DEGRADATION OF TRICLOSAN BY SULFATE RADICALS GENERATED BY METAL-MEDIATED ACTIVATION OF OXIDANTS

by

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Presented to the Faculty of the Graduate School of
The University of Texas at Arlington in Partial Fulfillment
of the Requirements
for the Degree of

DOCTOR OF PHILOSOPHY

THE UNIVERSITY OF TEXAS AT ARLINGTON

August 2012

ACKNOWLEDGEMENTS

The journey of my Ph.D. studies has been very fascinating with the challenges of combining academic work, family life, and church leadership, and I am indebted to the Almighty God who has strengthened me through it all. To Him is all the glory. Many individuals also contributed significantly towards my accomplishment and they are worthy of honor.

Words cannot express my profound gratitude to Prof. Hyeok Choi, as my research advisor and dissertation committee chair, for his continuous support, motivation, extraordinary scientific and professional guidance. He is a great mentor and an inspiration to me, and I am highly honored to have him as my coach and to be his first Ph.D. graduate.

I am grateful to the other members of my dissertation committee, Profs. Andy Kruzic and Melanie Sattler (Civil Engineering Department) for offering valuable advice, feedback, suggestions, encouragement and support throughout my study period at UTA, Prof. Qinhong Hu (Earth and Environmental Sciences Department) for his dedication, commitment, and guidance, especially during the analysis of some of my samples, and Prof. Yan Li (Mathematics Department) for her insightful directions and recommendations. I am also grateful to Prof. Kevin Schug, Dr. Samuel Yang, and Ms. Evelyn Wang (Chemistry and Biochemistry Department) for testing my samples in their analytical laboratory.

The staff in Civil Engineering Department contributed in diverse ways to make my studies at UTA a success and I am grateful to all of them. In particular, Sara Ridenour was of tremendous help. I also wish to acknowledge the contributions of my colleagues in Dr. Choi's research team and other environmental engineering research groups, friends, family members, and loved ones from all walks of life for their encouragement, motivation, and the moments we shared together.

I also thank the following institutions and organizations for their support in the form of fellowships, scholarships, awards, and grants: United States Geological Survey (USGS), Texas Water Research Institute (TWRI), American Chemical Society (ACS), Racetrac Petroleum Inc., The University of Texas at Arlington (UTA), Civil Engineering Department, and the Construction Research Center.

Most of all, I am very grateful to my dear wife, Gladys, who worked tirelessly, and children (John, Daniel and Deborah) for sacrificing the pleasures of a husband and father to give me all the support and encouragement to accomplish this dream of my life.

July 16, 2012

ABSTRACT

DEGRADATION OF TRICLOSAN BY SULFATE RADICALS GENERATED BY METAL-MEDIATED ACTIVATION OF OXIDANTS

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The presence of persistent and toxic compounds, especially pharmaceuticals and personal care products (PPCPs) in water resources has generated considerable scientific, regulatory, and public interests, requiring the development of cost-effective technologies for the management of PPCPs-contaminated water resources. In particular, triclosan (TCS, 5-chloro-2-(2,4-dichlorophenoxy)phenol), an important antimicrobial agent widely used in many PPCPs, has attracted significant attention due to its potential endocrine disrupting capabilities. In order to address these concerns, advanced oxidation processes (AOPs), resulting in the generation of stronger oxidizing species, typically hydroxyl radicals (HRs) and sulfate radicals (SRs), have been studied and proposed to be effective to degrade a wide variety of organic compounds. However,

most of the research studies and applications have been focused exclusively on hydroxyl radicals (HRs)-based AOPs.

I evaluated the potential of sulfate radicals (SRs)-based AOPs as a new environmental risk management option for PPCPs-contaminated water with a focus on the decomposition of TCS. Sulfate radicals, generated by the activation of peroxymonosulfate (PMS) and persulfate (PS) with transition metals, exhibited high potential for the decomposition and mineralization of PPCPs. A series of dose-response studies were conducted to optimize the doses of oxidants and metals for the degradation of TCS. The speciation of metals under different pH regimes, which is a key to understanding the efficiency of radical generation, was elucidated. However, additional studies are required in order to propose SRs-based AOPs for large scale practical applications, including identification of the reaction intermediates and monitoring of toxicity.

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CHAPTER 1

INTRODUCTION

1.1 Pharmaceuticals and Personal Care Products

Recent advances in environmental health and analytical chemistry make it possible to detect and identify many toxic organic compounds in the environment at trace levels (Daughton and Ternes, 1999; Halling-Sørensen, et al., 1998; Jones, et al., 2001; Khetan and Collins, 2007). Among these compounds, pharmaceuticals and personal care products (PPCPs) are the most significant (Ankley, et al., 2007; Caliman and Gavrilescu, 2009; Ellis, 2006; Snyder, et al., 2003). PPCPs include soaps, skin care products, insect repellants, sunscreens and cosmetics, and health care products such as birth-control hormones, antibiotics, blood lipid regulators, analgesics, anti-inflammatory drugs, and veterinary medicines. An interesting short article was published in *Chemical and Engineering News* in 2010 pointing out that when we swallow a drug for medical remediation, we are anticipating its effects on our body, without considering its final destination (Everts, 2010). The primary route of PPCPs in water resources is via wastewater treatment plants. Many pharmaceuticals are administered orally, incompletely metabolized, excreted in urine or feces and eventually end up in wastewater treatment plants. Similarly, chemicals in personal care products are washed down the drain and end up at wastewater treatment plants. In addition to discharge of wastewater effluent, PPCPs may enter the aquatic environment through the land-application of sludge as well as surface water runoff from industries (Halling-Sørensen, B., 1998).

The U.S. Geological Survey has reported the detection of PPCPs in several waterways throughout the US (Kolpin, et al., 2002). Many other studies have quantified a broad array of PPCPs in rivers, lakes, groundwater, and sediments throughout the world (Buser, et al., 1998; Heberer, 2002; Miller, et al., 2008; Singer, et al., 2002; Ternes, 1998). Discoveries that some PPCPs have global distribution, environmental persistency, presence in humans and wildlife (bioaccumulation), and likely carcinogenic toxicity, have resulted in the classification of some environmental contaminants in PPCPs as emerging chemicals of concern (ECCs) and endocrine disrupting compounds (EDCs). This has led to considerable scientific, regulatory, and public interest (Ankley, et al., 2007; Caliman and Gavrilescu, 2009).

The water and wastewater industries face a great challenge as a result of the growing concern of the public about the presence of PPCPs in water resources. Among many PPCPs, the US Environmental Protection Agency is worried about the potential for endocrine disruption resulting from human exposure to triclosan (TCS), the most widely used antimicrobial chemical in soaps, body washes, and toys (Erickson, 2010). **S**ulfamethoxazole (SMX), a sulfonamide bacteriostatic antibiotic, is reported to pose serious health risks associated with antibiotic resistance. The removal of acetaminophen (ATAP) from some popular analgesic combination products has been recommended (Muir, et al., 1997). Meanwhile, some industries continue to emphasize the benefits of some PPCPs in their products, suggesting that they are too useful to be abandoned. It is anticipated that there will be an increase in the discharge of PPCPs into water resources as the world's population increases and living standards improve. PPCPs are contemporary chemicals with inadequate systematic research studies on their physical removal and chemical decomposition, and historically have not been regulated with respect to discharge limits. However, with the growing concern and recent research findings about toxicity and endocrine disruption potentials even at trace levels, the removal and decomposition of PPCPs is gradually becoming an issue of concern to the water industry and regulatory agencies, thus the need to find effective tools for the management of PPCPs-contaminated water resources.

1.2 Triclosan

Among many PPCPs, triclosan (TCS) is of particular interest because of its extensive use in consumer products in spite of recent concerns about its health effects on humans and aquatic life. TCS, 5-chloro-2-(2, 4-dichlorophenoxy)phenol and commercially known as Irgasan, is an antimicrobial agent widely used in soaps, toothpastes, cosmetics and deodorants, kitchen accessories such as cutting boards and cooking utensils, as well as in textiles like athletic clothing and carpets (Adolfsson-Erici, et al., 2002; Erickson, 2010). The extensive use of TCS results in its discharge into wastewater and subsequently into surface waters (Kolpin, et al., 2002; Singer, et al., 2002). TCS has attracted significant concern because of the toxicity, prevalence and persistence of its derivatives during chlorination and photochemical degradation (Cooney, 2010; Orvos, et al., 2002; Rule, et al., 2005). TCS is similar in structure to endocrine disruptors like dioxins and furans and it has been found to interfere with the metamorphosis of frogs (Cooney, 2010; Matsumura, et al., 2005). It has been detected in human milk, urine and blood plasma, and algae and fish (Adolfsson-Erici, et al., 2002). It has also been detected in about 60% of US waterways, including drinking water samples, and was nominated for inclusion in the USEPA drinking water contaminant candidate list (Kolpin, et al., 2002; USEPA, 2008). Though EPA concluded in its 2008 reassessment of the safety of TCS that human exposure did not pose unacceptable risks, the agency is currently worried about the potential for antibiotic resistance and endocrine disruption resulting from human exposure to TCS and plans to reexamine the potential risks due to recent findings that TCS has potential estrogenic effects in rats (Erickson, 2010). Research studies show that disinfection byproducts (DBPs) of TCS, including 4,5-dichloro-2-(2,4-dichlorophenoxy)phenol, 5,6-dichloro-2-(2,4-dichlorophenoxy)phenol and 4, 5, 6-trichloro-2-(2, 4-dichlorophenoxy)phenol, have been found in waterways. It has been also reported that the photodegradation of TCS produces dioxins like 2, 8-dichlorodibenzo-*p*-dioxin, 2, 3, 7-trichlorodibenzo-*p*-dioxin, 1, 2, 8-trichlorodibenzo-*p*-dioxin and 1, 2, 3, 8-tetrachlorodibenzo-*p*-dioxin (Aranami and Readman, 2007; Fiss, et al., 2007; Latch, et al., 2003; Mezcua, et al., 2004; Rule, et al., 2005). TCS is stable, difficult to completely degrade in conventional water and wastewater treatment systems, and persistent in all environmental media (Bester, 2003; Heidler and Halden, 2007; Kolpin, et al., 2002; Singer, et al., 2002).

The removal of TCS, like many other PPCPs and recalcitrant organic contaminants in conventional wastewater treatment processes, has been examined. These treatment facilities are, however, not designed to remove low-level PPCPs, resulting in the discharge of such pollutants into aquatic environments (Castiglioni, et al., 2006; Heberer, 2002; McAvoy, et al., 2002; Miao, et al., 2005). It has also been reported that TCS rather destroys some protozoa that are beneficial to biological treatment processes (Krishnakumar et al., 2011). Physical separation processes such as activated carbon and membrane separation processes can effectively remove TCS from water resources. However, these processes, in addition to being very costly, do not decompose the contaminant but transfer it from one medium to another. The decomposition of TCS with chemical oxidants, including chlorine, ozone and permanganate, has also not been very effective.

1.3 Advanced Oxidation Technologies

In order to completely mineralize recalcitrant organic contaminants like TCS, recent research has focused largely on advanced oxidation processes (AOPs). AOPs include chemical oxidation, Fenton and photo Fenton processes, ultraviolet (UV)-based processes, photocatalytic redox processes, supercritical water oxidation, sonolysis, and electron beams and γ-rays irradiation. These processes typically involve the further activation of chemical oxidants, including hydrogen peroxide (H_2O_2), ozone (O_3), peroxymonosulfate (PMS, HSO_5^-), and persulfate (PS, $S_2O_8^{2-}$), to generate stronger oxidizing species, typically hydroxyl radicals (HRs) and sulfate radicals (SRs), which possess higher oxidation potentials than the parent oxidants added. The radical species decompose organic contaminants to simpler compounds and eventually mineralize them into simple inorganic compounds, CO_2 and H_2O (Anipsitakis and Dionysiou, 2003; Elmolla and Chaudhuri, 2009; Esplugas, et al., 2007; Huber, et al., 2003; Kim, et al., 2008; Klamerth, et al., 2010; Sirés, et al., 2007; Son, et al., 2009; Son, et al., 2010; Westerhoff, et al., 2005; Yang, et al., 2008; Yu, et al., 2006a; Yu, et al., 2006b). AOPs have been proven to be effective for the destruction of biologically toxic and non-degradable compounds including PPCPs, and have attracted significant interest in water treatment and soil and sediment remediation application.

Most research on the decomposition of organic contaminants including PPCPs has focused exclusively on HRs-based AOPs (Huang, et al., 2005; Kim, et al., 2008; Xu, 2001). HRs-based AOPs that have been typically used are Fenton and photo Fenton reactions, ultraviolet (UV)-based processes (UV/H_2O_2, UV/O_3, UV/TiO_2), photocatalytic processes, sonolysis and supercritical oxidation. Among the HRs-based AOPs, the Fenton reaction (the activation of H_2O_2 with Fe^{2+}) and its modifications are significant, where HRs are generated by the activation of oxidants with a transition metal and/or UV radiation (Elmolla and Chaudhuri, 2009). The Fenton reaction, however, has several drawbacks for its practical applications, including pH dependence, problems associated with iron oxidation and precipitation, slow kinetics of ferrous iron regeneration (non-catalytic nature), and scavenging of HRs by CO_3^{2-}/HCO_3^- (Klamerth, et al., 2010; Rivas, et al., 2001).

SRs-based AOPs have received significant attention in recent times in an attempt to overcome the limitations of the Fenton reaction and also to provide an alternative to HRs-based AOPs. The reaction mechanisms of SRs and HRs are very different. SRs attack organics more selectively by electron transfer while HRs react rapidly with organic molecules by initial hydroxylation or hydrogen abstraction, resulting in different reaction intermediates (Neta, et al., 1977; Neta, et al., 1988). SRs can be generated by the thermal, photolytic, or radiolytic activation of oxidants such as PMS and PS. SRs have been popularly generated from the photochemical activation of PMS and PS with UV radiation, however, there are challenges with its full scale application to water treatment. Alternatively, SRs are generated by the activation of PMS and PS with transition metals, as shown in Reactions 1.1 and 1.2 (Anipsitakis and Dionysiou, 2004a; Anipsitakis and Dionysiou, 2004b; Anipsitakis, et al., 2006; Ball and Edwards, 1958). SRs possess higher standard redox potential (2.5–3.1 V) than HRs (1.8–2.7 V) over a wide range of pH values (Anipsitakis and Dionysiou, 2004a).

$$\mathrm{HSO_5^-} + \mathrm{M^{n+}} \rightarrow \mathrm{M^{n+1}} + \mathrm{SO_4^{\bullet -}} + \mathrm{OH^-} \qquad (1.1)$$

$$\mathrm{H_2O_8^{2-}} + \mathrm{M^{n+}} \rightarrow \mathrm{M^{n+1}} + \mathrm{SO_4^{\bullet -}} + \mathrm{SO_4^{2-}} \qquad (1.2)$$

The applications of SRs-based AOPs for the decomposition of toxic recalcitrant organic contaminants have received significant attention in recent times (Anipsitakis, et al., 2005; Do, et al., 2009; Huang, et al., 2005; Liang, et al., 2004; Rastogi, et al., 2009; Yang, et al., 2007). SRs-based AOPs have been reported to be superior to HRs-based

AOPs for the decomposition of some organic contaminants, including 2,4-dichlorophenol, atrazine, and naphthalene (Anipsitakis and Dionysiou, 2003). In spite of their high potential to degrade organic contaminants, none of the previous research studies explored the application of SRs-based AOPs for the decomposition of PPCPs. The current research findings, health risk concerns over their presence in water resources, and the potential increase in their use call for a systematic research on the decomposition of PPCPs.

1.4 Objectives

Advanced oxidation processes (AOPs) have become very significant in the water industries due to the inability of conventional treatment systems to completely degrade some organic contaminants. The presence of recalcitrant compounds, particularly PPCPS in water, has generated a huge concern. AOPs are effective for treating water containing refractory, toxic, and non-biodegradable materials. Most of research studies and applications of AOPs have, however, focused exclusively on hydroxyl radicals (HRs), particularly Fenton reaction, which has several drawbacks for practical application. Recently, there have been some interests in SRs-based AOPs to decompose organic contaminants in water. However, there have been no systematic studies investigating the degradation of PPCPs using SRs-based AOPs.

This study investigates whether SRs generated by the transition metal-mediated activation of PMS and PS are effective to decompose PPCPs, and thus proposes new and alternative management options for PPCPs-contaminated water resources. A more detailed study is conducted on the decomposition of TCS using SRs-based AOPs. In order to achieve this goal, the study has three objectives.

To verify the potential of SRs-based AOPs to decompose PPCPs. Some important chemical oxidant/metal activating systems to generate SRs and HRs are examined, and the effectiveness of SRs- and HRs-based AOPs is compared (PMS/Fe vs. PS/Fe, PMS/Fe vs. H_2O_2/Fe, and PMS/Co vs. H_2O_2/Co).

To elucidate the influence of common oxidants (PMS and PS) and metals (Co, Cu, Fe, and Ag) as well as their doses. Optimum conditions for the decomposition of TCS by SRs-based AOPs are revealed.

To investigate the detailed changes in metal speciation (solid vs. dissolved and Me^{2+} vs. Me^{3+}) during the decomposition of TCS by SRs generated from the activation of PMS with Co and Fe at different pH conditions. The impact of pH-dependent metal speciation on TCS decomposition is elucidated.

1.5 Methodology

The detailed methodology for each experiment and test is included in the corresponding chapter.

CHAPTER 2

SULFATE RADICALS-BASED DECOMPOSITION OF PPCPs

2.1 Abstract

The presence of persistent and toxic pharmaceuticals and personal care products (PPCPs) in water resources has generated considerable scientific, regulatory, and public interests, requiring the development of cost-effective technologies for PPCP treatment. This study communicates that sulfate radicals (SRs)-based advanced oxidation technologies (AOTs) are promising as a new environmental risk management option for PPCPs-contaminated water [Nfodzo, P. and Choi, H. (**2011**) *Environ. Eng. Sci.* 28 (8) 605-609]. As probe PPCPs, triclosan, sulfamethoxazole, and acetaminophen were effectively decomposed and mineralized by the attack of SRs generated through the activation of peroxymonosulfate (PMS) and persulfate (PS) with iron. The PMS/Fe system was more effective than PS/Fe but less effective than H_2O_2/Fe (Fenton reaction) that produces hydroxyl radicals (HRs). However, when conjugated with cobalt, PMS showed outstanding reactivity towards PPCPs while negligible decomposition of PPCPs by H_2O_2 was observed. Insights and suggestions on PPCP decomposition by SRs were also discussed, including organic selectivity and system stability. As an alternative to established HRs-based AOTs, SRs-based AOTs would initiate researchers into new strategic plans to manage PPCPs and other emerging chemicals of concern in water resources.

2.2 Introduction

Recent advances in environmental health and analytical chemistry make it possible to detect and identify many toxic organic compounds in the environment. Among these compounds, pharmaceuticals and personal care products (PPCPs) are the most significant (Ankley, et al., 2007; Caliman and Gavrilescu, 2009; Ellis, 2006; Snyder, et al., 2003). In addition to soaps, skin care products, insect repellants, sunscreens, and cosmetics, PPCPs are associated with health care products, including birth-control hormones, antibiotics, blood lipid regulators, analgesics, anti-inflammatory drugs, and veterinary medicines (Ellis, 2006). Many studies have quantified a broad array of PPCPs in rivers, lakes, groundwater, and sediments (Ellis, 2006; Richardson and Brown, 1985). Discoveries that some PPCPs have global distribution, environmental persistency, presence in humans and wildlife (bioaccumulation), and likely carcinogenic toxicity, have generated considerable scientific, regulatory, and public interest (Caliman and Gavrilescu, 2009). Some environmental contaminants in PPCPs have been thus classified as emerging chemicals of concern and endocrine disrupting compounds (Ankley, et al., 2007; Caliman and Gavrilescu, 2009). PPCPs are generally stable and thus hard to fully degrade in conventional water and wastewater treatment systems. Some of them are highly resistant to biodegradation and chemical decomposition and thus persistent in all environmental media (Onesios, et al., 2009; Castiglioni et al., 2006).

Recently, special attention has been given to advanced oxidation technologies (AOTs) where extremely strong and transitional radical species such as hydroxyl radicals (HRs) and sulfate radicals (SRs) are generated from common oxidants to attack organic contaminants. As one of the most practical HRs-based AOTs, Fenton reaction (activation of H_2O_2 with Fe) and its modifications have been extensively researched to decompose PPCPs (Elmolla and Chaudhuri, 2009). HRs demonstrates much higher oxidation capability than the oxidants added and thus readily attack PPCPs. However, the Fenton reaction has several drawbacks for its practical applications, including pH dependence of the reaction, problems associated with iron oxidation and precipitation, slow kinetics of ferrous iron regeneration (non-catalytic nature), and scavenging of HRs by CO_3^{2-}/HCO_3^{-} (Anipsitakis et al., 2006)

Driven by the needs to overcome the limitations of the Fenton Reagent and to introduce stronger oxidants than HRs, SRs-based AOTs have been quite recently researched to establish the radical generation, organic decomposition kinetics, and reaction pathways and mechanisms (Anipsitakis and Dionysiou, 2003; Anipsitakis, et al., 2006). SRs have also been widely used for in situ remediation of contaminated groundwater and soil (Do, et al., 2009; Liang, et al., 2004). SRs, typically generated via catalytic activation of peroxymonosulfate (PMS) and persulfate (PS) with transition metals, possess higher standard redox potential (2.5–3.1 V) compared to HRs (1.8–2.7 V) over pH values. Heterogeneous generation of SRs has also been attempted to mitigate concerns about dissolved metal ions, resulting in the formation of insoluble particles that can be easily removed by filtration (Anipsitakis, et al., 2005; Yang, et al., 2008; Yang, et al., 2007). The reaction mechanisms of SRs with organics are basically similar to those of HRs via electron transfer, hydrogen abstraction and/or hydrogen addition mechanisms while SRs react more selectively by electron transfer (Neta, et al., 1977; Neta, et al., 1988), which makes SR-based AOTs unique.

