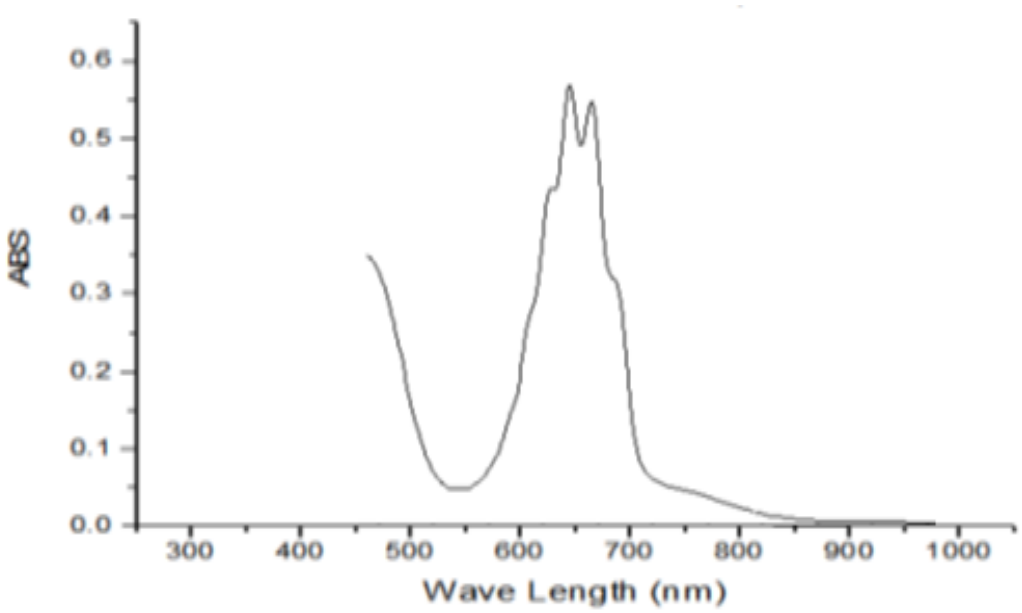


Figure 19. Sodium persulfate ($Na_2S_2O_8$) Wavelength Scan demonstrating the maximum absorbance at 650 nm

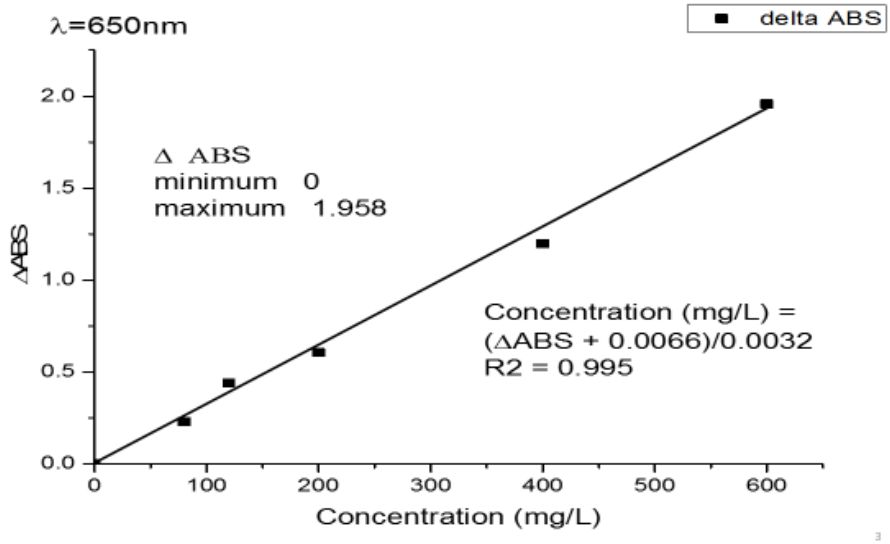


Figure 20. Calibration curve for calculating the concentration of sodium persulfate in the sample

3.7 Calculations

To calculate the concentration of sodium persulfate, the absorbance of each sample was measured using DR3900 spectrophotometer. The following calibration equations were then used to convert the absorbance into concentration. We maintained and calibrated the DR3900 spectrophotometer regularly. Each time the calibration was repeated.

$$PS\ Concentration\left(\frac{mg}{L}\right) = \frac{\Delta ABS + 0.0066}{0.0032}$$

These equations were developed through calibrations of the spectrophotometer and based on the Beer-Lambert Law that states:

$$Abs = -\frac{logI}{I_0} = \epsilon * l * c$$

Where:

I_0 : is the intensity of the light before reaching the spectrophotometer sample

I : is the intensity of the light after passing through the spectrophotometer sample

ϵ: is the molar extinction coefficient (L/mol.cm)

l: is the distance that the light travels the solution 31

c: concentration of the sample

For a on dilution multiply with 1, one-time dilution, we multiply the value obtained by 10, and for a two-time dilution, we multiply the value obtained by 100.

The percentage release was then calculated using the following equation:

$$\%\ SP\ Release = \frac{Concentration\left(\frac{mg}{L}\right) * volume\ (L)}{Load\ fraction\ of\ oxidant * mass\ of\ the\ pellet\ (mg)} * 100$$

The total percentage release is then only the sum of the percentage release at each specific sample.

3.8 Persulfate Activation and Bacteria Remediation

It was hypothesized that elevating the temperature, adding iron (Fe2+), base and combining with other oxidants would activate the persulfate and accelerate the remediation of coliforms while all the activators and persulfate were applied in control release matrix. CRP pellets comprised of the selected activator were manufactured by encapsulating the catalysts (Fe_2SO_4, $NaHCO_3$, and $KMnO_4$) into PVAc polymer. Kinetic release study for catalyst pellets were conducted to ensure that the pellets will defuse the materials rather than capturing them inside. After ensuring a sustainable release, the activator pellets along with PS pellet were applied for treating coliforms of contaminated water from lake.

3.8.1 Kinetic release of 25% $FeSO_4.7H_2O$ - 75% PVAc pellet. To evaluating iron release behavior from ferrous sulfate pellet, 1000 ml of DI water was taken in a glass beaker for one 25% Fe SO4.7H_2O - 75% PVAc Pellet. The test was done in triplicate. The beakers were kept under a continuous agitation with same size of stir bars. The same spinning speed of stir bar was maintained for each beaker as well. For the experiment, 5 ml of sample solution from each beaker was collected each 30-minute interval. Sampling was continued until 100% release was achieved.

The concentration of iron in the sample solution was measured using ‘iron TNT 585 vial test’ kit innovated and manufactured by Hach. The bar-coded reagent vials allow for automatic method detection and measurement by the spectrophotometer (DR 3900). The provided application instruction was followed.

In the reagent vial, 2ml of sample was taken. The cap replaced and the vial shaken 2 to 3 times horizontally until the contents dissolved fully. A wait time, after mixing, was 15 minutes was used. Then the vial was inserted into the spectrophotometer DR 3900.With the first spin of vial inside the spectrophotometer, the instrument scans the barcode and identifies the correct or associate parameter. The appropriate method and wavelength are automatically. On second spin the instrument takes ten readings, rejects any outliers and displays the average on the screen. The tenfold 360-degree measurement accounts for any potential scratches, fingerprints or other flaws in the glass.

Figure 21. Iron test reagent vial

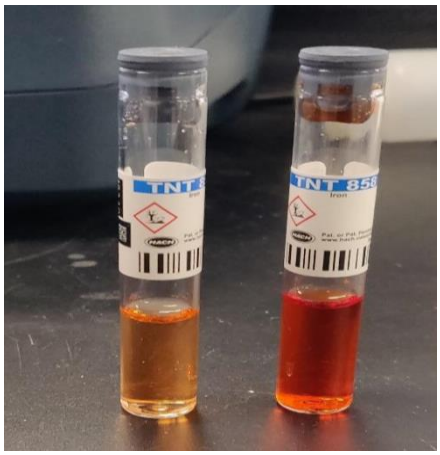


Figure 22. Vials with sample solutions

Figure 23. Identification of iron concentration in solution by bar-code determination method

The Hach TNT 585 kit can only measure concentration of iron between a range of 0.2-6 mg/L. Series dilutions were done while the concentration became higher than that range. The spectrophotometry reading indicated the out of range concentration by displaying the reading in red color.

Figure 24. Spectrophotometer dial displaying an out of range iron concentration in sample

3.8.2 Release of 20% $NaHCO_3$- 80% PVAc pellet. In 1000 ml of DI release behavior of 20% $NaHCO_3$- 80% PVAc Pellet was evaluated. The test was conducted in triplicate. With the release of base from pellet, pH of the water in the beaker increased. The gradual rise of pH in the water was measured with a Hach manufactured pH meter. Reading was taken in every 30 minutes.

Figure 25. pH meter used for evaluating release of base pellet

3.8.3 Release of 1% $KMnO_4$- 99% PVAc pellet. The pellets were then added to 1000 ml of DI water in beakers. Stir bars were placed in all of the beakers, and the beakers were stirred at the same rotation setting. For $KMnO_4$ release measurement, 10 ml from each beaker removed at time intervals of zero, 0.5, 1, 5, 10, 15, 20, 60, 120, and 180 minutes. The $KMnO_4$ concentration was measured using a Hach DR-3900 set at 525 nm absorbance wavelength. The concentration of $KMnO_4$ was determined by using the absorbency of the mass calibration curve (Figure 28). Triplicate measurements were taken for every 10 ml of solution. The experiments were repeated in triplicate for the pellets using the same procedure as described above.

