Advanced Oxidation of Tris-2-Chloroethyl Phosphate (TCEP) in Water

Huong Nguyen

B.S., Worcester Polytechnic Institute (WPI), 2010

Huong Nguyen

Professor John Bergendahl

Professor James O'Shaughnessy

A Thesis Submitted in Partial Fulfillment
of the Requirements for the
Degree of Master of Science at
Worcester Polytechnic Institute
2011

Acknowledgements

I would like to thank the Worcester Polytechnic Institute (WPI) Department of Civil and Environmental Engineering for financially supporting this project as well as providing me with financial assistance. I would also like to thank my advisor Professor John Bergendahl for providing with the opportunity to be involved in this project as well as for his expertise and time. Additionally, I would like to thank Professor Jeanine Plummer for her aid in using the Indigo Method. I would also like to thank Donald Pellegrino for his assistance in the laboratory. Lastly, I would like to thank Professor John O'Shaughnessy for being a part of my research committee.

Table of Contents

List of Tables

List of Figures

Abstract

Tris-2-chloroethyl phosphate (TCEP) is a biorecalcitrant flame retardant and plasticizer. It is a toxic and carcinogenic compound that is frequently detected in wastewater effluents and water bodies, including those used for drinking water, around the world. Due to the incomplete removal of TCEP from current wastewater and drinking water treatment facilities, effective treatment processes must be identified that will remove TCEP from water. This research investigated the effectiveness of Fenton's oxidation for removing TCEP from water. In laboratory scale experiments, batch reactions of aqueous TCEP solutions were conducted at different pH conditions and dosages of H_2O_2:Fe^{2+}:TCEP molar ratios. Samples were tested at pH values ranging from 2.5 to 4.5 and H_2O_2:Fe^{2+}:TCEP molar ratios from 5.0:0.5:1 to 200:5.0:1. TCEP concentrations were quantified by solid phase micro-extraction (SPME) followed by gas chromatography (GC). Complete removal of TCEP was achieved at equilibrium conditions with a molar ratio dose of 150:5:1 H_2O_2:Fe^{2+}:TCEP. The kinetics of TCEP removal were also investigated. Pseudo-first order rate constants for TCEP removal were obtained.

The effectiveness of ozonation was also investigated in this research. Batch reactions of aqueous TCEP at different doses of ozone were conducted at pH 7.0 ± 0.1. Ozonation was found to have no effect on the degradation of TCEP.

Chapter 1: Introduction

Organophosphorus compounds (OPs) consist predominantly of arylated and alkylated phosphates that are used as pesticides, plasticizers, flame retardants, antifoaming agents in hydraulic fluids, and extraction solvents [1,2]. Most of these compounds are produced in high quantities, on the order of ten thousand tons per annum [3]. Similar to many additives, OPs are usually mixed with and not chemically bonded to the host materials; therefore, they can be released into the surrounding environment [4]. In fact, they have been detected in several matrices including air [3, 2], sludge from wastewater treatment plants [5], and water samples [1, 6 - 9]. Detection of OPs in water is a particular concern due to the high mobility of the most polar species (i.e., chlorinated flame retardants) [4]. These high mobility polar species can pass through conventional wastewater treatment plants (WWTPs) and water treatment plants without significant removal. The presence of OPs in the aquatic environment may be a concern due to the potential human health and ecosystem effects, which are unknown at this time. Some of these compounds could be neurotoxic, e.g., tri-phenyl-phosphate (TPP) and tri-n-butyl-phosphates (TnBP), while others like tris-(1,3-dichloroisopropyl)-phosphate (TDCP) and tris-(2-chloroethyl)-phosphate (TCEP) are considered carcinogenic [11 - 14].

TCEP is a flame retardant and plasticizer used predominantly in rigid polyurethane foam. This flame retardant is one of the most frequently detected compounds in wastewater effluents and water bodies, including those used for drinking water, in the U.S., Europe, Canada, and Asia [7, 9, 11, 15 - 18]. TCEP does not meet the European Union (EU) PBT criteria (Persistence, Bioaccumulation, and Toxicity) as it is not bioaccumulative. According to the 2009 EU Risk Assessment Report [13], there is no need for further studies or reduction measures of TCEP in regards to the environment and human health. In spite of this risk assessment, TCEP is recognized to be carcinogenic, highly toxic, and persistent in the environment. Studies on rats indicate that this compound caused kidney and liver cancers as well as damage to testes and impairment to the reproductive system [11,19]. It has also been shown that TCEP is genotoxic, neurotoxic, and possibly mutagenic [8, 12]. In addition to being a health hazard, TCEP is a biorecalcitrant compound that is extremely resistant to degradation in conventional biological treatment processes [8, 14, 17]. Hence, TCEP has been found in WWTP effluents and finished drinking water at concentrations of up to 557 ng/L [8] and 99 ng/L [18], respectively.

Due to the incomplete removal of TCEP from current wastewater and drinking water treatment processes, assessment of alternative water treatment technologies have been conducted. Using adsorptive processes (metal salt coagulation, lime softening, powdered activated carbon) and oxidative processes (chlorine and ozone) in three different drinking water supplies, Westerhoff *et al.* [20] found that only powdered activated carbon was able to remove > 20 % of TCEP. Removal of TCEP using chlorine and ozone oxidation were < 20% and < 5% effective, respectively. No removal of TCEP was achieved with metal salt coagulation and lime softening. Using different nanofiltration membranes under different feed water conditions, Lee *et al*. [21] found that > 90% of TCEP was removed with membranes regardless of feed water conditions.

While nanofiltration membranes [21] has proven to effectively remove TCEP from water, advanced oxidation processes (AOPs) are treatment processes that can completely destroy the contaminant instead of transferring it to another phase. AOPs aim to mineralize organic contaminants by converting the organic contaminants to carbon dioxide and water by reaction with hydroxyl radicals (HO•). Hydroxyl radicals are a highly reactive oxidant that is often selected for treatment of waters contaminated with anthropogenic organic compounds.

Fenton's oxidation is an AOP that produces HO• through reaction of hydrogen peroxide (H_2O_2) with ferrous iron (Fe^{2+}) in aqueous solution. Fenton oxidation has been used to degrade a number of contaminants, including biorecalcitrant compounds. Pignatello [22] used Fe(II)/H_2O_2 for the degradation of herbicides 2,4-dichlorophenoxyacetic acid, 2,4,5-trichloroohenoxyacetic acid, and atrazine in aqueous solution. The destruction of phenolic compounds in water using Fe(II)/H_2O_2 was reported by Vella and Munder [23]. Perchloroethylene (PCE) and polychlorinated biphenyls (PCBs) adsorbed on sand were also effectively removed with Fenton reagent [24]. Reactions in these studies were pH sensitive, and acidic conditions were needed for effective treatment.

This research investigated the effectiveness of Fenton's oxidation for treating water contaminated with TCEP. It was hypothesized that production of hydroxyl radicals in Fenton's oxidation removes TCEP from water. Thus, the following objectives were developed:

- determine the influence of different operating parameters (e.g., pH, Fe^{2+} and H_2O_2 dosage)
- determine whether the oxidation process produces by-products
- determine the kinetic rate constants

In addition to Fenton's oxidation, ozone oxidation for removing TCEP was conducted at neutral pH.

Chapter 2: Fenton’s Oxidation

Background

Fenton's oxidation uses Fe^{2+} to initiate and catalyze the decomposition of H_2O_2 which produces HO• (Equation 1). The resulting HO• may then be scavenged by reacting with another Fe^{2+} or react with an organic compound [22]. See Equation 2.

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^{-} + HO^{\bullet} \qquad (1)$$

$$HO^{\bullet} + Fe^{2+} \rightarrow Fe^{3+} + HO^{-} \qquad (2)$$

Newly formed ferric ions catalyze the decomposition of H_2O_2 [25]. The radical chain mechanism for simple aqueous Fe^{3+} systems, involving no complexing ligands other than water, follows reactions shown in Equation 3-7 [22, 25]. As seen in Equation 1 and 7, H_2O_2 can act as an HO• initiator or a scavenger in Fenton's oxidation [25]. Table 1 summarizes reactions that occur in Fenton's oxidation.

$$Fe^{3+} + H_2O_2 \leftrightarrow Fe\text{–}OOH^{2^+} + H^{+} \qquad (3)$$

$$Fe\text{–}OOH^{2^+} \rightarrow HO_2^{\bullet} + Fe^{2+} \qquad (4)$$

$$Fe^{2+} + HO_2^{\bullet} \rightarrow Fe^{3+} + HO_2^{-} \qquad (5)$$

$$Fe^{3+} + HO_2^{\bullet} \rightarrow Fe^{2+} + O_2 + H^{+} \qquad (6)$$

$$HO^{\bullet} + H_2O_2 \rightarrow H_2O + HO_2^{\bullet} \qquad (7)$$

Accounting for the dissociation of water reaction, Walling [26] simplified the reaction in Equation 1 to the following:

$$2Fe^{2+} + H_2O_2 + 2H^{+} \rightarrow 2Fe^{3+} + 2H_2O + HO^{\bullet} \qquad (8)$$

