The Effectiveness of Persulfate in the Oxidation of Petroleum Contaminants in Saline Environment at Elevated Groundwater Temperature

by

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AUTHOR'S DECLARATION

I hereby declare that I am the sole author of this thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

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Abstract

In the past few decades, several aqueous oxidants have been employed (e.g., permanganate, persulfate) to remediate petroleum hydrocarbons. However, the majority of the research in this field has been focused primarily on the use of oxidants in treating fresh water at low groundwater temperature. In this study, bench experiments were carried out to investigate the effectiveness of persulfate (PS) as an oxidant to remediate petroleum hydrocarbons in alternative settings (saline environments at high groundwater temperature). Benzene, Toluene, Ethylbenzene, Xylenes (BTEX), Trimethylbenzenes (TMBs), and Naphthalene were the target organic compounds investigated.

Three important aspects were examined during this laboratory study: 1) the evaluation of (alkaline activated and non-activated) persulfate as a chemical oxidation agent; 2) the investigation of the effect of different temperatures (10°C versus 30°C); and 3) the examination of the effect of different persulfate concentration (20 versus 100 g/L) on the reactivity of persulfate.

The results showed the high potential of persulfate to remediate the target contaminants under certain conditions. In general, alkaline-activated persulfate showed a higher potential than the non-activated persulfate. However, precipitations of calcium hydroxide were observed due to the reaction between sodium hydroxide and the high concentration of calcium which will limit the use of alkaline-activated persulfate in this particular groundwater setting

The results also showed that the initial concentration of persulfate and the system temperature can play important roles in enhancing the effectiveness of PS to oxidize the target contaminants. For instance, the oxidation rate of the target contaminants was seen to be dramatically increased by increasing the persulfate addition from 20 to 100 g/L as well as with increasing the system temperature from 10°C to 30°C. However, increasing both factors (temperature and concentration) accelerated the decomposition rate of PS.

Lowering the system pH was tremendously successful in order to enhance the oxidation rate of all compounds. Moreover, the expected effect of the radicals scavenging at acidic pH by Cl$^-$ and Br$^-$,which was reported in the literatures (e.g., Pignatello et al., 2006; Grebel et al., 2010; Suri et al.,

2010), was not observed in this study which might be attributed to the contribution of the produced halogen radicals to the contaminant oxidation.

Acknowledgements

Dedication

To the memory of my mother and to my father, wife and my little angel Meshal.

I also dedicate this work to my older sister. Khadeeja, no matter what I say, I cannot thank you enough for your support, encouragement, and for being my first teacher.

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Chapter 1
Introduction

Many natural resources show some degree of anthropogenic impact, including the widespread contamination of groundwater by hazardous chemicals. Groundwater represents 98% of the available fresh water of the planet. Thus, protecting and restoring groundwater quality is of global strategic importance (Alvarez & Illman, 2006). Common organic groundwater contaminants include petroleum hydrocarbons. The extensive use of petroleum hydrocarbons as an energy source as well as raw materials for many synthetic products has resulted in widespread soil and groundwater contamination by this class of contaminants. Soil and groundwater contamination is commonly the result of unintentional release of chemical products that occurs during production, storage or transportation activities due to leaky underground storage tanks, pipelines, oil exploration activities, holding pits near production oil wells and refinery wastes. Once these contaminants enter the subsurface, they can persist as a non-aqueous phase liquid (NAPL) in the vadose zone and the near-water table zone in aquifers (Hamed, 2005). These hazardous releases in the environment are an ongoing concern that can result in long term contamination (Christensen & Larsen, 1993) that represents a significant technical and economical challenge because underground contamination is difficult to locate and remove by a traditional extraction and excavation method (Alvarez & Illman, 2006). Therefore, there is an urgent need for wider application of cost-effective, environmentally friendly in-situ remediation approaches that can be employed for the cleanup of contaminated sites.

Research and development over the last three decades have led to various subsurface remediation or controlling strategies such as: 1) containment of contaminated zones (e.g., concrete or slurry walls), 2) ex-situ treatment (e.g., excavation), 3) natural attenuation, and 4) in-situ treatment (e.g., in-situ bioremediation, chemical oxidation) (Domenico & Schwartz, 1998).

In-situ treatment or remediation approaches have become attractive due to favourable economics, simple preparation of the treatment solution, and the advantage of degrading contaminants in place. In-situ mass transformation techniques are based on the knowledge that many contaminants are

amenable to be fully or partially degraded by biological, chemical and physical processes. In-situ chemical oxidation (ISCO) is one of the promising remediation methodologies (Domenico & Schwartz, 1998). Compared with in-situ bioremediation which is typically limited by rates of contaminant desorption and dissolution (Ogram et al., 1985), the transformations in ISCO are near immediate, and therefore treatment is far more rapid than with biological techniques (Siegrist et al., 2006).

The application of ISCO as a remediation method for subsurface organic contaminants is still relatively new. Over the last 10 years, there has been a significant research and development in the employment of ISCO for the remediation of organic contaminants, especially NAPLs (e.g. Huling & Pivetz, 2006; Siegrist et al, 2006). ISCO technology involves injecting chemical oxidants (e.g., hydrogen peroxide or Fenton's reagent, persulfate, permanganate and ozone) into the vadose or saturated zone to reduce the contaminant mass through oxidization (Pignatello et al., 2006; Tsitonaki et al., 2010).

One of the recently used oxidants for ISCO application is sodium persulfate ($Na_2S_2O_8$). In addition to the advantages of having high water solubility and benign residual products, sodium persulfate (PS) is very stable and can persist in the subsurface for weeks (Huling & Pivetz, 2006). In this study, bench experiments were carried out to investigate the effectiveness of persulfate as an oxidation agent to remediate petroleum hydrocarbons in alternative settings (saline environments at high groundwater temperature). Benzene, Toluene, Ethylbenzene, and Xylenes (BTEX), Trimethylbenzenes (TMBs), and Naphthalene were the target investigated organic compounds during this project. The main objectives of this study were: 1) the evaluation of (alkaline activated and non-activated) persulfate as a chemical oxidation agent; 2) the investigation of the effect of different temperature ($10^{\circ}C$ versus $30^{\circ}C$); and 3) the examination of the effect of different persulfate concentration (20 versus 100 g/L) on the reactivity of persulfate.

1.1 Persulfate mechanism

When Persulfate salts are added to the water, they dissociate to persulfate anions (Eq. 1). These anions are strong oxidants and capable of electron transfer with an estimated standard oxidation potential of $E° = 2.01$ V, as written in Eq. 2 (House, 1962).

$$Na_2S_2O_8 \rightarrow 2Na^+ + S_2O_8^{2-} \tag{1}$$

$$S_2O_8^{2-} + 2\ e^- \rightarrow 2SO_4^{2-} \tag{2}$$

The persulfate anions are relatively stable oxidants and their reactivity may increase at low pH by yielding more reactive oxidants. In alkaline, neutral and diluted acid solutions (pH > 3; $[H^+] < 0.5M$), persulfate decomposes according to Eq. 3 (Kolthoff & Miller, 1951). In strongly acid solutions (pH < 3; $[H^+] > 0.5M$), the persulfate anions are catalyzed by hydrogen ions. Moreover, hydrolysis of the persulfate anion in strong acid will yield Caro's acid H_2SO_5 which hydrolyzes further to hydrogen peroxide H_2O_2 (Eq. 4 – 5) (Kolthoff & Miller, 1951; FMC, 2001). The produced H_2SO_5 or H_2O_2 are kinetically faster oxidants than persulfate anions and their reactivity with the organic contaminants are much faster (FMC, 2001).

$$S_2O_8^{2-} + H_2O \rightarrow 2HSO_4^- + ½\ O_2 \qquad (E°=2.01\ V) \tag{3}$$

$$H_2S_2O_8 + H_2O \rightarrow H_2SO_5 + H_2SO_4 \qquad (E°=1.81\ V) \tag{4}$$

$$H_2SO_5 + H_2O \rightarrow H_2O_2 + H_2SO_4 \qquad (E°=1.77\ V) \tag{5}$$

However, the reaction rates for persulfate ions with the organic contaminant becomes much faster when these ions generate free sulfate radicals ($SO_4^{•-}$) under free radical oxidation processes (e.g., heat, OH^-) Eq. 6 (Tsitonaki et al., 2010). With an oxidation potential of $E° = 2.60$ V, the sulfate radicals can effectively initiate radical chain reactions to oxidize organic compounds (i.e., M in Eq. 7) (Berlin et al., 1986). For instance, the oxidation rate for Benzene was observed to be five times faster when free sulfate radicals were generated (Neta et al., 1977).

$$S_2O_8^{-2} + (heat,\ OH^-) \rightarrow 2SO_4^{•-} \qquad (E°=2.60\ V) \tag{6}$$

$$SO_4^{•-} + M \rightarrow M^• + products \tag{7}$$

Moreover, radical interconversion reactions may occur in neutral and acid solutions to produce hydroxyl radicals (($^•OH$) $E° = 2.7$ V) Eq. 8 (Hayon et al., 1972). The rate for this reaction is relatively

slow ($K_8 < 3 \times 10^3$ M^{-1} s^{-1}). However, the reaction may become very rapid under alkaline conditions with a rate constant of ($K_9 = 6.5 \pm 1.0 \times 10^7$ M^{-1} s^{-1}) Eq. 9 (Hayon et al., 1972). Thus, hydroxyl radicals are likely the dominant radicals for organic oxidation under alkaline conditions. In contrast, sulfate radicals overcome hydroxyl radicals in neutral or acidic solutions (Liang et al., 2006). Much like the sulfate radicals, hydroxyl radicals can also initiate radical chain reactions to oxidize organic compounds (i.e., M in Eq. 10) (Berlin et al., 1986), or produce another oxidant such as hydrogen peroxide Eq. 11 (Waldemer et al., 2007). These studies demonstrate the complexity in persulfate chemistry and show that numerous reactions may be involved in the transformation process.

$$\text{All pHs: } SO_4^{\bullet-} + H_2O \rightarrow SO_4^{2-} + {}^{\bullet}OH + H^+ \tag{8}$$

$$\text{Alkaline pH: } SO_4^{\bullet-} + OH^- \rightarrow SO_4^{2-} + {}^{\bullet}OH \tag{9}$$

$$OH^{\bullet} + M \rightarrow M^{\bullet} + \text{products} \tag{10}$$

$$2OH^{\bullet} \rightarrow H_2O_2 \tag{11}$$
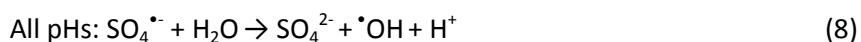
In terms of persulfate persistence, four reactions have been suggested to be responsible for the decomposition of PS (Kolthoff & Miller, 1951; House, 1962; Sra et al., 2010). Unanalyzed reaction through homolytic cleavage of PS to produce hydrogen sulfate and oxygen (Eq. 3), acid catalyzed reaction to yield Caro's acid (Eq. 5), free radical oxidation processes (Eq. 6), and persulfate reactions with transition metal catalysts and other reductants (e.g., reduced organic or inorganic). Accordingly, when constant concentration of PS is applied in two different systems, higher decomposition rate of PS would be expected in a strongly acid solution and/or in the presence of aquifer solids.