In spite of the high potential of SRs-based AOTs for the decomposition of recalcitrant organic contaminants, no research efforts have been given to the destruction of PPCPs. Since organic attack mechanisms of SRs are different from those of HRs and PPCPs are unique with great diversity in their molecular structure and chemical properties, the effectiveness of SRs-based AOTs to treat PPCPs-contaminated water should be immediately examined and publicized. In this study, I preliminarily test some important chemical oxidant/metal catalyst systems to generate SRs and HRs and compare their effectiveness to destroy PPCPs (PMS/Fe vs. PS/Fe, PMS/Fe vs. H_2O_2/Fe, PMS/Co vs. H_2O_2/Co).

Based on their unique nature and current significance, triclosan (TCS), sulfamethoxazole (SMX), and acetaminophen (ATAP) were selected as target PPCPs in this study, as summarized in Table 2.1. the molecular structures of the model PPCPs are shown in Figure 2.1. The US Environmental Protection Agency is recently worried about the potential for endocrine disruption resulting from human exposure to TCS, the most widely used antibiotic chemical in soaps, body washes, and toys (Erickson, 2010). SMX, as a sulfonamide bacteriostatic antibiotic, also poses health risks associated with antibiotic resistance. The removal of ATAP from some popular analgesic combination products has been issued (Muir, et al., 1997). Each of the PPCPs has its own molecular structure with unique moieties, which are the primary targets for the radical attack.

2.3 Materials and Methods

2.3.1 Chemicals

The model PPCPs, TCS, SMX, and ATAP were in the salt forms. The oxidants used were potassium peroxymonosulfate (PMS, KHSO5) derived from the triple salt, oxone, and potassium persulfate (PS, $K_2S_2O_8$), and hydrogen peroxide (H_2O_2). The transition metals used for the activation of the oxidants were ferrous sulfate (FeSO4), and cobalt sulfate ($CoSO_4$). HPLC grade acetonitrile and methanol were also used. All the chemicals were obtained from Sigma-Aldrich and used as received. The mass concentration of PPCPs was fixed at 9 mg/L in order to set a certain contamination situation in water resource (based on the lowest aqueous solubility of TCS at around 10 mg/L).

2.3.2 Generation of radical species

General experimental procedures for SRs-based AOTs and Fenton reaction were reported elsewhere (Anipsitakis and Dionysiou, 2003). PPCP degradation was performed in a 100 mL batch reactor. After short preliminary studies under different PPCP/oxidant/metal conditions, the molar ratios of PPCP to oxidant and oxidant to metal were fixed at 1:80 and 1:1, respectively, for all the experiments. The reason I set the molar (not mass) ratio of oxidant (or metal) to PPCP is to consider the stoichiometry of their reaction. The PPCP to oxidant ratio was increased to 1:10 for some experiments in order to make better comparisons. The initial pH was adjusted at 7.0 using 1 M sodium hydroxide to promptly compare the reactivities of SRs and HRs. No buffer solution was used to avoid any experimental complexities related to reaction between radicals and buffer species. The solution pH decreased to around 4.0 during the reaction as a result of acid generation during the decomposition of the oxidants and oxidation of contaminants as well as metal-related acidity.

2.3.3 Analysis

Sample of 0.5 ml was withdrawn at time of 0, 5, 10, 20, 30, 60, 120, 180, and 240 min. and immediately mixed with methanol, a quenching agent for HRs and SRs. Control experiments were also carried out with PPCP only, PPCP and Fe (no oxidant), or PPCP and oxidant (no Fe). All the experiments were triplicated.

The concentrations of PPCPs were determined with a reversed-phase high performance liquid chromatography (HPLC 1200 series, Agilent) consisting of a quaternary pump, C18 column, and ultraviolet (UV) detector. Briefly, a mixture of water and acetonitrile was used as the mobile phase at water:acetonitrile ratio of 25:75, 50:50, and 75:25 for TCS, SMX, and ATAP, respectively. The wavelengths for UV detection of TCS, SMX, and ATAP, which were pre-determined using a UV-visible spectrophotometer (UV 2550, Shimadzu), were set at 280 nm, 240 nm, and 265 nm, respectively. Total organic carbon (TOC) was monitored for 24 hrs. using a TOC analyzer (TOC-VCSH/CSN, Shimadzu).

Table 2.1 Molecular information of model PPCPs used in this study

PPCPs	Triclosan (TCS)	Sulfamethoxazole (SMX)	Acetaminophen (ATAP)
Usage	Antimicrobial	Antibiotic	Analgesic
Molecular Formula	$C_{12}H_7O_2Cl_3$	$C_{10}H_{11}O_3N_3S$	$C_8H_9O_2N$
Molecular Weight	289.5	253.3	151.2
Solubility	0.01g/L	0.61g/L	14 g/L

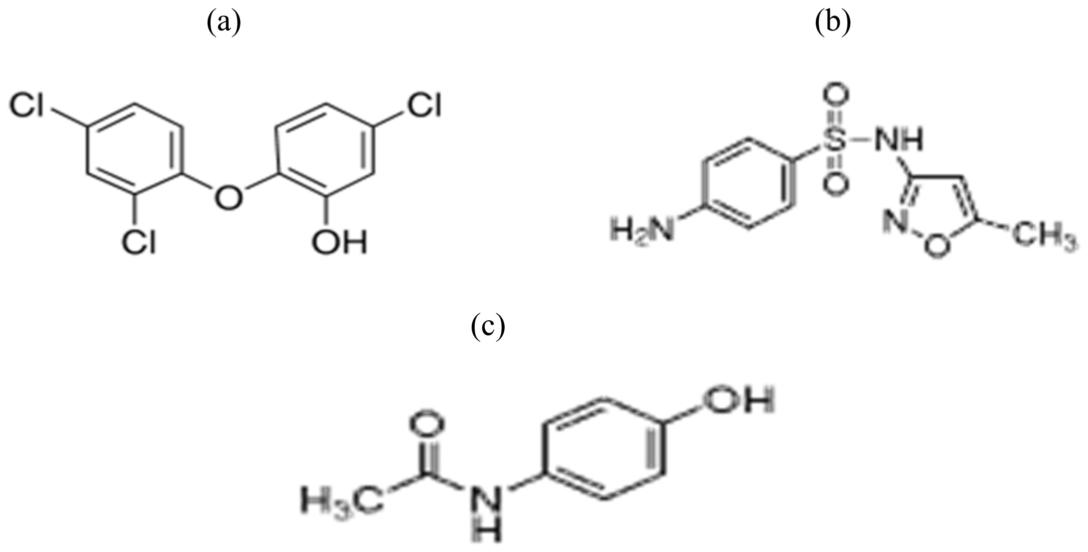


Figure 2.1 Molecular structure of model PPCPs (a) Triclosan (b) Sulfamethoxazole (c) Acetaminophen.

2.4 Results and Discussions

2.4.1 PPCP decomposition by PS/Fe and PMS/Fe

PS, PMS, and H_2O_2 alone showed negligible reactivity towards the PPCPs, implying that conventional oxidants are not effective to decompose the PPCPs. Figure 2.2 shows the decomposition of the PPCPs by PS/Fe system.

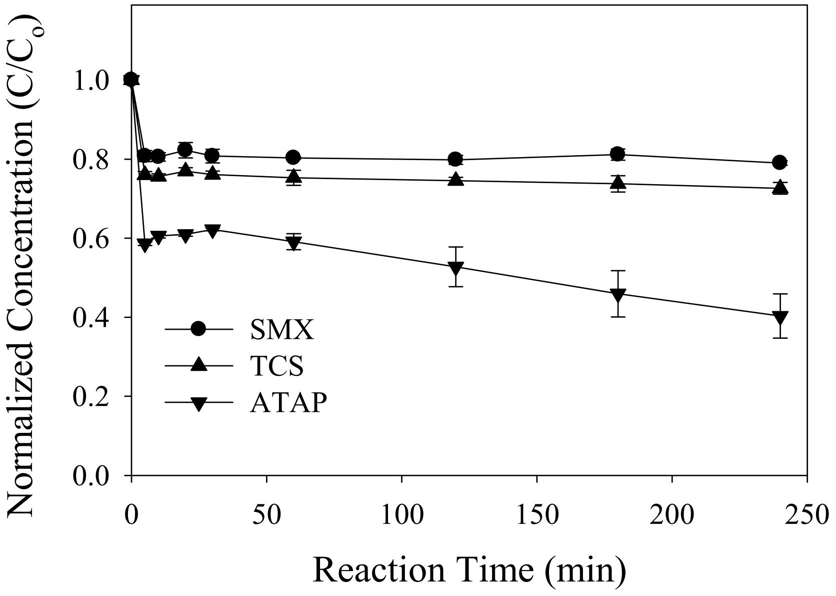


Figure 2.2 PPCP decomposition by SRs generated from PS/Fe (PPCP of 9 mg/l, molar ratio of PPCP:PS:Fe at 1:80:80, pH of 7). The error bars are the standard deviation of triplicated results.

After initial fast destruction of PPCPs within 5 min, no further decomposition was observed for TCS and SMX while 60% decomposition of ATAP was observed after 4 hrs. Unlike PS/Fe system, the decomposition of PPCPs by PMS/Fe system was immediate and complete within 30 min (SMX showed relatively slower kinetics), as shown in Figure 2.3.

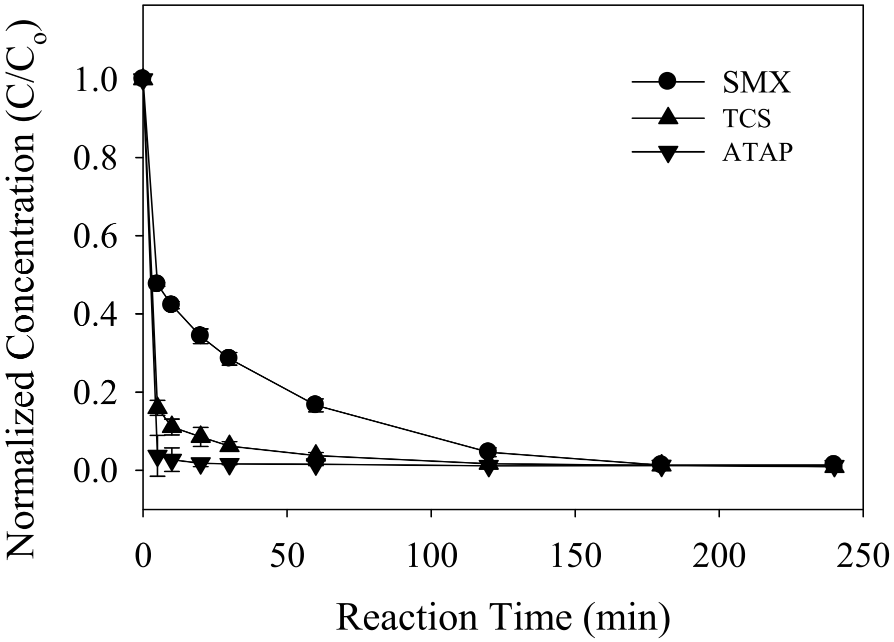


Figure 2.3 PPCP decomposition by SRs generated from PMS/Fe (PPCP of 9 mg/l, molar ratio of PPCP:PMS:Fe at 1:80:80, pH of 7). The error bars are the standard deviation of triplicated results.

Since the decomposition of PPCPs under the given conditions was too fast for us to distinguish the kinetics, the PMS concentration was much reduced and the result is shown in Figure 2.4. The PMS/Fe system even with 8 times lower PMS and Fe concentrations (PPCP:PMS:Fe of 1:10:10) was more effective than the PS/Fe system with PPCP:PS:Fe of 1:80:80.

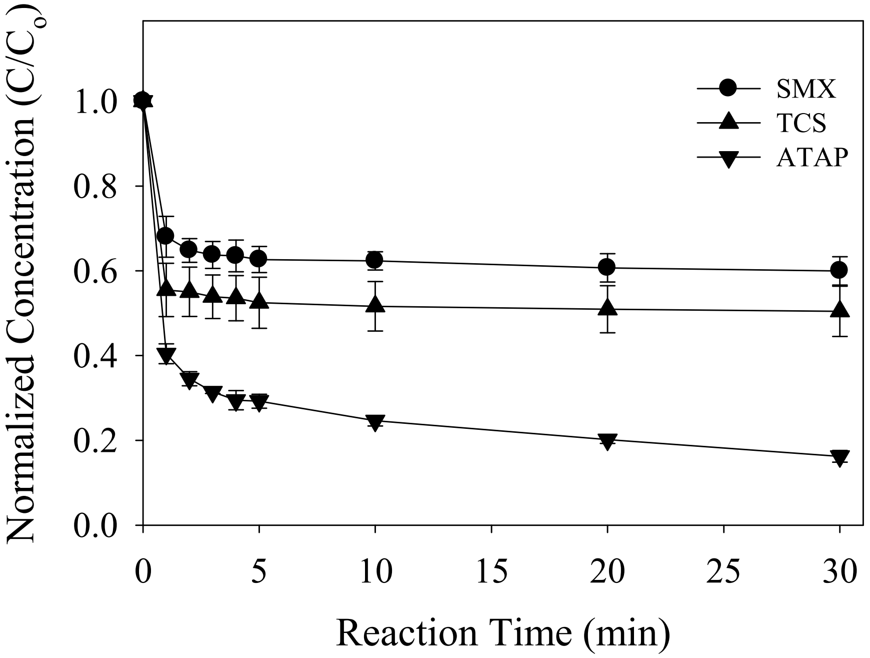


Figure 2.4 PPCP decomposition by SRs generated from PMS/Fe at a lower PMS loading. (PPCP of 9 mg/l, molar ratio of PPCP:PMS:Fe at 1:10:10, pH of 7). The error bars are the standard deviation of triplicated results. Inset shows PPCP decomposition.

When activated with Fe, PMS was more effective than PS for the decomposition of PPCPs due to the chemical stability of PS. Similar observations were reported for the decomposition of 2-chlorobiphenyl and 2,4-dichlorophenol (Anipsitakis and Dionysiou, 2004a; Rastogi, et al., 2009). However, the slow activation of PS was reported to be suitable for subsurface applications (Huang, et al., 2005; Killian, et al., 2007; Liang, et al., 2003; Liang, et al., 2004). The reactivity-saving characteristics of PS/Fe system would be beneficial to systems that are required to respond long term and low level release of PPCPs to the aquatic environment.

It is also known that the effectiveness of PMS and PS depends on conjugated transition metals (Anipsitakis and Dionysiou, 2004a). For the purpose of comparison with Fenton reaction, I focused exclusively on Fe (cheap, less toxic, and naturally abundant) in this study. Based on the results, the order of PPCP decomposition was consistent at ATAP > TCS > SMX, which calls for a follow-up study on detailed reaction mechanisms and pathways.

2.4.2 PPCP decomposition by PMS and H_2O_2 conjugated with Fe and Co

As shown in Figure 2.5, immediate decomposition of PPCPs by HRs was observed and their decomposition was not discriminated. The faster decomposition of PPCPs by H_2O_2/Fe is due to the nonselective hydroxylation of their functional groups by HRs. At a low oxidant dosage (compare Figures 2.4 and 2.6), it is noticed that H_2O_2/Fe performed better than PMS/Fe. However, interpretation on the comparative effectiveness between H_2O_2 and PMS should be limited to this specific case of using Fe as an oxidant activator. Other transition metals (e.g., Co Ag, Ni, Ru, Mn, Ce, and V) have been found to be more or less effective in the activation of H_2O_2 and PMS to generate HRs and SRs, respectively (Anipsitakis and Dionysiou, 2004a; Ball and Edwards, 1958).

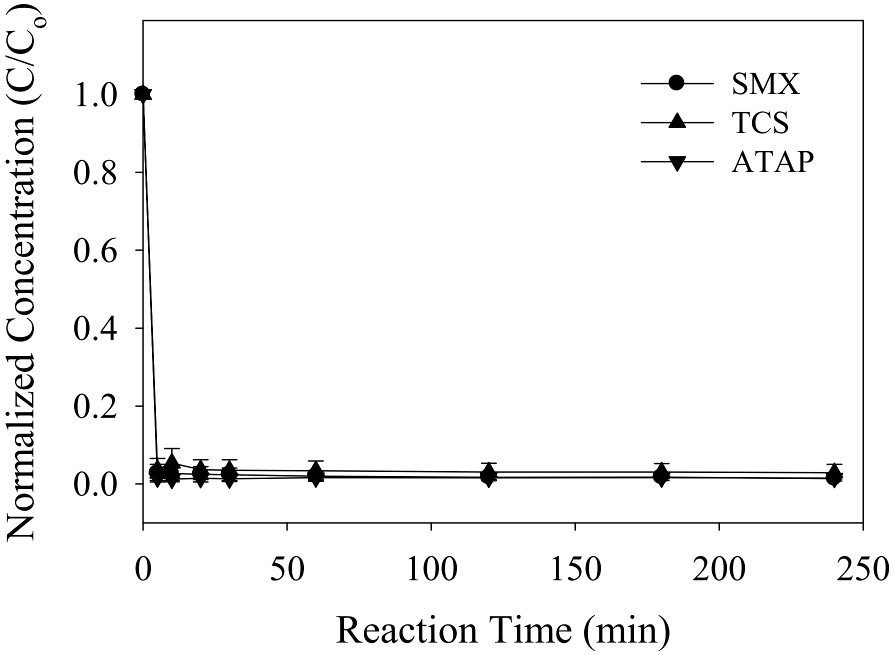


Figure 2.5 PPCP decomposition by HRs generated from H_2O_2/Fe (PPCP of 9 mg/l, molar ratio of PPCP:H_2O_2:Fe at 1:80:80, pH of 7). The error bars are the standard deviation of triplicated results.

As shown in Figure 2.7, completely different results were revealed when PMS and H_2O_2 were activated with Co. The PMS/Co system was as effective as H_2O_2/Fe system while H_2O_2/Co system did not show any reactivity towards SMX. This suggests that the use of a best-working catalyst among various transition metals would facilitate the generation of SRs and thus the decomposition of PPCPs. Cobalt was reported to be the best activator of PMS, and PMS/Co combination was shown to effectively decompose some recalcitrant organic contaminants that are resistant to HRs (Anipsitakis and Dionysiou, 2004a).

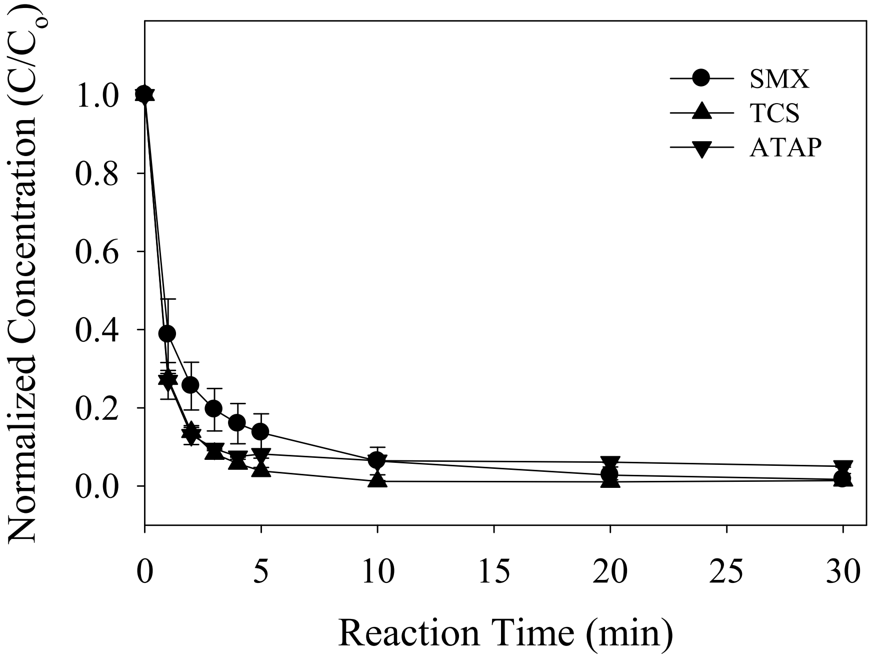


Figure 2.6 PPCP decomposition by HRs generated from H_2O_2/Fe at a lower H_2O_2 loading. (PPCP of 9 mg/l, molar ratio of PPCP:H_2O_2:Fe at 1:10:10, pH of 7). The error bars are the standard deviation of triplicated results.

Even though there has been a debate, Co conjugated with PMS was reported to behave as a catalyst (or at least catalyst-like) (Anipsitakis and Dionysiou, 2003; Kim and Edwards, 1995; Zhang and Edwards, 1992). Among several metals tested for the activation of PMS, Co exhibited a unique characteristic to decompose PMS with a second order kinetic, compared to a first order decomposition by all the other metals (Ball and Edwards, 1958). However, the use of Co as an oxidant activator should be with caution, considering its health and aesthetic aspects in addition to its reactivity (Anipsitakis, et al., 2005; Yang, et al., 2007).

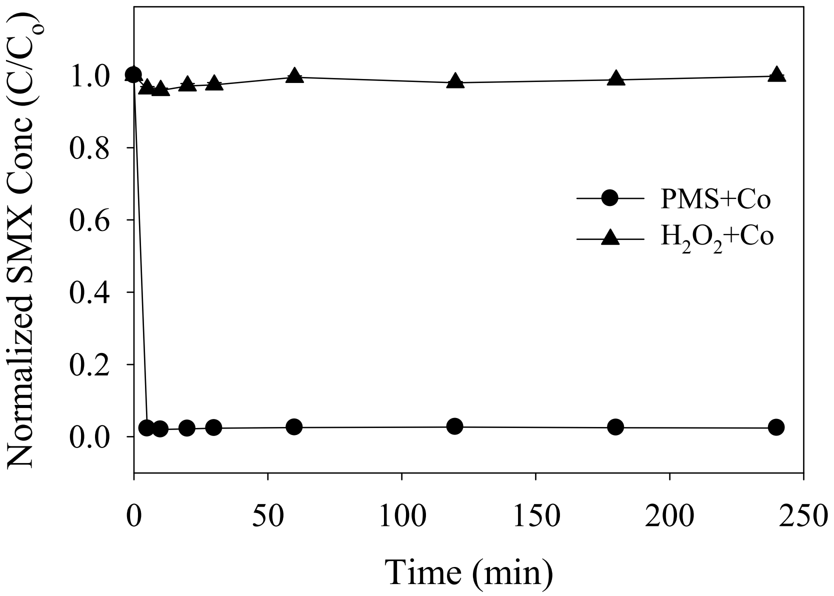


Figure 2.7 SMX decomposition by PMS/Co and H_2O_2/Co (SMX of 9 mg/l, molar ratio of SMX:PMS (or H_2O_2):Co at 1:10:10, pH of 7).