Equation 8 suggests that the presence of H^+ promotes the decomposition of H_2O_2, indicating that an acidic environment is needed to maximize production of HO•. Low pH also helps to keep ferrous and ferric iron in solution. Fenton's oxidation produces HO•, hydroperoxyl radicals, and organoradicals, however, HO• is the strongest oxidant in this process. Possessing an oxidation potential of 2.8 V, HO• reacts rapidly and non-selectively with most organic compounds (RH) by H-abstraction and addition to C-C unsaturated bonds [22, 25]. Abstraction of protons produces organic radicals (R•) that are highly reactive and can be further oxidized. See Equation 9.

$$RH + HO^{\bullet} \rightarrow H_2O + R^{\bullet} \rightarrow Further\ Oxidation \qquad (9)$$

Table 1: Summary of Fenton reaction [35]

Reaction		Constant k
$Fe^{2+} + H_2O_2 \rightarrow HO^\bullet + HO^- + Fe^{3+}$	(1)	$k_1 = 55 - 76\ M^{-1}\ s^{-1}$
$Fe^{3+} + H_2O_2 \rightarrow Fe - OOH^{2+} + H^+$	(2a)	$k_{2a} = 3.1 \times 10^7\ M^{-1}\ s^{-1}$
$Fe - OOH^{2+} + H_2O_2 \rightarrow + Fe(OH)(HO_2)^+$	(2b)	$k_{2b} = 32.0 \times 10^6\ M^{-1}\ s^{-1}$
$Fe - OOH^{2+} \rightarrow Fe^+ + HO_2^\bullet$	(3a)	$k_{3a} = 2.3 \times 10^{-3}\ s^{-1}$
$Fe(OH)(HO_2)^+ \rightarrow Fe^{2+} + HO_2^\bullet + OH^-$	(3b)	$k_{3b} = 2.3 \times 10^{-3}\ s^{-1}$
$HO^\bullet + Fe^{2+} \rightarrow Fe^{3+} + HO^-$	(4)	$k_4 = 4.3 \times 10^8\ M^{-1}\ s^{-1}$
$2HO^\bullet \rightarrow H_2O_2$	(5)	$k_5 = 5.3 \times 10^9\ M^{-1}\ s^{-1}$
$HO^\bullet + H_2O_2 \rightarrow H_2O_2 + HO_2^\bullet$	(6)	$k_6 = 3.3 \times 10^7\ M^{-1}\ s^{-1}$
$2HO_2^\bullet \rightarrow H_2O_2 + O_2$	(7)	$k_7 = 8.5 \times 10^5\ M^{-1}\ s^{-1}$
$RH + HO^\bullet \rightarrow H_2O + R^\bullet$	(8)	$k_8 = 1.3 \times 10^6\ M^{-1}\ s^{-1}$
$R^\bullet + H_2O_2 \rightarrow ROH + HO^\bullet$	(9)	$k_9 = 1.2 \times 10^6\ M^{-1}\ s^{-1}$
$R^\bullet + Fe^{3+} \rightarrow Fe^{2+} + products$	(10)	
$R^\bullet + Fe^{2+} \rightarrow Fe^{3+} + products$	(11)	
$R^\bullet + O_2 \rightarrow ROO^\bullet$	(12)	
$ROO^\bullet + Fe^{3+} \rightarrow Fe^{2+} + products$	(13)	
$ROO^\bullet + +Fe^{2+} \rightarrow Fe^{3+} + products$	(14)	

Materials and Methods

Chemicals

TCEP with 97% purity was purchased from Sigma-Aldrich (St. Louis, MO). All other chemicals used were of reagent grade and were purchased from Fisher Scientific (Pittsburg, PA).

Experiments

Fenton oxidation reaction. Equilibrium Fenton's oxidation experiments were conducted at room temperature (25 ± 1◦C) in 250 mL foil wrapped glass beakers with 1 in long Teflon^{TM}-coated stir barsand magnetic stir plates providing mixing. After dissolving $FeSO_4$ in purified water and adding TCEP, the solution pH was adjusted to pH 3.6 ± 0.1 using hydrochloric acid (HCl). Predetermined H_2O_2 doses were added to each beaker. Further experiments at varied pHs were conducted similarly, except in 40 mL glass vials. All equilibrium experiments were allowed to proceed for 24 h, found to be sufficient for equilibration to occur. Samples for kinetic runs were quenched by adding methanol (HPLC grade, Fisher Scientific) to a concentration ~ 3000 mg/L [27]. Kinetics experiments were conducted in 40 mL glass vials using 1 in long Teflon^{TM}-coated stir bars. Mixing was done at low speed to minimize vortex formation.

All water used was purified with an E-pure water system (ROpure ST/E-pure system, Barnstead/Thermolyne, Dubuque, IA). Glassware used was soaked in water and detergent for at least 24 h, then rinsed five times with water, and twice with E-pure water.

Gas Chromatography Analysis. Gas chromatography (GC) analyses were done on a 6890 Series GC, Agilent Technologies using a RTX-5MS silica column (30 m x 0.32 mm I.D., d_f = 0.25µm). A 65 µm poly(dimethylsiloxane)-divinylbenzene (PDMS-DVB) fiber was selected for solid phase micro-extraction (SPME) [2]. The temperature program was adopted from Ollers et al. [28]. The temperature was programmed as follows: 1 min at 90°C, first ramp 15°C min^{-1} to 150°C, 15 min at 150°C, second ramp 5 C min^{-1} to 200°C, 5 min at 200°C, third ramp 15° C min^{-1} to 290°C, 6 min at 290°C.

Prior to GC analyses, all samples were adjusted to pH 7.0 ± 0.1 using (sodium hydroxide) NaOH and HCl and subjected to centrifugation for 20 min at 2900 rpm for solid-liquid separation. Eighteen microliters (18 µL) of sample were transferred for analysis. Spike samples and controls (without Fe and/or H_2O_2) were included in every run. The limit of detection was 400 µg/L and retention time of TCEP was determined to be around 42 minutes. See Figure 1 for a representative chromatograph.

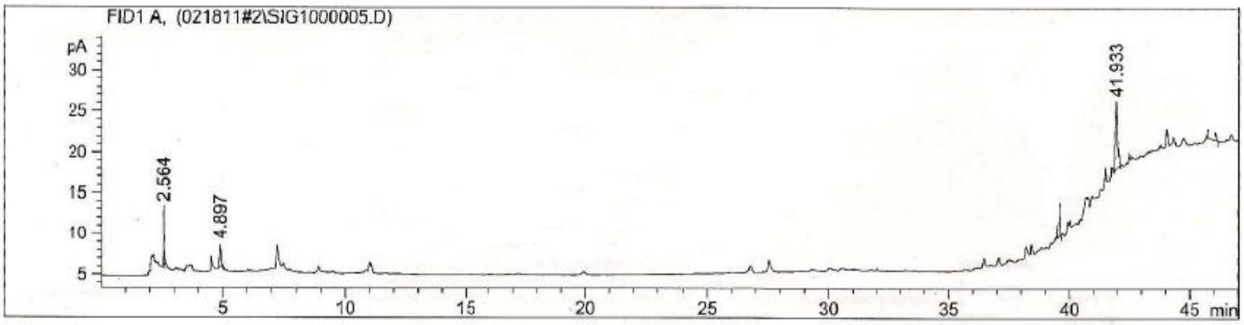


Figure 1: Chromatograph showing TCEP peak at ≈ 42 minutes

Following GC analysis, the unknown concentration of TCEP that remains after Fenton's oxidation was determined using a standard curve. A standard curve is a plot of known TCEP concentration as shown in Figure 2.

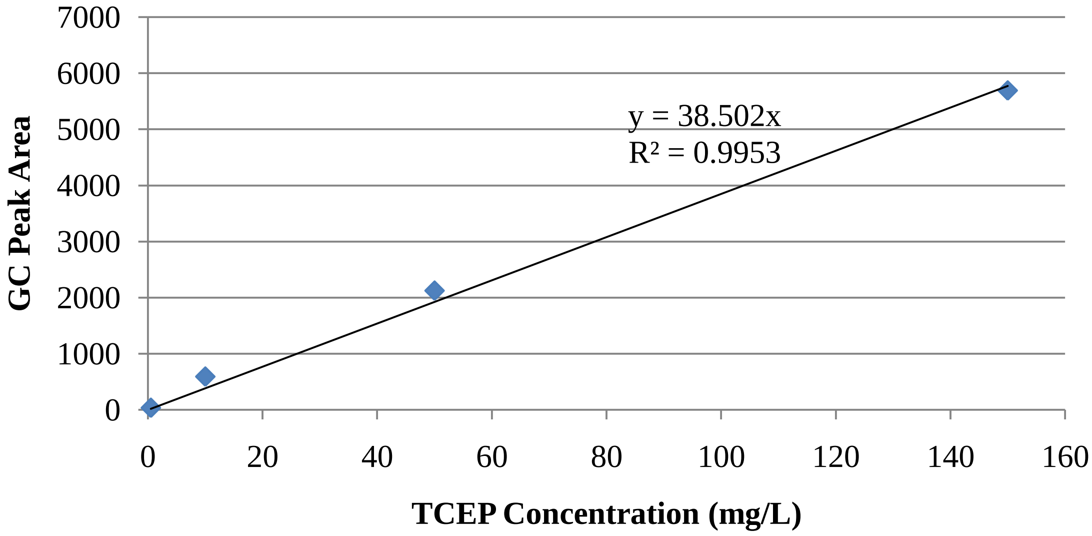


Figure 2: Standard curve of TCEP

Total Organic Carbon Analysis. Total organic carbon (TOC) was measured with a Shimadzu total organic carbon analyzer (Model 5000A, Shimadzu Corp., Japan). Twenty milliliter samples (20 mL) were collected for analysis. Epure water blanks and a spike sample were included in every run. Samples were placed in 40 mL parafilm wrapped vials with Teflon lined screw caps, and acidified with HCL to pH < 1 [27]. Samples were analyzed within two weeks after refrigeration.