1.2 Halide Ions Effect

There have been few studies examining the effect of halide ions on the contaminant destruction. For instance, significant increase in oxidation rate of estrogens with the addition of NaCl was reported (Suri et al., 2010). In contrast, Fenton oxidation of 1,2-dibromoethane was almost completely stopped by the addition of 1 mM NaBr (Pignatello et al., 2006). Cl$^-$ and Br$^-$ are well-known radical scavengers as it shown in Eq. 12 - 13 (Peyton, 1993); Eq. 14 - 17 (Grebel et al., 2010). Interestingly, traces of Br$^-$ in a NaCl stock were found to have a greater effect than Cl$^-$ itself, demonstrating the significant inhibition effect of Br$^-$ (Grebel et al., 2010). This consequence was attributed to the higher reaction rate of radicals with Br$^-$ than the one with Cl$^-$ Eq. 12 and 17. Still, both ions have the capability to react rapidly with the free radicals which as a result may slow or inhibit the oxidation of the target organics (Grebel et al., 2010).

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$$SO_4^{\bullet-} + Cl^- \rightarrow SO_4^{2-} + Cl^{\bullet} \qquad (K_{12\,for} = 2 \times 10^8 \text{ M}^{-1}\text{s}^{-1}) \qquad (12)$$

$$SO_4^{\bullet-} + Br^- \rightarrow SO_4^{2-} + Br^{\bullet} \qquad (K_{13\,for} = 3.5 \times 10^9 \text{ M}^{-1}\text{s}^{-1}) \qquad (13)$$

$$OH^{\bullet} + Cl^- \leftrightarrow ClOH^{\bullet-} \qquad (K_{14\,for} = 4.3 \times 10^9 \text{ M}^{-1}\text{s}^{-1}) \quad (14)$$
$$(K_{14\,rev} = 6.1 \times 10^9 \text{ M}^{-1}\text{s}^{-1})$$

$$ClOH^{\bullet-} + H^+ \leftrightarrow Cl^{\bullet} + H_2O \qquad (K_{15\,for} = 2.1 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}) \quad (15)$$
$$(K_{15\,rev} = 2.5 \times 10^5 \text{ M}^{-1}\text{s}^{-1})$$

$$OH^{\bullet} + Br^- \leftrightarrow BrOH^{\bullet-} \qquad (K_{16\,for} = 1.1 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}) \quad (16)$$
$$(K_{16\,rev} = 3.3 \times 10^7 \text{ M}^{-1}\text{s}^{-1})$$

$$BrOH^{\bullet-} + H^+ \leftrightarrow Br^{\bullet} + H_2O \qquad (K_{17\,for} = 4.4 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}) \quad (17)$$
$$(K_{17\,rev} = 1.4 \text{ M}^{-1}\text{s}^{-1})$$
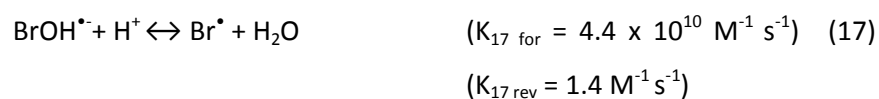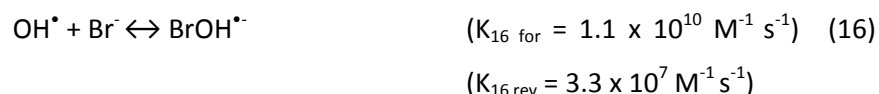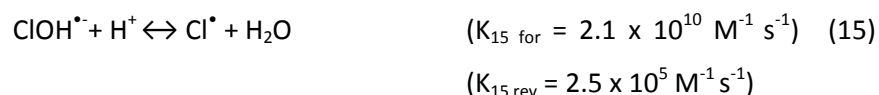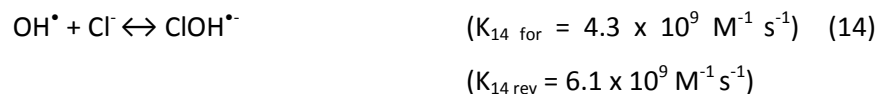
Moreover, these scavenging reactions were found to be more pronounced at low pH (Jayson et al., 1973). The destruction of cyclohexanol by $OH^{\bullet}$ was reduced in the presence of halides at low pH, and the destruction rate was reported to increase with increasing pH (Grebel et al., 2010). Similar observation was reported when Fenton reaction of 2,4-dichlorophenoxyacetic acid was inhibited due to the presence of $Cl^- > 0.01$ M at pH = 2.8 (Pignatello et al., 2006). The effect of pH on these results can be explained by comparing the rate constants for the forward and reverse reactions in Eq. 14 - 17 (Liao et al., 2001). In neutral and alkaline conditions, the rate constants for the reverse reactions in Eq. 14 was found to be slightly larger than the rate constants for the forward $OH^{\bullet}$ scavenging reactions. This indicates the high possibility of $OH^{\bullet}$ regeneration by dissociating back the formed halogen radicals. On the other hand, in acidic solution, the rate constants for the forward reactions in Eq. 15 and 17 were considerably larger than the rate constants for the reverse reactions, demonstrating high $OH^{\bullet}$ scavenging at low pH.

When radicals are scavenged by halide ions, they are converted to radical reactive halogen species (i.e., $Cl^{\bullet}$, $Br^{\bullet}$ in Eq. 15 - 17), that may take part in the contaminant oxidation but react more selectively with electron-rich organic compounds (Grebel et al., 2010). At 25ºC, standard reduction potentials (E°) of 2.59 V, 2.04 V have been proposed for $Cl^{\bullet}$ and $Br^{\bullet}$, respectively (Isse et al., 2011). Furthermore, the presences of halide ions might affect the decomposition rate of persulfate by increasing the solution ionic strength. Increasing the ionic strength by the addition of salt resulted in a lower decomposition rate of persulfate (Kolthoff & Miller, 1951). Although, the presence of halogen

radicals would appear efficient to treat contaminated water with electron-rich compounds, escalating the production of theses radicals might lead to the production of toxic gases (e.g., X_2 in Eq. 19) (Grebel et., 2010) which would limit its efficiency.

$$X^{\bullet} + X^{-} \leftrightarrow X_2^{\bullet -} \tag{18}$$

$$2X_2^{\bullet -} \rightarrow 2X_2 + 2X^{-} \tag{19}$$

1.3 Alkalinity Effect

Alkalinity, reported as $CaCO_3$, is another radical scavenger which may compete with the organic contaminants for the highly reactive radicals. In turn, this may affect the rate of contaminant oxidation. Lower oxidation rate of TCE was associated with increasing the level of carbonate (CO_3^{2-}) (Linag et al., 2006). Similarly, the oxidation rate of 1,4-dioxane by hydroxyl radical slowed down when bicarbonate (HCO_3^-) and carbonate were present (Mehrvar et al., 2001).

As the form of alkalinity anions present in a solution is pH dependent (e.g., CO_3^{2-}, HCO_3^-, H_2CO_3), the scavenging reaction rates by these anions are also expected to be affected by pH. Increasing the scavenging reaction rate with increasing pH has been experienced in many studies. This consequence can be attributed to the rapid decay of sulfate and hydroxyl radicals when they react with hydroxyl ions (OH^-) at alkaline pH (Dogliotti, 1967). Another possible reason is that the carbon dioxide formed from the oxidation of organic compounds may lead to the formation of more scavenging carbonate ions (Xu et al., 1989). However, increasing the production of CO_2 will bring about lower pH, which should increase the oxidation rate for the contaminants. Increasing the scavenging reaction rate under alkaline solution might also be explained by the dramatically different reaction rates of different alkalinity forms at different pH Eq. 20 - 24.For instance, the reaction rate in acidic solution pH ≤ 3.5, where H_2CO_3 would be the dominant species, is much slower comparing to that in a solution buffer at pH ≥ 6.35, where HCO_3^- is the dominant species. While in alkaline pH ≥ 10.33, CO_3^{2-} would be the dominant species and the rate of radical scavenging reaction is considerably faster. This hypothesis is in agreement with a study done by Liang et al. (2006). At a neutral pH, TCE oxidation by persulfate was not affected by the presence of bicarbonate/carbonate concentrations within the range of 0 - 9.20 mM. The author also reported a decrease in the TCE oxidation rate with an increase in the level of carbonate species at elevated pHs.

When radicals are scavenged by carbonate ions, they are converted to reactive carbonate radicals in the form of $CO_3^{\bullet-}$ regardless the radicals are scavenged by CO_3^{2-}, HCO_3^- or H_2CO_3 Eq. 20 (Zuo et al., 1999); Eq. 21 (Huie & Clifton, 1990); Eq. 22 - 23 (Buxton & Elliot, 1986); Eq. 24 (Czapski, 1999)). This has been confirmed after a pK_a of $CO_3^{\bullet-} < 0$ was reported (Czapski, 1999). The produced $CO_3^{\bullet-}$ is also a strong oxidant ($E° \approx 1.65$ V at pH = 7), and may oxidize but more selectively the electron-rich organic compounds by the electron transfer mechanism (Zuo et al., 1999; Mazellier et al., 2007). Moreover, at pH < 6, an increase in redox potential by 59 mV per pH unit was suggested by Linag (Linag et al., 2006). The authors also suggested that the yield redox potential is dependent to a lesser degree between 6 and 11 and is almost independent above a pH of 11 ($E° = 1.59$ V).

$$SO_4^{\bullet-} + CO_3^{2-} \rightarrow SO_4^{2-} + CO_3^{\bullet-} \qquad (K_{20} = 6.1 \times 10^6 \ M^{-1} s^{-1}) \qquad (20)$$

$$SO_4^{\bullet-} + HCO_3^- \rightarrow SO_4^{2-} + CO_3^{\bullet-} + H^+ \qquad (K_{21} = 2.8 \times 10^6 \ M^{-1} s^{-1}) \qquad (21)$$

$$OH^\bullet + CO_3^{2-} \rightarrow OH^- + CO_3^{\bullet-} \qquad (K_{22} = 3.0 \times 10^8 \ M^{-1} s^{-1}) \qquad (22)$$

$$OH^\bullet + HCO_3^- \rightarrow H_2O + CO_3^{\bullet-} \qquad (K_{23} = 8.5 \times 10^6 \ M^{-1} s^{-1}) \qquad (23)$$

$$OH^\bullet + H_2CO_3 \rightarrow H_2O + H^+ + CO_3^{\bullet-} \qquad (K_{24} = 7.0 \times 10^4 \ M^{-1} s^{-1}) \qquad (24)$$
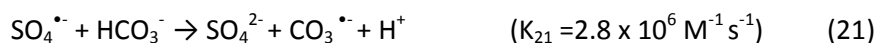
The impact of Br^-, Cl^-, and (bi)carbonate on the inhibition of the oxidation rates of contaminants at neutral pH was observed to follow this order: $Br^- > CO_3^{2-} > Cl^- > HCO_3^-$ (Grebel et al., 2010; Liao et al., 2001). When these constituents are present together in water, the opposite reaction behavior at different pH must be considered and the proper control of pH should be used to gain the highest efficiency from the radical oxidation process.