Figure 26. Kinetics release of potassium permanganate in water with agitation

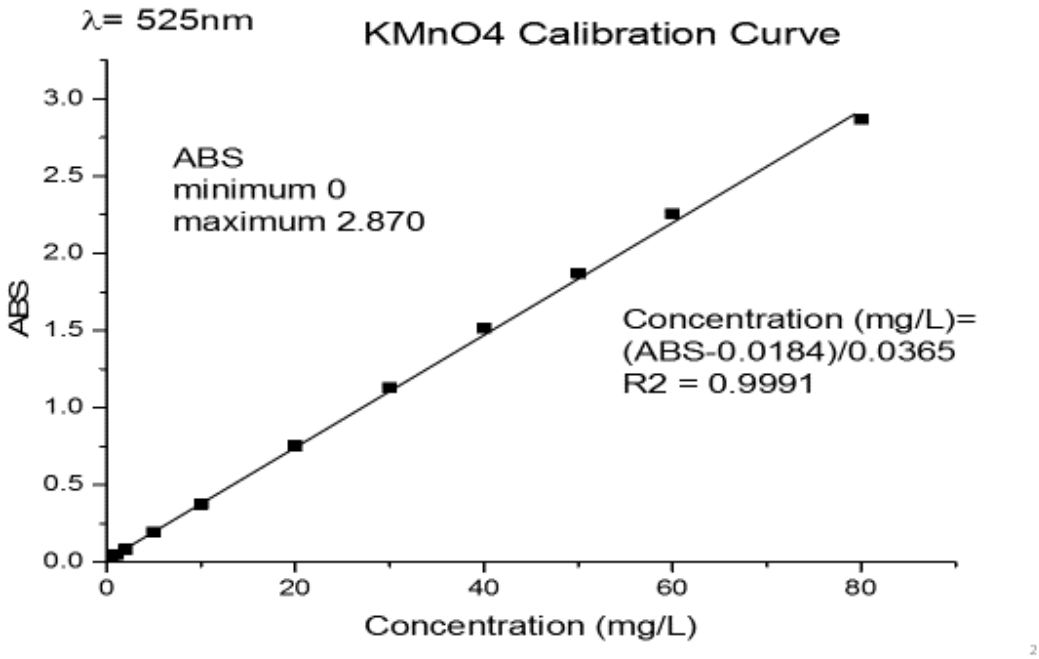


Figure 27. Calibration curve for calculating the concentration of potassium permanganate in the sample

3.9 Sample Location

Contaminated water from County Park Lake was used for the bacterial inactivation study. The park serves as a recreational site for the City of Greensboro. A coordinate of 30.07.44 N, 79.49.50w defines the location of the sampling area. The park has twined lake designated as Lake A and Lake B. A paddle boat facility is offered by Lake A and a fishing dock is situated on lake B. The circled point on the Map represented in (Figure 29) is the sampling point. This zone is duck and geese area. As objective of study was treating coliform bacteria from water, the location provides an ideal condition as it poses a high chance of fecal waste contamination.

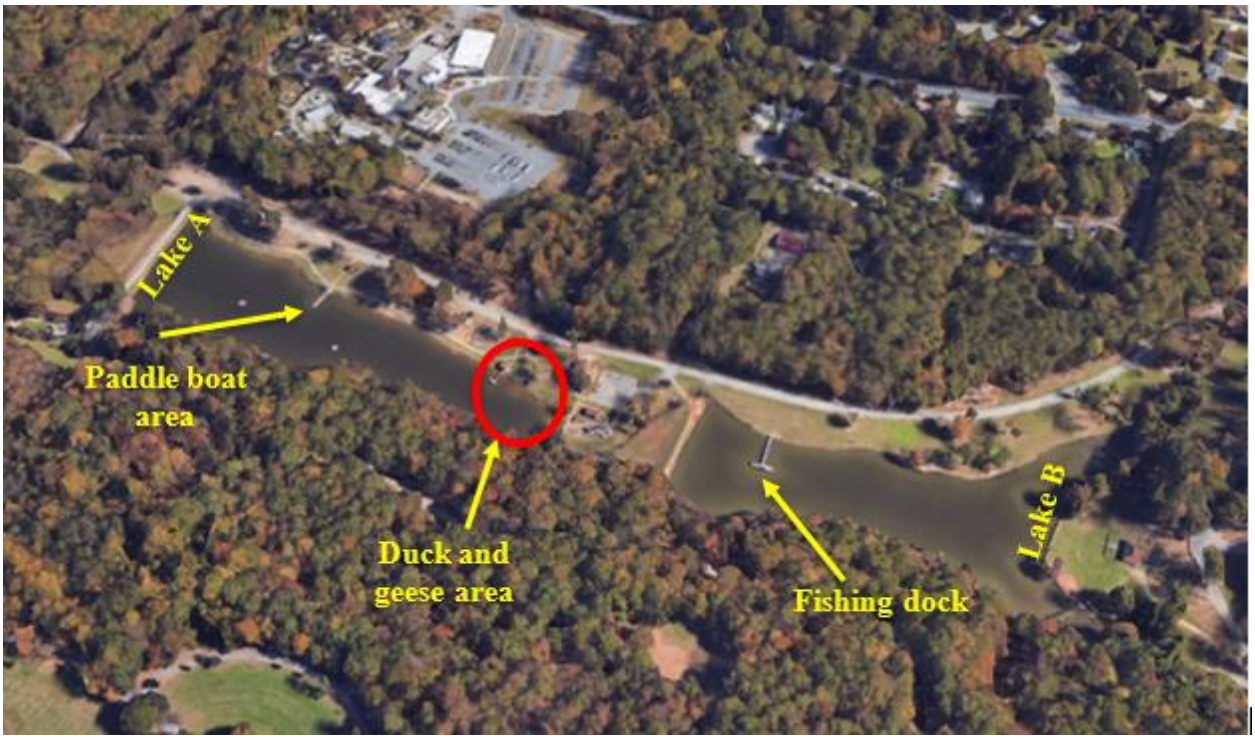


Figure 28. Site of contaminated water sample collection

3.10 Sample Collection

Sampling bottles, along with other experiment apparatus, were sterilized at 121°C for 15 minutes in an autoclave. For ensuring proper sterilization, a piece of autoclaved indicatory tape was placed on every item before sterilizing. The lids of all bottles were loosely closed as per autoclaving instruction. Bottles were labelled with the sampling date and location. Other instruments used for sample collection included gloves, safety goggles, Clorox wipes, paper towels, trash bags, and two sampling poles with adjustable lengths. A total of 25 litter of water sample were collected. To maintain the sample consistency, all the experiments were done with this reserve of water. The concentrations of active fecal coliform and E. coli bacteria within the lake water samples were measured on the day of collection to serve as a reference for calculating bacteria reduction. The IDEXX Colilert-24 MPN method was used to measure initial bacteria concentrations within untreated wastewater.

3.11 IDEXX Colilert-24

The concentration of coliform bacteria (Total coliform and E. Coli bacteria) in the sample water was ascertained using the IDEXX Colilert-24 Most Probable Number (MPN) method. For this test, one packet of Colilert reagent was mixed with 100 mL of sample water and poured into a Quanti-Tray. The Quanty-Trays are comprising of 49 large wells and 48 small wells. The tray was then heat-sealed using the Quanti-Tray Sealer and allowed to incubate at a temperature of 35±0.5 °C for 24 hours.

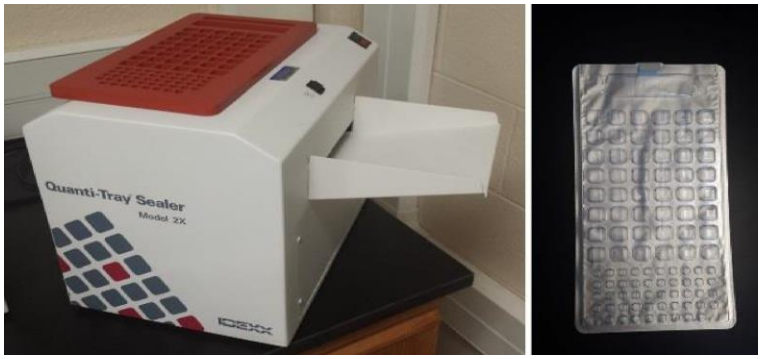


Figure 29. Quanti-Tray Sealer (left) and Quanti-Tray (right)

Figure 30. Quanti-Tray incubation

The reagent contains two enzyme substrates, a fluorogen, and chromagen which react with the galactosidase enzyme found in total coliforms and glucuronidase found in E. coli,

respectively. During subsequent incubation, incidence of coliform-positive reaction will be indicated by yellow colored tray wells in ambient light. E. coli-positive reaction will be specified by fluorescing wells under ultraviolet light (366 nm). To enumerate the most probable number of fecal coliform bacteria in the sample, the number of large and small yellow wells of each Quanti-tray was counted after 24 hours of incubation. These numbers corresponded to the rows and columns, respectively, of the IDEXX MPN table. The intersection of the row and column number represent the Most Probable Number of bacteria colonies forming units per 100 mL of water sample. The concentration for E. coli was obtained following the same procedure table reading using the number of fluorescing large and small wells.

3.12 Effect of Catalyst on Bacteria

To isolate the effect of catalyst on bacteria, the sample lake water was exposed to catalyst (Fe_2SO_4, $NaHCO_3$, and $KMnO_4$) pellets for 72 hours. The predetermined number of pellets were added to each beaker containing 1000 ml of contaminated water. To identify the effect of heat on bacterial growth, beakers containing 1000ml of sample water was placed in at 40^oC, which is the temperature used for heat activation of sodium persulfate. Control experiments were also conducted the whole time. 100 ml of samples were collected at 0, 24, 48, and 72 hours period from each beaker. Colilert reagent packet was added to the 100 mL sample and transferred into the Quanti-Tray. The Quanti-Tray was heat-sealed using the Quanti-Tray Sealer and incubated for 24 hours at a temperature of 35±0.5 °C. The concentration for total coliform and E. coli was obtained from MPN table.

3.13 Lake Water Disinfection

A continuous bacterial inactivation study was conducted to observe the coliform bacteria remediation ability of activated persulfate in control release polymer system. All the tests were

performed in triplicate. In this study, 20% sodium persulfate - 80% PVAc pellet was used. For iron activation a ratio of persulfate and Fe2+ of 1:1 and for $KMnO_4$ activation ratio of persulfate and permanganate of 10:1 was selected. For heat activation, a temperature of 40°C was determined and for alkaline activation pH 11 was maintained. 100 ml of samples were collected at every 3 hours and tests were continued until a complete remediation was obtained. The concentration of coliform bacteria was ascertained using the IDEXX Colilert-24 Most Probable Number (MPN) method.

Figure 31. Lab set up for bacteria remediation study

3.14 Methodology Summary

The following table summarizes the experiments conducted during this research study and briefly describes their purpose.