2.4.3 PPCP Mineralization by PMS/Fe

One of the most important features of AOTs is their capability to mineralize organic contaminants. The effectiveness of PMS/Fe system to mineralize PPCPs was investigated, as shown in Figure 2.8. ATAP and SMX with the highest and lowest decomposition kinetics, respectively, were tested. After 24 hr. reaction under the given conditions, 55% of SMX and 13% of ATAP were mineralized. Mineralization of recalcitrant compounds is known to take much longer time, compared to immediate transformation of target compounds to intermediates. SMX with the lowest decomposition kinetics was mineralized faster than ATAP with the highest decomposition kinetics.

Even though detailed investigation should be followed, the results imply that SRs are also effective for the mineralization of PPCPs.

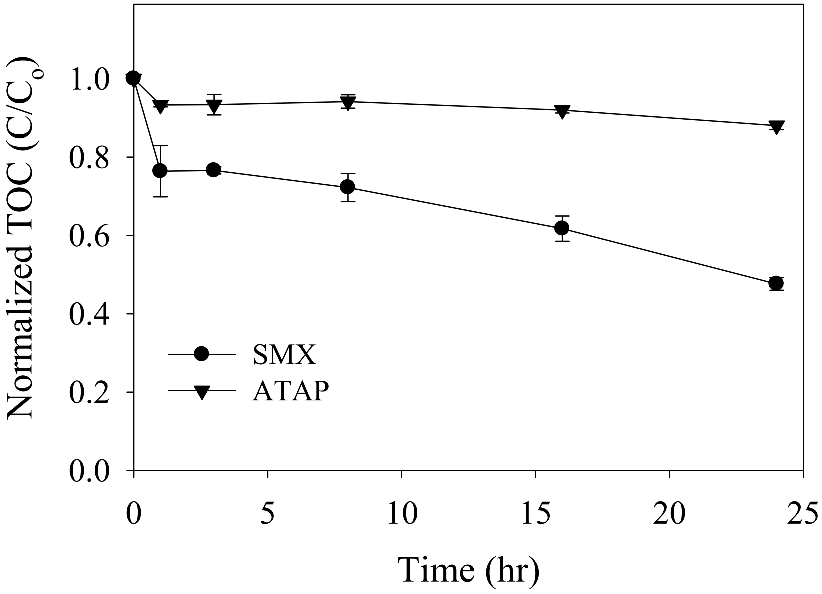


Figure 2.8 PPCP mineralization by SRs generated from PMS/Fe (PPCP of 9 mg/l, molar ratio of PPCP:PMS:Fe at 1:80:80, pH of 7). The error bars are the standard deviation of triplicated results.

2.5 Conclusion

Sulfate radicals-based processes were as effective as the Fenton reaction for the decomposition of PPCPs. Considering the simplicity of the radical generation, SRs-based AOTs are promising as a new environmental risk management option for PPCPs-contaminated water. The selective nature of SRs was confirmed, compared to nonselective HRs generated from Fe/H_2O_2. This study would initiate researchers into new strategic plans to manage PPCPs and other emerging chemicals of concern in water resources, where established Fenton reaction, one of the most practical HRs-based AOTs, shows substantial drawbacks (e.g., pH dependence of the reaction, slow kinetics of ferrous iron regeneration, and scavenging of HRs by CO_3^{2-}/HCO_3^{-}). However, in order to propose the SRs-based AOTs as a new environmental risk management option for PPCPs- and ECCs-contaminated water resources, detail investigation should be conducted, including i) examination of other transition metals to best activate PMS and PS and ii) identification of the speciation of the metals to verify catalytic and non-catalytic reaction. Decomposition pathways and mechanisms should be investigated since the organic attack mechanisms of the two radicals, SRs and HRs, have differences and thus different reaction intermediates are formed.

CHAPTER 3

TRICLOSAN DECOMPOSITION BY SULFATE RADICALS: EFFECTS OF OXIDDANT AND METAL DOSES

3.1 Abstract

The potential of metal-mediated activation of peroxymonosulfate (PMS) and persulfate (PS) to generate sulfate radicals (SRs) to degrade pharmaceuticals and personal care products, including triclosan (TCS) was demonstrated in the previous chapter. This section focuses on more detailed evaluation of the decomposition of TCS, emphasizing the reactivity of sulfate radicals (SRs) generated from the activation of PMS and PS by transition metals (Fe^{2+}, Co^{2+}, Cu^{2+}, and Ag^{+}). Special attention was given to understanding the effects of the oxidant and metal conjugations, and their doses [Nfodzo, P. and Choi, H. (**2011**), *Chem. Eng. J.* 174 (2-3) 629-634]. The results showed that the oxidants alone did not show any decomposition of TCS while SRs generated from the oxidant/metal conjugations were very effective to oxidize and mineralize TCS. In general, TCS was decomposed much faster with PMS than PS regardless of the metals conjugated. PMS/Co, PMS/Cu, and PS/Ag systems showed best reactivity with TCS while the other combinations exhibited negligible or much less TCS decomposition. More oxidants at a fixed oxidant:metal molar ratio resulted in faster decomposition of TCS, while excessive amounts of metals rather hindered the reaction due to undesired competition between the metal and TCS for SRs generated. Some metals, such as Co exhibiting catalytic behavior during the reaction, required less doses

than their stoichiometric amounts to fully activate the oxidants, whereas some (e.g., Fe) required more doses. A series of the dose-effect results implied there should be optimum doses of oxidants and metals to maximize TCS decomposition. As an alternative to established hydroxyl radicals, SRs exhibited high potential for the decomposition and mineralization of TCS.

3.2 Introduction

Triclosan (TCS), 5-chloro-2-(2,4-dichlorophenoxy)phenol, is an antimicrobial agent widely used in many pharmaceuticals and personal care products (PPCPs) (e.g., soap, toothpaste, cosmetics, and deodorants), kitchen accessories (e.g., cutting boards and cooking utensils), and textiles (e.g., athletic clothing and carpets) (Adolfsson-Erici, et al., 2002; Erickson, 2010). The extensive use of TCS has resulted in its discharge into wastewater and subsequently into surface waters (Kolpin, et al., 2002; Singer, et al., 2002). TCS has been detected in about 60% of US waterways and nominated for inclusion in the United States Environmental Protection Agency (EPA)'s drinking water contaminant candidate list (Kolpin, et al., 2002; EPA, 2008). In its 2008 assessment of the safety of TCS, EPA concluded that human exposure to TCS did not pose unacceptable risks. However, after an article demonstrating the potential estrogenic effects of TCS in rats was publicized in 2009, the agency has been currently worried about the potential of TCS for antibiotic resistance and endocrine disruption and planned to reexamine the potential risks of TCS (Erickson, 2010; Zorrilla, et al., 2009).

TCS, like many other PPCPs and recalcitrant organic compounds, is hard to completely degrade in conventional water and wastewater treatment processes and thus persistent in all environmental media (Heidler and Halden, 2007; Kolpin, et al., 2002; Singer, et al., 2002). For the decomposition and mineralization of such persistent organic contaminants, advanced oxidation technologies (AOTs) have been recently highlighted, where extremely strong and transitional oxidizing species such as hydroxyl radicals (HRs) and sulfate radicals (SRs) are typically generated to attack organic molecules (Anipsitakis and Dionysiou, 2003; Esplugas, et al., 2007; Huber, et al., 2003; Méndez-Díaz, et al., 2010; Westerhoff, et al., 2005). Among the AOTs, Fenton reaction (i.e., generation of HRs by the activation of H_2O_2 using Fe) has been the most widely researched for the decomposition of PPCPs. In particular, many studies on the decomposition of TCS have been conducted exclusively using Fenton reaction and other HRs-based AOTs (Sirés, et al., 2007; Son, et al., 2009; Son, et al., 2010). The Fenton reaction and its modifications, however, have several drawbacks for practical applications, including pH dependence of the reaction, problems associated with iron oxidation and precipitation, slow kinetics of ferrous iron regeneration (non-catalytic nature), and scavenging of HRs by CO_3^{2-}/HCO_3^- (Klamerth, et al., 2010; Rivas, et al., 2001).

Recently, there is a growing interest in SRs in comparison to well-established HRs (Anipsitakis and Dionysiou, 2003; Anipsitakis and Dionysiou, 2004a; Rastogi, et al., 2009). In my previous study, I communicated the potential of SRs-based AOTs to decompose PPCPs in water (Nfodzo and Choi, 2011a). SRs are typically generated by the activation of oxidants such as peroxymonosulfate (PMS, HSO_5^-) and persulfate (PS, $S_2O_8^{2-}$) with transition metals (Anipsitakis and Dionysiou, 2004a; Ball and Edwards, 1958). The reactivity of the oxidants with metals to generate SRs is unique and known to be complicated. Though Fe has many advantages as an oxidant activator (cheap, less toxic, and naturally abundant), use of other transition metals have been of interest. Ball and Edwards (Ball and Edwards, 1958) reported only 8 metals among 28 tested metals showed significant reactivity in activating PMS. Anipsitakis and Dionysiou (Anipsitakis and Dionysiou, 2004a) also reported that 14 out of 27 couples (3 oxidants and 9 metals) demonstrated significant reactivity towards the transformation of 2,4-dichlorophenol (2,4-DCP). The conjugation of PMS with Co was more effective than the Fenton reaction for the degradation of 2,4-DCP, naphthalene, and atrazine at neutral pH (Anipsitakis and Dionysiou, 2004a). In addition, the reaction largely depends on the dose of oxidants and metals. Excessive amounts of oxidant and metal were reported to potentially lead to undesired competition reactions to quickly consume SRs (Burbano, et al., 2003; Burbano, et al., 2005; Rastogi, et al., 2009).

As a result, my research focuses on the destruction of TCS, as an emerging chemical of concern (ECC), using SRs in my effort to propose SRs-based AOTs as an alternative to the most common and established HRs-based AOTs for the decomposition of ECCs. As a part of the research activities, the objective of this present study is to examine whether SRs are effective to destroy TCS or not. In addition to better understanding of the influence of common oxidants (PMS and PS) and metals (Co, Cu, Fe and Ag) as well as their doses on TCS decomposition, this study will provide the basis for the next phase on pH effects and TCS decomposition pathways under more focused conditions.

3.3 Materials and Method

3.3.1 Chemicals

TCS was in a salt form as irgasan. The oxidants used were potassium persulfate ($K_2S_2O_8$, PS) and potassium peroxymonosulfate ($KHSO_5$, PMS) derived from the triple salt, oxone. Three of the transition metals tested were in the form of salts: $CoSO_4$, $FeSO_4$ and Ag_2SO_4 while $CuSO_4$ was a volumetric solution. HPLC grade acetonitrile and methanol were used. All chemicals were obtained from Sigma-Aldrich and used as received. A stock solution of TCS in 9 mg/L (0.031mM), close to its aqueous solubility, was prepared in high-purity water.

3.3.2 Generation of sulfate radicals

SRs were generated by the activation of oxidants (PMS and PS) with metals (Co, Fe, Ag, and Cu). All the experiments were based on batch reaction at ambient temperature. Specific aliquot of TCS was transferred into a glass reactor and appropriate volumes of oxidant and metal stock solutions were added to achieve a 100 mL reaction solution with predetermined molar ratios of TCS, oxidant, and metal. After brief preliminary studies, the molar ratios of oxidant to TCS and oxidant to metal were fixed at 5:1 and 1:1, respectively, resulting in oxidant and metal concentrations of 0.155 mM. The basic ratios were also precisely adjusted to make it possible to best compare

TCS decomposition kinetics under various reaction conditions. Control experiments were conducted with TCS only, TCS/metal (no oxidant), and TCS/oxidant (no metal).

The initial pH of the reaction solution was adjusted at 7.0 to mimic natural water. No buffer solution was used to avoid any experimental complexities related to potential reactions between radicals and buffer species and to minimize any artificial control and thus simulate more natural situation (i.e., letting pH freely change). The solution pH in all the experiments immediately decreased to around 3-4 due to acid generation during the decomposition of the oxidants and TCS as well as metal-related acidity. Since the behavior of the pH change was very similar in all the experimental conditions, the reactivities of the oxidant-metal combinations were not discriminated by the pH change and thus detail discussion on pH effects was excluded. The solution was continuously agitated using a magnetic stirring bar. All the experiments were carried out in triplicates to ensure accurate data acquisition and interpretation.

3.3.3 Control of oxidant and metal doses

For some systems showing promising results, more detailed experiments were conducted to investigate the effects of oxidant and metal doses. For PMS/Co and PMS/Cu, the oxidant to TCS ratio was incremented to 1:1, 3:1, and 5:1, and for PMS/Fe, more oxidant was used at 1:1, 5:1, 10:1, 40:1, while maintaining the oxidant to metal ratio at 1:1 in order to determine the combined effect of oxidant and metal concentrations on TCS decomposition kinetics. In case of PS, only PS/Ag combination at oxidant to TCS molar ratios of 1:1, 5:1, 10:1, and 40:1 was tested since other metals conjugated with PS did not show any significant reactivity. The difference in the ratios was to reflect differences in the reactivity of the oxidant-metal conjugation for achieving complete transformation of TCS. In addition, the effect of the molar ratio of oxidant to metal on TCS oxidation was investigated in cases of PMS/Co, PMS/Fe and PS/Ag.

3.3.4 Analysis

Sample of 0.5 ml was drawn at time of 0, 10, 20, 30, 60, 90, 120, 180, and 240 min., immediately mixed with methanol, a well-known quenching agent for SRs, to stop further chemical reaction, and filtered through 0.45 µm syringe filters. The transformation of TCS was monitored with a reversed-phase high performance liquid chromatography (HPLC, 1200 series, Agilent) equipped with quaternary pump, C18 column, and ultraviolet (UV) detector. Analysis methods for TCS were reported in literature and were adopted for this study with slight modification (Xuefei, et al.,). A mixture of water and acetonitrile was used as the mobile phase at H_2O:ACN ratio of 25:75% v/v at a flow rate of 1 mL/min, TCS was detected at a wavelength of 280 nm, which was determined through preliminary study using UV-visible spectrophotometer (UV 2550, Shimadzu). Total organic carbon (TOC) was monitored for 12 hrs. to verify whether SRs have the capability to mineralize TCS using a TOC analyzer (TOC-VCSH/CSN, Shimadzu).

3.4 Results and Discussion

3.4.1 Validation of PMS/metal and PS/metal systems for TCS decomposition

TCS was very stable under ambient conditions over time. Control experiments employing either oxidant or metal only indicated no decomposition of TCS. The transition metal-mediated activation of oxidants is a complex process, resulting in the generation of several known and unknown radical species in addition to SRs and HRs. Previous studies on the degradation of organic contaminants by the activation of PMS and PS with transition metals showed that SRs are the predominant and significant species responsible for the decomposition of organic contaminants (Anipsitakis and Dionysiou, 2004a; Brandt and Eldik, 1995; Kim and Edwards, 1995; Zhang and Edwards, 1992). As shown in Figures 3.1 and 3.2, PMS and PS, when conjugated with metals (Fe, Co, Cu, and Ag), showed significant reactivity towards TCS.

This implies the system successfully generated SRs that are much stronger than the parent oxidants, in accordance with previous studies (Anipsitakis and Dionysiou, 2003; Anipsitakis and Dionysiou, 2004a; Rastogi, et al., 2009). Figure 3.1 shows TCS decomposition by PMS/metal combinations. Among the metals tested, Co and Cu were the most effective to generate SRs, achieving almost complete degradation of TCS within 10 min under the given conditions (high level of oxidants). In cases of Fe and Ag, there was an initial prompt decomposition of TCS within 10 min followed by slow decomposition. Similar results were reported elsewhere (Anipsitakis and Dionysiou, 2003; Anipsitakis and Dionysiou, 2004a; Rastogi, et al., 2009). This phenomenon is mainly associated with the intrinsic reactivity of the metal ions with the oxidants (e.g., Co and Cu are very reactive) as well as the change of the metal speciation during the reaction (i.e., regeneration of spent metal ions to more effective speciation).

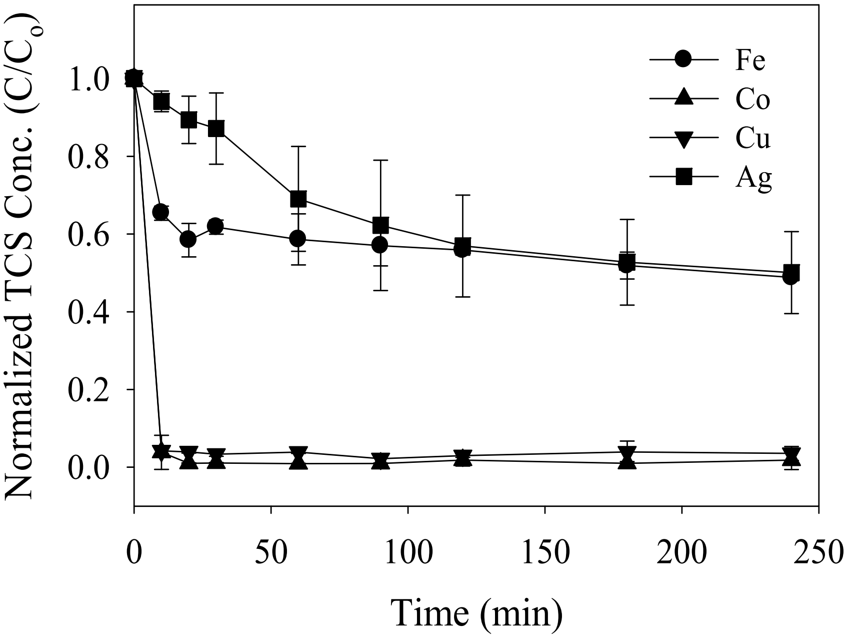


Figure 3.1 TCS decomposition by the activation of PMS with different metals. Molar ratio of TCS:PMS:metal = 1:5:5. The error bars are the standard deviation from triplicate experiments.

Metal ions added (ions II for Fe, Co, and Cu, and ions I for Ag) activate the oxidants to generate SRs, resulting in their prompt conversion to higher oxidation states (III and II), which are not effective to activate the oxidants. Meanwhile, there is also a reduction of ions (III and II) back to ions (II and I) but at much slower rate. As a result, once ions (II and I) initially added are completely consumed, SRs generation and thus TCS decomposition rely on the metal regeneration process, of which kinetics and mechanisms differ system-by-system.

As shown in Figure 3.2, TCS decomposition by PS/metal combinations was much slower compared to PMS/metal, similar to observations reported for the decomposition of 2-chlorobiphenyl and 2,4-DCP (Anipsitakis and Dionysiou, 2004a; Rastogi, et al., 2009).

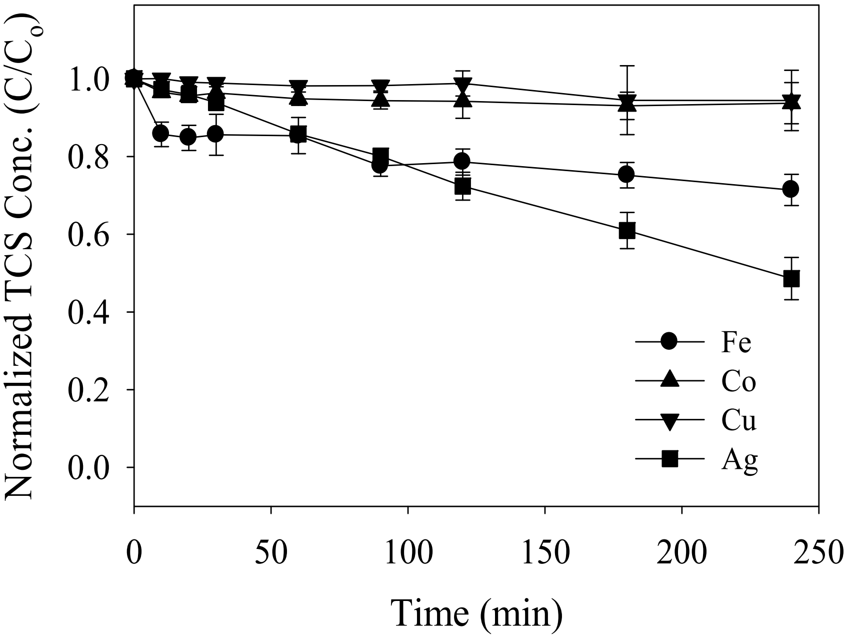


Figure 3.2 TCS decomposition by the activation of PS with different metals. Molar ratio of TCS:PS:metal = 1:5:5. The error bars are the standard deviation from triplicate experiments.

PS is known to be more stable with respect to its chemical decomposition, compared to PMS (Block, et al., 2004; Brown, et al., 2003; Sra, et al., 2010). Due to its slow activation and thus oxidant saving effects, PS has been preferentially used for in situ chemical oxidation of a broad range of organic contaminants including chlorinated alkanes and alkenes, polycyclic aromatic hydrocarbons, polychlorinated biphenyls, and methyl tert-butyl ether (Huang, et al., 2002; Liang, et al., 2003; Yukselen-Aksoy, et al., 2010). In Figure 3.2, PS conjugated with Ag showed slow but continuous decomposition of TCS over time. These features of PS might be beneficial to some scenarios required to respond to low level but long term contamination of water resources with TCS (Block, et al., 2004; Brown, et al., 2003).

The effectiveness of metals coupled with PS was completely different from that coupled with PMS. PS conjugated with Co and Cu showed no significant reactivity, achieving only 6.2% and 5.6% degradation of TCS in 4 hrs., respectively, while Fe and Ag were more effective in activating PS. PMS/Fe conjugation was faster than PS/Fe, and resulted in 51% and 29% degradation in 4 hrs. reaction time respectively. Although Fe showed some reactivity with both PMS and PS, the conjugations were not very effective for the degradation of TCS at this specified experimental condition. Among the metals, Ag was the best to activate PS but the worst to activate PMS. In general, these results were consistent with previous findings that Co and Ag are the best transition metals for the activation of PMS and PS, respectively (Anipsitakis and Dionysiou, 2004a; Ball and Edwards, 1958). With all the metals tested except for Ag, PMS was a more universal oxidant compared to PS, as it showed faster decomposition of TCS.