Chapter 2

Materials and Methods

2.1 Materials

Reagent grade sodium persulfate ($Na_2S_2O_8$>98%, Sigma Aldrich), diluted with ultra pure water, was used for the oxidation experiments. The contaminated groundwater that was used to conduct the experiments was collected from a site in Saudi Arabia. The collected sample from the site was analyzed by ALS laboratory group for specific conductance, alkalinity, total dissolved solids, anion and cation content. Standard methods (APHA 1998) were employed for all analyses. The characteristics of the groundwater sample are illustrated in **Table 2.1**. The groundwater sample containers were shipped to the laboratory on ice, then preserved with a 10% sodium azide solution (v/v) (Added 43 mL/4.3L =1 g/L) to inhibit biodegradation of organic compounds, and stored in the fridge until use.

Table 2.1 Characteristics of the groundwater

Alkalinity, Total (as CaCO3)	1020 mg/L	Barium (Ba)-Total	0.82 mg/L
Conductivity	10400 umhos/cm	Boron (B)-Total	3.62 mg/L
Total Dissolved Solids	5330 mg/L	Calcium (Ca)-Total	31 mg/L
pH	7.7	Iron (Fe)-Total	<0.50 mg/L
Chloride	3030 mg/L	Magnesium (Mg)-Total	33.1 mg/L
Bromide	5.6 mg/L	Manganese (Mn)-Total	0.624 mg/L
Fluoride	2.36 mg/L	Phosphorus (P)-Total	<0.50 mg/L
Nitrite-N	<1.0 mg/L	Potassium (K)-Total	<10 mg/L
Nitrate-N	<1.0 mg/L	Silicon (Si)-Total	16 mg/L
Sulphate	<20 mg/L	Sodium (Na)-Total	1940 mg/L
Aluminum (Al)-Total	<0.10 mg/L	Strontium (Sr)-Total	1.65 mg/L

2.2 Experimental Procedure

A laboratory batch experiment was carried out to evaluate the effectiveness of persulfate oxidation of selected VOCs over time. Twenty-five mL borosilicate VOA vials with PTFE septa and screw caps were employed as reaction systems. Batch reactor experiments were designed with (5 mL) headspace

to accommodate the expected gas production throughout the reaction. Temperature was maintained at 10°C or 30°C, by using constant temperature incubators. When using activated persulfate as an oxidant, pH was initiated at 12 by adding sodium hydroxide (NaOH). pH was then maintained between 10 and 12, when high concentrations of persulfate were added (100 g/L), by regularly adding NaOH through Mininert® valve caps. Vials containing only contaminated groundwater were prepared and used as control samples for the experiment. Initial VOCs analyses showed that the water samples contain 83 mg/L of BTEX, 2.9 mg/L of TMBs, and 0.3 mg/L of Naphthalene.

For the oxidation experiment, alkaline-activated and non-activated persulfate were added via syringe to the vials that contained VOC contaminated groundwater. The added oxidant was calculated to achieve a final concentration of 20 g/L or 100 g/L in the reaction vials. The reactors were then capped, shaken to completely mix, and incubated at 10°C or 30°C. During sampling, using a ground glass syringe (with a stainless steel syringe tip), 19.0 mL was removed for VOCs analyses and 0.5 mL for persulfate analyses. The analyses were performed at the Organic Chemistry Laboratory, Department of Earth and Environmental Sciences, University of Waterloo. Analyses of Benzene, Toluene, Ethylbenzene, Xylenes, Trimethylbenzenes, and Naphthalene were performed using a HP 5890 capillary gas chromatography (GC) equipped with a flame ionization detector and a HP7673A auto sampler. The GC calibration was checked with standards to verify the validity of the calibration within $\pm$ 10%. Dichloromethane (1 mL) was injected in the reactors followed by extraction and analysis as described by Freitas & Barker (2008). Bulk PHC fractions F1 (C_6 to C_{10}), F2 (C_{10} to C_{16}) and TPH (F1 + F2) were obtained from chromatographs generated during PHC analysis. Sodium persulfate concentrations were measured using the spectrophotometric methods of Huang et al. (2002). Tests were conducted in triplicate at time points 1, 8, 15, 26, 40, 56 and 98 days. One replicate was utilized for analysis of pH when required.

Chapter 3
Results and Discussion

Prior to the interpretation of the results, there is a main factor that should be considered and discussed. This factor might affect the oxidation rates of the contaminants rather than the oxidation potential of PS. The effectiveness of PS oxidation seems to be related to the initial concentration of the organic compounds, inorganic ions, and their kinetic reactions with the free radicals (Tsitonaki et al., 2010). It seems that for the same organic compound, a lower oxidation rate would be expected with higher concentrations as well as with the presence of inorganic species.

3.1 The Role of Temperature in the Oxidation of Petroleum Contaminants by Persulfate in Saline Environment

Generally, the reaction rate is temperature dependence. In most cases the rate of reaction doubles for every $10^{\circ}C$ rise in temperature (Tyagi, 2009). Increasing the temperature will increase the number of molecules having the minimum necessary energy, threshold energy, to be effective in producing chemical changes. Additionally, increasing the temperature will make molecules move faster and hence increase the chances for more collisions and reactions between molecules (Tyagi, 2009). Moreover, in persulfate chemical oxidation, sulfate free radical can be generated by activating persulfate thermally (Eq. 3). Therefore, at relatively higher system temperature ($30^{\circ}C$), a higher rate of sulfate and hydroxyl radical generation would be expected than a system with a temperature of $10^{\circ}C$. This would result in a higher rate of oxidation for the contaminants. Nevertheless, high temperature in some cases has been suggested to reduce the mineralization efficiency of the total organic carbon (Peyton, 1993). This was attributed to the extremely quick release of reactive radicals. Too many radicals will favour radical-radical reactions over radical-organic reactions which will reduce the organic oxidation efficiency. Thus, controlling temperature is essential to gain the most efficiency of radicals especially when radical scavengers are present in high concentration.

Figure (3.1 (a & b)) shows the influence of temperature over a range of ($10^{\circ}C$ - $30^{\circ}C$) on persulfate oxidation of Total Petroleum Hydrocarbons (TPH). Higher oxidation rate of TPH with PS at higher temperature was apparent in all experiment conditions.

At 10°C, control reactors that contained only contaminated groundwater demonstrated almost no change in all various gasoline compounds by processes other than the chemical oxidation. Insignificant TPH loss was observed in control reactors at 30°C, most likely due to the thermal treatment of Volatile Organic Compounds (VOCs) at 30°C. Nearly identical results were obtained in the PS experiment at 10°C. These results established the similarity between the thermal treatment at 30°C, without PS, and the contaminant oxidation by PS at 10°C. In contrast, the results from reactors contained PS at 30°C showed the capability of the oxidant to oxidize most of the target contaminants.

3.1.1 Oxidation with Non-Activated Persulfate

When non-activated PS was added at low temperature 10°C, more than 83% of the total organic compounds and 87% of the initial persulfate remained in the solution by the end of the experiment (**Figure 3.1 (a)**). These results demonstrated extremely low oxidation rate of the target contaminants by PS at low temperature, most likely due to the low sulfate anions reactivity with the organic compounds at low temperature. On the other hand, 50% of the initial PS concentration was decomposed when PS was activated thermally at 30°C. The thermally activated PS was capable to completely oxidize TPH in~98 days.

Although, higher decomposition rate of PS was observed at higher temperature, significant concentration of the oxidant remained in the reactors without being decomposed (**Figure. 3.2 (a)**).

The pH measurements that were conducted throughout the two experiments showed that the pH did not change in the lower temperature system while the pH dropped severely to values around 1.5 in the higher temperature system. Several reactions might contribute to this enormous drop of pH. First, Uncatalyzed degradation of persulfate through homolytic cleavage to produce hydrogen sulfate and oxygen perhaps accounted for some of the H^+ generation (Eq. 3). The organic oxidation might also contribute to the generated acidity. For instance, the oxidation of one mole of Benzene produces 30 H^+ as described in Eq. 25 (Sra, 2010). Finally, when the pH decreases to < 3 further H^+ production occurred due to the persulfate degradation through the acid-catalyzed reaction (Eq. 5).

$$C_6H_6 + 15S_2O_8^{2-} + 12H_2O \rightarrow 6CO_2 + 30SO_4^{2-} + 30H^+ \qquad\qquad (25)$$

According to the data in **Table 3.1,** 1,2,4-TMB was the most degradable compound with the addition of PS at $30°C$. Benzene was the most persistent compound and the high-to-low order of oxidation rates was: 1,2,4-TMB > 1,2,3-TMB > 1,3,5-TMB > Naphthalene > *P,M*-xylene > Toluene >O-xylene > Ethylbenzene > Benzene.

3.1.2 Oxidation with Alkaline-Activated Persulfate

It is worth noting that in the alkaline-activated PS experiments, the alkaline pH ≈12 was only attained initially; the pH was deliberately uncontrolled to avoid the expected scavenging reaction by carbonates at alkaline pH which was observed in a preliminarily experiment. In the preliminarily experiment, controlling pH at 12 showed a very limited potential of PS to oxidize the target contaminants after 40 days. The technique of not controlling the pH was tremendously successful in the higher temperature system $30°C$ in the current experiment. After five days, pH dropped to pH≈ 1.5 resulted in total removal of the organic compounds, most likely in neutral and acidic pH, during the first 56 days (**Figure 3.1 (b)**). In contrast, insignificant drop in pH was observed in the $10°C$ system and very slow oxidation rates for the organic compounds were observed with 75% of the total TPH remaining in solution. The slight drop in pH from 12 to 10 was perhaps not sufficient to prevent the free radicals from being scavenged by the carbonate species. The rate of PS decomposition was observed to be a temperature dependant (**Figure 3.2 (b)**). Higher decomposition rate of PS was seen at $30°C$ comparing to the one at $10°C$ where (48%) and (17%) of the initial PS concentration were decomposed, respectively. The data in **Table 3.1** showed that 1,2,3-TMB was the most rapidly degradable compound and the high-to-low order of the oxidation rates was: 1,3,5-TMB > 1,2,4-TMB > *P,M*-xylene > Toluene > O-xylene > Ethylbenzene > 1,2,3-TMB > Benzene > Naphthalene.

In general, alkaline-activated PS has showed an extremely high potential to oxidize the target contaminants. However, white precipitations of calcium hydroxide at a strong alkaline pH = 12 - 10 were observed due to the reaction between sodium hydroxide and calcium carbonate as presented in Eq. 26. These species were tested and differentiated from calcium carbonate ($CaCO_3$) by adding a

solution of HCl and no reaction was observed. The effect of these species on the water quality and the possibility of blocking the porous media in the field might undervalue the use of alkaline-activated PS in this particular groundwater setting.

$$CaCO_3 + 2\,NaOH \leftrightarrow Ca(OH)_2 + Na_2CO_3 \qquad\qquad (26)$$
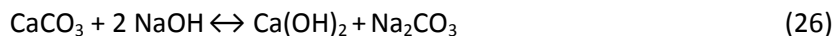
The data for the oxidation by PS for each compound exhibited a good fit to a pseudo-first-order model ($r^2 > 0.94$) by exponential regression analysis (**Table 3.1**). The k_{obs} for TMBs were the largest followed by Xylenes > Toluene > Ethylbenzene > Benzene > Naphthalene. The k_{ob} trend for some compounds in this study (e.g., xylenes and TMBs) is in disagreement with the reported trend for the same compounds by Sra (2010). This could be due to the difference in the initial concentration of the compound between the two studies. For the same organic compound, a lower oxidation rate would most likely be associated with higher concentrations (Tsitonaki et al., 2010). Although the TPH in this experiment was ~ 4 times higher than those in Sra (2010) experiment, the k_{ob} was higher. The oxidation rate coefficients in this study were ~ 2 to 6 times higher when non-activated PS was added in both experiments. This difference was likely due a slightly lower temperature (20°C) in Sra (2010) as opposed to the 30°C in this experiment. In contrast, the difference between the calculated k_{ob} when alkaline-activated PS was used in both studies was < 2.