	Study	Purpose
1	Kinetic release of 60% PS-40%PVAc high-bake pellet (10 min @120°C)	Assess release kinetics of PS from PVAc matrix and determine the

	control release pellet in water.	relationship between kinetics and baking time
2	Kinetic release of 60%PS-40%PVAc low-bake pellet (4 min @120ºC) control release pellet in water.	Assess release kinetics of PS from PVAc matrix and determine the relationship between kinetics and baking time
3	Kinetic release of 60%PS-40%PVAc high-bake pellet (10 min @120ºC) control release pellet in soil column.	Assess release kinetics of PS from PVAc matrix and determine existence of relationship between kinetics and baking time
4	Kinetic release of 60%PS-40%PVAc low-bake (4 min @120ºC) control release pellet in soil column	Assess release kinetics of PS from PVAc matrix and determine existence of relationship between kinetics and baking time
5	Post column analysis for high-bake pellet (10 min @120ºC) control release pellet	Assess the captured amount of PS in high-baked pellet after column study
6	Post column analysis for low-bake pellet (4 min @120ºC) control release pellet	Assess the captured amount of PS in low-baked pellet after column study
7	Kinetic release of 20%PS- 80%PVAc no-bake control release pellet in water	Assess release kinetics of PS from PVAc matrix.
8	Kinetic release of 25% Fe $SO_4.7H_2O$ - 75% (no-bake) PVAc pellet in water	Assess release kinetics of iron from PVAc matrix.
9	Kinetic release of 20 % $NaHCO_3$- 80%	Assess the increase in pH level with the

	PVAc pellet	release of $NaHCO_3$ from PVAc matrix.
10	Kinetic release of 1% $KMnO_4$- 99% PVAc pellets	Assess release kinetics of $KMnO_4$ from PVAc matrix.
11	Preliminary coliform inactivation study (with powder form and control release pellet form of PS)	To select the weight amount PS to be used in further study and to ensure the success of controlled release of PS.
12	Effect of catalyst on bacteria	To isolate the effect of catalysts (heat, Fe2+, NaHCO3, $KMNO_4$) on bacteria from PS
13	Bacteria inactivation study	Assess the disinfection efficiency of control release of sodium persulfate activated by different control release catalyst

CHAPTER 4

Results

4.1 Kinetic Release of Sodium Persulfate - Polyvinyl Acetate (PS-PVAc) Control Release Pellet

The introduction of this thesis stated the undesirable impacts of applying a liquid phase of oxidant for in-situ chemical oxidation of soil and groundwater remediation. Therefore, this thesis intended to explore an alternative solution by encapsulating solid sodium persulfate oxidant in PVAc polymers. With the aim to formulate a sustainable control structure, the preliminary experiments were conducted to determine the effect of baking time on the formation of pellets and its oxidant release rate. Kinetic release of PS-PVAc pellet was investigated in water and in the sand column to differentiate the release behavior between low-bake and high-bake formulation.

4.1.1 Kinetic release of PS-PVAc control release pellet in water. Kinetic release studies were conducted with 60% PS- 40% PVAc pellet of 0.5-inch diameter produced by using hand press. The pellets were then baked in the oven at the temperatures of 120^{o}C for different baking times. The objective of this test was to determine the effect of heat from baking on release and formation of the pellets. Therefore, we evaluated “high-baked” versus “low-baked” pellets. The high-baked pellets for this experiment contained were baked at 120-degree C for10 minutes, where the low-baked pellets were baked at 100-degree C for 4 minutes. PVAc exhibits an all carbon–carbon single bond backbone. Possessing a highly flexible backbone without side groups, properties of PVAc are substantially temperature dependent [80]. It was hypothesized that the PVAc polymer could encapsulate the oxidant within the polymer and the high-baked pellet could slower the release of the oxidant from the pellet.

Each pellet was allowed to release in 500 mL of deionized (DI) water for 3 hours. Beakers were kept under continuous agitation at ambient temperature. A calibration curve was developed to convert triplicate absorbance measurements on the 650 nm wavelengths to units of concentration (mg/ L). Table 2 displays percent release of high-baked and low-baked PS/PVAc pellets after 3 hours of kinetic release:

Table 2.

Percent release of high-baked and low-baked 60% PS-40% PVAc in water with agitation after 3 hours of release

PS - PVAc Pellet	**% Release**	**Average % Release**	**PS - PVAc Pellet**	**% Release**	**Average % Release**
High bake #1 (10 min – 120ºC)	94.99 %	(95.95 ± 1.4) %	Low bake #1 (4 min – 120ºC)	98.99	(99.57± 0.4) %
High bake #2 (10 min - 120ºC)	97.85 %		Low bake #2 (4 min – 120ºC)	99.98	
High bake #3 (10 min - 120ºC)	95.01 %		Low bake #3 (4 min – 120ºC)	99.73	

The data presented in Table 2, shows that high-baked pellets released at a rate slower than the low-baked pellet. The average total percent release of sodium persulfate from the 10-minute baked 60%PS-40%PVAC pellets is 95.95 ± 1.4, which is lower when compared to the 4-minute baked pellets which are at (99.57± 0.4) %. The value of % release appears that baking time has an impact on the kinetic release in water. The variances in release could be due to the polymer-polymer and polymer-oxidant bond, or the oxidant is "taped up" within the melted polymer during baking, therefore, once cooled, the pellet has captured the oxidant to delay the release. However, the difference in percent release is not high enough to have any significant difference statistically. PVAc polymer can encapsulate the oxidant within the pellet, and the baking time can slow or control the release of the oxidant from the pellet.

To compare the release profile of high-baked and low-baked pellet the average concentration as well as percentage release obtained from both types of pellet were plotted against time (figure 33 and 34). The blue color-coded data plotted on the graph represents the Average PS concentration in mg/L (left Y-axis) while the orange color coded data provides are presentation of the average % release (right Y-axis)

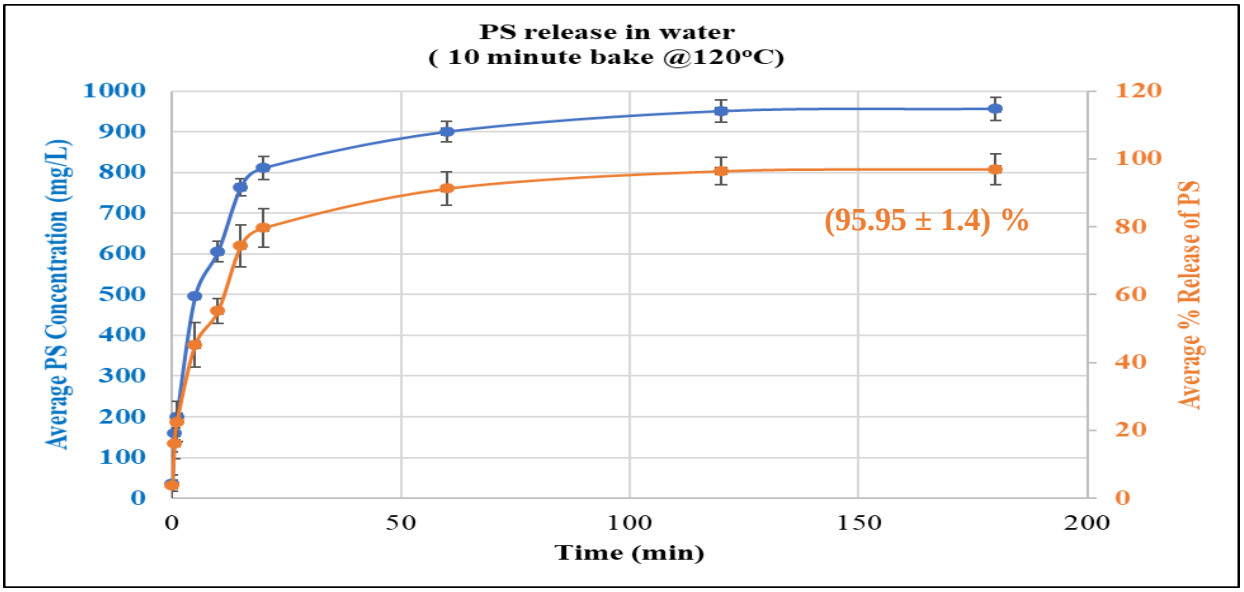


Figure 32. Average Concentration and Percentage Release in water of triplicate Runs (n=3) using 60% PS – 40% PVAc pellet, baked for 10 mins

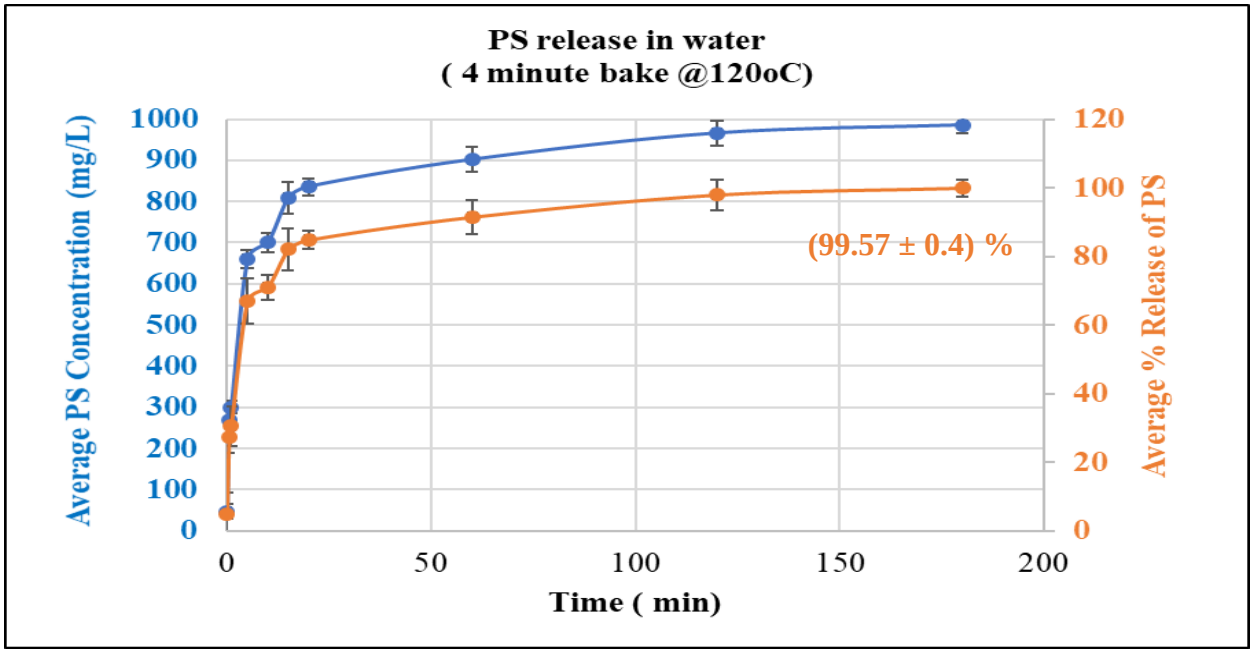


Figure 33. Average Concentration and Percentage Release in water of triplicate Runs (n=3) using 60% PS – 40% PVAc pellet, baked for 4 mins

The average sodium persulfate solution concentrations appeared to steadily increase over time with relatively small standard deviation for both high-baked and low baked formula.