Results and Discussion

Equilibrium Experiments

Experiments to determine the effect of varying doses of H_2O_2 and Fe^{2+} on the reduction in TCEP concentrations with 24 hours reaction time were conducted and results are illustrated in Figure 3.

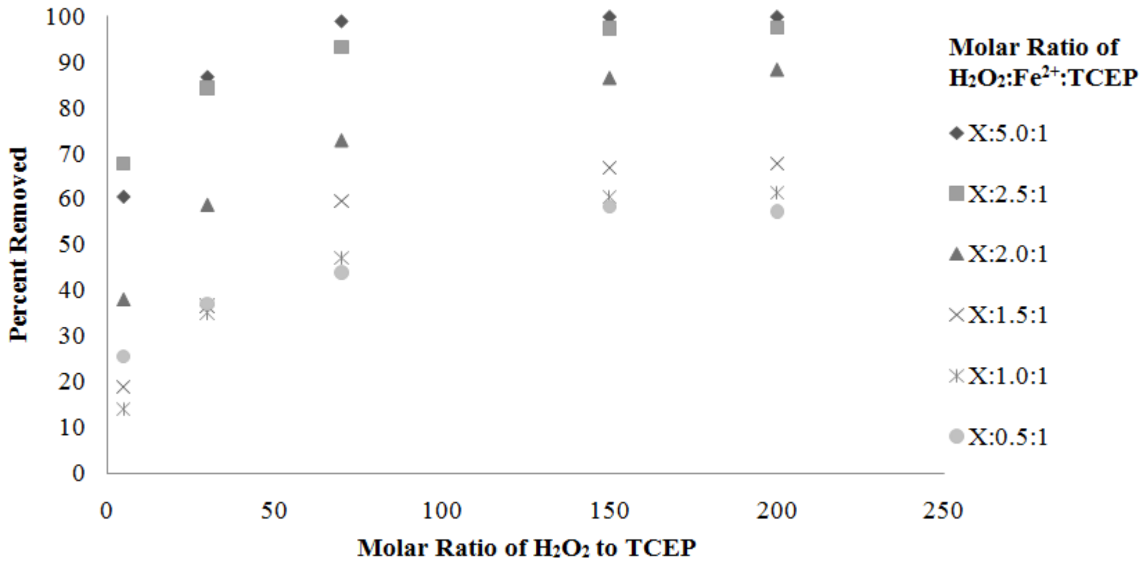


Figure 3: Effect of H_2O_2 and Fe^{2+} dose on Fenton's oxidation of TCEP in 24 h. Conditions: initial TCEP = 100 mg/L, initial pH 3.6 ± 0.1, and final pH 7.0 ± 0.1.

The lowest reduction in TCEP concentration occurred at Fe^{2+}:TCEP: molar ratio of 1.0:1 and 0.5:1. Despite a high H_2O_2:TCEPof 200:1, the Fe^{2+}:TCEP molar ratio of 1.0:1 and 0.5:1 achieved up to about 60% in TCEP reduction. The greatest reduction in TCEP concentration occurred at H_2O_2:Fe^{2+}:TCEP molar ratio of 150:5.0:1 with complete removal. However, the most efficient application of reactants occurred with doses between molar ratios 75:2.5:1 and 150:2.5:1. The reduction in TCEP concentration at these doses is approximately 95% but required half the Fe^{2+}concentration compared to the 150:5.0:1 molar ratio that resulted in100% removal. TCEP removal rates between doses of 75:2.5:1 and 150:2.5:1 is in the same range as those found by Watts and Linden [29]. Using photooxidation with $UV_{254\ nm}$ fluence of 6,000 mJ/cm^2 in a 50 mg/L H_2O_2 solution, they observed that greater than 95% of initial TCEP (5 mg/L) was removed from lake water.

The effect of Fe^{2+} on reduction of TCEP concentration was analyzed at 150:1 H_2O_2:TCEP molar ratio is shown in Figure 4.

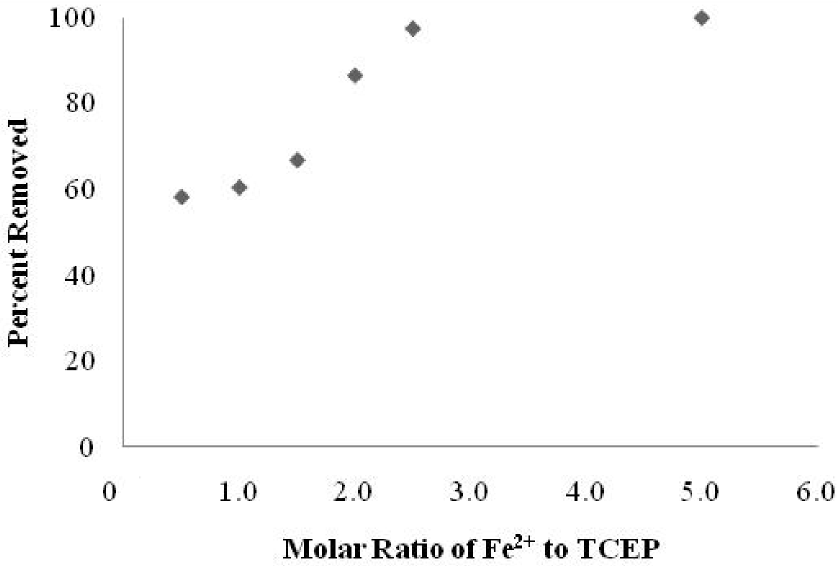


Figure 4: Effect of Fe^{2+} on Fenton's oxidation of TCEP in 24 h at 150:1 H_2O_2:TCEP molar ratio.

The trend shown in Figure 4 indicates that TCEP:Fe^{2+} molar ratios of 1.0:1 and 0.5:1 have approximately the same reduction in concentration. This pattern was the same for molar ratios of 5.0:1 and 2.5:1. The plot shows a gradual increase in reduction of TCEP concentration with increasing Fe^{2+} concentration, which illustrates that production of HO• increases with increasing Fe^{2+} concentration.

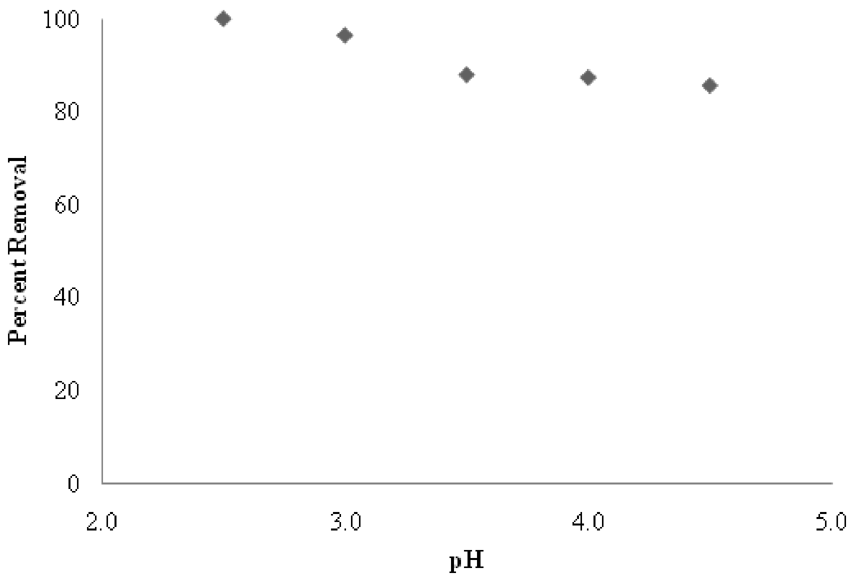


Figure 5: Effect of pH on Fenton's oxidation of TCEP in 24 h. Conditions: Initial TCEP = 100 mg/L and H_2O_2:Fe^{2+}:TCEP (molar ratio) = 75:2.5:1.

To determine the optimum solution pH, the reduction in TCEP concentration was determined at solution pHs between 2.5 and 4.5. The results are shown in Figure 5. The greatest reduction in TCEP concentration (100%) occurred at a solution pH of 2.5. At pH 3.0, TCEP concentration was reduced by 96%. For solution pH between 3.5 and 4.5, TCEP concentration was reduced by approximately 86%. Similar to previous studies [31, 32], the results show that optimum pH for Fenton oxidation is around pH 3.0.