3.1.3 Impact on Bulk PHC Fractions

Analyses for Petroleum Hydrocarbon (PHC) fractions (F1, F2, and F3) were conducted at the beginning of the experiments. F1 was accounted for 97% of the initial concentration while 2.9% and less than 0.1% were reported for F2 and F3, respectively. Due to the extremely low concentration of F2 and F3, the results for these particular fractions were neglected. However, the decomposition of F2 and F3 might cause an increase in the concentration of the lower molecular weight F1 and F2 which must be considered.

All control reactors demonstrated insignificant oxidation of F1 over the experiment period. Similar results were observed when PS was added in a low temperature system 10°C. In contrast, gradual decrease in F1 concentration was observed when PS was added in a high temperature system 30°C (**Figure 3.3 (a & b))**. However, a higher oxidation rate of F1 was apparent in the alkaline-activated

PS system than in the non-activated PS. Full removal of F1 was achieved in ~56 and ~89 days, respectively.
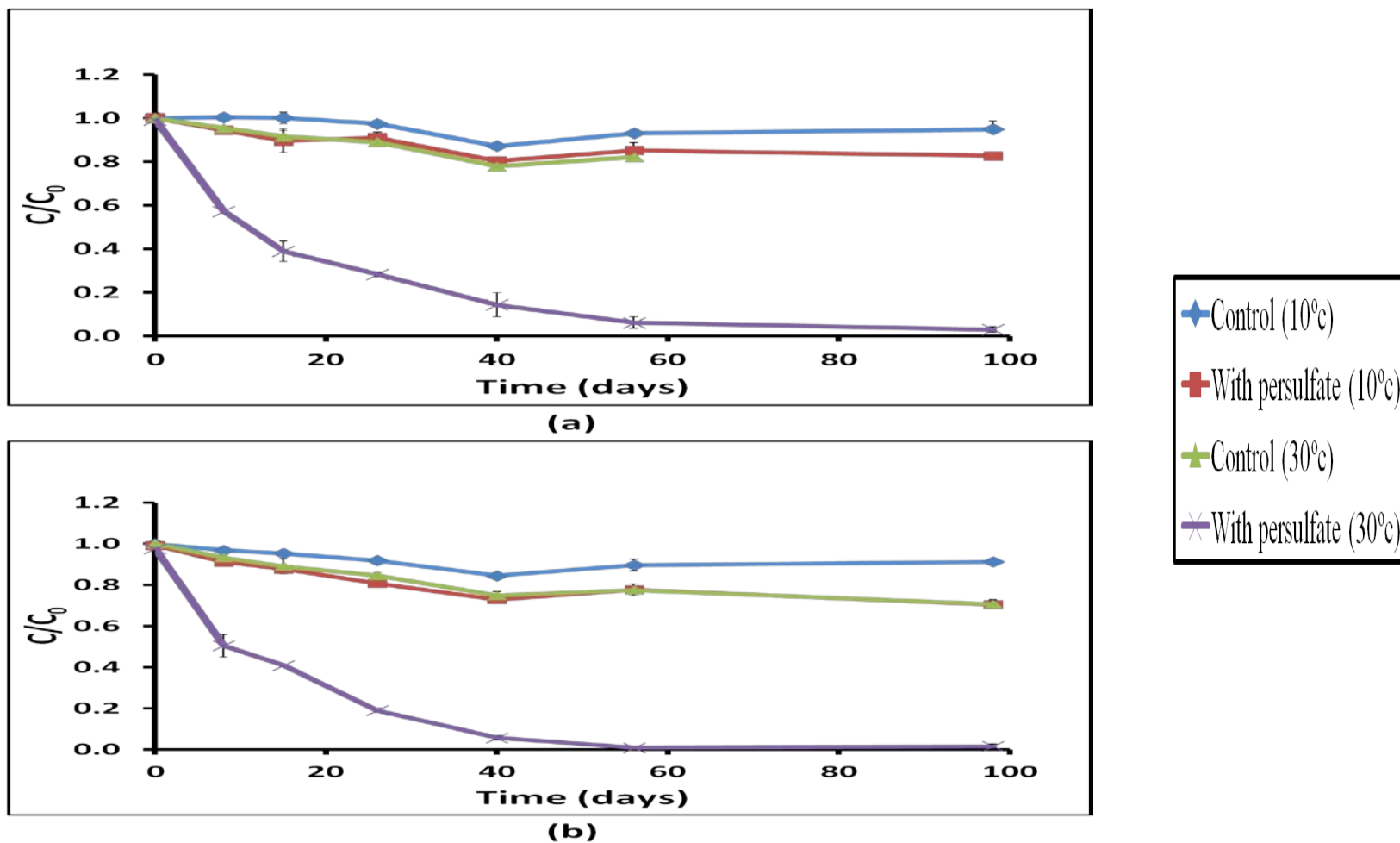
Figure 3.1 The effect of temperature (10⁰C vs. 30⁰C) on the oxidations of (TPH) by (a) non-activated PS and (b) alkaline-activated PS during the 98 days of the oxidation experiment.
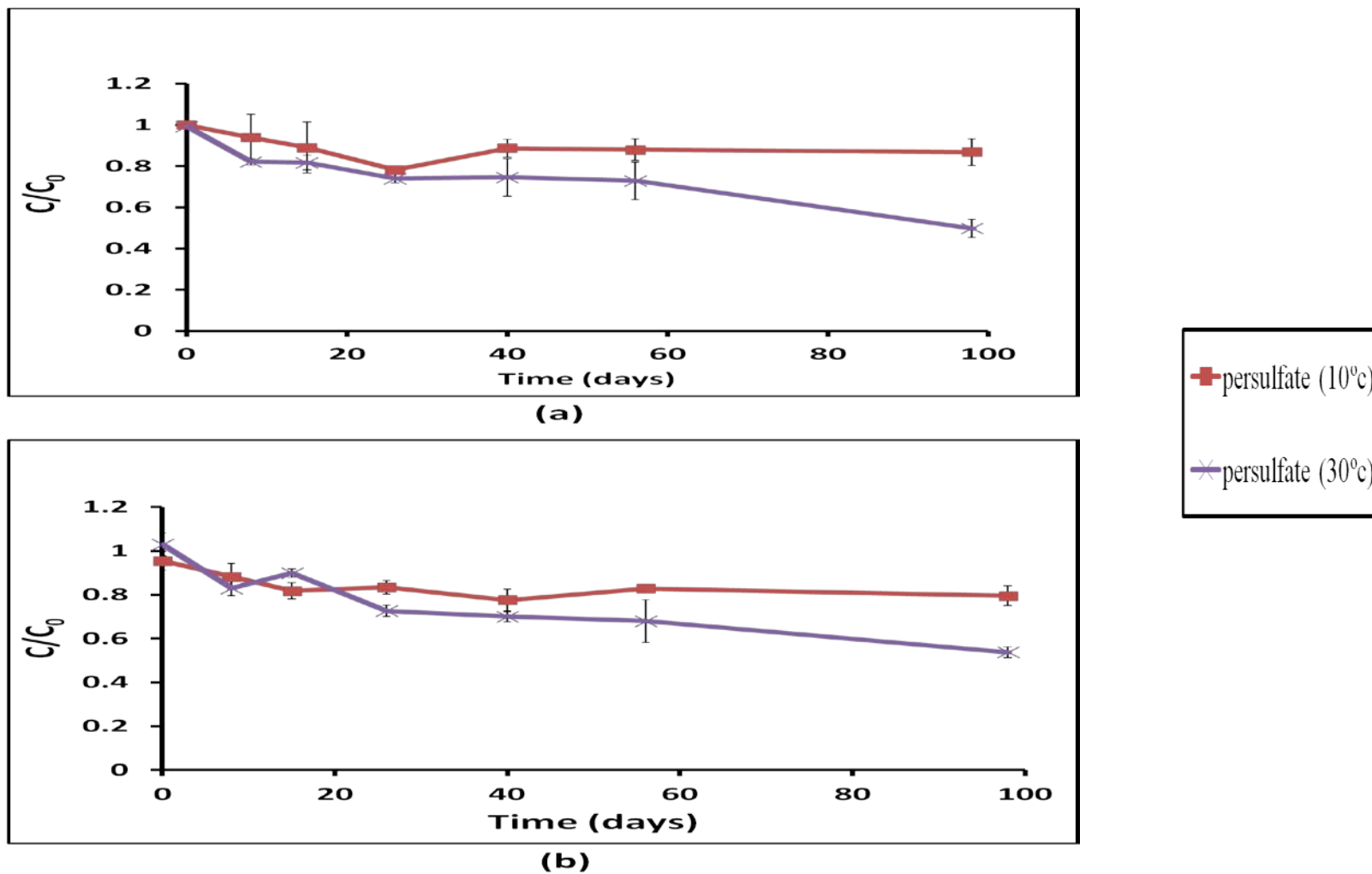
Figure 3.2 The concentration of the residual PS in both (a) non-activated PS and (b) alkaline-activated PS experiments of oxidizing TPH at (10⁰C and 30⁰C).
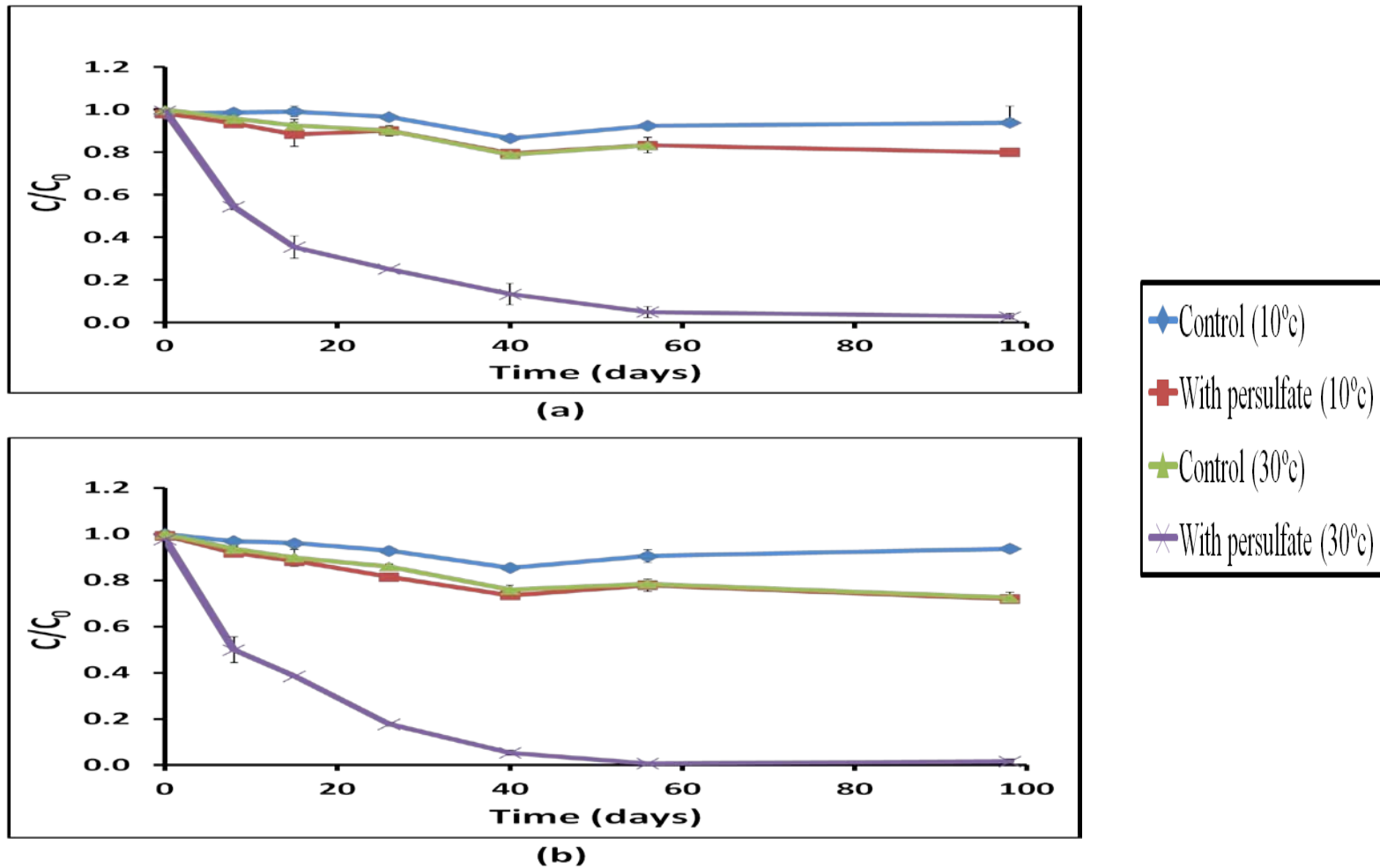
Figure 3.3 The effect of temperature (10⁰C vs. 30⁰C) settings on the oxidations of F1 by (a) non-activated PS and (b) alkaline-activated PS. The figure illustrates the change in concentrations during the 98 days of the oxidation experiments.