Similarities in the release profiles from high-baked and low-baked pellets were also observed. Chemical dissolution rates from slow-release oxidants generally characterized as an initial flush, followed by a slower and sustained release (Christenson, 2011; Kang et al., 2004; Lee & Schwartz, 2007). In this experiment. Both profiles exhibited three sequential release phases: (1) a relatively high initial burst release; (2) a steady, slow and sustained increase in solution concentration; (3) a relative plateau in the concentration change. For instance, the high-baked sample displayed an average of 79.7± 2.1 % oxidant release during the first 20-minute initial burst. Percent release increased at a steady rate from 20 minutes to 120 minutes and at the end of 2 hours, the high-baked pellet released 95.04 ± 1.6 % of total persulfate from pellets. The final "segment" of the curve displays a very small rate of change in present release. The last hour of the test only contributed a release of 0.9 1± 1.4 %, which makes the total average of (95.95 ± 1.4) % release after 3 hours of experiments. This pattern is typical for monolithic matrix-type slow-release systems, where particle release is governed by the dissolution of soluble oxidants and then an occurrence of diffusive transport behavior through secondary permeability formed within the matrix (Lee & Schwartz, 2007). Based on this data of oxidant release from all structures at both bake time best fit zero order kinetic models as higher R^2 value(0.422) compared to first and second order models.

The visual observation regarding the structural alteration of high-baked and low-baked pellet exhibited that the low-baked PS pellets dissolve within 20 minutes from the start of the experiment (Figure 35). Figure 35 shows the pellet in water between 5 minutes to 3 hours, which shows the pellet dissolved. The high baked pellets maintained their physical shape (Figure 36). As seen in Figure 36, the high-baked pellets removed after 3 hours were not completely dissolved and remained intact.

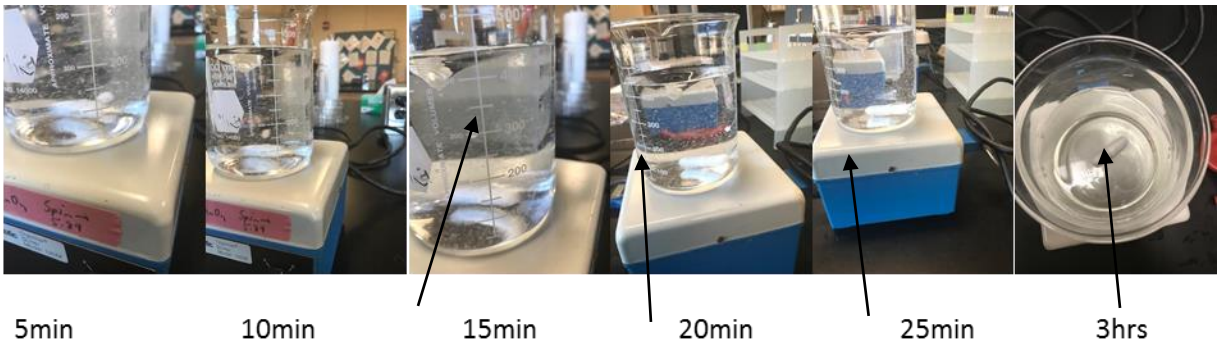


Figure 34. Kinetics release of PS low-baked pellets was dissolving completely within 20 min. Arrows point to the pellet in the beaker. Pellet particles visible in beaker after 25 minutes but not an intact pellet and pellet completely dissolved by the 3-hour time

Figure 35. PS high-baked pellets post 3 hours of kinetic release experiments

4.1.2 Kinetic release of PS-PVAc control release pellet in sand column. In column experiment, average percentage release, as well as an average concentration of 60 % PS and 40 % PVAc of high-bake and low-bake controlled release pellets, were determined. A closed system using Chromaflex (Kontes) glass (ID: 2.5 cm, length: 15 cm, v= 73.63 ml) was used for the experiment. To establish excellent sinking conditions for the controlled release pellets, the constant flow rate was maintained within the soil column using a peristaltic pump acquired from

(Cole Parmer Instrument Company) with pH 8 solution. Aliquots of 10 ml samples were continuously collected in a patterned time interval for 5 hours. The column experiments for both the high-bake and low-bake pellets were done in triplicate. Compaction was performed using a shaker attached to the soil column.

Table 3.

Percent release of high baked and low baked 60% PS-40% PVAc in sand column for 5 hours

PS - PVAc Pellet	**% Release**	**Average % Release**	**PS - PVAc Pellet**	**% Release**	**Average % Release**
High bake #1 (10 min – 120ºC)	21.77%	(17.87± 3.54) %	Low bake #1 (4 min – 120ºC)	89.02	(82.69± 4.58) %
High bake #2 (10 min – 120ºC)	14.85 %		Low bake #2 (4 min – 120ºC)	78.33	
High bake #3 (10 min – 120ºC)	16.99 %		Low bake #3 (4 min – 120ºC)	80.72	

Alike the oxidant release in water, in the soil column, control release pellet baked for 4-minutes, appear to release the oxidant at a higher rate than the pellets baked at a baking time of 10-minutes (Table 3). The low-baked pellet delivered an average percent release of 82.69 ± 4.58. The high baked pellets present the percentage release of sodium persulfate of 17.87 % with a

standard deviation of 3.54. The low percentage release of PS in the high baked pellets highly confirms a controlled release of the oxidants for 5 hours from the start of the experiment. This result ensures that longer baking time results in increased control of the oxidant's release from the polymer matrix.

In case of column study, a constant flow of water was supplied through the sand pile. The pellet was placed at the middle of the sand column. So, the pellets were only exposed to a very slow laminar flow of water through sand. This could be a reason of slower diffusion rate of PS from PVAc pellets, compared to kinetic release study of the pellet in water only. On the other hand, the sample was collected from the end point of the column. There is decent chance that an amount of PS got trapped within the sand while passing the sand path after diffusion and exhibited a lower average % release than release in water.

Plotting measured oxidant concentration versus time (min) for each sample for both high-baked and high-baked 60% PS- 40% PVAc produced the following curves (figure 37 and 38):

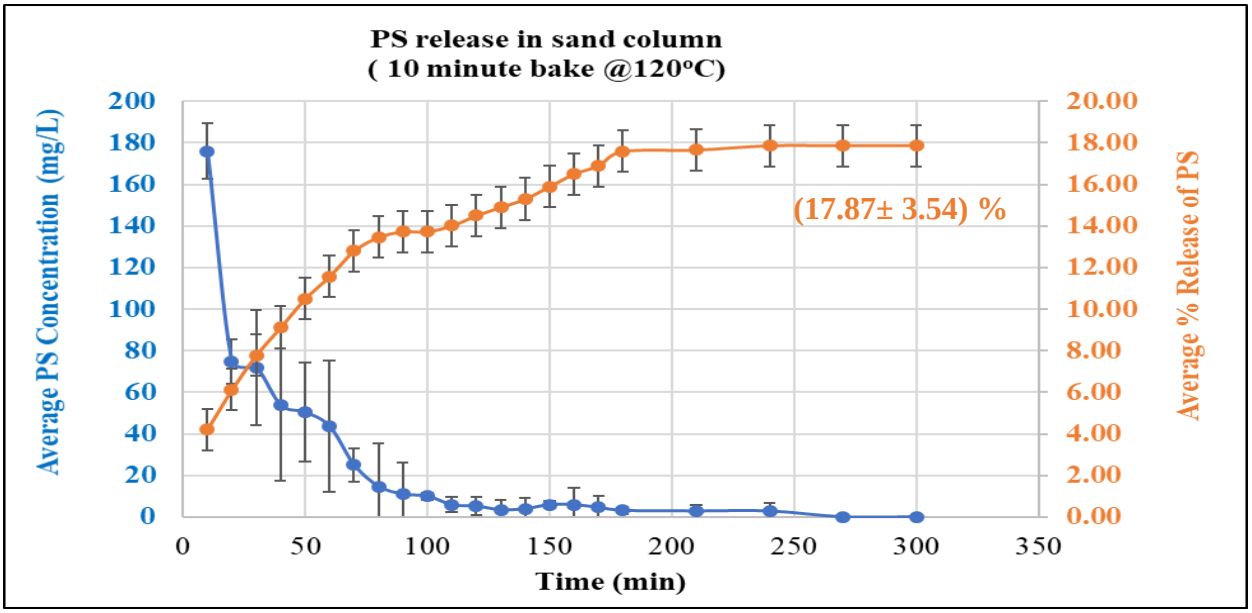


Figure 36. Average Concentration and Percentage Release in sand column of triplicate Runs (n=3) using 60% PS – 40% PVAc pellet, baked for 10- mins