Figure 5 indicates that the efficiency of Fenton's oxidation decreases with increasing pH. This decrease in efficiency is likely due to the oxidation of Fe^{2+} to Fe^{3+} and subsequent precipitation of Fe^{3+} as oxyhydroxide complexes, which decreases the iron concentration in solution [31]. This results in a decrease in HO• production.

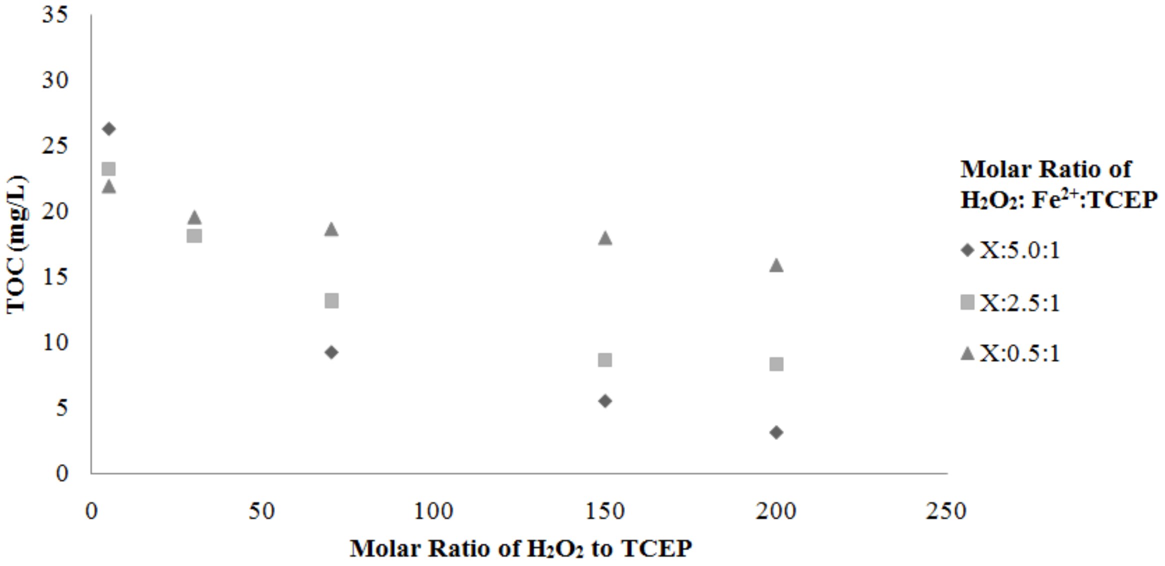


Figure 6: Remaining TOC after 24 h Fenton's oxidation of TCEP. Conditions: Initial TCEP = 100 mg/L and pH 3.6 ± 0.1.

As illustrated in Figure 6, the greatest TOC reduction (88%) occurred with a dose of 200:5.0:1 H_2O_2:Fe^{2+}:TCEP molar ratio. Compared to molar ratios of 200:0.5:1 and 200:2.5:1, the molar ratio of 200:5.0:1 reduced TOC by an average of more than 42%. The reduction of TOC indicated the mineralization of TCEP and its byproducts. However, a fraction of TCEP intermediates still retains its organic form as TOC did not reach zero under the conditions tested.

Kinetics Experiments

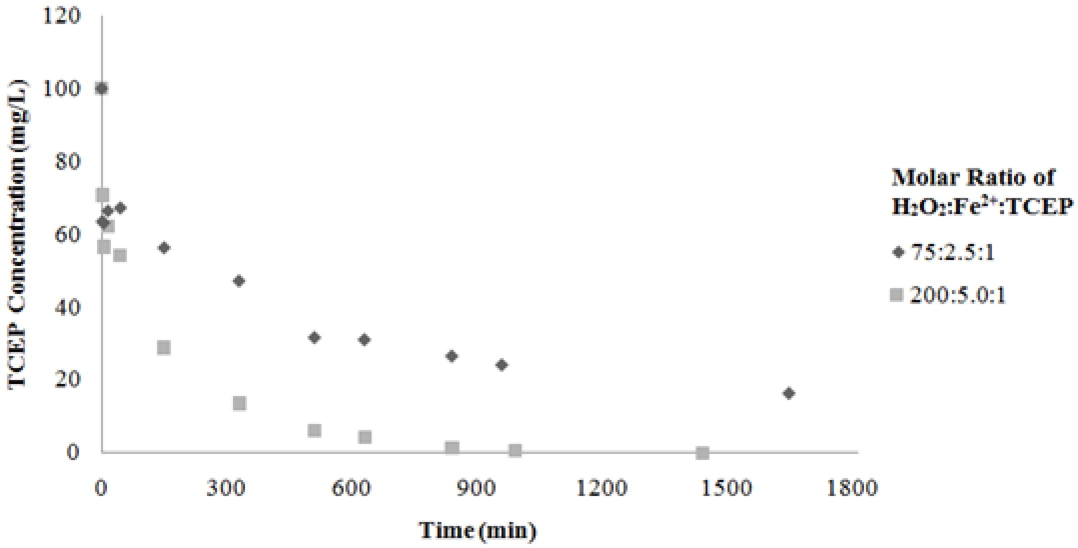


Figure 7: Remaining TOC after 24 h Fenton's oxidation of TCEP. Conditions: Initial TCEP = 100 mg/L and pH 3.6 ± 0.1.

The degradation of TCEP at H_2O_2:Fe^{2+}:TCEP molar ratios of 75:2.5:1 and 200:5.0:1 over time is shown in Figure 7. The degradation of TCEP with these reactant doses occurred most rapidly within the first 300 min, with oxidation continuing through 24 h. The dose with molar ratio of 200:5.0:1 achieved 100% removal in 24 h. Molar ratio 75:2.5:1 reduced TCEP concentration by 84% in approximately 24 h.

The results in Figure 7 show that TCEP degradation rate is somewhat slower when compared to other Fenton oxidation studies. For example, Arnold *et al.*[31] reported the complete removal of atrazine (initially 30 mg/L) in less than 30 s using a 1:1 molar ratio of H_2O_2:Fe^{2+}. Bergendahl and Thies [27] were able to degrade over 99% of MTBE (initially 1000 µg/L) within 10 min using 250 mg/L Fe^0 and 220:1 molar ratio H_2O_2:MTBE. And Vella and Munder [23] removed about 90% of phenol (1 mg/L) using a 17:1 molar ratio of H_2O_2:phenol and a 10:1 molar ratio of $H_2O_2:Fe^{2+}$ in 15 min. However, in this work up to 24 h was needed for effective treatment.

A possible explanation to the slow TCEP degradation rate is due to the inhibition of HO• formation, which can be affected by pH, iron oxidation state, and iron chelation [33]. In the case of TCEP, the phosphate moieties could be the inhibitor as phosphate has been reported to inhibit HO• production [23,34 , 35]. Siedlecka *et al*. [35] studied the effect of inorganic anions (i.e. Cl^-, ClO_4^-, SO_4^-, and $H_2PO_4^-$) on the effectiveness of Fenton's oxidation treating contaminated MTBE water. They found that $H_2PO_4^-$ played a major role in the suppression of MTBE degradation. The main mechanism for this retardation could be due to complex reactions with Fe^{+2} and Fe^{+3} ions. However, formation of inorganic radicals and scavenging of less reactive radicals could also be contributing factor. See Table 2 for complex reactions with Fe^{+2} and Fe^{+3} ions.

Table 2: Complex reactions with Fe^{+2} and Fe^{+3} [35]

Reaction (k)		Log
$Fe^{2+} + Cl^{-} \rightarrow FeCl^{+}$	(1)	0.45
$Fe^{3+} + Cl^{-} \rightarrow FeCl^{2+}$	(2)	0.82
$Fe^{3+} + 2Cl^{-} \rightarrow FeCl_2^{+}$	(3)	1.01
$Fe^{2+} + SO_4^{2} \rightarrow FeSO_4$	(4)	1.36
$Fe^{3+} + SO_4^{2} \rightarrow FeSO_4^{+}$	(5)	2.59
$Fe^{3+} + 2SO_4^{2} \rightarrow Fe(SO_4)_2^{-}$	(6)	3.65
$Fe^{2+} + H_2PO_4^{-} \rightarrow FeH_2PO_4^{+}$	(7)	2.75
$Fe^{3+} + H_2PO_4^{-} \rightarrow FeH_2PO_4^{2+}$	(8)	5.84
$Fe^{3+} + H_2O_2 \rightarrow Fe(HO_2)^{2+} + H^{+}$	(9)	- 2.50
$Fe(HO_2)^{2+} + H_2O_2 \rightarrow Fe(OH)(HO_2)^{+} + H^{+}$	(10)	-3.70

Another postulated explanation is the recalcitrant nature of TCEP intermediates. Watts and Linden [29] found that if initial TCEP in solution is >5%, only 1/5 of the initial DOC is bio-available. Thus, a significant amount of TCEP intermediates retains the recalcitrant properties of TCEP. Future research should focus on identifying TCEP intermediates and their properties.