Table 3.1 List of the rate constants of different VOCs observed at 10⁰C and 30⁰C after the 98 days oxidation experiments with non-activated and alkaline-activated PS

Compound	PS condition	Temperature (°C)	Initial pH	Final pH	Initial concentration (μg/L)	Final concentration (μg/L)	Kobs x 102 (h–1)	R²	t$_{1/2}$ (day)
Benzene	Non-activated	10	7.5	7	22339	20370	4.56	0.96	364.7
	Non-activated	30	7.5	1.5	22336	2	236.4	0.96	7.0
	Activated	10	12	10	22757	17377	17.76	0.99	93.6
	Activated	30	12	1.5	22178	4	222.48	0.98	7.5
Toluene	Non-activated	10	7.5	7	42487	32073	6.48	0.96	256.7
	Non-activated	30	7.5	1.5	42628	4	226.56	0.99	7.3
	Activated	10	12	10	43097	26985	23.28	0.98	71.4
	Activated	30	12	1.5	42729	5	221.28	0.97	7.5
Ethylbenzene	Non-activated	10	7.5	7	3663	2705	6.72	0.94	247.5
	Non-activated	30	7.5	1.5	3688	328	312.72	0.99	5.3
	Activated	10	12	10	3722	2210	11.52	0.94	144.4
	Activated	30	12	1.5	3701	223	62.16	0.95	26.8
P,M-xylene	Non-activated	10	7.5	7	10112	6085	12.24	0.99	135.9
	Non-activated	30	7.5	1.5	10181	0	377.04	0.99	4.4
	Activated	10	12	10	10270	5856	12.96	0.98	128.3
	Activated	30	12	1.5	10223	1	215.76	0.99	7.7
O-xylene	Non-activated	10	7.5	7	6208	4371	8.64	0.99	192.5
	Non-activated	30	7.5	1.5	6260	11	150.72	0.99	11.0
	Activated	10	12	10	6259	4224	9.12	0.98	182.4
	Activated	30	12	1.5	6235	7	164.4	0.99	10.1
1,3,5-Trimethyl-Benzene	Non-activated	10	7.5	7	456	144	28.56	0.99	58.2
	Non-activated	30	7.5	1.5	461	0	264.48	0.94	6.3
	Activated	10	12	10	457	179	22.56	0.99	73.7
	Activated	30	12	1.5	455	1	142.08	0.97	11.7
1,2,4-Trimethyl-Benzene	Non-activated	10	7.5	7	1927	1385	7.92	0.99	210.0
	Non-activated	30	7.5	1.5	1947	1	185.28	0.99	9.0
	Activated	10	12	10	1956	1184	11.52	0.95	144.4
	Activated	30	12	1.5	1949	2	166.32	0.99	10.0
1,2,3-Trimethyl-Benzene	Non-activated	10	7.5	7	533	291	15.12	0.99	110.0
	Non-activated	30	7.5	1.5	539	3	274.8	0.98	6.1
	Activated	10	12	10	539	334	11.04	0.98	150.7
	Activated	30	12	1.5	536	1	156	0.99	10.7
Naphthalene	Non-activated	10	7.5	7	327	241	7.44	0.99	223.5
	Non-activated	30	7.5	1.5	332	1	161.52	0.99	10.3
	Activated	10	12	10	332	158	18	0.99	92.4
	Activated	30	12	1.5	330	0	259.68	0.98	6.4

3.2 The Effect of Persulfate Concentration in the Oxidation of Petroleum Contaminants by Persulfate in Saline Environment

In general, reaction rates are concentration dependent. This is due to the large increase in the number of high energy collisions for the reaction (Tyagi, 2009). Moreover, the production rate of free radicals can be enhanced by increasing the oxidant concentration (Huang et al., 2002). Therefore, a higher rate of free radicals generation would be expected in a system with a relatively higher PS concentration of (100 g/L) than a system with PS concentration of (20 g/L). This apparently would result in a higher rate of oxidation for the contaminant.

Figure 3.4 (a & b) illustrates the influence of increasing the initial PS concentration from 20 g/L to 100 g/L on the oxidation of (TPH). Higher oxidation rate of TPH at higher PS concentration was observed in all experiments.

Control reactors that contain only dissolved gasoline components demonstrated insignificant loss of any monitored gasoline compounds or TPH. In contrast, the results from reactors that contained PS showed large losses of most target contaminants. However, the oxidation rate of the target contaminants was considerably increased by increasing PS concentration from 20 to 100 g/L.

3.2.1 Oxidation with Non-Activated Persulfate

At a constant temperature, higher oxidation rate of the total organic compounds was observed with increasing initial concentration of non-activated PS. For instance, at a constant temperature of 10°C, increasing PS concentration from 20 to 100 g/L was responsible for enhancing the total oxidation of contaminants from 17% to 62% during the 98 days period (**Figure 3.4 (a)**). Moreover, the effect of increasing PS concentration was enhanced at the higher constant temperature (30°C). This led to almost total oxidation of the target contaminants (**Figure 3.4 (b)**). This enhancement in the oxidation rates could be explained by the increase of both the concentration of oxidant and the temperature (Huang et al., 2002). This result is in agreement with a study done by Navarro et al. (2007) where

temperature and PS concentration were reported to significantly accelerate 1,4 dioxane oxidation. The fast release of reactive free radicals may cause them to be scavenged by the existing ions (e.g. chloride and bromide ions) in the water. The positive aspect of this process could the production of free halogen radicals that will also oxidize the target contaminants. However, the negative side of this process is the fact that this might end up producing toxic gases (e.g. Cl_2, Br_2). A pale brown gas with a bleach smell was observed, most likely bromine gas, in the reactor with 100 g/L of PS at 30°C. However, further analysis is required to accurately identify the produced gases in the reactor cells. Thus, controlling concentration and temperature is essential to maximize the effectiveness of radicals, especially when radical scavengers are present in groundwater at high concentrations.

3.2.2 Oxidation with Alkaline-Activated Persulfate

In this case, increasing the initial PS concentration from 20 to 100 g/L enhanced the rate of oxidation for the target contaminants by alkaline-activated PS.

In a constant low temperature system at 10° C, increasing the initial PS concentration dramatically increased the oxidation rate of the organic compounds. For instance, the addition of 100 g/L of PS resulted in a total oxidation for the organic compounds in almost 56 days. In contrast, only 29% of the total contaminants were oxidized over the 98 days period when lower concentrations (20 g/L) of alkaline-activated PS were used (**Figure 3.5 (a)**). Similar but more pronounced results were observed in a constant high temperature system 30° C. While it took 40 days for the organic compounds to be fully oxidized when low concentrations (20 g/L) of PS were added, full oxidation was achieved in less than one week when higher concentrations (100 g/L) of PS was used (**Figure 3.5 (b)**).

The pH of the solutions in all experiments decreased from the initial pH values due to the generation of H^+ during PS decomposition (Eq. 3). As expected, decreased in the pH levels and larger decomposition rates of PS were observed to be associated with increasing the concentrations of PS in the experiments as demonstrated in **Figures 3.6 & 3.7**. This is due to the larger generation of H^+ ions during the oxidation of the contaminants at the high PS concentration settings (Eq. 25). The significant decrease of pH to ≤ 3 caused the PS to decompose much faster presumably through the acid-catalyzed reaction (Eq. 4).

During the batch experiment at low PS concentrations (20 g/L), the pH was initially ≈ 12. Throughout the experiment, the pH was deliberately uncontrolled to avoid the expected scavenging reaction by carbonate at high pH values that was observed in the preliminary experiment. On the other hand, for the high PS concentration (100 g/L) experiment, the pH was monitored and maintained between 10 and 12 by adding sodium hydroxide during sampling. This experiment was conducted to investigate the ability of high PS concentrations in reducing the expected scavenging reaction by carbonate species at high pH. Controlling pH was achieved by regularly adding NaOH through Mininert valve caps during the sampling points. This technique was successful in a system with a low temperature of 10°C. However, controlling the pH at 30°C was not successful as the pH dropped rapidly from pH ≈ 12 to pH ≈ 3 in the first three days of the experiment and before the first sampling point was performed. This result indicated that most of the oxidation of the contaminants in this particular condition occurred in a neutral and acidic pH.

Precipitations of calcium hydroxide were observed during the alkaline-activated PS which might undervalue the use of alkaline activation in this particular groundwater setting. These Precipitates are most likely the results of the reaction between sodium hydroxide and calcium carbonate as shown in Eq. 26. Further to that, a pale brown gas with a bleach smell was also observed during this experiment suggesting the formation of toxic gases such as Br_2 gas. The high concentration of PS could be the reason behind the formation of bromine gases, because the increase of PS concentrations amplified the chances for more collision between these reactive radicals and other inorganic species (e.g. chloride, bromide) as described in Eq. 19.