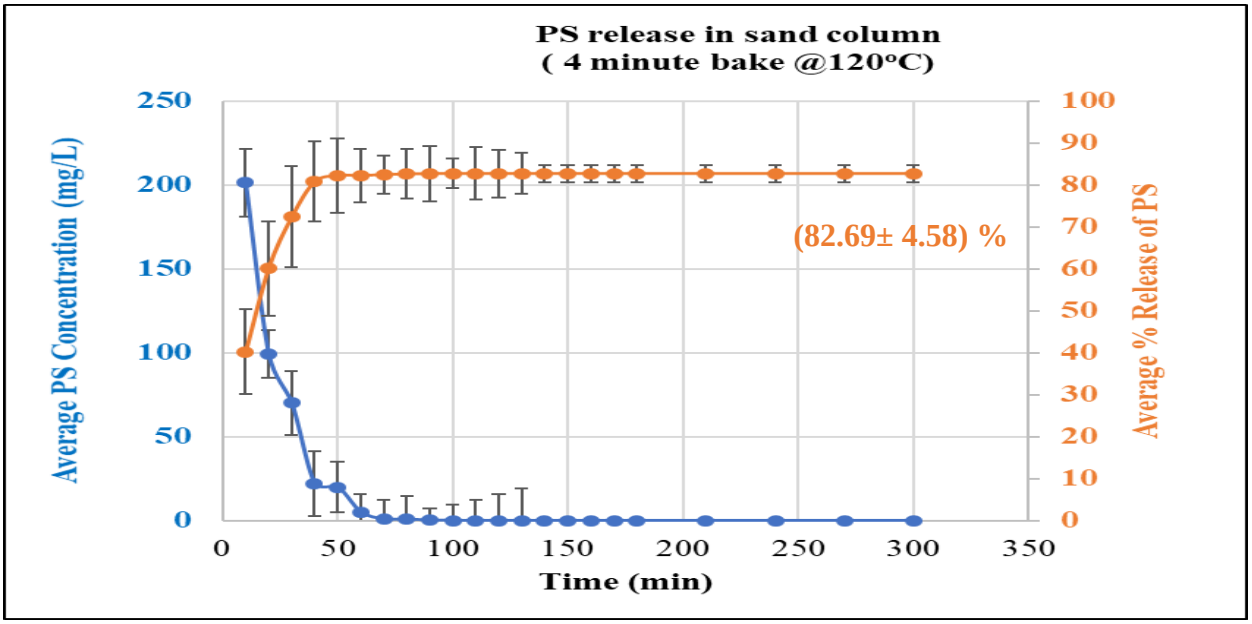


Figure 37. Average Concentration and Percentage Release in sand column of triplicate Runs (n=3) using 60% PS – 40% PVAc pellet, baked for 4-mins

Average sodium persulfate solution concentrations steadily decrease over time with relatively small standard deviation for both high-baked and low baked formula. Similarities in the release profiles from high-baked and low-baked pellets were also observed. (S. Liang et al., 2011) conducted a column study for laboratory-scale in situ oxidation barrier system (prepared from a mixture of sodium persulfate, cement, sand, and water). The release profile from their column study is highly comparable with the release profile of control release polymer pellet, which comprises with a high initial blast release followed by a very slow change in concentration. Low-bake PS/PVAc pellet release 82.69% of sodium persulfate with a standard deviation of 4.58. This high release of sodium persulfate is thought to be mainly because low baked PS pellets disassociate oxidant faster. DR-3900 measurements indicated that most of the of sodium persulfate from the low-baked pellet had diffused from the polymer within 60 minutes from the start of the experiment.

Upon observing the release behavior of low-baked and high-baked pellet in soil, an efficient approach of application can be prescribed. Deployment of a combination of low-baked and high-baked pellet could employ a long term, single application control release treatment. Where, the low-baked pellet could provide the initial oxidant supply to the higher contamination plume and the high-baked pellet could diffuse oxidant at a slow rate but through a very long period and take into account of any contaminant rebound.

4.2 Post Column Analysis

Low baked pellets released all most all oxidant in the sand column within 60 minutes from the start of the experiment, while high baked pellets continuously released oxidant over the 5 hours sand column runs. Following 5 hours of sand column experiment, the pellets were removed from the sand column and immersed in DI for 24 hrs. The pellets surface was pitted, and the average dry mass was (41.02 ±2.92) % of the initial mass. The original tablet shape and diameter of both low baked and high baked pellets remained unchanged after the pellets were removed from the sand column run (figure 39). In figure 39, the photo of the low-baked pellets appears to be more crystalline, whereas, the high-baked appears not to have the crystalline surface such that crystals are not visible. After running the pellets in the soil column, the pellets were added to 200 ml of DI water. Table 4 shows the remaining oxidant released in the water post-use in the soil column. The low bake released 5.13 ± 1.73% representing the near-complete release of the oxidant in the soil column run, whereas the high-bake pellet still contained oxidant in the pellet post-use in the sand column and released 51.06 ± 5.53% oxidant.

Table 4.

Post Columns analysis after 24 hours

Post column study	Percentage release (%) SP in 200 DI water
Low-bake 60%PS-40%PVAc pellet	5.13 ± 1.73
. High-bake 60%PS-40%PVAc pellet	51.06 ± 5.53

Figure 38. pellets post sand column experiment, low- baked (left), B: high-baked (right)

4.3 Statistical Analysis

In order to reveal any significant difference in oxidant release behavior related to various baking time, two-sided t-test was conducted. A t-test is a type of inferential statistic test, used to determine if there exists a significant difference between the means of two groups, which may be related in certain features. It is one of the popular statistical hypothesis tests in which the test statistic follows a t-distribution of a group, under the null hypothesis. An analytical programing software called 'R' was used to test the validity of hypothesis testing described as follow:

$$H_o: \mu \text{ Control} = \mu 1 = \mu 2 = \cdots.$$

$$H_a: \mu \text{ Control} \neq \mu 1 \neq \mu 2 \neq \cdots.$$

The test is based on the F-test statistic which fundamentally compares the ratios of the mean square error as well as the mean square leading to a suggested variability that exists between groups to that of within the groups studied. When performing the two-way t-test, a P-value is obtained and compared to a significance level of 0.05 or 95 %. In case the obtained p-value is lower than that of the significance level chosen, we fail to reject the null hypothesis and accept that there exists no statistical difference between the groups studied. On the other hand, if they obtained P-value is greater than the significance level, we reject the null hypothesis and accept the alternate hypothesis conceding that at least one of the groups is statistically different from the other groups chosen.

In our case, average concentrations obtained with low-baked and high-baked pellet triplicate release experiment are used to determine if the baking duration has significant implication in concentration changes within our preferred significance level.:

Table 5.

Output of the analysis for statistical comparison between the release concentrations obtained from the kinetic release experiment of high-baked vs low-baked control release pellet in water

t- Value	Degree of Freedom **df**	**P- Value**	Significance level **α**
0.42794	17.962	0.6738	0.05

Table 6.

Output of the analysis for statistical comparison between the release concentrations obtained from the kinetic release experiment of high-baked vs. low-baked control release pellet in sand column

t- Value	Degree of Freedom **df**	**P- Value**	Significance level **α**
0.54538	41.111	0.5884	0.05

From table 5, table 6, we can observe that the p values obtained, resulted in values that are higher than the significance level of α=0.05. which is suggesting that enough evidences did exist between the groups to reject the null hypothesis that states that our variable sample are equal (Ho : μ1=μ2…) consequently suggesting that there is no significant statistical difference between the concentrations obtained and thus pertains that the baking time did not have a significant effect on the release concentrations within our soil samples tested.

4.4 Bacteria Inactivation with PS in Control Release Polymer System

Fecal contaminated samples collected from 'County park' lake was used to conduct a bacterial inactivation study. Results from this experiment were used to assess the disinfection efficiency of control release of sodium persulfate activated by different control release catalyst.

4.4.1 Preliminary coliform inactivation study. To ensure that, sodium persulfate has the capability to remediate coliform bacteria, a preliminary bacteria inactivation study was performed. This part of experiment was also important to decide the mass amount of sodium persulfate salt that would be used in the control release matrix. In this experiment 0.1gm, 0.3gm and 0.5gm of powder sodium persulfate salt were added to 3 beakers each containing 1000ml of contaminated water from the sample reserve from the lake. To find the initial coliform count,

IDEXX Quanti-Trays was prepared at the beginning (t=0) of the experiments. A sample of 100 ml from each beaker was collected every 12 hours until complete remediation was achieved. The result showed that both 0.3 g and 0.5g of sodium persulfate were able to achieve complete decontamination of both total coliform and E. Coli at 12 hours. From the result, we decide to use the 0.3 g mass amount of sodium persulfate in control release form for the next step of the study. For the ease of wrapping and also for employing higher control in oxidant release, pellets were made with 20 weight % PS embedding in 80% weight PVAc polymer. Each PS-PVAc pellet weighed 0.5gm in total mass, and 0.1 gm of that weight was contributed by sodium persulfate salt. For the next level of the study, we used three 20%PS-80%PVAc pellets for each PS-catalyst combination. In a preliminary study, 20%PS- 80%PVAc pellets containing total 0.3gm of PS were added to the same amount (1000ml) of contaminating water, and the control release form of sodium persulfate was not able to inactivate coliforms at 12 hours. Figure 40 displays the Quanti trays after 12 hours of treatment with different mass amount of sodium persulfate, applied in both powder and pellet form.

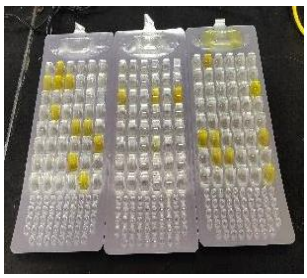
(a) Control @12 h;
average Total Coliform (TC) count = **>2419.2 mpn/100ml**

(b) Treatment with 0.1g PS (powder) @ 12 h;

Average Total Coliform (TC) count = **31.33 mpn/100ml**

(c)Treatment with 0.3 g PS (powder) @ 12 h;

Average Total Coliform (TC) count = **<1 mpn/100ml**



(d) Treatment with three 20%PS-80%PVAc (0.3 g mass amount of PS in control release form) @12h;

Total Coliform (TC) count = **8.3 mpn/100ml**

Figure 39. Triplicated Total coliform Quanti-Trays after 12 hours of treatment hours of treatments.

IDEXX Quanti-Trays were run in triplicate. The control showed a total coliform count greater than 2419.2 mpn/100 ml at the beginning of the study (t=0). The count remains unchanged after 12 hours of exposure to coliform contained lake water in the test environment (figure 40a). After

12 hours of treatment, 0.1g of powder PS was able to reduce the number of total coliform in 100ml of contaminated water to 31.33 mpn/100ml (figure 40b) , while 0.3g of PS powder achieved complete coliform inactivation and reduced the total coliform to less than 1mpn/100ml (Figure 40 c). On the other hand, controlled release treatment by 20%PS-80%PVAc displayed that after 12 hours of decontamination, the total coliform count was 8.3 mpn/100ml, even though the mass amount of PS in PS-PVAc pellets was 0.3g (Figure 40d). While comparing the Quanti tray count for treatment with 0.3gm direct powder PS and treatment with 0.3gm of control release PS, the results demonstrate that the rate of bacteria inactivation by control release PS was slower than direct PS application. This count indicates the success of control release bacteria decontamination by PS-PVAc matrix.