The oxidant/metal systems showing perceptible decomposition of TCS under the experimental conditions can be grouped into i) PMS/Co and PMS/Cu for immediate decomposition of TCS and ii) PMS/Fe, PMS/Ag and PS/Ag for slow decomposition of TCS (Anipsitakis and Dionysiou, 2004a; Anipsitakis, et al., 2006; Ball and Edwards, 1958; Sra, et al., 2010). The activation of oxidants by transition metals is known to follow a complex mechanism with several distinguishable steps. Nyberg and Larsson (Nyberg and Larsson, 1973) suggested that transition metals form complexes with PMS and PS in three different ways; complexes without sulfur coordination, complexes with dominant sulfur coordination, and complexes with both sulfur and oxygen coordination. The reactivity of metals thus depends on the type of complex coordination. Complexes with sulfur coordination result in stronger bonds and thus better reactivity than those with oxygen coordination (Brandt and Eldik, 1995). PMS/Co results in a complex with sulfur coordination while PMS/Cu results in a complex with both sulfur and oxygen coordination (Nyberg and Larsson, 1973). In addition, Co conjugated with PMS has been reported to exhibit catalytic behavior (Anipsitakis and Dionysiou, 2003; Kim and Edwards, 1995; Zhang and Edwards, 1992) and Co decomposes PMS uniquely at second-order kinetic to generate SRs, compared to first-order decomposition by all the other metals (Ball and Edwards, 1958). Similarly, Cu was reported to demonstrate catalytic properties in the transformation of organic compounds (Komiya, et al., 1997). PMS/Ag, on the other hand, results in a complex with oxygen coordination (Nyberg and Larsson, 1973), which may account for its low reactivity. However, it has been reported that Ag decomposes PS at second-order kinetic (Nyberg and Larsson, 1973), which possibly explains the fast decomposition of TCS in Figure 3.2.

3.4.2 Effect of oxidant dose on TCS decomposition

Some promising combinations of oxidant and metal were further tested to investigate the effect of oxidant dose while oxidant to metal ratio was fixed at 1:1. Figures 3.3 and 3.4 show the TCS decomposition at different PMS and PS concentrations, respectively. In spite of the relatively high oxidation potentials of PMS at 1.75 eV and PS at 2.01 eV (House, 1962; Spiro, 1979), even high concentration of the oxidants alone (40 times higher than TCS concentration) in the absence of metals showed negligible decomposition of TCS. In all cases, adding more oxidant resulted in better TCS decomposition..

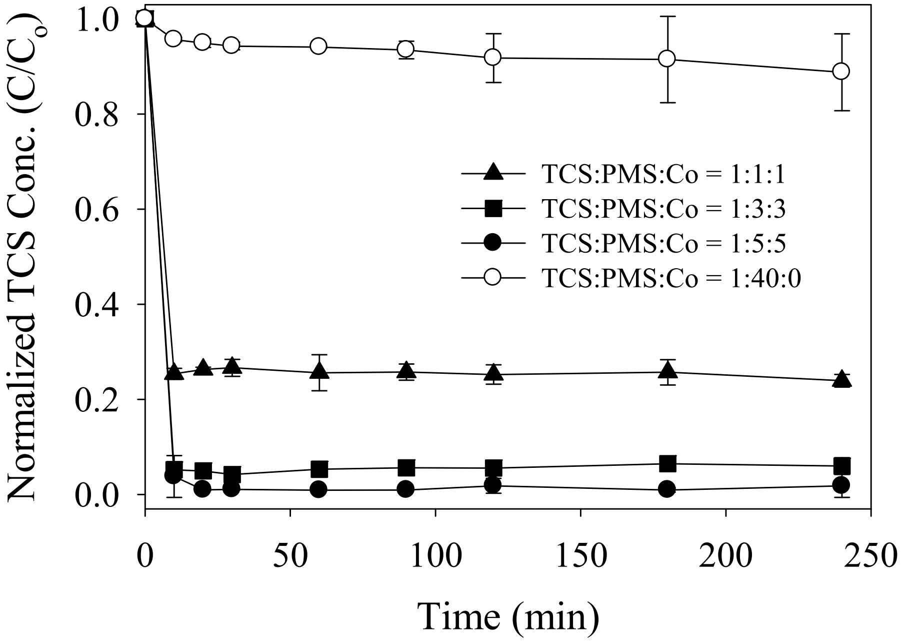


Figure 3.3 TCS decomposition by the activation of PMS with Co at different TCS:PMS molar ratios. Molar ratio of PMS:Co = 1:1, except for the control without metal. The error bars are the standard deviation from triplicate experiments.

However, interpretation of the results should be limited to this specific condition with oxidant/metal ratio at 1:1. In Figure 3.1, it was difficult to determine the comparative effectiveness between Co and Cu to decompose TCS since the concentrations of the oxidant and the metals were high enough to immediately decompose TCS. At lower oxidant dose as shown in Figures 3.3 and 3.4, the difference in the reactivities of Co and Cu was apparent.

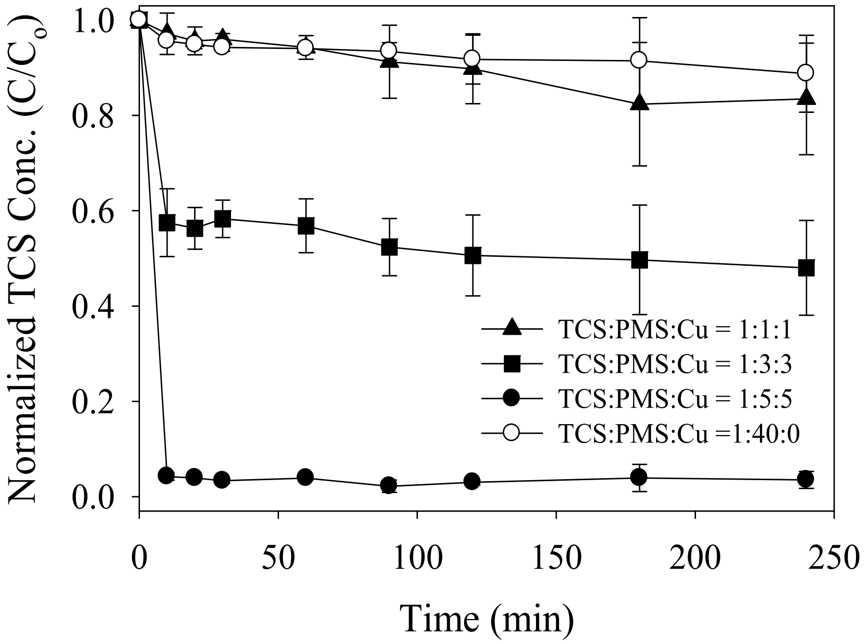


Figure 3.4 TCS decomposition by the activation of PMS with Cu at different TCS:PMS molar ratios. Molar ratio of PMS:Cu = 1:1, except for the control without metal. The error bars are the standard deviation from triplicate experiments.

In case of Co, even small dose of PMS achieved significant decomposition of TCS. Anipsitakis and Dionysiou (Anipsitakis and Dionysiou, 2003) also reported similar observation that PMS/Co system resulted in 99% transformation of 2,4-DCP at a molar ratio of 1:3. Meanwhile, more PMS, when conjugated with Cu, was needed to achieve the similar level of TCS decomposition. At the given condition, Co was found to the best activator for PMS.

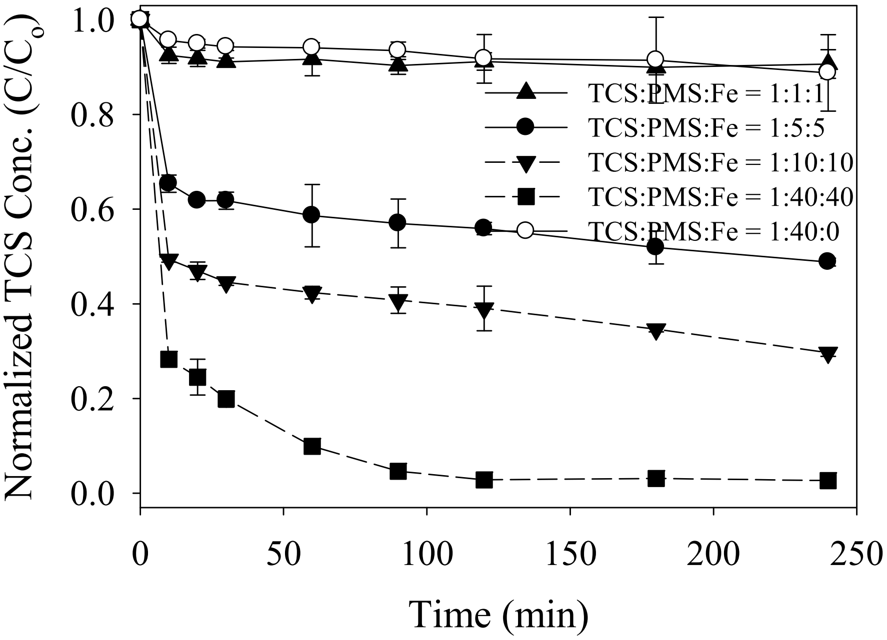


Figure 3.5 TCS decomposition by the activation of PMS with Fe at different TCS:PMS molar ratios. Molar ratio of PMS:Fe = 1:1, except for the control without metal. The error bars are the standard deviation from triplicate experiments.

Figure 3.5 shows the results of the effect of PMS dose when conjugated with Fe. Since PMS/Fe system showed relatively low efficiency, compared to PMS/Co and PMS/Cu, much higher PMS dose, up to 1:40, was tested. Considerable improvement in the degradation of TCS over increase in PMS dose was observed. It should be noted that the dose of metals seems very high in this molar ratio configuration but their actual mass concentration is not so high. Although Fe is not as effective as Co and Cu as an activator of PMS for TCS decomposition, it should be emphasized that Fe is, in many cases, abundant in natural water enough to activate PMS.

For TCS decomposition by PS, only Ag showing some reactivity with PS was further examined. Figure 3.6 shows the influence of PS concentration on TCS decomposition at constant PS/Ag molar ratio of 1/1. Increasing PS dose from a PS/TCS molar ratio of 5/1 to 10/1 resulted in an increase in the decomposition of TCS from 22% to 90% in 2 hrs. The PS/Ag system looks similar to PMS/Fe (Figure 3.5) with respect to TCS decomposition effectiveness. However, it is notable that TCS was slowly but continuously decomposed by PS/Ag, compared to initial immediate followed by more or less stagnant decomposition of TCS by PMS/Fe. This is mainly due to differences in the regeneration kinetics of the metal ions and in the chemical stability of the oxidants, as explained previously. In addition, the kinetics of TCS decomposition by PS showing likely a zero-order reaction was different from that by PMS following a pseudo first-order kinetic. Table 3.1 summarizes the oxidant dose and reaction time required to achieve over 95 % degradation of TCS under the given experimental conditions.

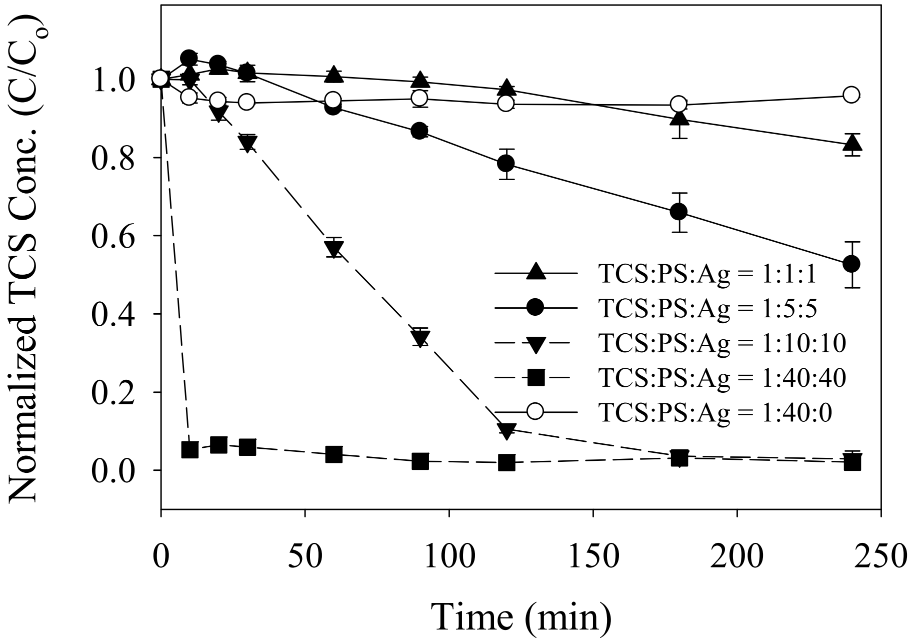


Figure 3.6 TCS decomposition by the activation of PS with Ag at different TCS:PS molar ratios. Molar ratio of PS:Ag = 1:1, except for the control without Ag. The error bars are the standard deviation from triplicate experiments.

Table 3.1 Oxidant dose and reaction time required to achieve over 95% TCS degradation

Conjugate	Oxidant:TCS molar ratio	Reaction time, min	Final pH
PMS/Co	3:1	10	4.3
PMS/Cu	5:1	10	4.1
PMS/Fe	40:1	120	2.7
PS/Ag	40:1	10	3.1
PS/Ag	10:1	180	4.1

3.4.3 Effect of metal dose on TCS decomposition

Since one of the objectives of this study is to find optimum reaction conditions for TCS decomposition by SRs, more attention was given to PMS/Co and PS/Ag system showing the best reactivity in each oxidant case, and PMS/Fe with more practical application potential. In particular, the effect of metal concentration was investigated. The results are intriguing. As shown in Figure 3.7, increasing Co concentration at fixed PMS dose (comparison among 1:1:1, 1:1:3, and 1:1:5) rather inhibited TCS decomposition and increasing PMS concentration at fixed Co dose (comparison among 1:1:1, 1:3:1, and 1:5:1) also interrupted TCS decomposition.

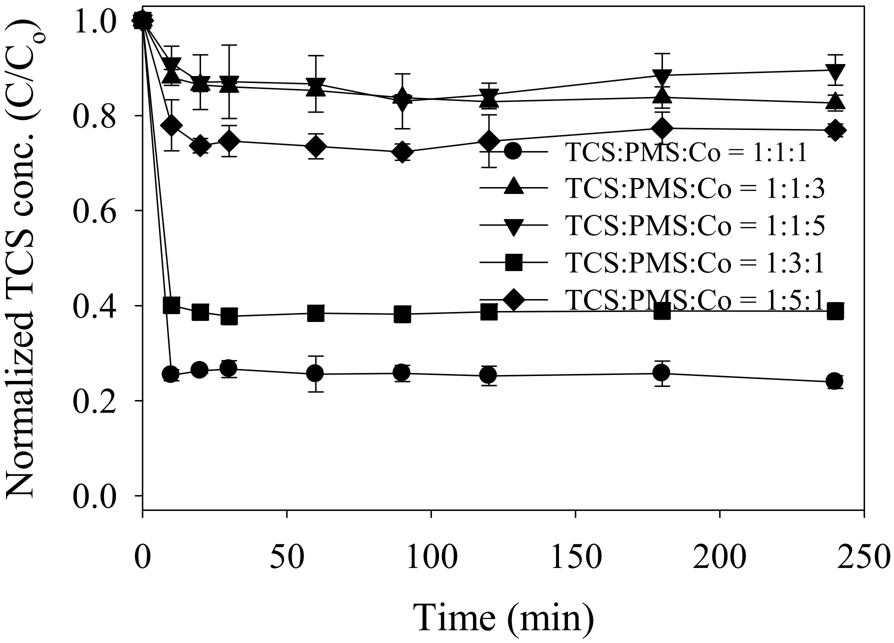


Figure 3.7 TCS decomposition by the activation of PMS with Co at different PMS:Co molar ratios. The error bars are the standard deviation from triplicate experiments.

Meanwhile, PMS/Fe combination showed slightly different trends, as shown in Figure 3.8. Increasing Fe concentration at fixed PMS dose (comparison among 1:10:10, 1:10:20, and 1:10:30) inhibited TCS decomposition while increasing PMS concentration at fixed Fe dose (comparison among 1:10:10, 1:20:10, and 1:30:10) facilitated TCS decomposition.

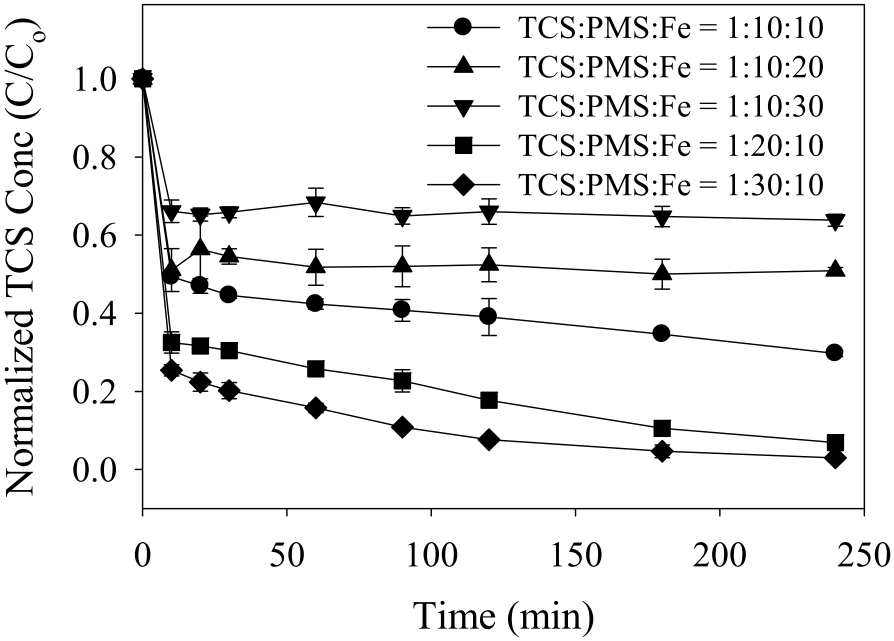


Figure 3.8 TCS decomposition by the activation of PMS with Fe at different PMS:Fe molar ratios. The error bars are the standard deviation from triplicate experiments.

The results suggest that more oxidants and metals, in general, generate more SRs for faster decomposition of TCS, while excessive amount of oxidants and metals might be rather undesirable.

$\mathrm{Fe^{2+} + HSO_5^- \rightarrow Fe^{3+}\,SO_4^{\bullet-} + OH^-}$ $\quad (\mathrm{k = 3.0 \times 10^4\,M^{-1}s^{-1}})$ (3.1)

$\mathrm{Fe^{2+} + SO_4^{\bullet-} \rightarrow Fe^{3+} + SO_4^{2-}}$ $\quad (\mathrm{k = 3.0 \times 10^8\,M^{-1}s^{-1}})$ (3.2)

$\mathrm{HSO_5^- + SO_4^{\bullet-} \rightarrow SO_5^{\bullet-} + SO_4^{2-} + H^+}$ $\quad (\mathrm{k < 1.0 \times 10^5\,M^{-1}s^{-1}})$ (3.3)

As shown in Reactions 3.1 - 3.3, the presence of excessive amounts of metal ions (in this case, $\mathrm{Fe^{2+}}$) and oxidants (PMS) is detrimental to organic decomposition because SRs generated are also promptly consumed by their further reaction with the metal and oxidant (note the reaction rate constants) (Burbano, et al., 2003; Burbano, et al., 2005). Even though it is difficult to directly compare the two systems because different molar ratios for Co and Fe were tested (in fact, at the similar ratio scale, the reactivity change of PMS/Fe was too small, as mentioned previously), the results implied the presence of optimum oxidant and metal concentration to best decompose TCS with respect to their molar ratios.

Meanwhile, in case of PS conjugated with Ag, some interesting results were found as shown in Figure 3.9. Both increasing Ag concentration at fixed PS dose (comparison among 1:10:10, 1:10:20, and 1:10:30) and increasing PS concentration at fixed Ag dose (comparison among 1:10:10, 1:20:10, and 1:30:10) facilitated TCS decomposition. As pointed out previously, gradual decomposition of TCS by PS/Ag system is clearly seen over time, compared to immediate TCS decomposition by PMS/Co and PMS/Fe systems.

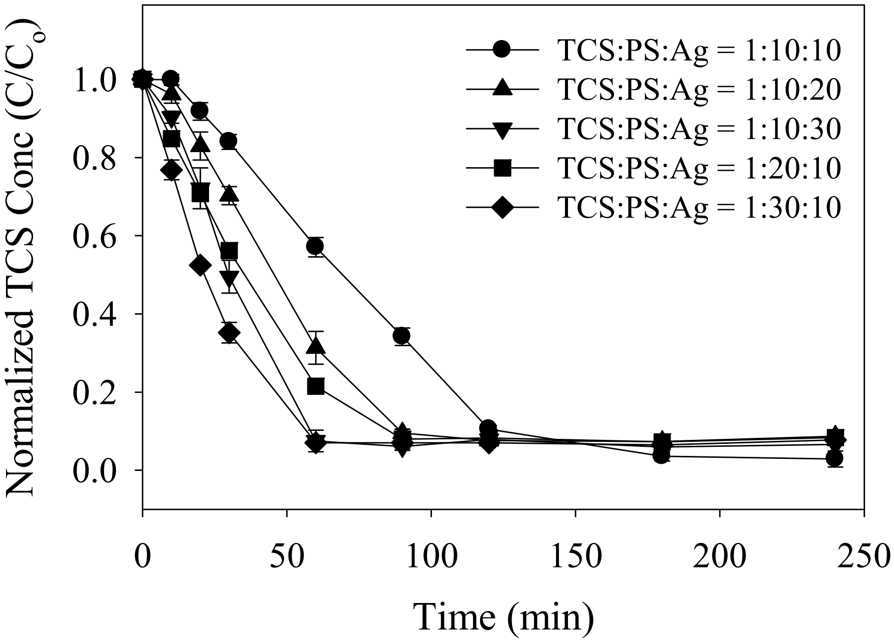


Figure 3.9 TCS decomposition by the activation of PS with Ag at different PS:Ag molar ratios. The error bars are the standard deviation from triplicate experiments.