In general, the data for the oxidation by PS for each compound exhibited a good fit to a pseudo-first-order model by exponential regression analysis (**Tables 3.2 & 3.3**). The observed pseudo-first-order rate constants (k_{obs}) were found to increase with the increase of PS concentrations.

3.2.3 Impact on Bulk PHC Fractions

All control reactors demonstrated insignificant oxidation of F1 over the experiment period. Similar results were observed at a constant temperature system of 10°C when 20 g/L of PS was used in both

non-activated and alkaline-activated settings. In contrast, gradual decreases in F1 concentrations were observed when 100 g/L of PS was used in both non-activated and alkaline-activated settings at $10^{\circ}C$ (**Figure 3.8 (a) & 3.9 (a))**, respectively. The trend of decreasing F1 with increasing the concentration of PS was much more pronounced in the high temperature system $30^{\circ}C$ (**Figure 3.8 (b) & 3.9 (b))**. This result indicated that both increasing temperature and PS concentration were responsible for increasing the production rate of free radicals which enhanced the total F1 oxidation. In general, highest oxidation rate of F1 was observed in alkaline-activated PS at high PS concentrations (100 g/L).
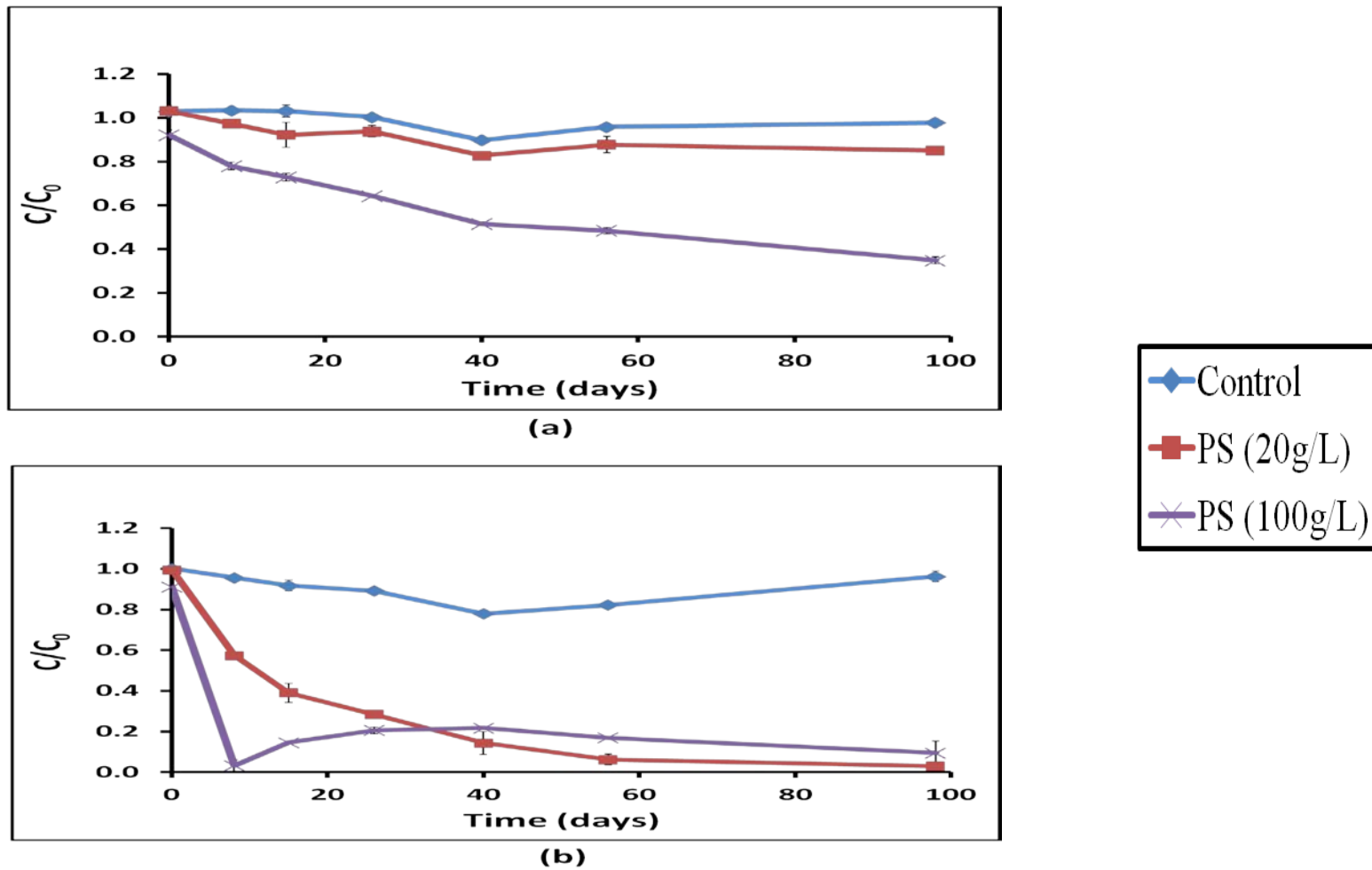
Figure 3.4 The effect of increasing the concentration of non-activated PS from 20 to 100 g/L on the oxidation of (TPH). The figures above show the change of concentrations during the 98 days of the oxidation experiments at (a) 10⁰C and (b) 30⁰C.

Figure 3.5 The effect of increasing the concentration of alkaline-activated PS from 20 to 100 g/L on the oxidation of (TPH). The two figures illustrate the change in concentration of TPH during the 98 days of the oxidation experiments at (a) 10⁰C and (b) 30⁰C.

Figure 3.6 The effect of increasing the concentration from 20 to 100 g/L on the decomposition rate of non-activated PS at (a) 10⁰C and (b) 30⁰C.
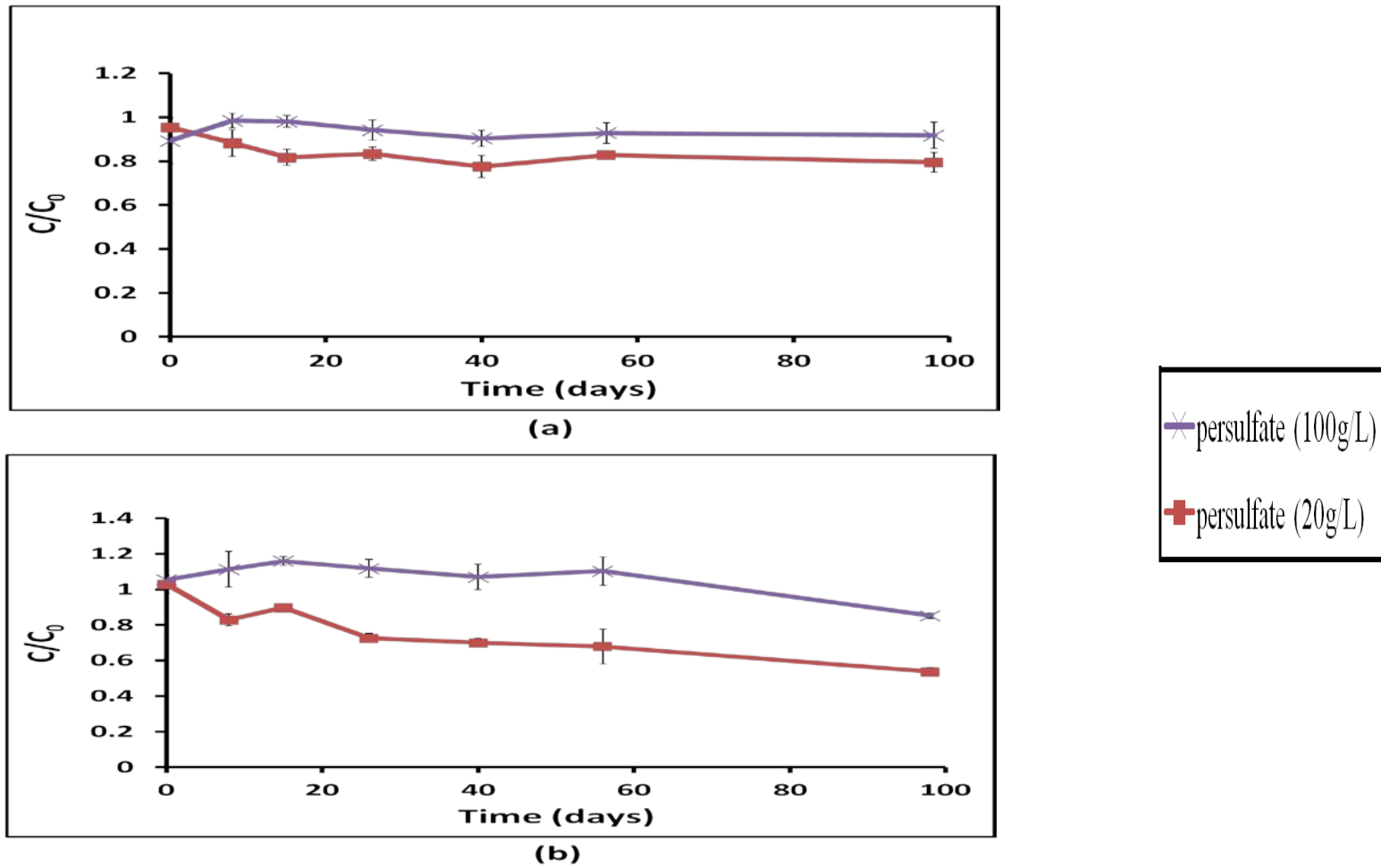
Figure 3.7 The effect of increasing the concentration from 20 to 100 g/L on the decomposition rate of alkaline-activated PS at (a) 10⁰C and (b) 30⁰C.
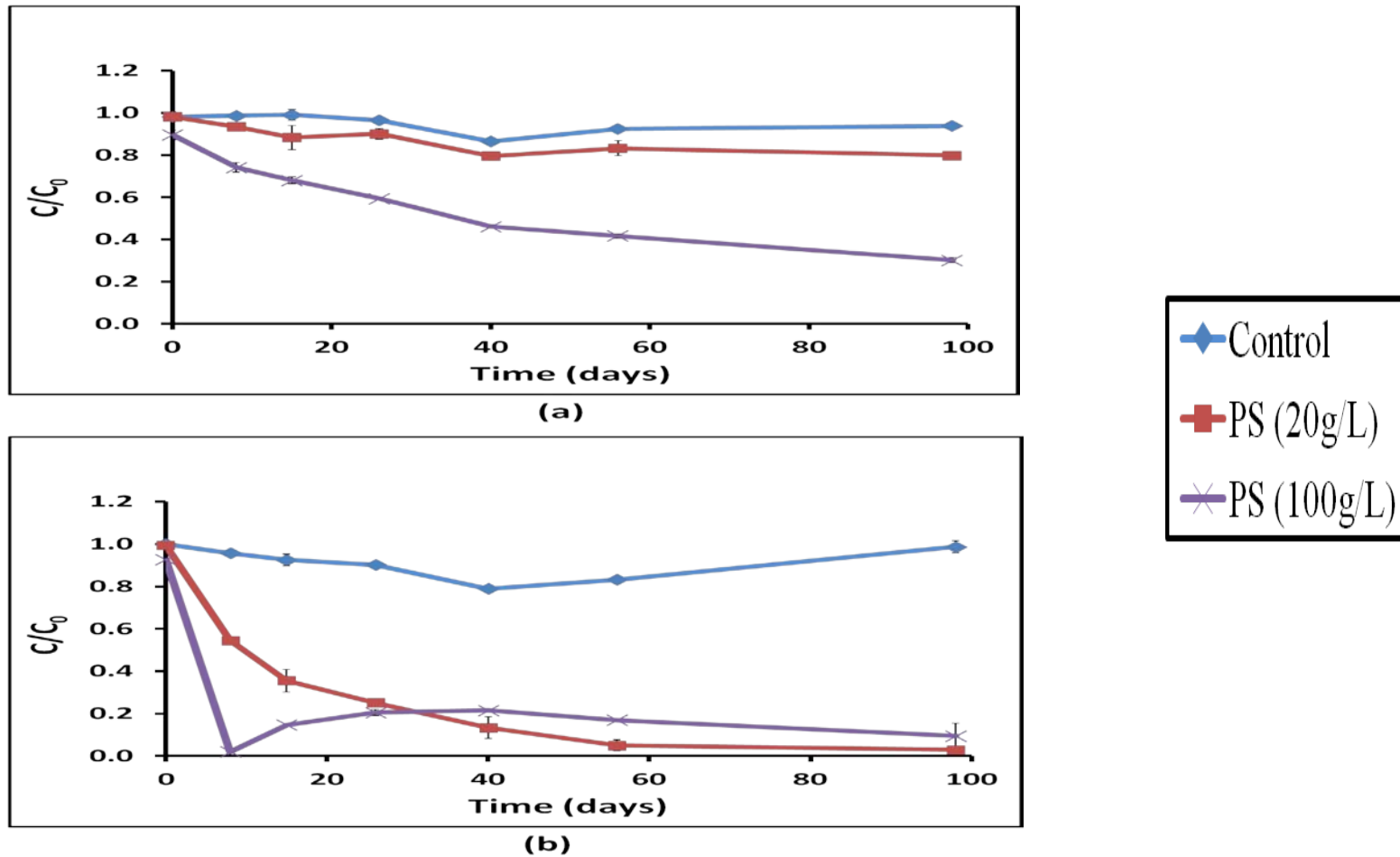
Figure 3.8 The effect of increasing the concentration of non-activated PS from 20 to 100 g/L on the oxidation of (F1). The above figures show the change of concentrations of F1 during the 98 days of the oxidation experiments at (a) 10⁰C and (b) 30⁰C.