4.4.2 Kinetic release of 20% PS- 80%PVAc pellets – not baked. To investigate the kinetic release behavior of 20% PS- 80%PVAc pellets that are unbaked, a kinetic release study was performed following the same method as the previous kinetic release study of high-bake and low-bake pellet. As from previous kinetic release experiments, no statistical significance of baking time was found on oxidant release, for bacteria remediation study, no-bake pellets were used. Kinetic release experiment was conducted in triplicate with continuous agitation. At the end of three hours of study, the pellets released an average of 98.95% of the mass of oxidant contained. Figure 41 displays the oxidant release profile of 20% PS- 80%PVAc, no-bake pellet.

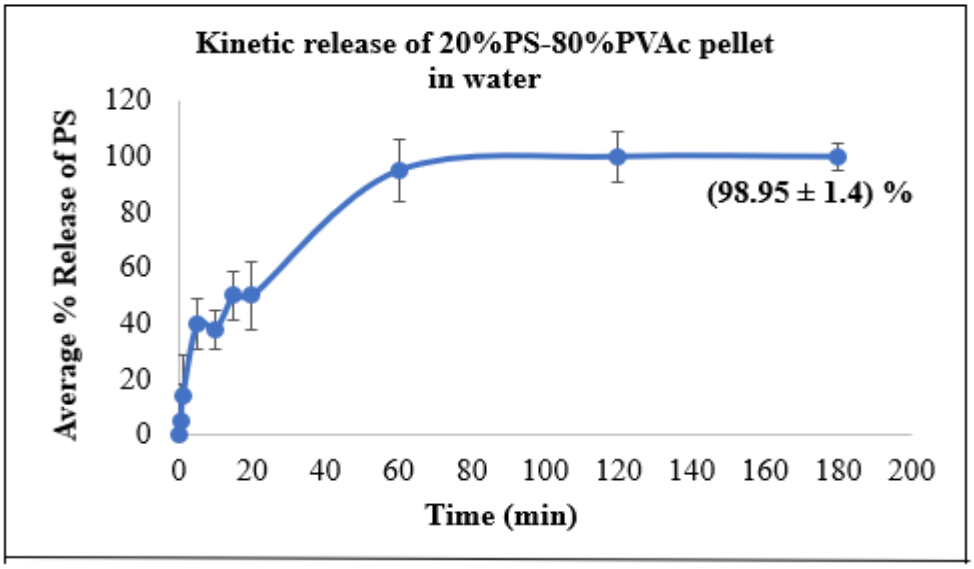


Figure 40. Average percentage release in the water of triplicate runs (n=3) using 20% PS-80%PVAc pellets (Not Baked)

The plot above displays that, the average concentration of sodium persulfate solution increased over time with moderate standard deviation. Alike kinetic release of high-baked and low baked pellet, oxidant dissolution profile of no-bake 20%PS-40%PVAc pellet portrayed an initial flush release followed by a slower and sustained release and a relative plateau in the concentration change at the ending segment. At the end of three hours of triplicate release experiment, the pellets released an average of 98.95% of the mass of oxidant contained.

4.4.3 Kinetic release of catalyst pellets. To activate persulfate in a complete control release matrix catalyst were also encapsulated in PVAc pellet. For controlled persulfate activation 25% Fe $SO_4.7H_2O$ - 75% PVAc, 20 % $NaHCO_3$- 80% PVAc, 1% $KMnO_4$- 99% PVAc pellets were produced and tested for sustainable kinetic release to ensure a sustainable release, kinetic release study was conducted.

4.4.3.1 Kinetic release of 25% Fe $SO_4.7H_2O$ - 75% PVAc pellet. To quantify the ability to release Fe^{2+} from 25% Fe $SO_4.7H_2O$ - 75% PVAc pellet, kinetic release study was conducted

in triplicate for this pellet formulation. The test was done in triplicate under continuous agitation. The concentration of Fe^{2+}in the solution was measured every 30minuets for 3 hours. Iron pellets appeared to release 100% iron within the experimental time frame (figure 42).

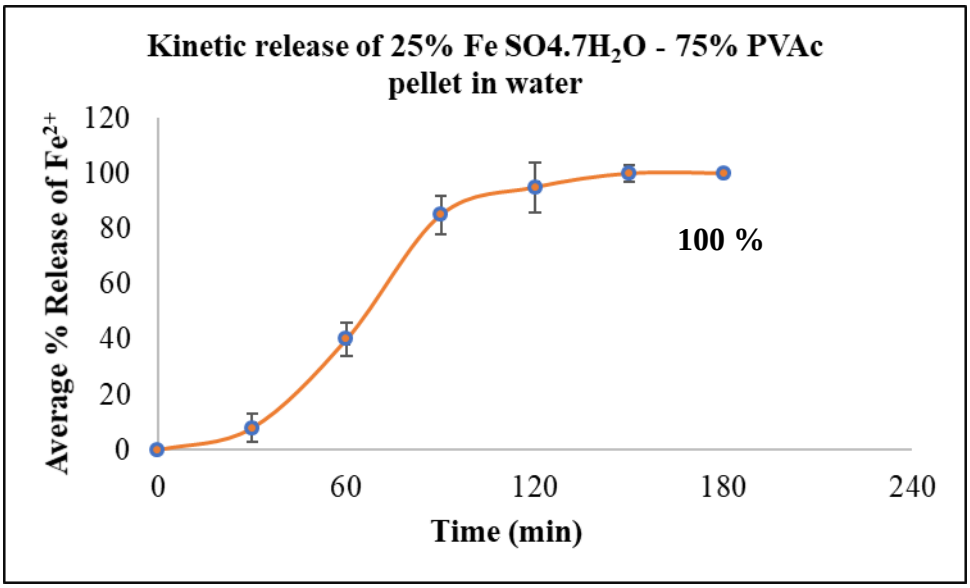


Figure 41. Average percentage release in the water of triplicate runs (n=3) using 25% Fe $SO_4.7H_2O$ - 75% PVAc pellet

The release profile of ferrous sulfate pellet exhibited two sequential release phases, a steady and sustained increase in solution concentration, followed by a very slow change in concentration segment. This result is also seen in previous work by other researchers investigating controlled release (Kambhu et al., 2017; S. Liang et al., 2011). Within the first 90 minutes the pellet release 85% of the total Fe^{2+} from the pellet and in the next 90minute remaining 15% was released. For the control experiment, the same mass amount of ferrous salt was mixed into an equal amount of DI water. The concentration of iron in the sample solution was measured using barcoded 'iron TNT 585 vial test' kit with the assistance of spectrophotometer (DR 3900). Because of high solubility $FeSO4.7H_2O$, the DR-3900 measurements of control solution showed a very high iron

concentration immediately. While achieving the same concentration from control release pellet acquired 120 min of kinetic release time. This verifies that the controlled release of Fe2+ is attainable.

For an effective iron activation of persulfate, a ratio of PS: Fe2+ of 1:1 is essential. Molecular mass of $FeSO4.7H_2O$ is 278, which includes 56 molecular mass of Fe^{2+}. While producing the control release iron-PVAc pellet, to deliver 0.1g of Fe^{2+} during PS activation process, the pellet should contain 0.5g of $FeSO4.7H_2O$ encapsulated in the polymer to achieve the desired delivery concentration. For the ease of pellet production and to ensure complete encapsulation, more polymer was needed to encapsulate the FeSO4 salt hence leading to a greater production of pellets. For every PS pellet, three iron pellets were needed to maintain the PS:Fe^{2+} ratio of 1:1. Because of higher number of pellets produced, the surface area available for chemical diffusion was higher. This could be a reason for higher percent release of iron from pellets. Moreover, the concentration of Fe2+ was measured by using 'iron test vial kit'. However, the kit could only measure a limited range of iron concentration. While using the kit, a series dilution was conducted to complete the measurement.

Iron activation of persulfate is one of the most popular activation techniques. However, a high dose of iron can promote $SO4^{\cdot-}$ scavenging and subsequently reduces the overall degradation rate and efficiency [81]. Therefore, it is essential to optimize iron dosing to achieve effective activation. The control release approach for iron supply to the system could ensure slower and continuous delivery of iron, instead of applying total lode at a time by following traditional method. By limiting iron supply, an efficient solution for $SO4^{\cdot-}$ scavenging problem could be achieved. Thus, establishment of control release iron approach can improve the

remediation applications by providing a sustained iron delivery to overcome scavenging issues with a single application and can lower overall project costs.

4.4.3.2 Kinetic release of 20 % $NaHCO_3$- 80% PVAc pellet. To compute the potential to increase pH level, kinetic release experiment of 20 % $NaHCO_3$- 80% PVAc pellet was performed in 1000 ml of DI water. The initial pH of the solution was 6. The pH reading was taken every 30 minutes. For control, the same mass amount of powder $NaHCO_3$ was added to 1000ml of DI water. Control release base pellet showed a slow, gradual increase of pH for the first 90 minutes of the experiment, and of the rest of the study time, the sample solution maintained the same pH level (pH=8). Kinetic release experiment was conducted for 300 minutes. To increase the pH value up to the required level (pH=11) extra amount of powder $NaHCO_3$ was added. However, neither the control test nor the controlled release sodium bicarbonate appeared to raise the pH value in their respective solutions.