The complexities of each system make it difficult to make a general conclusion. In addition, different results on the effects of oxidant and metal doses on the degradation of organic contaminants were reported in literatures (Burbano, et al., 2003; Rastogi, et al., 2009; Romero, et al., 2010; Vicente, et al., 2011). Rastogi *et al.* reported a molar ratio of 1:1 as an optimum for the degradation of 2-chlorobiphenyl in PMS/Fe system (Rastogi, et al., 2009). Romero *et al.* reported that dose of PS greater than molar ratio of 1:1 resulted in higher degradation of diuron in PS/Fe system (Romero, et al., 2010).

Metals react differently with oxidants, and 1:1 (stoichiometric) molar ratio of oxidant to metal may not necessarily be an optimum, as also suggested by other studies (Anipsitakis and Dionysiou, 2004a; Burbano, et al., 2005; Liang, et al., 2003; Rastogi, et al., 2009). The reactivity of oxidant/metal systems seems to be also specific to target compounds to oxidize. Some metals (e.g., Co) were reported to exhibit catalytic effects during the reaction and thus require dose much less than the stoichiometric ratio while others may not demonstrate true catalytic effect in the entire process, requiring dose in excess of the stoichiometric requirement to fully activate the oxidant. As mentioned, however, the presence of excessive metal ions may result in an undesired competition for SRs between metal ions and target organic compounds.

3.4.4 Mineralization of Triclosan by Sulfate Radicals

Transformation of TCS molecular structure to intermediates (i.e., disappearance of TCS) was reported in the previous sections while the possibility of complete mineralization of TCS by SRs was unknown. TOC change in the less effective PMS/Fe system even at high concentration (TCS:PMS:Fe=1:40:40) and the more effective PMS/Co system even at low concentration (TCS:PMS:Co=1:3:3) was briefly monitored, as shown in Figure 3.10. As expected, mineralization of TCS took much longer time, compared to its immediate disappearance. The results clearly indicate that both PMS/Co and PMS/Fe systems have high potential to completely mineralize TCS. In spite of much higher doses of PMS and Fe, the system was less effective for TCS mineralization compared to PMS/Co system. The result is consistent with the results on

TCS decomposition demonstrated previously. This also supports likely-catalytic behavior of the activation of PMS by Co, as discussed. Although a detailed mineralization test is under investigation in conjugation with a focused study on pH effects on metal speciation, SRs generation, and TCS decomposition, the results are promising enough to demonstrate the capability of the oxidant/metal systems to completely mineralize TCS.

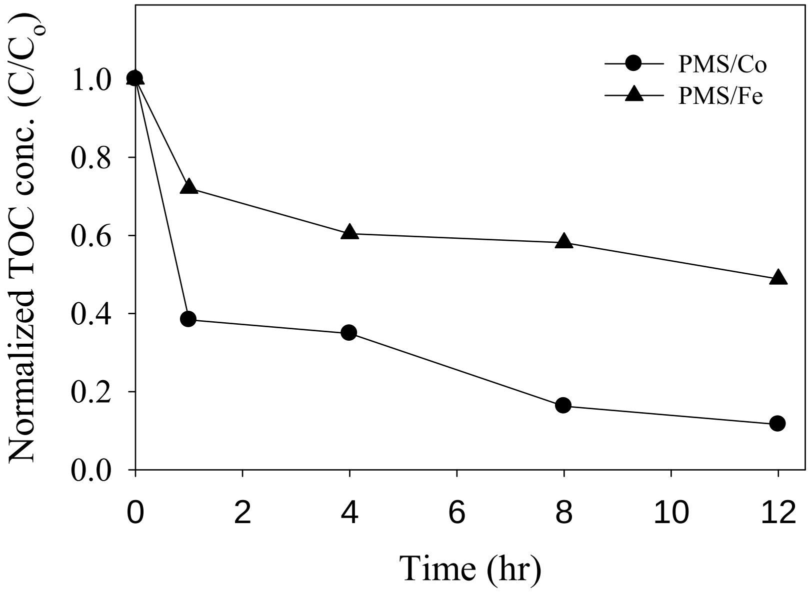


Figure 3.10 TCS mineralization by the activation of PMS with Co and Fe. Note that different molar ratios were used at TCS:PMS:Co = 1:3:3 and TCS:PMS:Fe = 1:40:40.

3.5 Conclusion

TCS was effectively decomposed by SRs generated from common oxidants (PMS and PS) conjugated with transition metals while the oxidants alone did not show any decomposition of TCS. The extent of TCS decomposition varied depending on the configuration of oxidant-metal conjugation and their doses. In general, PMS was more effective than PS for the decomposition of TCS. PMS/Co and PMS/Cu showed immediate decomposition of TCS while PMS/Fe, PMS/Ag and PS/Ag exhibited slow decomposition of TCS. TCS decomposition was faster with increasing doses of oxidant and metal, however, excessive amounts of oxidant and metal rather inhibited the decomposition reaction. An oxidant:metal molar ratio of 1:1 (stoichiometric amount) was found not to be necessarily an optimum for the decomposition of TCS. Although in-depth study on understanding of the detailed reaction mechanisms, including metal speciation change, is further needed, this study on SRs-based AOTs, as an alternative to established HRs-based AOTs, provides water authorities and industries with a sound and promising solution for the remediation of contaminated water with TCS and other PPCPs.

CHAPTER 4

IMPACTS OF pH-DEPENDENT METAL SPECIATION ON TRICLOSAN DECOMPOSITION

4.1 Abstract

The effectiveness of different oxidant/metal conjugations to decompose triclosan was reported in the previous chapter. The effects of the oxidant and metal doses were elucidated, showing diversity in the nature of TCS degradation with different oxidant/metal systems. The results from the previous studies suggest possible intrinsic reactivity of the oxidants and metals that require further investigations. A major factor to the understanding of the generation of radical species and thus the decomposition of organic contaminants is the catalytic/non-catalytic nature of the oxidation reaction. However, metal speciation has not been properly highlighted in previous studies probably due to associated analytical challenges. In this study, I investigated the detailed changes in metal speciation (solid vs. dissolved and Me^{2+} vs. Me^{3+}) in Co/PMS and Fe/PMS systems over time and correlated it with TCS decomposition at different pH conditions [Nfodzo, P., Hu, Q. and Choi, H., *Water Science Technology: Water Supply* (In press, doi:10.2166/ws.2012.059)]. A rapid oxidation of Co^{2+} to Co^{3+} and Fe^{2+} to Fe^{3+} generally corresponded with the pseudo-steady state decomposition kinetics of TCS after its initial fast decomposition. I also found the presence of a potential threshold concentration of metals to effectively activate PMS. Fe required a higher

threshold concentration than Co. A strong catalytic activity was observed for Co/PMS system in particular at pH 3 where most of Co added was present in the form of dissolved Co^{2+}. The pH impacts were different for Co/PMS and Fe/PMS, and TCS oxidation was fast at pH 5 for Co and pH 3 for Fe. However, long term mineralization of TCS seemed less dependent on pH conditions.

4.2 Introduction

Recently, the presence of pharmaceuticals and personal care products (PPCPs) in water resources has raised great attention. Many PPCPs have been classified as emerging chemicals of concern and endocrine disrupting compounds. In particular, triclosan (TCS, 5-chloro-2-(2,4-dichlorophenoxy)phenol), an antimicrobial agent widely used in PPCPs, has attracted significant concern because of the toxicity and prevalence of its derivatives. Since recent findings about the estrogenic effects of TCS in rats, the US Environmental Protection Agency (EPA) is particularly worried about the potential for antibiotic resistance and endocrine disruption resulting from human exposure to TCS (Zorrilla et al., 2009). The EPA is subsequently re-examining the potential health risks of TCS (Erickson, 2010).

TCS, like many other recalcitrant organic contaminants, is not degraded completely in conventional water and wastewater treatment processes and thus persistent in all environmental media. Moreover, TCS destroys some protozoa that facilitate biological treatment processes (Krishnakumar et al., 2011). Responding to the growing concerns, recent studies have focused largely on advanced oxidation processes

(AOPs), which rely on the generation of transitional reactive free radicals, particularly hydroxyl (HRs, $^{\bullet}OH$) and sulfate (SRs, $SO_4^{\bullet-}$) radicals as strong oxidizing species (Anipsitakis and Dionysiou , 2004; Son et al., 2007). The radicals have been proven to be effective for the degradation of a wide variety of organic compounds. For the degradation of organic contaminants including TCS, most of research efforts have been put into the application of HRs-based AOPs, such as Fenton reaction (activation of H_2O_2 with Fe), photo-Fenton (activation of H_2O_2 with UV radiation), and photocatalysis (activation of photocatalysts under UV radiation) (Sires et al., 2007; Son et al., 2009; Son et al., 2010). More recently, there has also been a growing interest in the application of SRs-based AOPs. SRs are typically generated by the metal-mediated activation of common oxidants such as peroxymonosulfate (HSO_5^-, PMS) and persulfate ($S_2O_8^{2-}$, PS), as shown in Reactions (4.1) and (4.2) (Anipsitakis and Dionysiou, 2003). In particular, these technologies have been reported to be effective for the decomposition of TCS (Nfodzo and Choi, 2011a).

$$\mathrm{HSO_5^- + M^{n+} \rightarrow M^{n+1} + SO_4^{\bullet-} + OH^-} \tag{4.1}$$

$$\mathrm{H_2O_8^{2-} + M^{n+} \rightarrow M^{n+1} + SO_4^{\bullet-} + SO_4^{2-}} \tag{4.2}$$

The effectiveness of the metal/oxidant systems to generate such radicals is dependent on the availability of useful metal species in the reaction environment. Since homogeneous systems are much more effective than heterogeneous systems with respect to reaction kinetics, dissolved metal species are preferred to solid state metal species. In particular, the presence of low oxidation state ions, such as Fe^{2+} and Co^{2+}, is important for the activation of oxidants, as demonstrated in Reactions 4.1 and 4.2. Consequently, the ability of a metal/oxidant system to maintain an adequate amount of useful metal species (i.e., dissolved Fe^{2+} and Co^{2+}) determines the efficiency of SR generation and the catalytic/non-catalytic nature of the overall reaction. Some metals demonstrate catalytic behaviors in the activation of oxidants and thus require small doses to decompose contaminants while others require large doses to achieve similar results (Anipsitakis and Dionysiou, 2003; Nfodzo and Choi, 2011b; Zhang and Edwards, 1992; Kim and Edwards, 1995; Ball and Edwards, 1958).

In spite of the importance of metal speciation in solution as a key to understanding the efficiency of SR generation and catalytic/non-catalytic nature of the oxidation reaction during the metal-mediated AOPs, there have been few research studies focusing on measuring metal species over the reaction time and thus correlating the metal speciation with organic decomposition. Measuring metal species in real time poses many analytical challenges. Changes in metal species are radical over time, especially in oxygenated environments (Safarzadeh-Amiri et al., 1996), and they are also dependent on pH conditions. Some previous studies reported simply concentration of either total metal or total dissolved metal initially added (Anipsitakis and Dionysiou, 2004). Even the presence of a potential threshold concentration of Co minimally required to activate PMS was proposed in previous studies, but researchers reported only total dissolved Co concentration added (Anipsitakis and Dionysiou, 2003). This might have resulted in shallow explanations on observed organic decomposition kinetics in AOPs.

In this study I, for the first time, traced detailed changes in metal species during the decomposition of TCS by SRs at different pH conditions. PMS, which shows a better reactivity than PS, was exclusively focused in this study (Nfodzo and Choi 2011b). The efficiencies of Co/PMS and Fe/PMS systems for the decomposition and mineralization of TCS were correlated with the changes in metal speciation. Among many transition metal activators, Co and Fe were selected because Co is known to be the best metal activator for PMS and Fe is naturally abundant in water resources (Anipsitakis and Dionysiou, 2004; Safarzadeh-Amiri et al., 1996).

4.3 Materials and Methods

4.3.1 Chemicals

TCS was in the salt form as irgasan. Potassium peroxymonosulfate ($KHSO_5$) was derived from the triple salt, oxone. Other chemicals including iron (II) sulfate (Fe^{2+}), iron (III) sulfate (Fe^{3+}), and cobalt sulfate (Co^{2+}) were obtained as salts. Standard iron (Fe) and cobalt (Co), sodium hydroxide (NaOH), and nitric acid (HNO_3) were obtained as volumetric solutions. These chemicals and analytical chemicals including HPLC grade acetonitrile and methanol were obtained from Sigma-Aldrich and used as received. The chemicals for ion chromatography analysis, including Metpac PDCA eluent, MetPac PAR post column eluent, and 4-(2-pyridylazo) resorchol monosodium salt, were obtained from Dionex. Phosphate buffers were prepared from the salts of sodium phosphate monobasic monohydrate ($H_2NaPO_4 \cdot H_2O$) and sodium phosphate dibasic heptahydrate ($HNa_2PO_4 \cdot 7H_2O$) obtained from Sigma-Aldrich. Solution of TCS was prepared at 9 mg/L (0.031 mM, close to its aqueous solubility). All reaction solutions were prepared in high-purity water. The standard solutions of Fe and Co were prepared in 2% ultra-pure HNO_3 solution.

4.3.2 Generation of sulfate radicals and decomposition of triclosan

SRs were generated by the activation of PMS with Co2+ and Fe2+. All the experiments were conducted in a batch reactor at ambient temperature. Specific aliquot of TCS was transferred into a glass reactor, and appropriate volumes of PMS followed by Co2+ and Fe2+ stock solutions were added to achieve a 100 mL reaction solution with predetermined molar ratios of TCS, PMS, and metal. Experiments were conducted to investigate the effects of pH on the species of Co and Fe and consequently on the simple disappearance and complete mineralization of TCS. Since preliminary experiments showed the immediate disappearance of the original molecular form of TCS by self-ionization at pH above 8.1, I focused on the experiments exclusively at pH 3.0, 5.0, and 7.0 using phosphate buffers. The use of phosphate buffers in maintaining solution pH in reactions involving oxidizing radicals is a common practice.

In my previous studies on TCS decomposition, PMS:metal molar ratio of 1:1 was most effective, and TCS:PMS molar ratio of 1:3 when conjugated with Co and 1:40 when conjugated with Fe resulted in a rapid decomposition of TCS (Nfodzo and Choi, 2011b). In order to retard the reaction kinetics and thus to effectively monitor the metal species change, PMS dosage was slightly reduced in this study to TCS:PMS at 1:2 for PMS/Co and TCS:PMS at 1:10 for PMS/Fe while PMS:metal ratio was fixed at 1:1. Control experiments with TCS only, TCS/metal (without PMS), and TCS/PMS (without metal) were conducted to validate the mechanism of TCS decomposition. The solution was continuously agitated using a magnetic stirring bar. Some of the experiments were conducted in triplicates to ensure accurate data acquisition and interpretation.

4.3.3 Measurement of triclosan and total organic carbon

For the determination of TCS disappearance, sample of 0.5 ml was drawn at 15 minutes intervals for 2 hrs., immediately mixed with methanol as a quenching agent for SRs to stop further chemical reaction, and filtered through 0.45 μm syringe filters. Samples for total organic carbon (TOC) analysis to determine TCS mineralization were drawn at time of 1, 2, 3, 6, 12, 18 and 24 hr, and immediately mixed with sodium nitrite as an inorganic quenching agent for SRs. The disappearance of molecular TCS was monitored with a reversed-phase high performance liquid chromatography (HPLC, 1200 series, Agilent) equipped with a quaternary pump, C18 column, and ultraviolet (UV) detector. A mixture of water and acetonitrile was used as the mobile phase at water:acetonitrile ratio of 25:75% v/v with a flow rate of 1 ml/min. The UV detector was operated at a wavelength of 280 nm for TCS detection. The TOC concentration was monitored by measuring the non-purgeable organic carbon concentration using a TOC analyzer (TOC-VCSH/CSN, Shimadzu).

4.3.4 Identification of metal species

The concentrations of the various metal species were monitored over time in order to make distinctions between solid metals and dissolved metals and to identify the oxidation states of dissolved metals. Total metal concentration added to the initial reaction solution and dissolved metal concentration in filtered samples was measured eventually to determine solid metal concentration. In filtered samples, specific ionic species (Co^{2+} and Fe^{3+}) was instantaneously measured and compared to total dissolved metal concentration to determine the concentration of other ionic species (Co^{3+} and Fe^{2+}). Measurements of the ionic species were performed with an ion chromatograph (IC) (LC 20, Dionex), comprising UV-visible multiple wavelength detector (AD 25), gradient pump (GP 50), IonPac analytical column (CS5A, Dionex), IonPac guard column (CG5A, Dionex), automated sampler (AS 40), and a postcolumn pneumatic controller. MetPac PDCA eluent was used as the mobile phase at a flow rate of 1.0 mL/min and MetPac PAR was used as post-column reagent at a flow rate of 0.5 mL/min. Measurements of total metal and dissolved metal concentrations were carried out using a quadrupole inductively coupled plasma–mass spectrometry (ICP–MS) system (PerkinElmer/SCIEX, Sheldon, CT) after the samples were acid-digested.

4.4 Results and Discussion

The solution pH governs the speciation and reactivity of metals and thus the generation of SRs and the decomposition of TCS. The effects of pH at 3, 5, and 7 on the speciation of Co and Fe and consequently on the kinetics of TCS degradation were examined. It has been reported that at pH values of above 8.1 (pKa of TCS), TCS exists primarily in its ionic form (Lindström et al. 2002) as shown in Figure 4.1. This was also confirmed in my preliminary studies. At pH 9.0 and 11, no evidence of the presence of initial molecular TCS added in solution was observed at all times. Since my focus was on the transformation of the original molecular form of TCS over time at different pHs, reactions at pH 9 and 11 were excluded from further investigation.

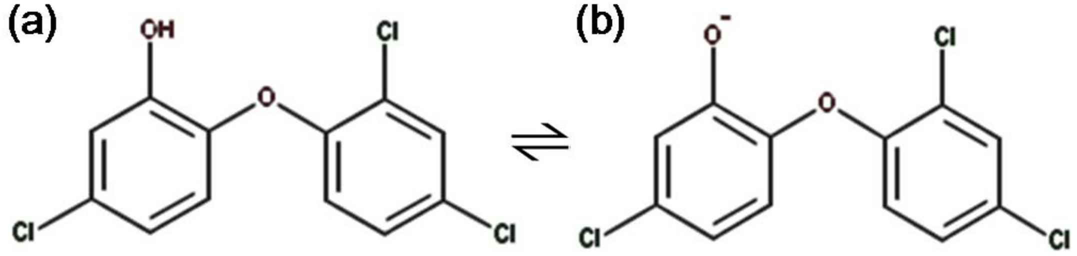


Figure 4.1 Molecular and ionized structures of TCS with acid dissociation constant pKa of 8.1 (a) Phenolic form at pH<8.1 (b) Phenolate form at pH >8.1.

4.4.1 Cobalt speciation and triclosan decomposition

The decomposition of aqueous TCS by the Co-mediated system was significantly affected by pH, as shown in Figure 4.2. The decomposition of TCS ranged from 60% to 95% for 2 hrs. and was more effective at pH 5 compared to pH 7 and 3.

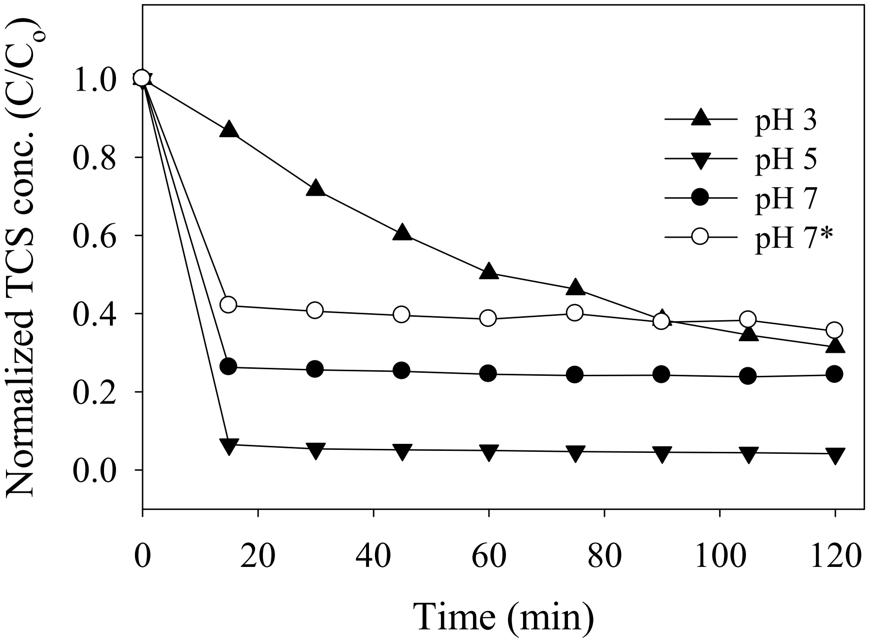


Figure 4.2 Effect of pH in a Co/PMS system over time on TCS decomposition For the reaction, chemicals were added in order of TCS, PMS, and Co, while for pH7*, chemicals were added in order of PMS, Co, and TCS. $[TCS]_o$=9 mg/L, $[Co^{2+}]_o$=3.66 mg/L, and $[PMS]_o$=19.14 mg/L.

Other studies also confirmed that near pH 5 is optimal for organic decomposition by Co/PMS system (Anipsitakis and Dionysiou, 2003; Yang et al., 2009). The kinetics of TCS decomposition is somewhat interesting. A non-catalytic reaction evidenced by an initial rapid decomposition followed by a pseudo-steady state was observed at pH 5 and 7 while a catalytic-like activity was demonstrated at pH 3 showing slow but continuous decomposition of TCS over time. Although much more rapid TCS decomposition was observed at pH 7 than at pH 3 within first 15 min, TCS decomposition at pH 3 was eventually comparable to that at pH 7 after 2 hrs. It has been reported that SRs have the potential to react with H_2O under neutral conditions and with hydrogen ions under acidic conditions, as shown in Reactions 4.3 and 4.4 (Buxton and Greenstock 1988; Spinks and Woods 1990). As a result, SRs generated are immediately transformed to less effective species, which hinders the decomposition of TCS.

$$\mathrm{SO_4^{\bullet -}} + \mathrm{H_2O} \rightarrow \mathrm{SO_4^{2-}} + \mathrm{OH^-} + \mathrm{H^+} \tag{4.3}$$

$$\mathrm{SO_4^{\bullet -}} + \mathrm{H^+} + \mathrm{e^-} \rightarrow \mathrm{HSO_4^{\bullet -}} \tag{4.4}$$

In order to elucidate the catalytic/non-catalytic behavior of the oxidation reaction, Co species was monitored over time. The kinetics of TCS decomposition is somewhat interesting. A non-catalytic reaction evidenced by an initial rapid decomposition followed by a pseudo-steady state was observed at pH 5 and 7, while a catalytic-like activity was seen at pH 3, showing slow but continuous decomposition of TCS over time. Considering that the heterogeneous activation of oxidants by solid state metals is not as effective as the homogeneous activation by dissolved metal ions, determining fractional changes of the solid state and ionic state metals was of particular interest. As shown in Figure 4.3, although a small amount of Co precipitates were found at pH of 7 and 5, a high level of dissolved Co species was always maintained at all pH values. The dissolved Co species at above 2.7 mg/L is considered to be enough to activate PMS, according to the concept of a cobalt threshold concentration (Anipsitakis and Dionysiou 2003). Due to the similar behavior of the dissolved Co fraction over time under different pHs, it did not explain well the unique TCS decomposition kinetics shown in Figure 4.2. Some of the dissolved Co species may not be effective to activate PMS.