Reaction Kinetics

The reaction describing TCEP degradation with advanced oxidation is:

$$TCEP + OH\bullet \rightarrow products \qquad (10)$$

Hence, the rate equation for TCEP degradation is written as:

$$\frac{dC_{TCEP}}{dt} = -k_{TCEP} \times C_{TCEP} \times C_{OH\bullet} \qquad (11)$$

Where C_{TCEP} is the concentration of TCEP, and $C_{OH\bullet}$ is the concentration of HO•.

To simplify the kinetic analysis of advance oxidation, HO• concentration is often assumed to be at steady state [27]. Using this assumption, Equation 11 is simplified to a pseudo-first-order rate equation and integrated to:

$$\ln\left(\frac{C_{TCEP}}{C_{TCEP,0}}\right) = -k_{TCEP}t \qquad (12)$$

Employing linear regression to the data to obtain the degradation rate constant for Equation 12, k_{TCEP} was found to be 5.2×10^{-3} min^{-1}. The kinetic model using the k_{TCEP} determined from linear regression is plotted in Figure 8 with the experimental TCEP data for the 200:5.0:1 reactant dose.

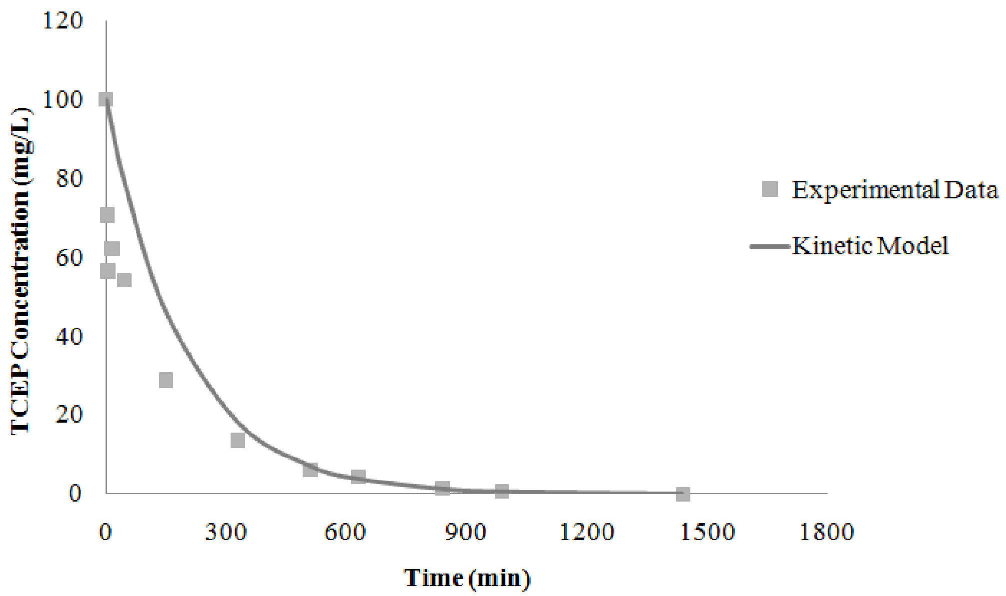


Figure 8: Measured and kinetic model values of TCEP concentration. Conditions: initial TCEP = 100 mg/L, H_2O_2:Fe^{2+}:TCEP molar ratio of 200:5.0:1, and pH 3.6 ± 0.1.

The rate constant found in this study is somewhat lower than those found when using other AOPs. Echigo *et al*. [15] found the pseudo-first-order rate constants for TCEP removal using O_3/UV, O_3/H_2O_2, and UV radiation with and without H_2O_2 to be around 0.1 min^{-1}, 0.1 min^{-1}, 0.92 min^{-1}, and 0.52 min^{-1}, respectively. In addition, for the O_3/UV and O_3/H_2O_2 processes they found that the TCEP degradation rate decreased as initial TCEP concentration increased. Similar to Westerhoff *et al*. [20], they were not able to detect degradation of TCEP with simple ozonation. Note that the rate constants found by Echigo *et al*. [15] were calculated based on the concentration in the initial 5 minutes. This is because after 5 minutes they found that the degradation of organophosphates deviates from first-order kinetics and became slower. Their explanation for this occurrence is the consumption of available HO• by the oxidized products of organophosphates. However, as previously mentioned, phosphate could be inhibiting HO• production in different AOPs.

Chapter 3: Ozone Oxidation

Background

Ozone (O_3) is a strong oxidant with an oxidation potential of 2.07 V. Primarily ozone is used for disinfection and for odor and taste control in drinking water treatment. Ozone is an unstable gas that must be generated on-site through an ozone generator. The chemistry involved in the formation of ozone is shown in Equations 13 and 14 [37, 38].

$$O_2 + energy \rightarrow O + O \quad (13)$$

$$O + O_2 \rightarrow O_3 \quad (14)$$

The energy required to separate the oxygen molecule (O_2) into oxygen atoms (O) is usually supplied by an electric discharge with a peak voltage from 8 to 20 kV, depending on the ozone generator. The ozone generator is fed oxygen or air. Dry, particle-free air, oxygen, or oxygen-enriched air passed through a narrow gap within the ozone generator will produce ozone. The gap has a glass or ceramic dielectric on one side and a stainless steel ground electrode on the other side. High-energy discharge is generated across the gap by an alternating current. This current creates a voltage cycle between the dielectric and electrode. The yield of ozone depends on voltage, frequency, and the type and quality of the feed gas. Once ozone is generated, the gas is passed through a gas absorption device for ozone transfer into aqueous solution [37, 38].

In aqueous solution, ozone is very unstable and is very reactive with a number of constituents in drinking water. Ozone also undergoes a spontaneous decomposition or auto-decomposition in aqueous solution. Auto-decomposition of ozone consists of a complex chain reaction process that involves several free radical species. Decomposition may be initiated by hydroxide ions (e.g., high pH values), natural organic material, ferrous ions, addition of H_2O_2, or irradiation with ultraviolet light. Reactions shown in Equations 15-20 illustrate the auto-decomposition scheme using hydroxide ion as the initiator [38].

$$OH^- + O_3 \rightarrow HO_2 + {O_2}^- \tag{15}$$

$$HO_2 \rightarrow H^+ + {O_2}^- \tag{16}$$

$${O_2}^- + O_3 \rightarrow O_2 + {O_3}^- \tag{17}$$

$${O_3}^- + H^+ \rightarrow HO_3 \tag{18}$$

$$HO_3 \rightarrow O_2 + OH \tag{19}$$

$$OH + O_3 \rightarrow HO_2 + O_2 \tag{20}$$

Materials and Methods

Chemicals

TCEP with 97% purity was purchased from Sigma-Aldrich (St. Louis, MO). All other chemicals used were of reagent grade and were purchased from Fisher Scientific (Pittsburg, PA).

Experiments

All water used was purified with an E-pure water system (ROpure ST/E-pure system, Barnstead/Thermolyne, Dubuque, IA). Glassware used was soaked in water and detergent for at least 24 h, then rinsed five times with water, and twice with E-pure water.

Indigo Method for Measuring Ozone. The concentration of ozone in water was measured by using the Indigo Method. Ozone dosage was measured by transferring diluted ozonated water into 40 mL glass vials. Each vial of diluted ozonated water was combined with 3.8 mL of solution containing trisulfonated indigo [39]. The total volume of ozonated water and trisulfonated indigo solution was 38 mL. Ozonated water decolorizes the indigo dye. Using a 4.5 cm cell, the decolorization of samples was measure at 600 nm by the UV Spectrophotometer (Cary 50 Scan Series,Varian). See Standard Methods [39] for details on the Indigo Method. The concentration of ozone is calculated using the equation below.

$$\frac{mg\ O_3}{L} = \frac{(V_{total})(\Delta\ Absorbance)}{f\ x\ b\ x\ V} \qquad (21)$$

where:

Δ A = difference in absorbance between sample and blank

b = path length of cell, cm

V = volume of ozonated water, mL

f = 0.42

To adjust for dilution, the calculated ozone concentration from Equation 21 was multiplied by the factor below:

$$\frac{mg\ O_3}{L} = \frac{(Calculated\ O_3\ )(Vol.of ozone\ and\ epure)}{Volume\ of\ ozone} \tag{22}$$

Ozone Oxidation. Ozone oxidation experiments were conducted at room temperature (25 ± 1◦C) in 40 mL glass vials. Ozone was generated using an air fed L-25 ozone generator from Ozonology Inc. (Northbrook, IL). The ozone generator was set at an air flow of 2 SCFH, at 24 psi, and with an ozone generation of 95 V. Ozone passed through a glass gas dispersion tube (Model 7197-18, Ace Glass, New Jersey) and into a 500 mL glass cylinder for 1.5 h. Prior to ozonation, water was adjusted to pH 7.0 ± 0.1 using hydrochloric acid (HCl) or sodium hydroxide (NaOH). Ozonated water was immediately transferred into vials with different volume of TCEP water that has been adjusted to pH 7.0 ± 0.1. Ozonated water was transferred quickly and carefully into different vials to minimize the dissipation of ozone. The combined volume of TCEP and ozonated water was 40 mL. Vials were slowly rotated end-over-end 5 times. All ozone oxidation experiments were allowed to proceed for 5 minutes prior to gas chromatography (GC) analysis. See Chapter 2for details of the GC analysis.