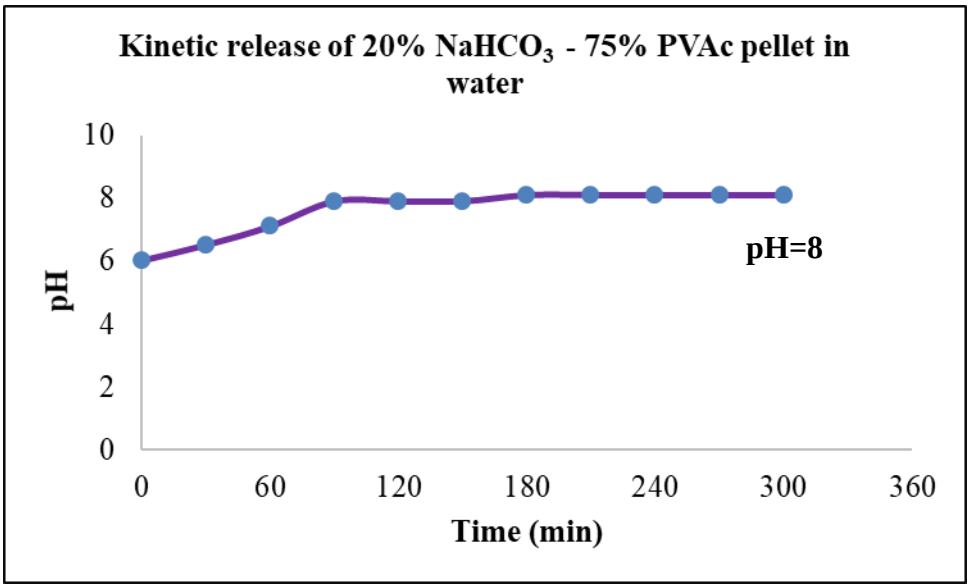


Figure 42. Average percentage release in the water of triplicate runs (n=3) using 20 % $NaHCO_3$-80% PVAc pellet

As for base activation of sodium persulfate, a pH 11 is mandatory, to increase the pH value, liquid sodium hydroxide was added. From the release behaviors of control release base, we concluded that complete controlled base activation of PS by sodium bicarbonate is not attainable because we only reached a pH of 8 after 300 minutes of exposure.

Where the pH scale runs from 0 to 14, with 0 representing acidic solutions like battery acid and 14 representing alkaline solutions like liquid drain cleaner, $NaHCO_3$ pH rests around 8.4 on the pH scale.. The effect of $NaHCO_3$ could be influenced by the current pH of water, but it is not possible to raise the pH above 8.4. For future studies, persulfate activation with sodium carbonate (Na_2CO_3) is suggested for employing control release base activation as literature refers that, when dissolved in water, Na_2CO_3 tends to form solutions with pH values between 11 and 12.

4.4.3.3 Kinetic release of 1% $KMnO_4$- 99% PVAc pellets. The release behavior of 1**%** $KMnO_4$- 99% PVAc Pellet was evaluated. The test was conducted in triplicate. Samples were collected at a patterned interval. The concentration of KMnO4 was measured using a Hach DR-3900 set at 525 nm absorbance wavelength. The concentration of KMnO4 was determined by using the absorbency of the mass calibration curve.

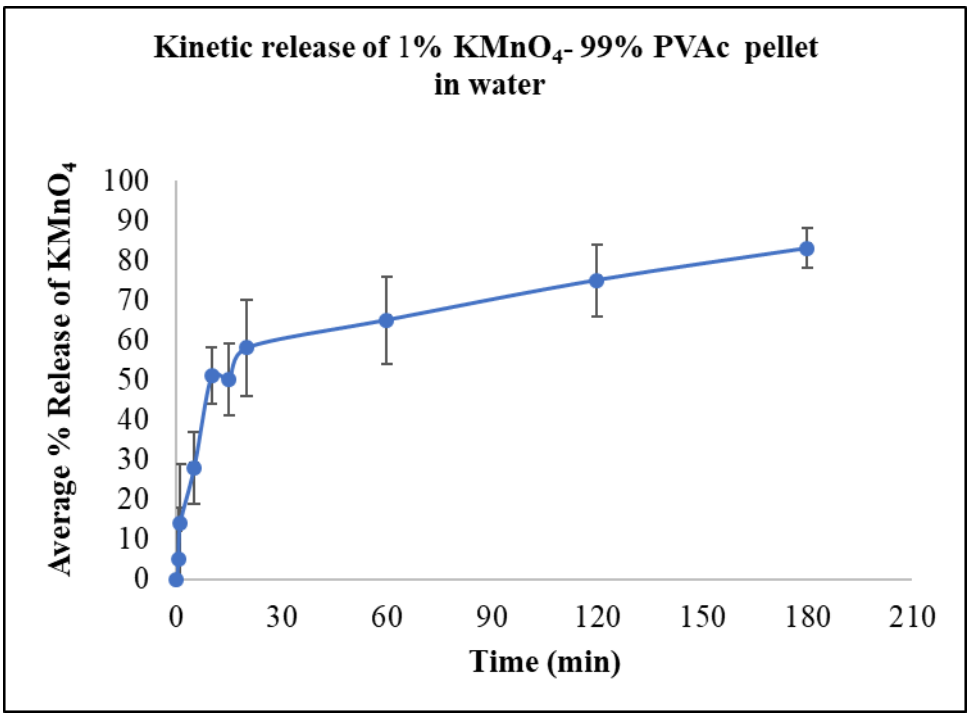


Figure 43. Average percentage release in water of triplicate runs (n=3) using 1**%** $KMnO_4$- 99% PVAc Pellet

The release profile can be characterized by a dramatic peak early in concentration, followed by a sustained decrease in concentration to finally reach a plateau. This pattern is typical for monolithic matrix-type slow-release systems, where the chemical release is governed by the dissolution of soluble oxidants and then an occurrence of diffusive transport particle through secondary permeability formed within the matrix (Lee & Schwartz, 2007). The $KMnO_4$ on the external edges of the matrix dissolves readily, which leads to an initial spike in the amount of MnO_4 released.

Several researches have confirmed that in situ chemical oxidation of $KMnO_4$ produces MnO_2 as a byproduct. The presence of MnO_2 can be visually confirmed through the dark to brown color. Initial production of colloidal size particles of MnO_2 follows an agglomeration process, which creates larger particles (Crimi & Taylor, 2007). The accumulation of MnO_2

affects the subsurface atmosphere significantly by alternating the subsurface hydraulic conductivity as well as permeability (Li & Schwartz, 2004). Thus, solid form of MnO_2 can lead to critical modifications into the treatment effectiveness.

While MnO_2 has negative impacts on in situ contaminate remediation, it can be employed as an effective catalyst for persulfate activation to remove contaminant efficiently. The objective of using $KMnO_4$ along with the PS in bacteria activation study is to promote a sustainable combined treatment approach where $KMnO_4$ loaded pellet could establish a sustained supply of persulfate activator.

Our research team has already confirmed the formation of MnO_2 during the kinetic release of $KMnO_4$ through XPX analysis. For this particular thesis study, the concentration of MnO_2 was not measured through XPX analysis, however, during a visual investigation of the effect of $KMnO_4$ on coliform contaminated lake water an accumulation of MnO_2 was observed. In Figure 45, the brown deposits at the bottom of the beaker may be MnO_2 formation.

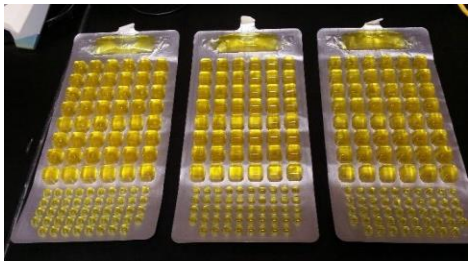
Figure 44. Accumulation of MnO2 during kinetic release of $KMnO_4$ pellet

4.5 Effect of Catalyst on Bacteria

The investigation was conducted to identify any significant effect (removal or growth) of bacteria based on the selected catalyst (e.g. heat, $NaHCO_3$, Fe^{2+} or $KMnO_4$). Contaminated lake water from the sample reserve was exposed to the controlled release catalyst pellets for 72 hours. In order to establish a baseline for comparison, IDEXX Quanti-Trays for control samples were prepared in triplicate on the day experiment. Result of bacteria counts exhibited that the heat, base, and iron have little to no effect of coliform decontamination. However, $KMnO_4$ appeared to pose substantial bacteria removal potential and therefore is feasible as the oxidant used in pellets for bacteria.

As, untreated samples contained high concentrations of both total coliform and E. coli, for bacterial growth investigation, the sample was diluted before performing IDEXX Colilert measurement to render quantifiable values. None of the activators exposed any effect on coliform growth as well. Figure 46 displays the Quanti trays after 72 hours of exposure to different catalysts applied in ($NaHCO_3$, Fe^{2+} or $KMnO_4$) pellet form.

(a) Control @ 72 h;
average Total Coliform (TC) count = **>2419.2 mpn/100ml**



(b) Bacteria Contaminated water from Country Park + Heat @ 72 h;
average Total Coliform (TC) count = **>2419.2 mpn/100ml**

(c) Bacteria Contaminated water from Country Park + Fe^{2+} @ 72 h;
average Total Coliform (TC) count = **>2419.2 mpn/100ml**

(d) Bacteria Contaminated water from Country Park + NaHCO3 @ 72 h;
average Total Coliform (TC) count = **>2419.2 mpn/100ml**

(a) Bacteria Contaminated water from Country Park + $KMnO_4$ @ 72 h;
average Total Coliform (TC) count = **1 mpn/100ml**

Figure 45. Effect of persulfate activation catalyst on total coliform

IDEXX Quanti-Trays were run in triplicate. The control presented an average total coliform count greater than 2419.2 mpn/100 ml at the beginning of the study (t=0). The count remains unchanged after 72 hours exposure of coliform contained lake water in the test

environment (figure 46a). After 72 hours of study, the resulting total coliform counts exhibited that heat (figure 46b), and iron (figure 46c) and base (figure 46d), have insignificant effect of coliform inactivation and did not reduce bacteria levels. As like the control study, all of the bacteria contaminated water + activator pellet combination provided same count of total coliform (>2419.2 mpn/100ml). In contrast to the control with heat, base or iron (Figures 46a - c), we see that the $KMnO_4$ exhibited extensive bacteria removal potential (Figure 46d). Within the experimental time frame, $KMnO_4$ reduced the coliform count from 2419.2 mpn/100 ml down to 1mpn/100ml.

4.6 Bacteria Inactivation Study

Bacterial inactivation study was conducted to observe the coliform bacteria decontamination ability of activated persulfate in control release polymer system. All the combination of controlled release catalyst and PS were allowed to release in 1000ml of contaminated lake water. All the tests were performed in triplicate. Bacteria concentrations were enumerated at every 3 hours of oxidative treatment using the IDEXX Colilert detection technique. The treatment continued until complete decontamination was achieved. It was hypothesized that that heat, Fe2+, $NaHCO_3$, and $KMnO_4$ would activate the persulfate and accelerate the remediation of coliforms while all the activators and persulfate are applied in a control release system. Observations from this experiment supposed to be attributed to the controlled release PS activation success indication, translated from the disinfection strength of the oxidant-catalyst combinations. Table 7 presents the total coliform count and Table 8 presents the E. Coli coliform counts for every 3 hours of treatment until complete fecal coliform inactivation was achieved.