Figure 3.9 The effect of increasing the concentration of alkaline-activated PS from 20 to 100 g/L on the oxidation of (F1). The figures illustrate the change in F1 concentrations over the 98 days of the oxidation experiments at (a) 10°C and (b) 30°C.

Table 3.2 List of the rate constants of different VOCs observed at (10⁰C) with different PS concentrations (20 g/L and 100 g/L) after the 98 days of the oxidation experiments by non-activated and alkaline-activated PS.

Compound	PS condition	PS concentration (g/L)	Initial pH	Final pH	Initial concentration (µg/L)	Final concentration (µg/L)	Kobs x 102 (h-1)	R^2	$t_{1/2}$ (day)
Benzene	Non-activated	20	7.5	7	22339	20370	4.56	0.97	364.7
	Non-activated	100	7.5	5.8	20167	14822	6.96	0.97	239.0
	Activated	20	12	10	22757	17377	6	0.94	277.2
	Activated	100	12	10.5	19983	2045	104.88	0.97	15.9
Toluene	Non-activated	20	7.5	7	42487	32073	6.48	0.97	256.7
	Non-activated	100	7.5	7	37063	305	120.48	0.95	13.8
	Activated	20	7.5	5.8	43097	26985	10.56	0.95	157.5
	Activated	100	12	10	36893	107	170.4	0.96	9.8
Ethylbenzene	Non-activated	20	12	10.5	3663	2705	6.72	0.94	247.5
	Non-activated	100	7.5	7	3254	13	142.8	0.94	11.6
	Activated	20	7.5	7	3722	2210	11.52	0.95	144.4
	Activated	100	7.5	5.8	3253	52	180.72	0.96	9.2
P,M-xylene	Non-activated	20	12	10	10112	6085	12.24	0.99	135.9
	Non-activated	100	12	10.5	9219	23	149.28	0.99	11.1
	Activated	20	7.5	7	10270	5856	12.96	0.98	128.3
	Activated	100	7.5	7	9352	16	371.28	0.93	4.5
O-xylene	Non-activated	20	7.5	5.8	6208	4371	8.64	0.99	192.5
	Non-activated	100	12	10	5619	20	137.28	0.97	12.1
	Activated	20	12	10.5	6259	4224	8.64	0.94	192.5
	Activated	100	7.5	7	5615	25	392.88	0.96	4.2
1,3,5-Trimethyl-Benzene	Non-activated	20	7.5	7	456	144	28.8	0.99	57.8
	Non-activated	100	7.5	5.8	416	9	299.28	0.99	5.6
	Activated	20	12	10	457	179	22.32	0.98	74.5
	Activated	100	12	10.5	423	0	261.12	0.97	6.4
1,2,4-Trimethyl-Benzene	Non-activated	20	7.5	7	1927	1385	7.92	0.99	210.0
	Non-activated	100	7.5	7	1859	1	190.8	0.99	8.7
	Activated	20	7.5	5.8	1956	1184	11.52	0.96	144.4
	Activated	100	12	10	1860	0	13.2	0.94	126.0
1,2,3-Trimethyl-Benzene	Non-activated	20	12	10.5	533	291	15.12	0.99	110.0
	Non-activated	100	7.5	7	488	0	246.24	0.97	6.8
	Activated	20	7.5	7	539	334	10.8	0.97	154.0
	Activated	100	7.5	5.8	486	0	915.84	0.95	1.8
Naphthalene	Non-activated	20	12	10	327	241	7.44	0.99	223.5
	Non-activated	100	12	10.5	290	0	326.88	0.96	5.1
	Activated	20	7.5	7	332	158	17.04	0.98	97.6
	Activated	100	7.5	7	288	0	256.8	0.93	6.5

Table 3.3 List of the rate constants of different VOCs observed at (30⁰C) with different PS concentrations (20 g/L and 100 g/L) after the 98 days of the oxidation experiments by non-activated and alkaline-activated PS.

Compound	PS condition	PS concentration (g/L)	Initial pH	Final pH	Initial concentration (µg/L)	Final concentration (µg/L)	Kobs x 102 (h-1)	R²	$t_{1/2}$ (day)
Benzene	Non-activated	20	7.5	1.5	22336	2	236.4	0.97	7.0
	Non-activated	100	7.5	1	20938	4	1113.36	0.99	1.5
	Activated	20	12	1.5	22178	4	241.68	0.94	6.9
	Activated	100	12	3	19849	8	1908.24	0.99	0.9
Toluene	Non-activated	20	7.5	1.5	42628	4	531.84	0.97	3.1
	Non-activated	100	7.5	1	38018	10	2208	0.99	0.8
	Activated	20	12	1.5	42729	5	506.88	0.95	3.3
	Activated	100	12	3	35931	2	29997.6	0.99	0.1
Ethylbenzene	Non-activated	20	7.5	1.5	3688	328	401.76	0.99	4.1
	Non-activated	100	7.5	1	3324	2941	2.88	0.99	577.5
	Activated	20	12	1.5	3701	223	397.2	0.94	4.2
	Activated	100	12	3	3150	5127	1940.64	0.99	0.9
P,M-xylene	Non-activated	20	7.5	1.5	10181	0	597.6	0.97	2.8
	Non-activated	100	7.5	1	9353	0	2194.32	0.99	0.8
	Activated	20	12	1.5	10223	1	612.24	0.97	2.7
	Activated	100	12	3	9049	0	2733.12	0.99	0.6
O-xylene	Non-activated	20	7.5	1.5	6260	11	515.52	0.97	3.2
	Non-activated	100	7.5	1	5727	64	137.28	0.97	12.1
	Activated	20	12	1.5	6235	7	492.24	0.97	3.4
	Activated	100	12	3	5454	108	2205.6	0.99	0.8
1,3,5-Trimethyl-Benzene	Non-activated	20	7.5	1.5	461	0	588	0.97	2.8
	Non-activated	100	7.5	1	418	0	1810.32	0.99	0.9
	Activated	20	12	1.5	455	1	686.88	0.95	2.4
	Activated	100	12	3	403	0	1799.52	0.99	0.9
1,2,4-Trimethyl-Benzene	Non-activated	20	7.5	1.5	1947	1	839.52	0.95	2.0
	Non-activated	100	7.5	1	1892	8	1734.96	0.99	1.0
	Activated	20	12	1.5	1949	2	691.2	0.96	2.4
	Activated	100	12	3	1795	6	2247.84	0.99	0.7
1,2,3-Trimethyl-Benzene	Non-activated	20	7.5	1.5	539	3	664.32	0.98	2.5
	Non-activated	100	7.5	1	494	26	3933.12	0.99	0.4
	Activated	20	12	1.5	536	1	331.44	0.98	5.0
	Activated	100	12	3	468	108	1844.4	0.99	0.9
Naphthalene	Non-activated	20	7.5	1.5	332	1	588.72	0.95	2.8
	Non-activated	100	7.5	1	298	0	1709.28	0.99	1.0
	Activated	20	12	1.5	330	0	151.2	0.98	11.0
	Activated	100	12	3	278	0	1688.64	0.99	1.0

3.3 Conclusion and Suggestions

Three important aspects were examined during this laboratory study: 1) the effect of activation (alkaline activation) of PS on the effectiveness of PS as a chemical oxidation agent; 2) investigating the effect of different temperatures (10°C versus 30°C) on the reactivity of PS; and 3) examining the effect of different PS concentrations (20 versus 100 g/L) on the oxidation rates by PS on selected organic contaminants.

The results showed the high potential of PS to oxidize the target contaminants under certain conditions. In general, the alkaline-activation of PS has demonstrated an enhancement of the oxidation capabilities of PS on the target contaminants when compared with the potential of the non-activated PS. However, precipitations of calcium hydroxide that observed during this experiment, which are believed to be caused by the reaction between sodium hydroxide and calcium carbonate, will undervalue the use of alkaline-activated PS in this particular groundwater setting. Moreover, increasing the concentration of PS was not favored in all experimental conditions. This is due to the accumulation of solid precipitations as well as the production of pale brown gases, most likely Br_2, as products of the reactions between the free radicals and the presence of high concentrations of inorganic species (e.g., bromide) in this specific water sample that was used for the experiment.

The results also showed that both the initial concentration of PS and the system temperature can play important roles in the reactivity of PS. For instance, the oxidation rate of the target contaminants was observed to increase dramatically by increasing the concentration of PS from 20 to 100 g/L. Similarly, the oxidation rate coefficients increased by increasing the system temperature from 10°C to 30°C. These results demonstrated that the effect of PS on oxidizing the target contaminants is a site specific and can vary from one site to another based on the chemical characteristics of the groundwater as well as the temperature of the groundwater in the site. Therefore, in the systems where the groundwater temperature is naturally elevated, the application of PS will naturally enhance and increasing the PS concentration will further enhance and speed up the oxidation process. On the other hand, utilizing PS as an oxidation agent in low temperature system in an effective way might require both enhancements (thermal and high concentrations) in order to achieve the same yield as the scenario in elevated temperature aquifers.