Results and Discussion

Ozone oxidation of TCEP does not remove TCEP from water as shown in Table 2. This result is similar to those of Echigo *et al.* [15] and Westerhoff *et al.* [30]. Although the actual TCEP concentration is higher than the theoretical TCEP, the data indicate no TCEP removal. The reason for the discrepancy between the theoretical and actual TCEP concentration is unknown.

Table 3: Ozone oxidation

Volume of TCEP (L)	Volume of Ozonated Water (L)	Theoretical TCEP Concentration (mg/L)	Actual TCEP concentration (mg/L)
0.005	0.035	12.5	20.88
0.01	0.03	25	39.25
0.02	0.02	50	61.63
0.03	0.01	75	87.38
0.035	0.005	87.5	87.36

Chapter 4: Conclusions and Future work

Conclusions

TCEP is a flame retardant and plasticizer. The compound is a toxic and carcinogenic compound that has been frequently detected in wastewater effluents, surface water, and finished drinking water worldwide. Previous work has shown that Fenton's oxidation is an effective method for removing recalcitrant compound from water [22, 23, 24, 27]. The objective of this study was to determine the effectiveness of treating TCEP contaminated water with Fenton's oxidation and ozone oxidation.

Fenton's oxidation was found to be an effective treatment method for TCEP contaminated water. Fenton's oxidation removed 100% of TCEP with a H_2O_2:Fe^{2+}:TCEP molar ratio of 1:150:5 at pH 3.6 ± 0.1. Both GC and TOC analysis indicate mineralization of TCEP by products. Kinetic experiments show complete removal of TCEP within 24 h. However, the TCEP degradation rate is somewhat slower when compared to other Fenton's oxidation studies [23, 27, 32]. The pseudo-first-order rate constant for TCEP was found to be 5.2E-3 min^{-1}.

Ozone oxidation was found to be ineffective in removing TCEP from water which agrees to the findings by Echigo *et al.* [15] and Westerhoff *et al*. [20].

Engineering Implications and Future Work

Fenton's oxidation of TCEP contaminated water is effective on a laboratory scale using purifed water. Future research should consider the effectiveness of Fenton's oxidation in other water matrices and identify the products of TCEP oxidation. In addition, several design issues should be addressed prior to implementing this method for contaminated water treatment. These issues include: 1) field scale reactor design; 2) reaction time based on treatment goals; 3) how pH is adjusted in the system; 4) how H_2O_2 is introduced in the system; 5) where H_2O_2 is introduced in the reactor (e.g., at the beginning of the reactor or sequentially along the length of the reactor 6) the need for pre-treatment of contaminated water to remove interfering chemicals/anions; and 7) the need for post-treatment (i.e. adjustment to a neutral pH).

Other AOPs such as UV/TiO_2, $UV/TiO_2/H_2O_2$, and etc. should also be considered and evaluated. Optimum Fenton's oxidation occurs at pH around 3.0, which is much lower than the natural water pH range of 6.0-9.0 [40]. Thus, additional post treatment costs would be incurred to bring the treated water pH back to neutral. This cost can be avoided using other AOPs such as UV/H_2O_2. Watts and Linden [29] demonstrated the effectiveness of using UV/H_2O_2 in removing 90 % of TCEP from water. Adjustment of pH is not necessary in UV/H_2O_2 treatments; however, if high energy consumption is needed to remove the contaminants then the cost of energy can be more expensive than pH adjustment. Therefore, cost considerations should be carefully evaluated.

A batch system was used in these laboratory studies; however, for actual treatment a continuous-stirred tank reactor (CSTR) or a plug-flow reactor (PFR) may be more suitable. Advantages of a

CSTR are good mixing and good temperature control. Advantages of a PFR are high reaction conversion and no moving parts [40].

References

1. Fries, E. and Puttmann, W. Occurrence of organophosphate esters in surface water and ground water in Germany. J. Environ. Monit., 2001; 3: 621-626.

2. Rodriguez, I., Calvo, F., Quintana, J.B., Rubi, E., Rodil, R. and Cela, R. Suitability of solid-phase microextraction for the determination of organophosphate flame retardants and plasticizers in water samples. J. Chromatography A., 2006; 1108: 158-165.

3. Andresen, J. and Bester, K. Elimination of organophosphate ester flame retardants and plasticizers in drinking water purification. Water Research, 2006; 40: 621-629.

4. Garcia-Lopez, M., Rodriguez, I. and Cela, R. Development of a dispersive liquid-liquid microextraction method for organophosphorus flame retardants and plastizicers determination in water samples. J. Chromatography A., 2007; 1166: 9-15.

5. Marklund, A., Andersson, B. and Haglund, P. Organophosphorus Flame Retardants and Plasticizers in Swedish Sewage Treatment Plants. Environ. Sci. Technol., 2005; 39: 7423-7429.

6. Andresen, J.A., Grundmann, A. and Bester, K. Organophosphorus flame retardants and plasticisers in surface waters. Sci. Total Environ., 2004; 332: 155-166.

7. Focazio, M., Kolpin, D., Barnes, K., Furlong, E., Meyer, M., Zaugg, S., Barber L. and Thurman, M. A national reconnaissance for pharmaceuticals and other organic wastewater contaminants in the United States – II) Untreated drinking water sources. Sci. Total Environ., 2008; 402: 201-216.

8. Fries, E. and Puttmann, W. Monitoring of the three organophosphate esters TBP, TCEP and TBEP in river water and ground water. J. Environ. Monit., 2003; 5: 346-352.

9. European Union (EU), 2009. European Union Risk Assessment Report of TCEP. Retrieved from http://www.baua.de/de/Chemikaliengesetz-Biozidverfahren/Dokumente/RAR-068.pdf?__blob=publicationFile&v=1

10. Garcia-Lopez, M., Rodriguez, I. and Cela, R. Development of a dispersive liquid-liquid microextraction method for organophosphorus flame retardants and plastizicers determination in water samples. J. Chromatography A., 2007; 1166: 9-15.

11. Environment Canada, 2009. Ethanol, 2-chloro, phosphate (3:1) (Tris(2-chloroethyl)phosphate [TCEP]). Retrieved from http://www.ec.gc.ca/substances/ese/eng/challenge/batch5/batch5_115-96-8.cfm

12. Environmental Protection Agency (EPA), 1988. Tris (2-chloroethyl) Phosphate: Information Review. Rockville, MD: Dynamac Corp.

13. European Union (EU), 2009. European Union Risk Assessment Report of TCEP. Retrieved from http://www.baua.de/de/Chemikaliengesetz-Biozidverfahren/Dokumente/RAR-068.pdf?__blob=publicationFile&v=1

14. Meyer, J. and Bester, K. Organophosphate flame retardants and plasticisers in wastewater treatment plants. J. Environ. Monit., 2004; 6: 599-605.

15. Echigo, S., Yamada, H., Matsui, S., Kawanishi, S., and Shishida, K. Comparison Between O_3/VUV, O_3/H_2O_2, VUV, and O_3 Processes for the decomposition of Organophosphoric Acid Triesters.

16. Kolpin, D., Furlong, E., Meyer M., Thurman, E., Zaugg, S., Barber, L. and Buxton, H. Pharmaceuticals, Hormones, and other Organic Wastewater Contaminants in U.S. Streams, 1999-2000: A National Reconnaissance. Environ. Sci. Technol., 2002; 36: 1202-1211.

17. Reemtsma, T., Quintana, J., Rodil, R., Garcia-Lopez, M. and Rodriguez, I. Organophosphorus flame retardants and plasticizers in water and air: 1. Occurrence and fate. Trends Analyt. Chem., 2008; 27(9): 227-237.

18. Stackelberg, P. Furlong, E., Meyer, M., Zaugg, S., Henderson, A. and Reissman, D. Persistence of pharmaceutical compounds and other organic wastewater contaminants in a conventional drinking-water-treatment plant. Sci. Total Environ., 2004; 329: 99-113.

19. U.S. Department of Health and Human Services, 2009. Draft toxicological profile for Phosphate Ester Flame Retardants.

20. Westerhoff, P., Yoon, Y., Snyder, S. and Wert, E. Fate of Endocrine-Disruptor, Pharmaceutical, and Personal care Product Chemicals during Simulated Drinking Water Treatment Processes., 2005; 39: 6649-6663.

21. Lee, S., Nguyen, Q., Lee, E., Kim, S., Lee, S., Jung, Y., Choi, S. and Cho, J. Efficient removals of tris (2-chloroethyl) phosphate (TCEP) and perchlorate using NF membrane filtrations. Desalination, 2008; 221: 234-237.

22. Pignatello, J.J., dark and Photoassisted Fe3+ Catalyzed Degradation of Chlorophenoxy Herbicides by hydrogen Peroxide. Environ. Sci. Technol., 1992; 26: 944-951.