Table 7.

Total coliform concentrations per 100 mL for control release treatment

Treatment time (h)	Only PS (MPN/100ml)	PS+heat (MPN/100ml)	Ps+Fe2+ (MPN/100ml)	PS+base (MPN/100ml)	Base (PS + $KMNO_4$) (MPN/100ml)
0	2419.2	2419.2	2419.2	2419.2	2419.2
3	72.93	75.8	49.5	6.76	<1
6	41.73	38.23	1	<1	<1
9	25.63	14.73	<1	<1	<1
12	8.67	1	<1	<1	<1
15	5.20	<1	<1	<1	<1
18	3.77	<1	<1	<1	<1
21	3.06	<1	<1	<1	<1
24	2.01	<1	<1	<1	<1
27	1	<1	<1	<1	<1
30	<1	<1	<1	<1	<1

Table 8.

E. Coli concentrations per 100 mL for control release treatment

Treatment time (h)	Only PS (MPN/100ml)	PS+heat (MPN/100ml)	Ps+Fe2+ (MPN/100ml)	PS+base (MPN/100ml)	PS+ $KMnO_4$ (MPN/100ml)
0	185.47	190.35	179.99	191.8	178.2
3	61.13	63.73	3.9	6.4	<1

6	38.83	33.96	1	<1	<1
9	21.96	13.73	<1	<1	<1
12	7.13	1	<1	<1	<1
15	3.43	<1	<1	<1	<1
18	3.40	<1	<1	<1	<1
21	1.7	<1	<1	<1	<1
24	1	<1	<1	<1	<1
27	<1	<1	<1	<1	<1
30	<1	<1	<1	<1	<1

From the total coliform and E. Coli count presented in table 7 and 8, they show that 'PS- only' (non-activated) treatment required longer to reduce bacteria levels than the 'PS- catalyst' treatment system. The least effective system was heat activation as 'PS +heat' system which 'obtained highest time (15 hours) to complete the disinfection process among all other 'PS-catalyst' combination. 'PS-Only' treatment took 30 hours to complete the treatment process, which is two times higher than complete bacteria inactivation time by heat activation system. PS+ Fe2+, PS+base, PS+$KMnO_4$. The PS+Fe2+ required 9 hours to complete reduce bacteria levels to <1 mpn/100 ml. The PS+base required 6 hours and the PS+$KMnO_4$ required 3 hours for reduction to <1 mpn/100 ml. This proves that the hypothesis is true, that heat, Fe2+, $NaHCO_3$, and $KMnO_4$ can activate the persulfate and accelerate the remediation of coliforms while all the activators and persulfate were applied in a control release system. Figure 47 displays the comparison among required treatment time for each combination of PS and activator:

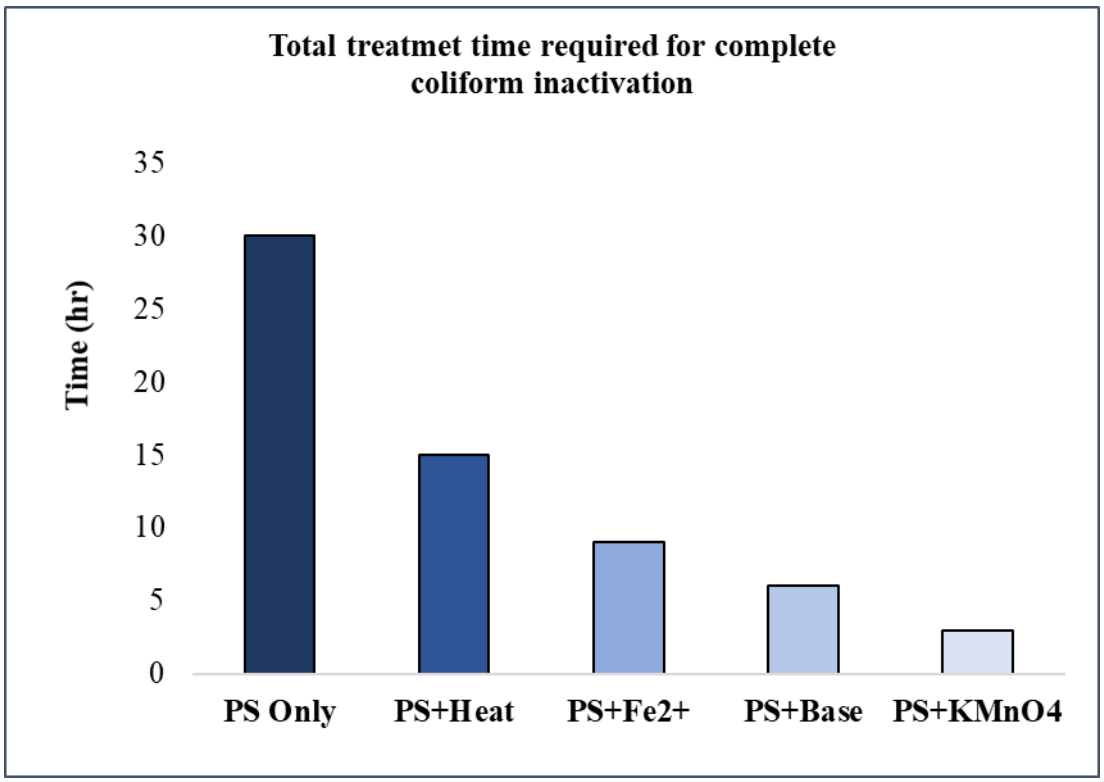


Figure 46. Comparison of total time required for complete bacteria remediation by different persulfate activation system

Base activation and permanganate activation seem to be the best persulfate activation in controlled release system, while the activation capacity is translated from the system's coliform inactivation efficiency. However, from the kinetic release CRP base pellet, it was evidenced that solid phase of base ($NaHCO_3$) does not have the capability to increase the pH level up to the required value. To create the optimum basic environment for persulfate activation, liquid form of base (NaOH) was added in the system. Application of liquid phased base might contribute to higher rate of sulfate free radical generation thus increased the bacteria remediation rate. On the other hand, $KMnO_4$ presented a high potential of bacteria inactivation when the effect of permanganate (excluded from persulfate) on contaminated lake water was isolated in the preliminary study. A debate was raised about the contribution permanganate and activated persulfate during the treatment process. $KMnO_4$ was supposed to create MnO_2 and thus activate

the persulfate. From the kinetic release of control release $KMnO_4$ pellet, it was evidenced that generation of MnO_2 requires longer release time. Nevertheless, control release 'PS-$KMnO_4$' system accomplished complete bacteria inactivation only in 3 hours. Because the $KMnO_4$ deactivated the bacteria within 3 hours, MnO_2 was not produced within the experimental timeframe. Longer treatment times with $KMnO_4$ may yield the production of MnO_2 which should be considered as a potential concern for controlled release persulfate activation. Literature supports that the production of MnO_2 positively impacts the activation of persulfate. Therefore, for sites where a mixture of chemicals is the focus for the remediation efforts, the use of $KMnO_4$ with persulate and result in advantageous co-reactions to reduce chemical contamination. In this study, the goal was to evaluate bacteria. Therefore, future research in the use of $KMnO_4$ activation of persulfate to treat contaminants is warranted to evaluate effectiveness of controlled release $KMnO_4$+persulfate.

On another observation, all of the treatment system showed a high inactivation of coliforms within the first 3 hours, followed by a slow and steady coliform decrease. For example, for 'PS Only' treatment system, total coliform count dropped from 2419.2mpn/ 100ml to 72.93mpn/100ml within the first 3 hours of treatment and from 72.93mpn/100ml to complete total coliform inactivation (<1 mpn/100ml) was achieved by 27 hours. This inactivation pattern is comparable to the oxidant release profile of PS-PVAc control release pellets where the chemical dissolution rates from slow-release persulfate exorbitated an initial flush, followed by a slower and sustained release.

CHAPTER 5

Discussion and Future Research

Application of controlled-release polymer systems (CRPS) serves as a novel advancement in the in-situ chemical remediation of water resources. By providing sustainable delivery, oxidants encapsulated in biodegradable polymers such as PVAc (polyvinyl Acetate) can increasing contaminate remediation efficacy and lower the overall project costs.

Kinetic release study was conducted for two formulations (low-bake and high-bake) of 60%PS-40%PVAc pellet to identify the effect of baking time on the release of CRP pellet. Result of the kinetic releasees in water showed a comparable percentage release of 95.95 ± 1.4 % for high-baked structure and 99.57± 0.4% for low-bake structure. On the contrary, high-baked controlled release pellets tested in sand column showed an average release percentage of 17.87±3.54% where average release percentage for low bake pallet was 82.69 ± 4.58%. But there was no significant effect of baking time on oxidant release rate was confirmed while statistical analyses were performed.

Bacterial inactivation study was conducted to observe the coliform bacteria decontamination ability of persulfate, activated in control release polymer matrix. For this part of the examination, all the catalysts (Fe^{2+}, $NaHCO_3$, $KMnO_4$) as well as persulfate were encapsulated in PVAc polymer separately. Kinetic release study of each catalyst exhibited sustainable release behavior. Experimental results for the bacteria inactivation study confirms the success in persulfate activation process in control release system. Control releasee heat and iron activation was able to compete decontamination in 15 hours and 9 hours. Non-activated persulfate required 30 hours to complete the treatment. Control release of base activation was partially achieved.

For future work, because control release of sodium persulfate is a relatively new remediation approach, a number of potential studies exists for future research. Future research is needed to understand persulfate encapsulation in other polymers, which could be tested to identify the best combination. FTIR analysis could be done to monitor the chemical changes of pellet over time to ensure long term stability. Treatment of persulfate amenable organic component could be tested in control release form. For effective contaminant removal, persulfate activation is essential. Research can be extended for persulfate activation in control release system. Chemical analysis can be conducted to detect the rate of sulfate free radical generation.

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