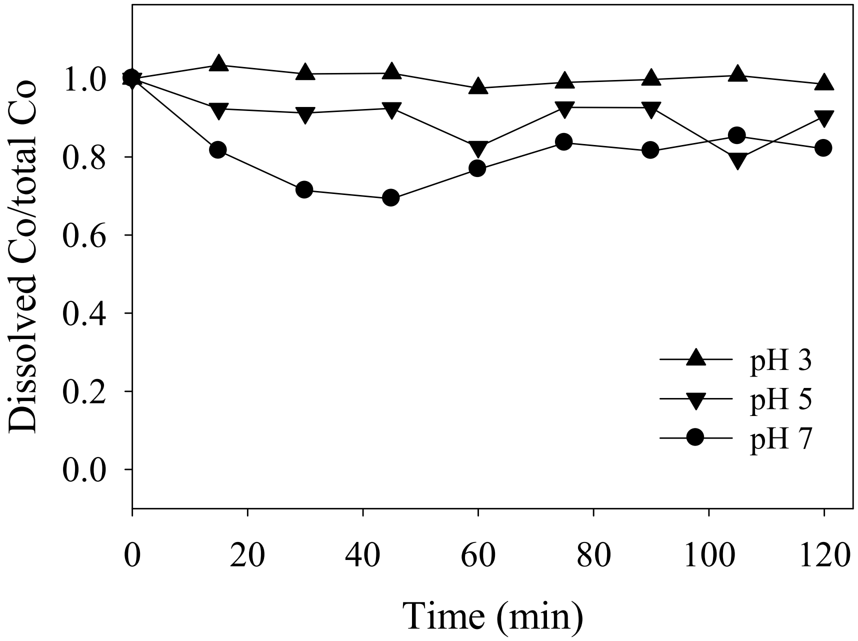


Figure 4.3 Effect of pH in a Co/PMS system over time on Fraction of dissolved Co/total. Co $[TCS]_o$=9 mg/L, $[Co^{2+}]_o$=3.66 mg/L, and $[PMS]_o$=19.14 mg/L.

As a result, I focused on tracing the oxidation state of dissolved Co ions in order to elucidate the catalytic/non-catalytic behavior of the oxidation reaction. Figure 4.4 shows changes in the ionic Co species during the reaction. As expected from Reaction 4.1, maintaining a high concentration of Co^{2+} is important for inducing the catalytic behavior of the overall reaction in order to continuously generate SRs and thus decompose TCS. At pH 3, the steady-state high concentration of Co^{2+} at above 3.5

mg/L could explain the continuous decomposition of TCS over time observed in Figure 4.2.

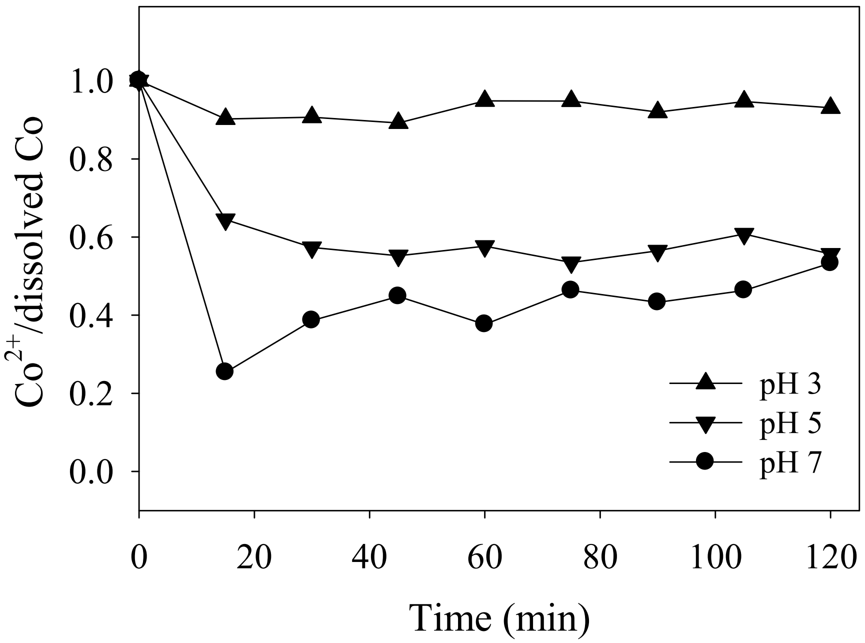


Figure 4.4 Effect of pH in a Co/PMS system over time on Fraction of Co^{2+}/dissolved Co. $[TCS]_o$=9 mg/L, $[Co^{2+}]_o$=3.66 mg/L, and $[PMS]_o$=19.14 mg/L.

$$Co^{3+} + HSO_5^- \rightarrow Co^{2+} + SO_5^{\bullet -} + H^+ \quad (4.5)$$

During the production of SRs, Co^{2+} is converted to Co^{3+} (note Reaction 1). The generated Co^{3+} can also react with PMS to transform back to Co^{2+} (note Reaction 4.5). However, the reduction of Co^{3+} to Co^{2+} is generally slower than the oxidation of Co^{2+} to Co^{3+} (Reactions 4.1 and 4.2), resulting in accumulation of Co^{3+} in the reaction solution. This is one of possible explanations on why many Fenton-like reactions show non-catalytic behavior in organic oxidation. However, the Co regeneration process is known to be somewhat enhanced under certain conditions. The Co/PMS system at pH 3 seemed successful in regenerating Co^{2+} at all times. On the other hand, a rapid oxidation of Co^{2+} to Co^{3+} was observed at pH 5 and 7. The initial fast decomposition of TCS can be explained by the initial prompt conversion of Co^{2+} to Co^{3+} at pH 5 and 7. Although a certain level of Co^{2+} was continuously maintained, TCS decomposition was almost idle. Similar results showing an initial sharp drop followed by no further reaction were reported by other researchers (Anipsitakis and Dionysiou 2004; Rastogi et al. 2009). One notable explanation for this behavior is the presence of a potential threshold concentration of Co^{2+} minimally required to activate PMS. Anipsitakis and Dionysiou reported a minimum concentration of 0.72 mg/L of Co for the effective degradation of 2,4-dihlorophenol (Anipsitakis and Dionysiou 2003). Threshold concentrations might vary depending on the ratio of oxidant and metal added as well as target contaminants.

For all the experiments, reactants were added in the order of TCS, PMS and Co^{2+}. PMS alone does not decompose TCS and thus addition of Co^{2+} initiates the decomposition of TCS. Co^{2+} is, however, converted to Co^{3+} while TCS is decomposed. In a separate test, I first added PMS and Co^{2+} before TCS injection. As shown in Figure 4.2, there was a substantial decrease in TCS decomposition when TCS was added later. Significant amount of Co^{2+} added was already converted to Co^{3+} during its instantaneous reaction with PMS before TCS addition. The results so far suggested the importance of the presence of dissolved Co^{2+} ions for activating PMS to generate SRs and catalytically decompose TCS.

4.4.2 Iron speciation and triclosan decomposition

Similarly to the Co/PMS system, the decomposition of aqueous TCS by the Fe/PMS system was significantly affected by pH conditions, as shown in Figure 4.5.

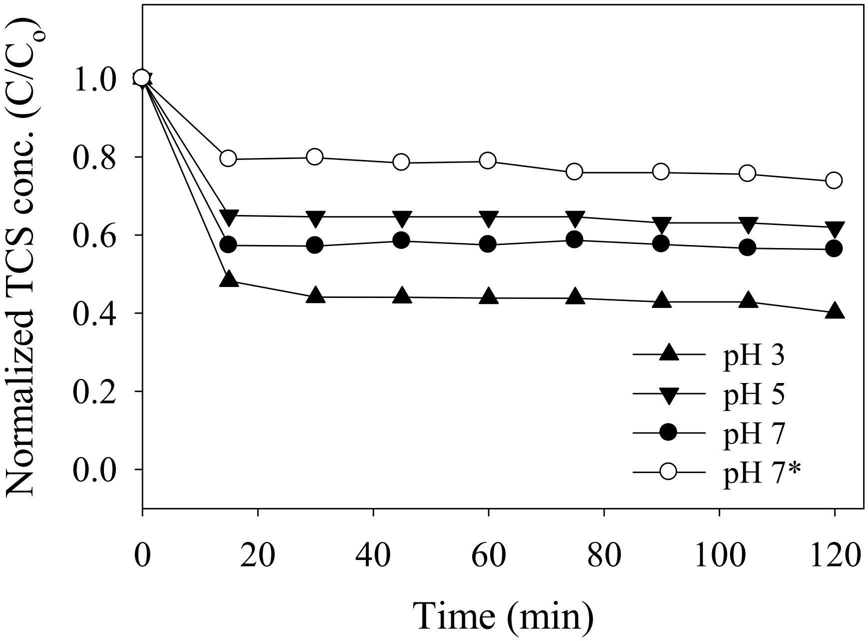


Figure 4.5 Effects of pH in a Fe/PMS system over time on TCS decomposition. For the reaction, chemicals were added in order of TCS, PMS, and Fe while for pH7*, chemicals were added in order of PMS, Fe, and TCS. $[TCS]_o$=9 mg/L, $[Fe^{2+}]_o$=17.36 mg/L, and [PMS]=94.69 mg/L.

The transformation of TCS ranged from 35% to 60%. The highest TCS decomposition occurred at pH 3. Other studies also reported pH 3 as the best condition of Fe/PMS systems for the decomposition of organic compounds, such as polychlorinated biphenyls (PCBs) (Rastogi et al. 2009). Their study showed that decreasing reaction pH in a Fe/PMS system generally increased the oxidation kinetics of PCBs. In this present study, pH 7 was marginally better than pH 5. The slightly different observation might be related to the selective nature of SR attack to specific target organic molecules.

At pH 5, Fe was mainly present in solid form, as shown in Figure 4.6. This was consistent with the lowest TCS decomposition observed at pH 5.

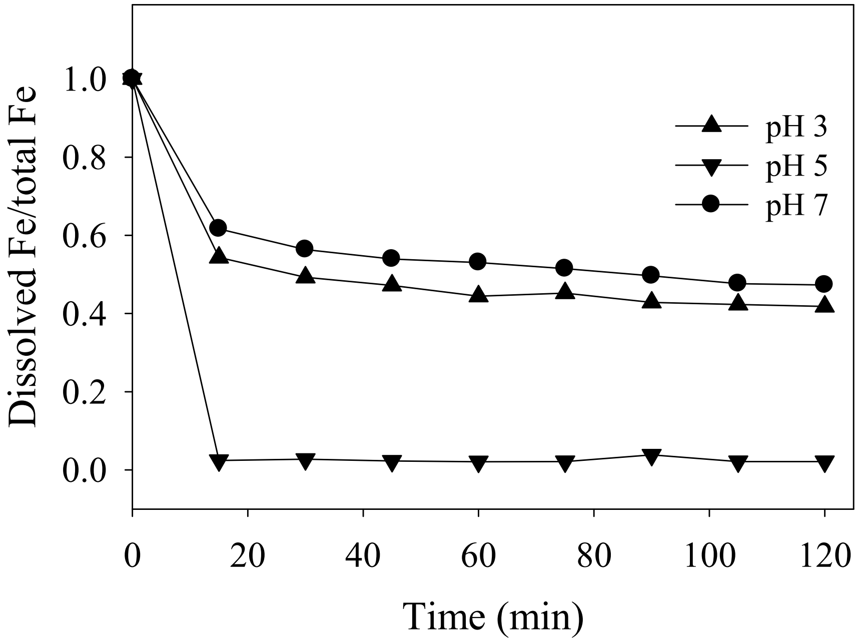


Figure 4.6 Effects of pH in a Fe/PMS system over time on Fraction of Dissolved Fe/total Fe $[TCS]_o$=9 mg/L, $[Fe^{2+}]_o$=17.36 mg/L, and [PMS]=94.69 mg/L.

On the other hand, a significant amount of dissolved Fe ions were maintained at pH 3 and 7. As mentioned previously, the amount of reactive dissolved species such as Fe^{2+} is more important than total dissolved Fe. However, measuring Fe^{2+} concentration in real time is challenging especially under oxygenated environments since Fe^{2+} readily oxidizes to Fe^{3+} in the presence of any measurable amount of dissolved oxygen in water (Snoeyink and Jenkins 1980).

Figure 4.7 shows the fraction of Fe^{2+} ions/total dissolved Fe over time. Fe^{3+} ions were found to be dominant at pH 3 and 7.

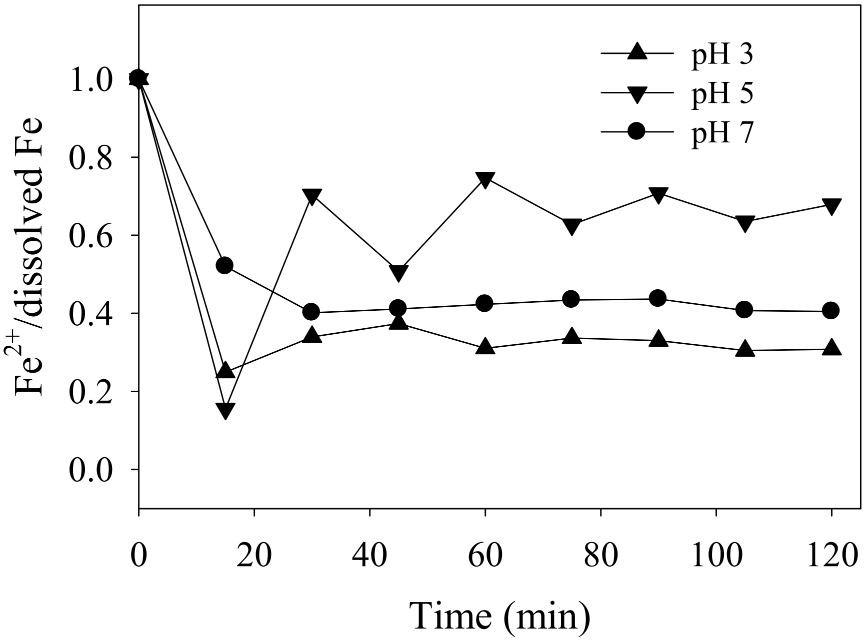


Figure 4.7 Effects of pH in a Fe/PMS system over time on Fraction of Fe^{2+}/dissolved Fe. $[TCS]_o$=9 mg/L, $[Fe^{2+}]_o$=17.36 mg/L, and [PMS]=94.69 mg/L.

The initial fast oxidation of Fe^{2+} to Fe^{3+} resulted in a pseudo-steady state TCS decomposition, as observed in Figure 4.5. The result is in agreement with previous studies on Fenton reaction, where the slow Fe regeneration kinetics from Fe^{3+} back to Fe^{2+} is a major drawback of the technology for organic decomposition (Klamerth et al. 2010). Although a fairly high concentration of Fe^{2+} was still maintained in the solution (4 mg/L at pH 3 and 5 mg/L at pH 7), TCS decomposition did not progress promptly, suggesting the presence of a potential threshold concentration of Fe^{2+} to effectively activate PMS. The importance of maintaining high concentration of Fe^{2+} was also examined by changing the order of chemical addition, as shown in Figure 4.3(a). There was a substantial reduction in the efficiency of the PMS/Fe system when TCS was added later after Fe^{2+} ions pre-reacted with PMS and thus some of them already transformed to Fe^{3+}.

4.4.3 Comparison of the effects of pH on Co/PMS and Fe/PMS systems

Although both Co- and Fe-mediated systems effectively generated SRs and decomposed TCS, different impacts of pH on the metal speciation and TCS disappearance were exhibited. Co was mostly dissolved at all pH values tested whereas a fairly high amount of Fe was precipitated and thus not available for the homogeneous activation of PMS. TCS disappearance ranged from 45% to 95% in the Co/PMS system and was more effective at pH 5, while it ranged from 35% to 60% in the Fe/PMS system (even with much higher Fe concentration than Co) and was more effective at pH 3. The large amount of Fe^{2+} required to activate PMS suggests a high threshold concentration of Fe^{2+}, which accounts for the non-catalytic nature of the Fe/PMS system. On the other hand, the steady-state high concentration of Co^{2+} resulting from the effective Co regeneration from Co^{3+} back to Co^{2+} enhanced the catalytic-like activity of the Co/PMS system at pH 3. A potential threshold concentration of Co^{2+} was much lower than Fe^{2+}.

4.4.4 Triclosan mineralization

Mineralization of TCS is another important parameter to evaluate the effectiveness of the metal/PMS systems. Reduction of TOC by Co/PMS and Fe/PMS systems was monitored over 24 hrs, as shown in Figures 4.8 and 4.9. Generally, pH conditions did not significantly affect the mineralization of TCS, except for Co/PMS at pH 7.

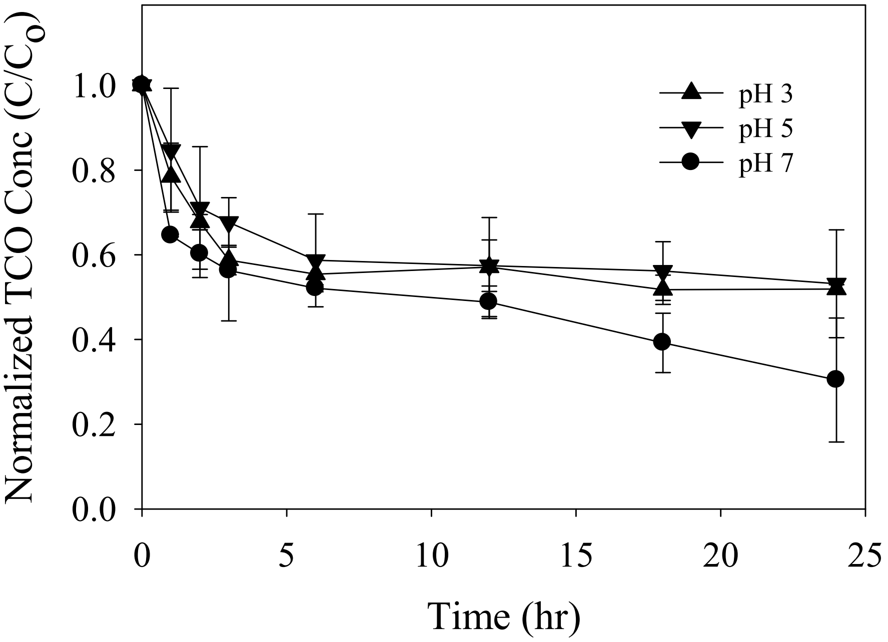


Figure 4.8 Effect of pH on TCS mineralization over time in Co/PMS system $[TCS]_o$=9 mg/L, $[Co^{2+}]_o$=3.66 mg/L, $[PMS]_o$=19.14 mg/L.

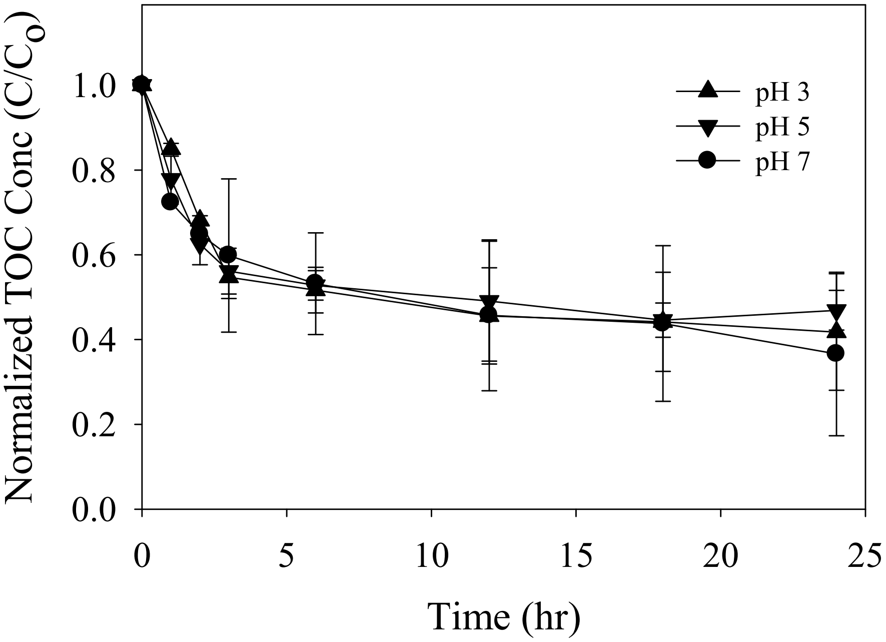


Figure 4.9 Effect of pH on TCS mineralization over time in Fe/PMS system
$[TCS]_o$=9 mg/L, $[Fe^{2+}]_o$=17.36 mg/L, $[PMS]_o$=94.69 mg/L.

The Co/PMS was much more effective than Fe/PMS, considering a lower dose of Co (TCS/PMS/Co of 1:2:2) was used than Fe (TCS/PMS/Fe of 1:10:10), which is consistent with the observation on the disappearance of original molecular TCS. The disappearance rate of molecular TCS reached a pseudo-steady state within 15 minutes in most cases, while the mineralization of TCS continuously progressed over the prolonged time. This suggests that SRs might attack preferentially some reaction intermediates rather than the original molecular TCS at some point during the reaction.