23. Vella, P. A. and Munder, J.A. Toxic Pollutant Destruction. In: Tedder, D.W. and Pohland, F.G. Emerging Technologies in Hazardous Waste Management III. American Chemical Society, Washington, 1993: 85-105.

24. Sato, C., Leung, S.W., Bell, H., Burkett, W.A. and Watts, R.J. Decomposition of Perchloroethylene and polychlorinated biphenyls with Fenton’s reagent. In: Tedder, D.W., Pohland, F.G. (Eds.), Emerging Technologies in Hazardous Waste Management III. American Chemical Society, Washington, 1993: 343-356.

25. Neyens, E. and Baeyens, J. A review of classic Fenton's peroxidation as an advanced oxidation technique. J. Haz. Mater., 2003; B98: 33-50.

26. Walling, C. Fenton's Reagent Revisited. Acc. Chem. Res., 1975; 8: 125-131.

27. Bergendahl, J. and Thies, T. Fenton's oxidation of MTBE with zero-valent iron. Water Research, 2004; 38: 327-334.

28. Oller, S., Singer, Heinz, fassler, P. and Muller, S. Simultaneous quantification of neutral and acidic pharmaceuticals and pesticides at the low-ng/l level in surface and waste water. J. of Chromatography A, 2001; 911: 225-234.

29. Watts, M. and Linden, K. Photooxidation and subsequent biodegradability of recalcitrant tri-alkyl phosphates TCEP and TBP in water. Water Research, 2008; 42: 4949-4954.

30. Westerhoff, P., Yoon, Y., Snyder, S. and Wert, E. Fate of Endocrine-Disruptor, Pharmaceutical, and Personal care Product Chemicals during Simulated Drinking Water Treatment Processes., 2005; 39: 6649-6663.

31. Arnold, S., Hickey, W. and Harris, R. Degradation of Atrazine by Fenton's Reagent: Condition Optimization and Product Quantification. Environ. Sci. Technol., 1995; 29: 2083-2089.

32. Hickey, W., Arnold, S. and Harris, R. Degradation of atrazine by Fenton's reagent: condition optimization and product quantification. Environ. Sci. Technol., 1995; 29(8): 2083-2089.

33. Lindsey, M. and Tarr, M. Quantitation of hydroxyl radical during Fenton oxidation following a single addition of iron and peroxide. Chemosphere, 2000; 41: 409-417.

34. Hawkins, P., Poyner, D., Jackson, t., Letcher, A., Lander, D. and Irvine, R. Inhibition of iron-catalysed hydroxyl radical formation by inositol polyphosphates: a possible physiological function for myo-inositol hexakisphosphate. Biochem. J., 1993; 294: 929-934.

35. Siedlecka, E., Wieckowska, A., and Stepnowski, P. Influence of inorganic ions on MTBE degradation by Fenton's reagent. J. Hazardous Materials, 2007; 147: 497-502.

36. Watts, M.J., 2008. Photochemical degradation of aqueous organics in chlorinated solutions. Doctoral dissertation, Duke University, Durham, NC.

37. Rakness, K. Ozone in drinking water treatment. American Water Works Association, Denver, 2005:1-4.

38. Singer, P. and Reckhow D. Chemical Oxidation, McGraw Hill, 1999: 12.18-12.19.

39. APHA, AWWA, and WEF. Standard methods for the examination of water and wastewater. 4500-O3 Ozone (Residual). APHA, Washington, 2005: 4-144 – 4-146.

40. Engwall, M., 1997. Mineralization of creoste and pentachlorophenol by photo-assisted Fenton's oxidation. Master's Thesis, University of Connecticut, New Hartford, CT.

Appendix A: Standard Curve Results

Conditions initial TCEP 100 mg/L, initial pH 3.6 ± 0.1, and final pH 7.0 ± 0.1. Samples run on 9/01/2010.

TCEP Concentration (mg/L)	**TCEP Retention time (mins)**	**TCEP Peak Area**
0.5	41.91	38.62
10	41.88	594.65
50	41.91	2126.63
150	41.95	5694.15

Appendix B: Gas Chromatography (GC) Results

Molar Ratio of X:5.0:1 of H_2O_2:Fe^{2+}:TCEP.

Conditions initial TCEP 100 mg/L, initial pH 3.6 ± 0.1, and final pH 7.0 ± 0.1. Samples run on 9/01/2010.

H_2O_2 Molar Ratio	TCEP Peak Area	Calculated TCEP Concentration	% TCEP Removed
200.00	0.00	0.00	100.00
150.00	0.00	0.00	100.00
70.00	27.41	0.98	99.02
30.00	370.68	13.22	86.77
5.00	1109.14	39.57	60.43
Control Fe^{2+}	2960.45	105.62	-5.62
Control H_2O_2	2550.21	90.98	9.02

Molar Ratio of X:2.5:1 of H_2O_2:Fe^{2+}:TCEP.

Conditions initial TCEP 100 mg/L, initial pH 3.6 ± 0.1, and final pH 7.0 ± 0.1. Samples run on 10/05/2010.

H_2O_2 Molar Ratio	TCEP Peak Area	Calculated TCEP Concentration	% TCEP Removed
200.00	92.76	2.41	97.59
150.00	96.60	2.51	97.49
70.00	253.16	6.58	93.42
30.00	599.72	15.58	84.42
5.00	1236.33	32.11	67.89
Control H_2O_2	2622.24	93.55	6.45

Molar Ratio of X:2.0:1 of H_2O_2:Fe^{2+}:TCEP.

Conditions initial TCEP 100 mg/L, initial pH 3.6 ± 0.1, and final pH 7.0 ± 0.1. Samples run on 10/19/2010.

H_2O_2 Molar Ratio	TCEP Peak Area	Calculated TCEP Concentration	% TCEP Removed
200.00	447.98	11.64	88.36
150.00	517.67	13.45	86.55
70.00	1045.32	27.15	72.85
30.00	1590.43	41.31	58.69
5.00	2390.44	62.09	37.91

0.00	4459.05	115.81	-15.81
Control H_2O_2	2650.21	94.55	5.45

Molar Ratio of X:1.5:1 of H_2O_2:Fe^{2+}:TCEP.			
Conditions initial TCEP 100 mg/L, initial pH 3.6 ± 0.1, and final pH 7.0 ± 0.1. Samples run on 10/28/2010.			
H_2O_2 Molar Ratio	TCEP Peak Area	Calculated TCEP Concentration	% TCEP Removed
200.00	1246.85	32.38	67.62
150.00	1276.87	33.16	66.84
70.00	1556.94	40.44	59.56
30.00	2443.75	63.47	36.53
5.00	3123.63	81.13	18.87
Fe^{2+} Control	3495.61	90.79	9.21

Molar Ratio of X:1.0:1 of H_2O_2:Fe^{2+}:TCEP.			
Conditions initial TCEP 100 mg/L, initial pH 3.6 ± 0.1, and final pH 7.0 ± 0.1. Samples run on 09/18/2010.			
H_2O_2 Molar Ratio	TCEP Peak Area	Calculated TCEP Concentration	% TCEP Removed
200.00	1081.76	38.59	61.41
150.00	1107.63	39.52	60.48
70.00	1481.27	52.85	47.15
30.00	1817.73	64.85	35.15
5.00	2409.15	85.95	14.05
Fe^{2+} Control	3664.94	95.18	4.82

Molar Ratio of X:0.5:1 of H_2O_2:Fe^{2+}:TCEP.			
Conditions initial TCEP 100 mg/L, initial pH 3.6 ± 0.1, and final pH 7.0 ± 0.1. Samples run on 10/14/2010.			
H_2O_2 Molar Ratio	TCEP Peak Area	Calculated TCEP Concentration	% TCEP Removed
200.00	1646.74	42.77	57.23
150.00	1607.99	41.76	58.24
70.00	2159.67	56.09	43.91
30.00	2421.30	62.89	37.11
5.00	2860.52	74.30	25.70
control Fe^{2+}	3497.86	90.85	9.15

Spike 100 mg/L	3336.15	119.02	-19.02

Effect of Fe^{2+} on Fenton's oxidation of TCEP at 150:1 H_2O_2: TCEP molar ratio			
Conditions initial TCEP 100 mg/L, initial pH 3.6 ± 0.1, and final pH 7.0 ± 0.1. Samples run on 10/15/2010.			
$FeSO_4$ Molar Ratio	TCEP Peak Area	Calculated TCEP Concentration	% TCEP Removed
5.00	0.00	0.00	100.00
2.50	96.60	2.51	97.49
2.00	517.67	13.45	86.55
1.50	1276.87	33.16	66.84
1.00	1107.63	39.52	60.48
0.50	1607.99	41.76	58.24
Spike 100 mg/L	4861.63	126.27	-26.27

Effect of pH on Fenton's oxidation of TCEP at 75:2.5:1 H_2O_2:Fe^{2+}:TCEP molar ratio			
Conditions initial TCEP 100 mg/L, initial pH 3.6 ± 0.1, and final pH 7.0 ± 0.1. Samples run on 10/30/2010.			
Initial pH	TCEP Peak Area	Calculated TCEP Concentration	% TCEP Removed
2.50	0.00	0.00	100.00
3.00	138.06	3.59	96.41
3.50	465.92	12.10	87.90
4.00	489.49	12.71	87.29
4.50	41.86	555.89	85.56

Appendix C: Total Organic Carbon (TOC) Results

Molar Ratio of X:5.0:1 of H_2O_2:Fe^{2+}:TCEP.
Conditions initial TCEP 100 mg/L, initial pH 3.6 ± 0.1, and final pH 7.0 ± 0.1. Samples run on 09/16/10.