4.5 Conclusion

This study has demonstrated the detailed changes in metal speciation in Co/PMS and Fe/PMS systems over time and correlated it with TCS decomposition under different pH regimes. I proved that a rapid oxidation of Co^{2+} to Co^{3+} and Fe^{2+} to Fe^{3+} deteriorates the effective decomposition of TCS and the potential threshold concentration of Fe is much higher than that of Co. A strong catalytic activity was also observed for a Co/PMS system in particular under pH 3, where Co^{3+} seemed to be effectively regenerated back to Co^{2+}. The pH effects on the metal speciation and reactivity were quite different for Co and Fe. Overall, it was concluded that SRs radicals generated from the Co/PMS and Fe/PMS systems are effective to mineralize TCS under various pH conditions. This study contributes towards taking an important first step in understanding the catalytic/non-catalytic nature of the metal-mediated activation of PMS.

CHAPTER 5

RECOMMENDATIONS AND APLLICATION POTENTIALS

5.1 Recommendations for future studies

In my dissertation, I have demonstrated the effectiveness of SRs-based AOTs for the degradation of PPCPs, in particular TCS, and elucidated the critical reaction conditions for the generation of SRs by the metal-mediated activation of common oxidants. There is, however, concern over the uncertainty of the possible toxicity of the degradation intermediates of PPCPs. It is well-known that HRs exhibit nonselective organic attack while SRs show some selectivity. The mechanisms of SRs attack to organics are basically similar to those of HRs, occurring via electron transfer, hydrogen abstraction, and/or hydrogen addition. However, SRs react more selectively by electron transfer (Neta *et al*., 1977, 1988), making both HRs- and SR-based AOPs unique and distinct from each other. In spite of the high potential for complete degradation of TCS in water by AOPs, there have been few research studies on the reaction mechanisms. In particular, no attempt has been made so far to determine the degradation intermediates of TCS resulting from SRs-based AOPs. Moreover, most studies to determine the degradation intermediates of TCS using HRs-based AOPs have focused on photolytic processes with emphasis on the presence or absence of dioxins as degradation intermediates .

The transition metal-mediated AOPs, including the original Fenton reaction (generation of HRs by the activation of H_2O_2 with Fe^{2+}) and generation of SRs by the activation of PMS and PS with transition metals, have high potentials of practical applicability for the treatment of TCS-contaminated water resources. A future study is needed to determine the intermediates, mechanisms, and pathways for TCS degradation by SRs-based AOPs in comparison to HRs-based AOPs. It is also necessary to establish the toxicity of the reaction intermediates in order to propose these processes as a practical management option for TCS-contaminated waters. With the emergence of nanomaterials currently driving research efforts to develop nanotechnological applications for water treatment, further studies involving the activation of common oxidants with nano-size metal particles in heterogeneous systems are also recommended. Since UV can be absorbed by oxidants, UV- oxidant systems, instead of metal activators, will be of high interest for the decomposition of PPCPs.

The studies in this dissertation have been conducted exclusively by spiking high purity water with PPCPs, future studies should be extended to the application of these systems to real water and wastewater samples, and investigate the influence of natural organic matter and other co-existing substances in natural water systems on the degradation of PPCPs.

5.2 Potential Applications

The transition metal-mediated activation of PMS and PS provides a new tool for the management of specialty industrial wastewater containing organic contaminants as well as transition metals. Industries, including nuclear energy and technology, photographic, paper and pulp, textiles, and electroplating, can take advantage of this technology. The metals in such wastewaters can be utilized to activate appropriate oxidants and generate radicals for the degradation of recalcitrant organic contaminants present in the wastewater.

In situ chemical oxidation, a process that conventionally involves the injection of common oxidants into groundwater and sediments for the purpose of contaminant destruction can also be greatly enhanced by the application of metal-mediated activation of oxidants since several metals are naturally abundant in these environments.

APPENDIX A

SAMPLES OF EXPERIMENTAL RESULTS

EXPERIMENTAL RESULTS

TREATMENT: SMX + PS+ Fe	DATE: 8/31/2010
REACTION VOLUME: 100 mL	INITIAL pH: 7
SAMPLE VOLUME: 0.5 mL	DILUTION: 2

TIME (min)	SMX CONCENTRATION (μg/L)		
	1	2	3
0	4500	4500	4500
5	3701	3577	3624
10	3679	3585	3609
20	3705	3611	3785
30	3705	3645	3552
60	3610	3601	3630
120	3647	3549	3580
180	3671	3704	3579
240	3532	3549	3584

Experimental Conditions

Molar ratio of SMX:PS:Fe =1:80:80

SMX concentration = 9.0 mg/L

PMS concentration = 672 mg/L

Fe concentration = 139 mg/L

EXPERIMENTAL RESULTS

TREATMENT: SMX + H_2O_2+ Fe	DATE: 9/2/2010
REACTION VOLUME: 100 mL	INITIAL pH: 7
SAMPLE VOLUME: 0.5 mL	DILUTION: 2

TIME (min)	SMX CONCENTRATION (µg/L)		
	1	2	3
0	4500	4500	4500
5	2161	2120	2140
10	1938	1857	1904
20	1631	1463	1534
30	1323	1200	1329
60	815	668	761
120	254	152	215
180	60	60	58
240	57	68	58

Experimental Conditions

Molar ratio of SMX:H_2O_2:Fe =1:80:80

SMX concentration = 9.0 mg/L

H_2O_2 concentration = 85 mg/L

Fe concentration = 139 mg/L

EXPERIMENTAL RESULTS

TREATMENT: SMX + PMS+ Fe	DATE: 8/31/2010
REACTION VOLUME: 100 mL	INITIAL pH: 7
SAMPLE VOLUME: 0.5 mL	DILUTION: 2

TIME (min)	SMX CONCENTRATION (µg/L)		
	1	2	3
0	4500	4500	4500
5	65	64	242
10	65	66	229
20	61	58	213
30	67	55	195
60	61	49	154
120	52	Undetected	100
180	Undetected	Undetected	79
240	Undetected	Undetected	62

Experimental Conditions

Molar ratio of SMX:PMS:Fe =1:80:80

SMX concentration = 9.0 mg/L

PMS concentration = 766 mg/L

Fe concentration = 139 mg/L

EXPERIMENTAL RESULTS

TREATMENT: SMX + PMS+ Fe	DATE: 11/3/2010
REACTION VOLUME: 100 mL	INITIAL pH: 7
SAMPLE VOLUME: 0.5 mL	DILUTION: 2

TIME (min)	SMX CONCENTRATION (µg/L)		
	1	2	3
0	4500	4500	4500
1	3285	2852	3047
2	2991	2771	2987
3	2943	2704	2956
4	2920	2667	2985
5	2907	2660	2892
10	2839	2696	2880
20	2799	2558	2835
30	2769	2526	2801

Experimental Conditions

Molar ratio of SMX:PMS:Fe =1:10:10

SMX concentration = 9.0 mg/L

PMS concentration = 96 mg/L

Fe concentration = 17 mg/L

EXPERIMENTAL RESULTS

TREATMENT: TCS + PMS+ Fe	DATE: 12/10/2010
REACTION VOLUME: 100 mL	INITIAL pH: 7
SAMPLE VOLUME: 0.5 mL	DILUTION: 2

TIME (min)	TCS CONCENTRATION (µg/L)		
	1	2	3
0	4500	4500	4500
10	3000	1934	2884
20	2792	1901	2766
30	2723	1784	2838
60	2429	1616	2847
90	2400	1575	2728
120	2556	1354	2473
180	2225	1366	2446
240	2171	1124	2224

Experimental Conditions

Molar ratio of TCS:PMS:Fe =1:5:5

TCS concentration = 9.0 mg/L

PMS concentration = 48 mg/L

Fe concentration = 9 mg/L

EXPERIMENTAL RESULTS

TREATMENT: TCS + PMS+ Co	DATE: 12/10/2010
REACTION VOLUME: 100 mL	INITIAL pH: 7
SAMPLE VOLUME: 0.5 mL	DILUTION: 2

TIME (min)	TCS CONCENTRATION (µg/L)		
	1	2	3
0	4500	4500	4500
10	400	54	63
20	44	53	39
30	48	44	55
60	39	46	40
90		47	41
120	49	37	
180	29	67	37
240		42	

Experimental Conditions

Molar ratio of TCS:PMS:Fe =1:5:5

TCS concentration = 9.0 mg/L

PMS concentration = 48 mg/L

Co concentration = 9 mg/L

EXPERIMENTAL RESULTS

TREATMENT: TCS + PMS+ Cu	DATE: 12/11/2010
REACTION VOLUME: 100 mL	INITIAL pH: 7
SAMPLE VOLUME: 0.5 mL	DILUTION: 2

TIME (min)	TCS CONCENTRATION (µg/L)		
	1	2	3
0	4500	4500	4500
10	214	196	
20	168	186	
30	167	134	
60	164	186	
90	158	140	
120	151		
180	86		
240			

Experimental Conditions

Molar ratio of TCS:PMS:Cu =1:5:5

TCS concentration = 9.0 mg/L

PMS concentration = 48 mg/L

Cu concentration = 10 mg/L

EXPERIMENTAL RESULTS

TREATMENT: TCS + PMS+ Ag	DATE: 12/13/2010
REACTION VOLUME: 100 mL	INITIAL pH: 7
SAMPLE VOLUME: 0.5 mL	DILUTION: 2

TIME (min)	TCS CONCENTRATION (µg/L)		
	1	2	3
0	4500	4500	4500
10	4500	4438	4500
20	4449	4015	4483
30	4453	3728	4440
60	4118	2996	2964
90	3934	2805	2347
120	3447	2682	2181
180	3133	2497	2067
240	2935	2464	1911

Experimental Conditions

Molar ratio of TCS:PMS:Ag =1:5:5

TCS concentration = 9.0 mg/L

PMS concentration = 48 mg/L

Ag concentration = 34 mg/L

EXPERIMENTAL RESULTS

TREATMENT: TCS + PMS+ Co DATE: 7/23-25/2011
REACTION VOLUME: 100 mL
SAMPLE VOLUME: 0.1 mL DILUTION:10

TIME (min)	Co^{2+} CONCENTRATION (µg/L)		
	pH 3	pH 5	pH 7
0	366.0	366.0	366.0
15	325.7	235.0	77.7
30	347.2	209.9	104.2
45	342.1	204.6	117.4
60	350.1	191.4	109.5
75	355.3	199.4	146.5
90	347.4	209.9	133.3
105	360.6	194.4	149.1
120	347.4	202.0	165.0

Experimental Conditions

Molar ratio of TCS:PMS:Co =1:2:2

TCS concentration = 9.0 mg/L

PMS concentration = 19 mg/L

Co concentration = 4 mg/L

EXPERIMENTAL RESULTS

TREATMENT: TCS + PMS+ Co	DATE: 7/23-25/2011
REACTION VOLUME: 100 mL	
SAMPLE VOLUME: 0.5 mL	DILUTION: 2

TIME (min)	TCS CONCENTRATION (μg/L)		
	pH 3	pH 5	pH 7
0	4500	4500	4500
15	3899	294	1181
30	3224	244	1151
45	2714	232	1134
60	2266	224	1101
75	2082	213	1086
90	1729	205	1091
105	1552	199	1072
120	1415	188	1094

Experimental Conditions

Molar ratio of TCS:PMS:Fe =1:2:2

TCS concentration = 9.0 mg/L

PMS concentration = 19 mg/L

Co concentration = 4 mg/L

EXPERIMENTAL RESULTS

TREATMENT: TCS + PMS+ Co DATE: 7/30-31/2011
REACTION VOLUME: 100 mL
SAMPLE VOLUME: 0.5 mL DILUTION: 6

TIME (hr)	NPOC (ppm)		
	pH 3	pH 5	pH 7
0	0.727	0.727	0.727
1	0.611	0.691	0.471
2	0.483	0.591	0.409
3	0.445	0.462	0.348
6	0.422	0.483	0.383
12	0.0.355	0.449	0.335
18	0.394	0.444	0.249
24	0.383	0.452	0.146

Experimental Conditions

Molar ratio of TCS:PMS:Co =1:2:2

TCS concentration = 9.0 mg/L

PMS concentration = 19 mg/L

Co concentration = 4 mg/L

EXPERIMENTAL RESULTS

TREATMENT: TCS + PMS+ Fe DATE: 7/30-31/2011
REACTION VOLUME: 100 mL
SAMPLE VOLUME: 0.5 mL DILUTION: 6

TIME (min)	NPOC (ppm)		
	pH 3	pH 5	pH 7
0	0.727	0.727	0.727
1	0.611	0.594	0.524
2	0.489	0.480	0.471
3	0.372	0.436	0.342
6	0.348	0.366	0.325
12	0.273	0.284	0.241
18	0.261	0.345	0.224
24	0.233	0.317	0.167

Experimental Conditions

Molar ratio of TCS:PMS:Fe =1:10:10

TCS concentration = 9.0 mg/L

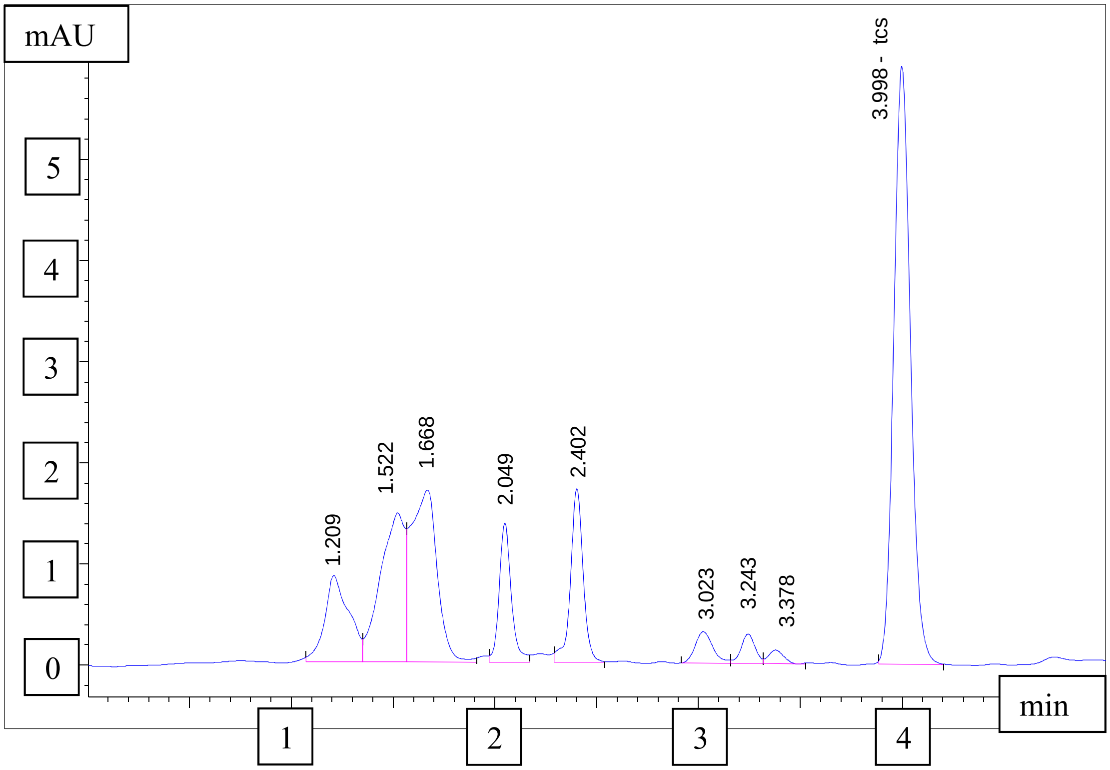
PMS concentration = 96 mg/L

Fe concentration = 17 mg/L

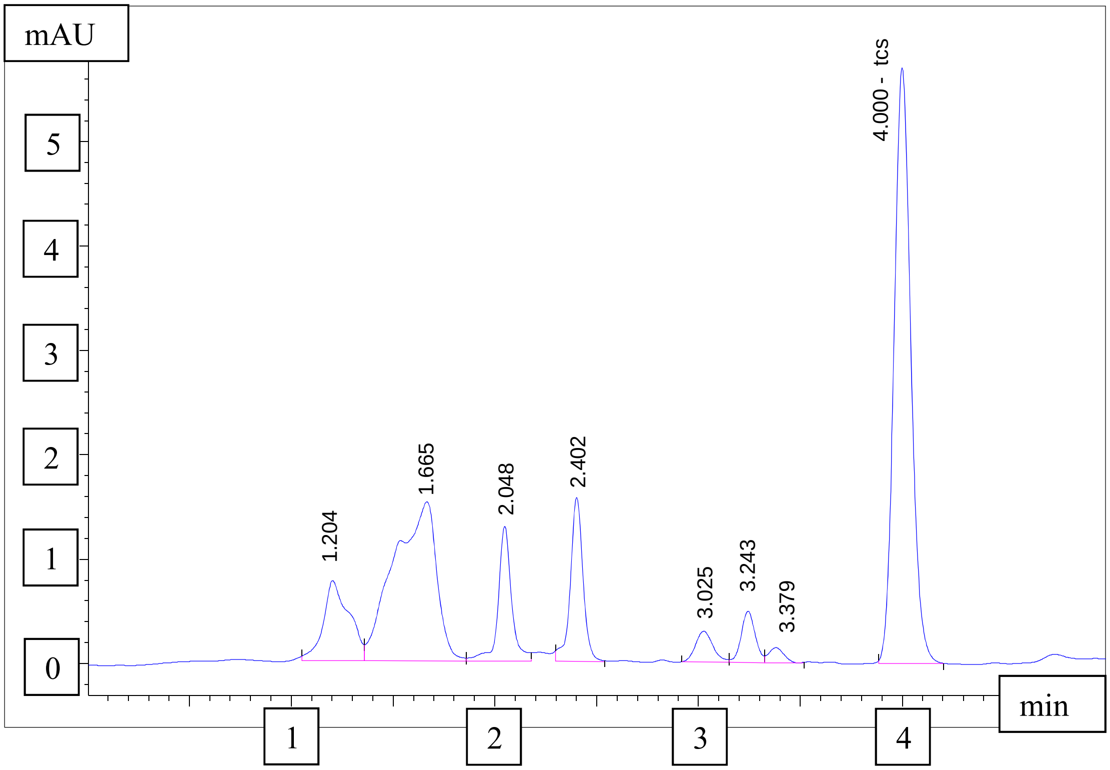
APPENDIX B
SAMPLES OF CHROMATOGRAMS

```
Sample Name: tcs+pms+fe-10-1
=========================================
Acq. Operator   : Prince                        Seq. Line:   22
Injection Date  : 12/15/2010 4:16:27 PM               Inj:    1
Inj Volume: 20.0 µl
Acq. Method     :C:\CHEM32\1\DATA\TCS\PMS-FE PS-AG 1-10 (7) 2010-
                 12-15 14-03-00\TCS CAL 0-10 MG.M
Analysis Method: C:\CHEM32\1\DATA\TCS\PMS-FE PS-AG 1-10 (7)
                  2010-12-15 14-03-00\022-2201.D\ DA.M (TCS CAL
                  0-10 MG.M, From Data File)

         External Standard Report
================================================================
Calib. Data Modified  :      8/18/2010 1:47:33 PM Multiplier: 1.0000
Dilution:                      1.0000
Signal 1: VWD1 A, Wavelength=280 nm
RetTime  Type     Area     Amt/Area    Amount   Grp   Name
 [min]          [mAU*s]
-------|------|----------|----------|----------|--|---------------
  3.998 BB       33.87873   65.98079 2235.34520    tcs
Totals:                              2235.34520
```



```
Sample Name: tcs+pms+fe-20-1
    =========================================
    Acq. Operator   : Prince                          Seq. Line:   19
    Injection Date  : 12/15/2010 3:57:22 PM                 Inj:    1
    Inj Volume: 20.0 µl
    Acq. Method     :C:\CHEM32\1\DATA\TCS\PMS-FE PS-AG 1-10 (7) 2010-
                      12-15 14-03-00\TCS CAL 0-10 MG.M
    Analysis Method: C:\CHEM32\1\DATA\TCS\PMS-FE PS-AG 1-10 (7)
                      2010-12-15 14-03-00\019-1901.D\ DA.M (TCS CAL
                      0-10 MG.M, From Data File)
    =================================================================
             External Standard Report
    ==================================================================
    Calib. Data Modified  :      8/18/2010 1:47:33 PM Multiplier: 1.0000
    Dilution:                     1.0000
    Signal 1: VWD1 A, Wavelength=280 nm
    RetTime  Type     Area     Amt/Area    Amount   Grp   Name
     [min]          [mAU*s]
    -------|------|----------|----------|----------|--|---------------
      4.000 BB       32.73579   65.98079 2159.93359    tcs
    Totals:                              2159.93359
```

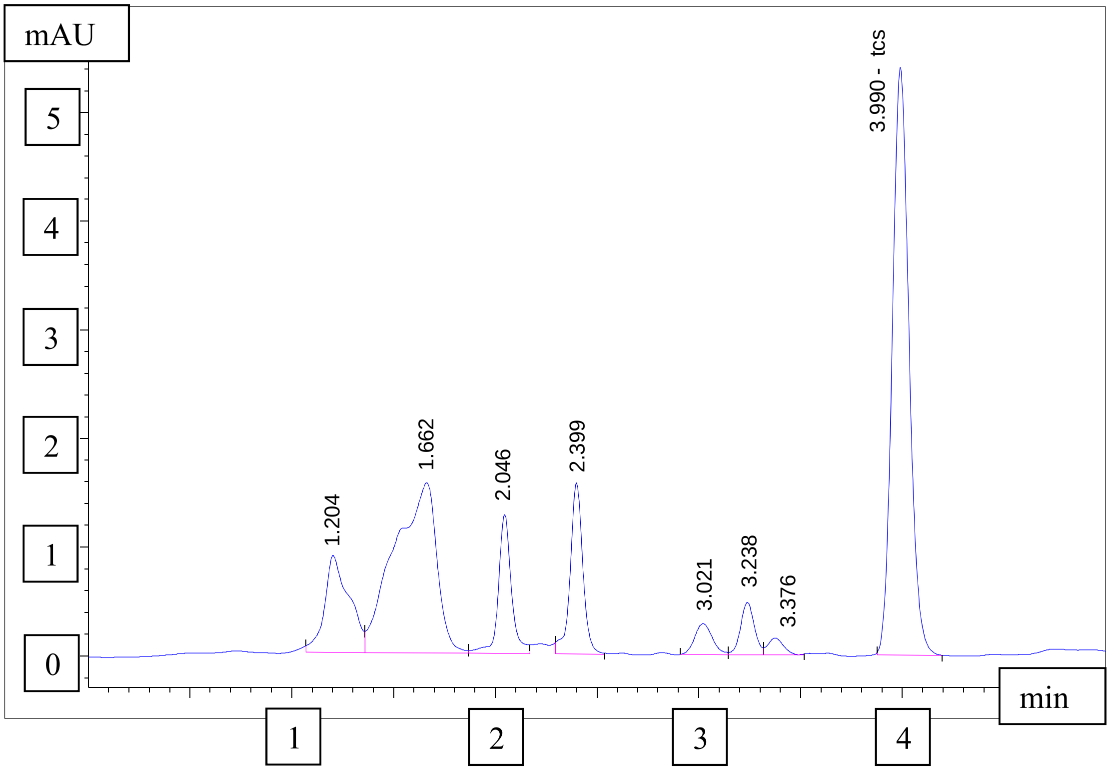


Sample Name: tcs+pms+fe-30-1

```
=========================================
Acq. Operator   : Prince                          Seq. Line:   16
Injection Date  : 12/15/2010 3:38:20 PM                 Inj:    1
Inj Volume: 20.0 µl
Acq. Method     :C:\CHEM32\1\DATA\TCS\PMS-FE PS-AG 1-10 (7) 2010-
                  12-15 14-03-00\TCS CAL 0-10 MG.M
Analysis Method: C:\CHEM32\1\DATA\TCS\PMS-FE PS-AG 1-10 (7)
                  2010-12-15 14-03-00\016-1601.D\ DA.M (TCS CAL
                  0-10 MG.M, From Data File)
=================================================================
         External Standard Report
=================================================================
Calib. Data Modified  :      8/18/2010 1:47:33 PM Multiplier: 1.0000
Dilution:                     1.0000
Signal 1: VWD1 A, Wavelength=280 nm

RetTime  Type     Area     Amt/Area    Amount    Grp   Name
 [min]          [mAU*s]
-------|------|----------|----------|----------|--|---------------
  3.990 BB       30.89598   65.98079 2038.54150    tcs

Totals:                              2038.54150
```



Sample Name: tcs+pms+fe-60-1

```
=========================================
Acq. Operator   : Prince                          Seq. Line:   13
Injection Date  : 12/15/2010 3:19:24 PM                 Inj:    1
Inj Volume: 20.0 µl
Acq. Method     :C:\CHEM32\1\DATA\TCS\PMS-FE PS-AG 1-10 (7) 2010-
                  12-15 14-03-00\TCS CAL 0-10 MG.M
Analysis Method: C:\CHEM32\1\DATA\TCS\PMS-FE PS-AG 1-10 (7)
                  2010-12-15 14-03-00\013-1301.D\ DA.M (TCS CAL
                  0-10 MG.M, From Data File)
=================================================================
         External Standard Report
=================================================================
Calib. Data Modified  :      8/18/2010 1:47:33 PM Multiplier: 1.0000
Dilution:                     1.0000
Signal 1: VWD1 A, Wavelength=280 nm
RetTime  Type     Area     Amt/Area    Amount    Grp   Name
 [min]          [mAU*s]
-------|------|----------|----------|----------|--|---------------
  3.989 BB       27.84811   65.98079 1837.44046    tcs

Totals:                              1837.44046
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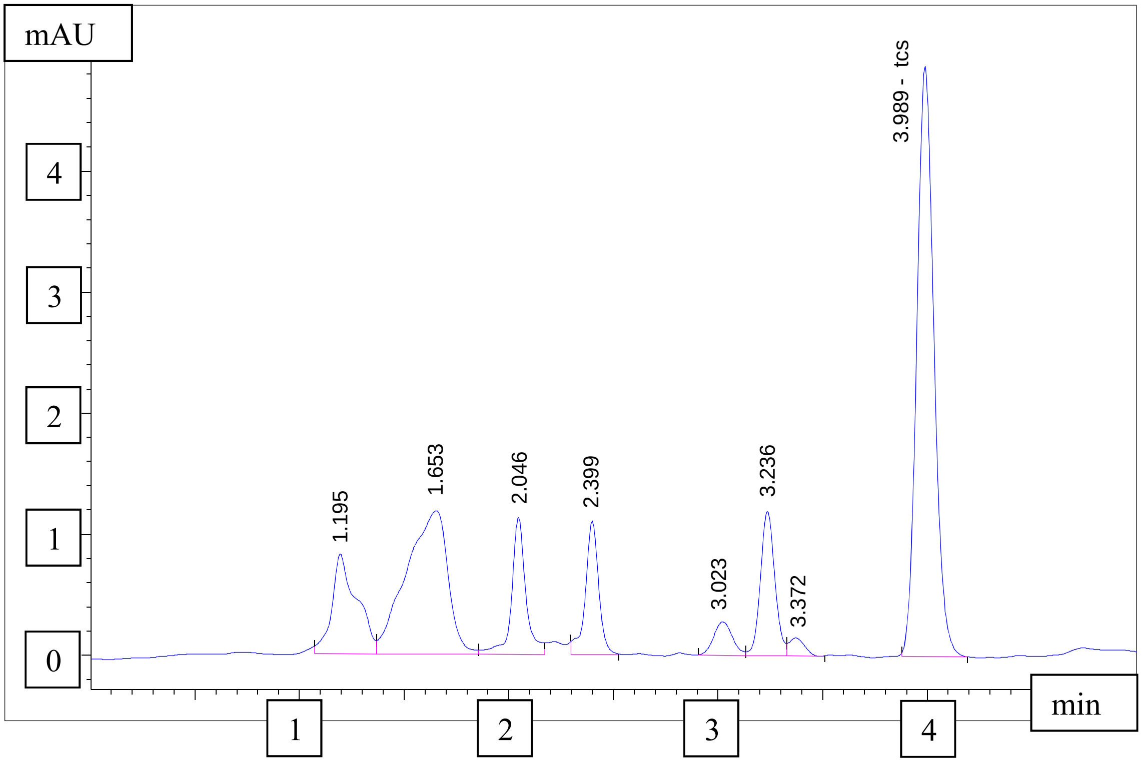
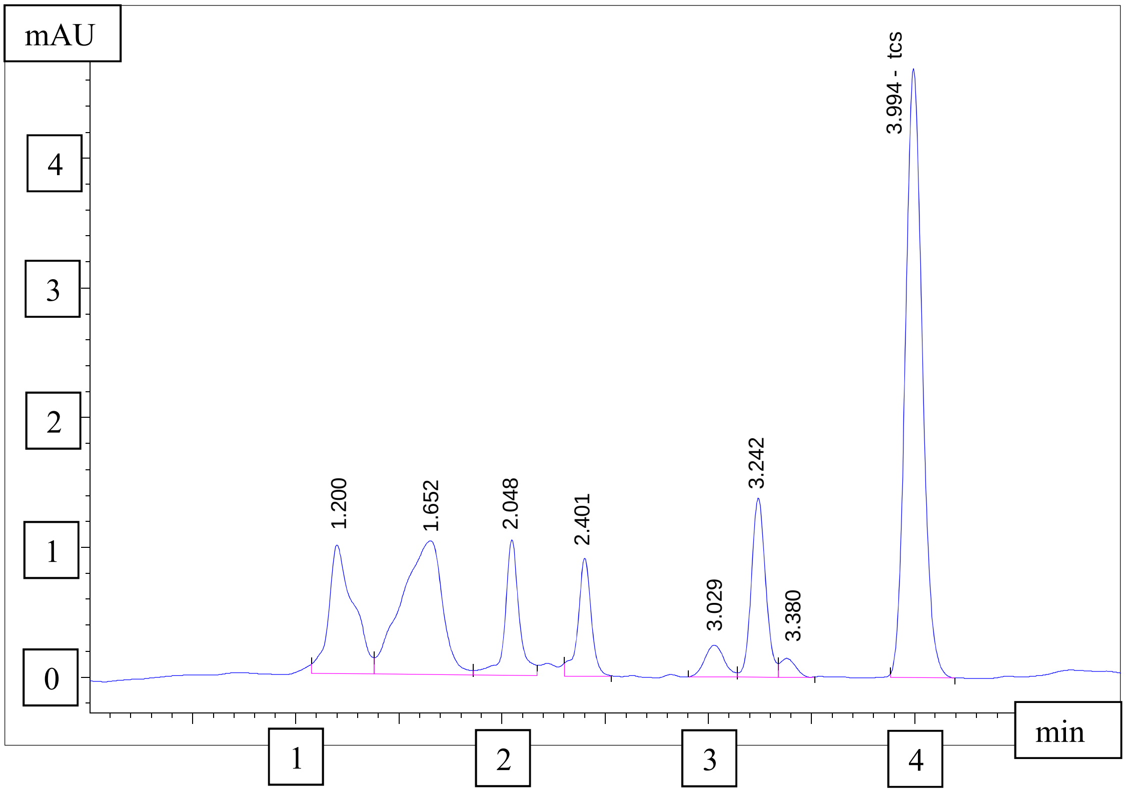


```
Sample Name: tcs+pms+fe-90-1
```

```
=========================================
Acq. Operator   : Prince                          Seq. Line:   10
Injection Date  : 12/15/2010 3:00:19 PM                 Inj:    1
Inj Volume: 20.0 µl
Acq. Method     :C:\CHEM32\1\DATA\TCS\PMS-FE PS-AG 1-10 (7) 2010-
                  12-15 14-03-00\TCS CAL 0-10 MG.M
Analysis Method: C:\CHEM32\1\DATA\TCS\PMS-FE PS-AG 1-10 (7)
                  2010-12-15 14-03-00\010-1001.D\ DA.M (TCS CAL
                  0-10 MG.M, From Data File)
=================================================================
         External Standard Report
=================================================================
Calib. Data Modified  :      8/18/2010 1:47:33 PM Multiplier: 1.0000
Dilution:                     1.0000
Signal 1: VWD1 A, Wavelength=280 nm
RetTime  Type     Area     Amt/Area    Amount    Grp   Name
 [min]          [mAU*s]
-------|------|----------|----------|----------|--|---------------
  3.994 BB       26.82908   65.98079 1770.20396    tcs
Totals:                              1770.20396
```



Sample Name: tcs+pms+fe-120-1

```
=========================================
Acq. Operator   : Prince                         Seq. Line:   7
Injection Date  : 12/15/2010 2:41:17 PM                Inj:   1
Inj Volume: 20.0 µl
Acq. Method     :C:\CHEM32\1\DATA\TCS\PMS-FE PS-AG 1-10 (7) 2010-
                  12-15 14-03-00\TCS CAL 0-10 MG.M
Analysis Method: C:\CHEM32\1\DATA\TCS\PMS-FE PS-AG 1-10 (7)
                  2010-12-15 14-03-00\007-0701.D\ DA.M (TCS CAL
                  0-10 MG.M, From Data File)
=================================================================
         External Standard Report
=================================================================
Calib. Data Modified  :      8/18/2010 1:47:33 PM Multiplier: 1.0000
Dilution:                     1.0000
Signal 1: VWD1 A, Wavelength=280 nm
RetTime  Type     Area     Amt/Area    Amount   Grp   Name
 [min]          [mAU*s]
-------|------|----------|----------|----------|--|---------------
  3.993 BB       23.97890   65.98079 1582.14647    tcs

Totals:                              1582.14647
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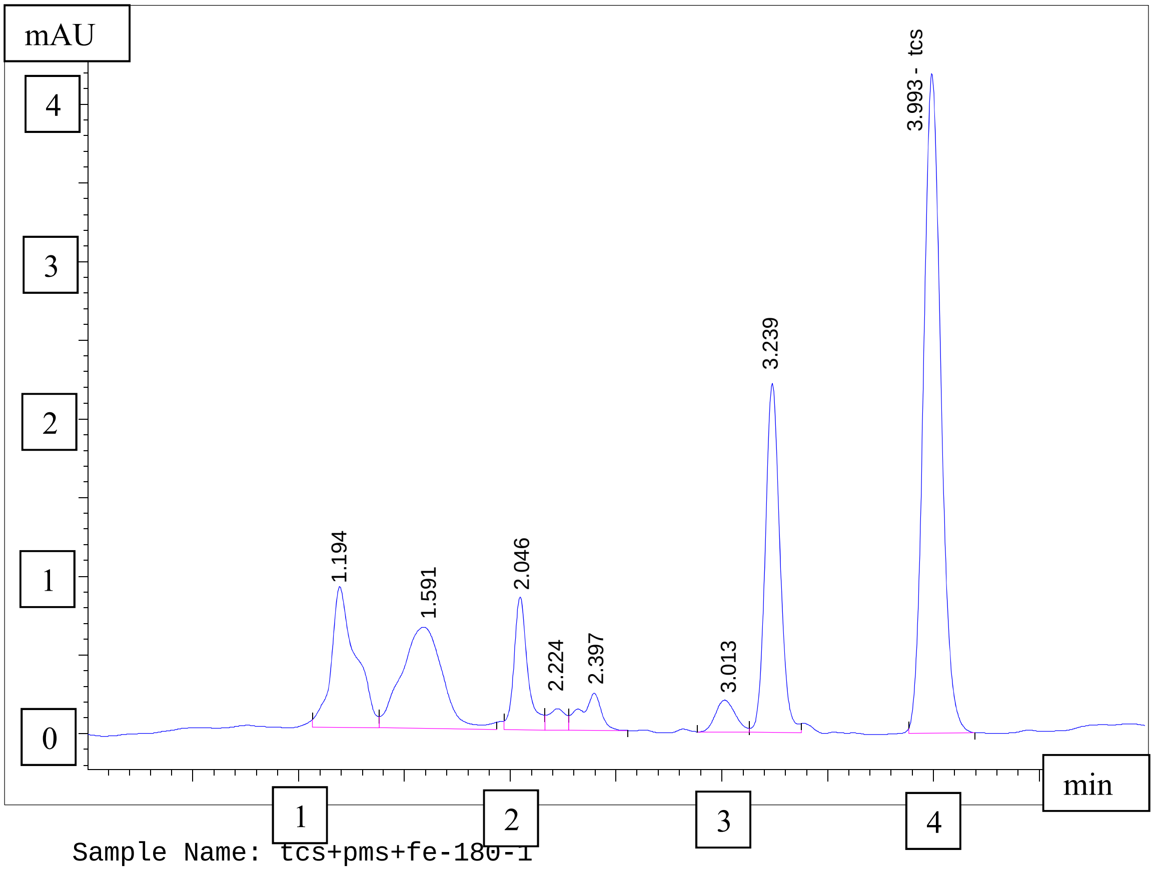

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                 0-10 MG.M, From Data File)
=================================================================
         External Standard Report
=================================================================
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Dilution:                     1.0000
Signal 1: VWD1 A, Wavelength=280 nm
RetTime  Type     Area     Amt/Area    Amount   Grp   Name
 [min]          [mAU*s]
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Totals:                              1562.30736
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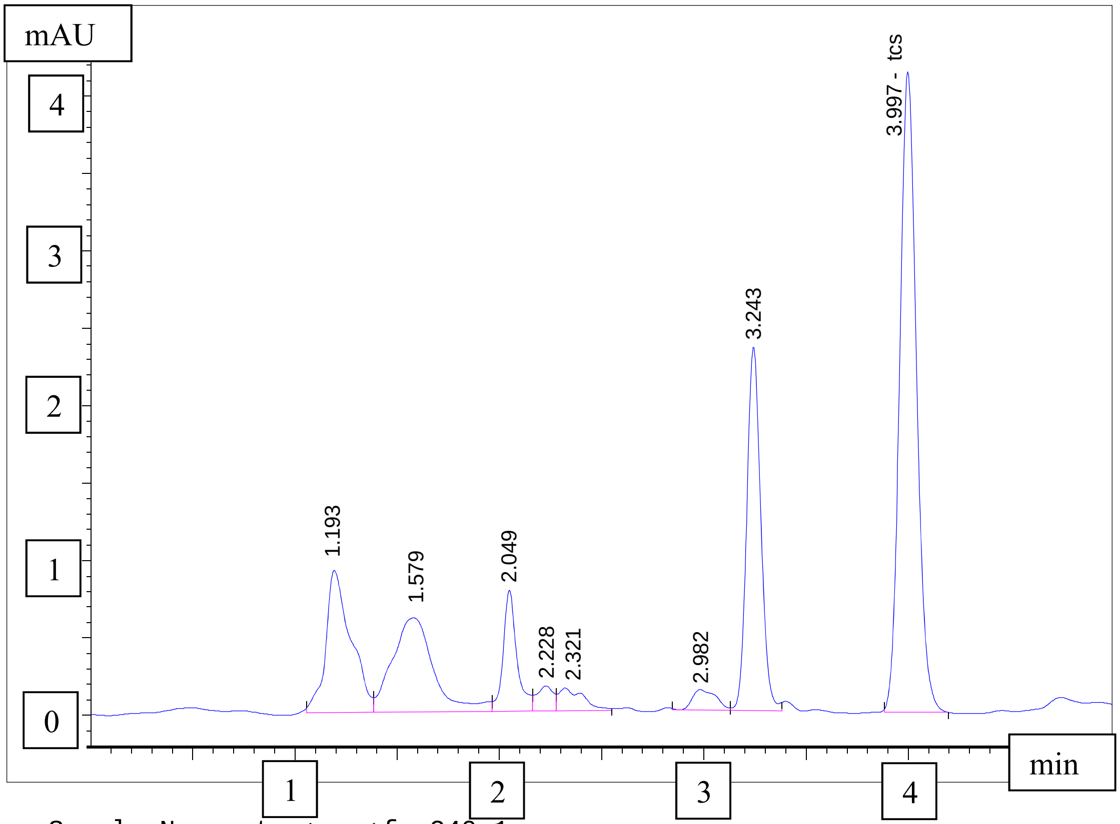

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                  12-15 14-03-00\TCS CAL 0-10 MG.M
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Dilution:                     1.0000
Signal 1: VWD1 A, Wavelength=280 nm
RetTime  Type     Area      Amt/Area    Amount    Grp   Name
 [min]          [mAU*s]
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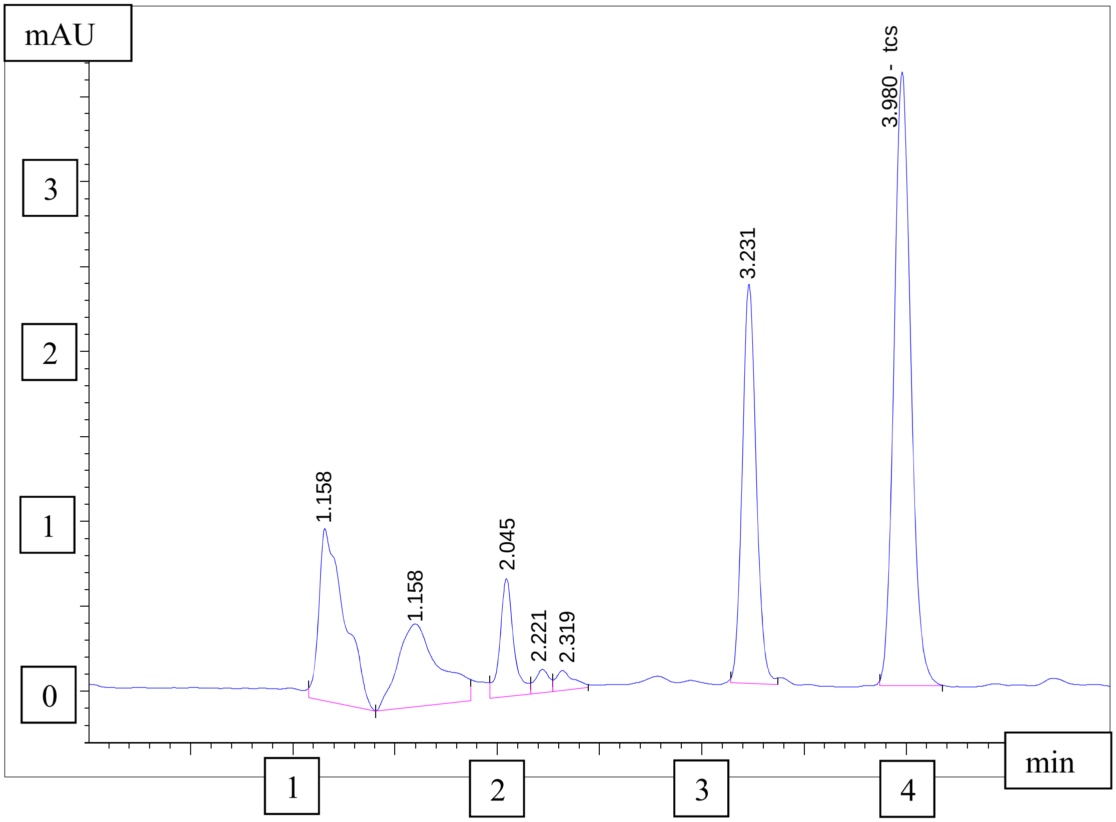

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BIOGRAPHICAL INFORMATION

Prince Albert Nfodzo obtained his BS degree in Civil Engineering at the University of Science and Technology, Ghana, during which he undertook a project on ‘Treatability Studies on Brewery wastewater’. He pursued his academic and professional interests further with a MS degree in Environmental Engineering and Project Management at the University of Leeds, United Kingdom. As part of his MS degree, he investigated the reliability of BIOWIN, a wastewater treatment plant model, for modeling wastewater treatment plants in the United Kingdom. He enrolled as a Ph.D. student in Civil Engineering at the University of Texas at Arlington in January 2008 and investigated the effectiveness of sulfate radicals-based advanced oxidation processes for the decomposition of pharmaceuticals and personal care products. His works have been presented at several prestigious conferences. From his Ph.D. research studies, he has published three research articles in *Environmental Engineering Science*, *Chemical Engineering Journal*, and *Water Science and Technology: Water Supply*. He is also co-author of two book chapters. His hard work earned him several international and national awards. Mr. Nfodzo’s long term professional goal is to secure an academic position in an institution of higher education where he can combine teaching and research in the field of environmental engineering to contribute towards providing a safer environment.