H_2O_2	TOC (mg/L)
200.00	3.18
150.00	5.57
70.00	9.27
30.00	35.91
5.00	26.27

Molar Ratio of X:2.5:1 of H_2O_2:Fe^{2+}:TCEP.
Conditions initial TCEP 100 mg/L, initial pH 3.6 ± 0.1, and final pH 7.0 ± 0.1. Samples run on 09/17/10.

H_2O_2	TOC (mg/L)
200.00	8.32
150.00	8.65
70.00	13.16
30.00	18.11
5.00	23.20

Molar Ratio of X:0.5:1 of H_2O_2:Fe^{2+}:TCEP.
Conditions initial TCEP 100 mg/L, initial pH 3.6 ± 0.1, and final pH 7.0 ± 0.1. Samples run on 09/20/10.

H_2O_2	TOC (mg/L)
200.00	15.95
150.00	18.02
70.00	18.69
30.00	19.59
5.00	21.94

Appendix D: Kinetics Results

Molar Ratio of 75:2.5:1 of H_2O_2:Fe^{2+}:TCEP.

Conditions initial TCEP 100 mg/L, initial pH 3.6 ± 0.1, and final pH 7.0 ± 0.1. Samples run on 10/21/10.

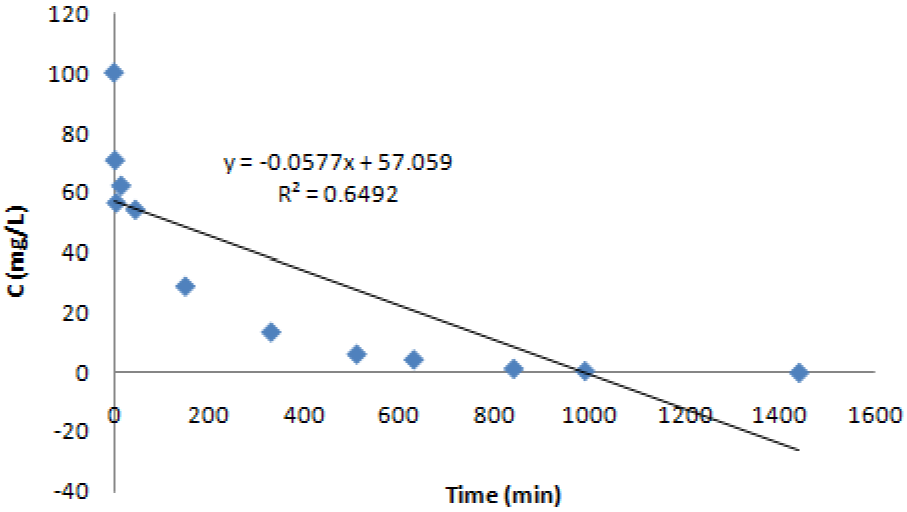
Time (min)	TCEP Peak Area	Calculated TCEP Concentration	% TCEP Removed	C (mg/L)	ln C/Co	1/C (1/(mg/L))
1650	631.69	16.41	83.59	16.41	#DIV/0!	0.06
960	931.72	24.20	75.80	24.20	-1.42	0.04
840	1024.85	26.62	73.38	26.62	-1.32	0.04
630	1198.55	31.13	68.87	31.13	-1.17	0.03
510	1220.75	31.71	68.29	31.71	-1.15	0.03
330	1818.59	47.23	52.77	47.23	-0.75	0.02
150	2169.26	56.34	43.66	56.34	-0.57	0.02
45	2589.41	67.25	32.75	67.25	-0.40	0.01
15	2557.85	66.43	33.57	66.43	-0.41	0.02
5	2429.57	63.10	36.90	63.10	-0.46	0.02
2	2446.66	63.55	36.45	63.55	-0.45	0.02
0	0.00	100.00	0.00	100.00	0.00	0.01

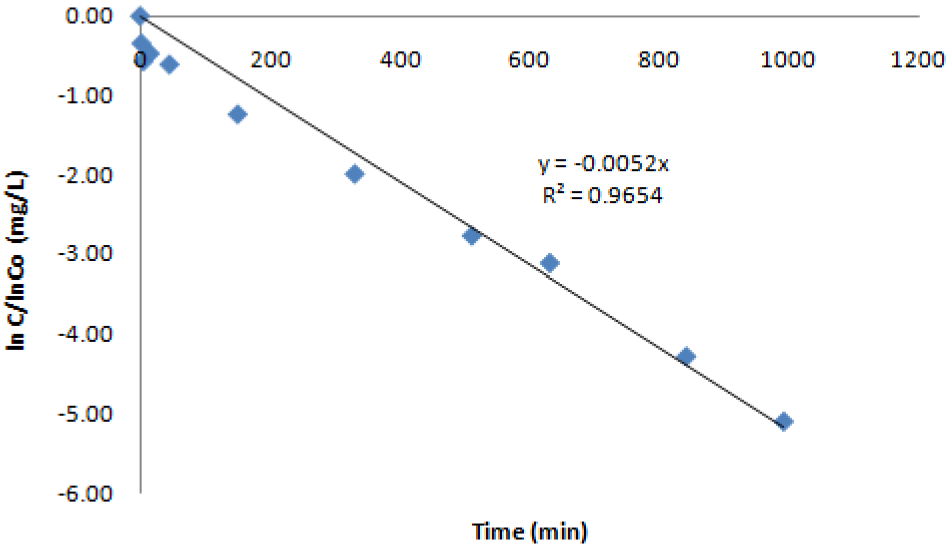
Molar Ratio of 200:5.0:1 of H_2O_2:Fe^{2+}:TCEP.

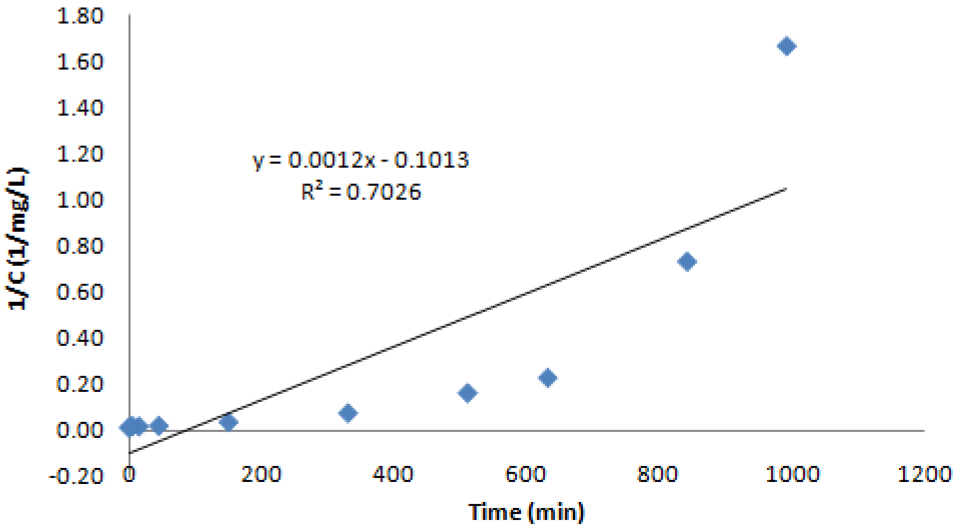
Conditions initial TCEP 100 mg/L, initial pH 3.6 ± 0.1, and final pH 7.0 ± 0.1. Samples run on 10/30/10.

Time (min)	TCEP Peak Area	Calculated TCEP Concentration	% TCEP Removed	C (mg/L)	lnC/C0	1/C (1/(mg/L))
1440	0.00	0.00	100.00	0.01	-9.21	100.00
990	23.11	0.60	99.40	0.60	-5.12	1.67
840	52.68	1.37	98.63	1.37	-4.29	0.73
630	169.77	4.41	95.59	4.41	-3.12	0.23
510	239.32	6.22	93.78	6.22	-2.78	0.16
330	523.22	13.59	86.41	13.59	-2.00	0.07
150	1112.42	28.89	71.11	28.89	-1.24	0.03
45	2086.64	54.20	45.80	54.20	-0.61	0.02
15	2395.38	62.21	37.79	62.21	-0.47	0.02
5	2175.75	56.51	43.49	56.51	-0.57	0.02
2	2722.05	70.70	29.30	70.70	-0.35	0.01
0	0.00	100.00	0.00	100.00	0.00	0.01

Plots are based on molar ratio of 200:5:1 of H_2O_2:Fe^{2+}:TCEP.






y = 0.0012x - 0.1013
R² = 0.7026
1/C (1/mg/L)
1.80
1.60
1.40
1.20
1.00
0.80
0.60
0.40
0.20
0.00
-0.20
0
200
400
600
800
1000
1200
Time (min)