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The decrease of the system's pH was very helpful in avoiding the expected scavenging action of free radicals by carbonate species at alkaline pH, which resulted in a greater oxidation rate for all compounds. Moreover, the effect of the expected scavenging of radicals at acidic pH by Cl^- and Br^- in all experiments conditions was minimized perhaps due to the production of free halogen radicals that contributed in oxidizing the target compounds as well.

Chapter 4

Monitoring Oxidation of BTEX by Persulfate in Groundwater Using Stable Isotopes

Overview:

In this study, bench top batch experiments were carried out to investigate the roles that carbon and hydrogen isotope analyses can play in the assessment of the effectiveness of persulfate as an oxidation agent to remediate petroleum hydrocarbons in saline environments at elevated groundwater temperature.

The chemical oxidation of Benzene, Toluene, Ethylbenzene, ρ-Xylenes and o-Xylenes by non-activated PS at 30ºC, was accompanied by significant carbon isotope fractionations with isotope enrichment factors of -2.0‰, -1.6‰, -1.6‰, -0.6‰ and -1.4‰, respectively. Similar results were observed when alkaline-activated PS was used with carbon enrichment factors of -2.0‰, -1.2‰, -1.1‰, -0.4‰ and -1.3‰, respectively.

In contrast, the chemical oxidation by PS was associated with insignificant hydrogen isotope fractionations, when it is compared to the average hydrogen fractionations during transformations by other chemical or biochemical processes, with isotope enrichment factors of -10.9‰, -6.6‰, -2.5‰, -5.6‰ and -9.4‰ for Benzene, Toluene, Ethylbenzene, ρ-Xylenes and o-Xylenes, respectively. Similar results were observed when alkaline-activated PS was utilized with hydrogen enrichment factors of -10.6‰, -6.4‰, -2.1‰, -7.4‰ and -7.1‰, respectively.

Two-dimensional isotope fractionations were also calculated and ʌ values were obtained in non-activated PS experiment were 5.5, 4.1, 1.6, 9.3, and 6.7 for Benzene, Toluene, Ethylbenzene, ρ-Xylene and o-Xylene, respectively. Nearly identical results were observed with the alkaline-activated PS experiment were the ʌ values were 5.3, 5.3, 1.9, 18.5, and 5.5, respectively. The data obtained in these experiments demonstrated the potential of utilizing the two-dimensional isotope analyses to assess the transformation pathway and to show the differences in the isotope fractionations when compounds undergoes chemical oxidation or biodegradation.

4.1 Introduction

Due to the widespread use of petroleum products, the soluble, mobile and toxic monoaromatics Benzene, Toluene, Ethylbenzene, and Xylenes (BTEX), has become contaminants of major concern in groundwater. For example this group can make up to 18% (w/w) in a standard gasoline blend (Christensen et al., 1996). As the result of terrestrial oil spills and leaking underground storage tanks, contamination of shallow aquifers by these chemicals has become a serious environmental problem. Research and development over the last three decades have led to various subsurface remediation or controlling strategies such as: 1) containment of contaminated zones (e.g., concrete or slurry walls), 2) ex-situ treatment (e.g., excavation), 3) natural attenuation, and 4) in-situ treatment (e.g., in-situ bioremediation, chemical oxidation) (Domenico and Schwartz, 1998).

The application of in-situ chemical oxidation (ISCO) as a remediation method of subsurface organic contaminants is still relatively new. Over the last 10 years, there has been significant research and development in ISCO for the remediation of organic contaminants (e.g. Hood, 2000; Watts & Teel, 2006). ISCO technology involves the injection of chemical oxidants (e.g., hydrogen peroxide or Fenton's reagent, persulfate, permanganate and ozone) into the vadose or saturated zone to reduce the contaminant mass through oxidization (Masten & Davis, 1997; USEPA, 1999; Nimmer et al., 2000). In the past few decades, several aqueous oxidants have been employed to remediate petroleum hydrocarbons (e.g., Huling & Pivetz, 2006; Siegrist et al, 2006; Tsitonaki et al., 2010). One is sodium persulfate ($Na_2S_2O_8$). In addition to the advantages of having high water solubility and benign residual products, sodium persulfate (PS) is very stable and can persist in the subsurface for weeks (Huling & Pivetz, 2006). The persistence of PS in the subsurface will allow for advective, dispersive, and diffusive mechanisms to transport PS away from the injection locations to ensure greater coverage of the treatment zone (Sra et al., 2010).

However, under field conditions, concentrations of hydrocarbons can decrease due to displacement of contaminated water by the injected persulfate solution rather than oxidation of hydrocarbons. Moreover, hydrocarbon concentrations may remain elevated even though destruction occurs, due to continuous dissolution of hydrocarbons from the source zone of the light non-aqueous phase liquid (NAPL). Therefore, it is very useful to couple this study with an isotopic investigation to better understand which processes are active and how extensive the remedial reactions have been. This in

turn will help to successful use of compound specific isotope analysis (CSIA) as a monitoring tool in real life scale treatments at field sites. In this study, the isotopic fractionation factors of carbon and hydrogen that are associated with the chemical oxidation of BTEX by PS were determined.

CSIA is a technique that provides isotopic characterization of individual compounds. In recent years, the use of CSIA in groundwater contaminant studies have become a valuable methodology that is employed routinely in field studies as an indicator of chemical and biological degradations of organic contaminants in groundwater (e.g., Sturchio et al., 1998; Slater et al., 2001; Schmidt et al., 2004; Fischer et al., 2009). The study of isotopes in groundwater contaminated with organic has provided unambiguous proof of its oxidation and provided an in-situ measurement of the rate of oxidation (e.g., Hukeler et al., 2001; Morasch et al., 2002; Mancini et al., 2003; Fischer et al., 2008). In most of the ISCO studies, decreasing concentrations of parent hydrocarbons and increasing the concentration of by-products have been used as indicators of contaminant destruction. Therefore, measurements of the isotope values of organic contaminants in groundwater samples can be utilized as an additional line of evidence. For example, the stable isotope ratios of carbon ($^{13}C/^{12}C$) during oxidation are expected to show gradual ^{13}C enrichment in the remaining residues, indicating preferential oxidation of ^{12}C-enriched molecules. The measured isotope variation, which is usually reported in delta notation $\delta^{13}C$, is defined by the following equation.

$$\delta^{13}C(‰) = \left(\frac{(^{13}C/^{12}C)_{compound}}{(^{13}C/^{12}C)_{ref}} \right) - 1 \times 1000‰ \qquad (1)$$

Here, $(^{13}C/^{12}C)_{compound}$ is the isotope ratio of the organic compound, $(^{13}C/^{12}C)_{ref}$ is the isotopic ratio of the international reference material (V-PDB, Vienna Pee Dee Belemnite for carbon) and $\delta^{13}C_{compound}$ is the isotopic ratio of the specific compound in any sample. All isotopic values are reported in permil (‰) relative to an international reference material by using the delta notation (δ). Moreover, the Rayleigh equation has been employed to calculate the isotopic enrichment factor (ε), the ratio between the specified isotopic abundance and the natural abundance of that isotope. For instance, the quantification of carbon isotopic enrichment can be expressed as shown in Eq. 2.

$$1000 \ln \left(\frac{\delta^{13}C + 1000}{\delta^{13}C_0 + 1000} \right) = \left(\frac{\varepsilon}{1000} \ln f \right)$$

(2)

Where, $\delta^{13}C_0$ is the initial carbon isotopic ratio when it has not yet been degraded and $\delta^{13}C$ is the isotopic ratio after oxidation has occurred; f is the fraction of the compound remaining at this stage of oxidation and ε is the isotopic enrichment factor.

Moreover, the transformation pathways can be characterized more precisely by using a two-dimensional isotope fractionation analysis (2D-CSIA) (Elsner et al., 2005; Zwank et al., 2005; Fischer et al., 2008; 2009; Herrmann et al., 2009). Prior to the isotope-sensitive bond change, carbon and hydrogen fractionation are equally influenced by rate limitations (Elsner et al., 2005). Therefore, any rate limitations that mask the values of the kinetic isotope effect (KIE) are cancelled out and the ratio between the isotope enrichment factors for the two elements can be seen as a fingerprint of the initial bond cleavage reaction within a distinct oxidation pathway (Herrmann et al., 2009). The lambda notation (Λ) is used for the ratio between the isotope enrichment factors for the two elements (Herrmann et al., 2009). For instance, the slope of the linear regression for hydrogen ($\Delta\delta^2H$) versus carbon ($\Delta\delta^{13}C$) is given in Eq. 3. Alternatively, Λ values can be assessed by the ratio of hydrogen to carbon isotope enrichment factors.

$$(\Lambda_{bulk}) = \Delta\delta^2H \; / \; \Delta\delta^{13}C \approx \varepsilon H_{bulk} / \; \varepsilon C_{bulk}$$

(3)

4.2 Experimental

4.2.1 Materials

Reagent grade sodium persulfate ($Na_2S_2O_8$>98% -Sigma Aldrich), diluted with ultra pure water, was used for the oxidation experiments. Contaminated groundwater, used to conduct the experiments, was collected from a site in Saudi Arabia. Samples of site groundwater were analyzed by ALS laboratory

group for specific conductance, alkalinity, total dissolve solids, anion and cation content. Standard methods (APHA 1998) were employed for all analysis and characteristics of the groundwater are presented in **Table 2.1**. Groundwater samples were shipped to the laboratory on ice, then preserved with a 10% sodium azide solution (v/v) (Added 43 mL/4.3L =1 g/L) to inhibit biodegradation of organic compounds, and stored in the fridge until they were used.

4.2.2 Experimental Procedure

A laboratory batch experiment was carried out to evaluate the effectiveness of persulfate oxidation of BTEX over time. Twenty-five mL borosilicate VOA vials with PTFE septa and screw caps were employed as reaction systems. Batch reactor experiments were designed with (5 mL) headspace to accommodate any expected gas production throughout the reaction. Temperatures were maintained at $10^{\circ}C$ and $30^{\circ}C$, by using constant temperature incubators. Vials containing only contaminated groundwater were prepared and used as control samples for the experiment. Initial BTEX concentration was analyzed and the results are shown in **Table 4.1**.

Table 4.1 Initial BTEX concentrations

Compound	Concentration (mg/L)
Benzene	22
Toluene	41.1
Ethylbenzene	3.6
P-xylene	9.8
O-xylene	6.1

4.2.3 Concentration measurements

For the oxidation experiment, persulfate was added via syringe to the vials that contained contaminated groundwater. The added oxidant was calculated to achieve a final concentration of 20g/L in the reaction vials. The reactors were then capped, shaken, (to completely mix and reach equilibrium), and incubated at $10^{\circ}C$ or $30^{\circ}C$. For sampling, a ground glass syringe (with a stainless

steel syringe tip) was used and 19.0 mL was removed from the reactor vial for BTEX analyses and 0.5 mL for persulfate analyses. The analyses were performed at the Organic Chemistry Laboratory, Department of Earth and Environmental Sciences, University of Waterloo. Analyses of Benzene, Toluene, Ethylbenzene, and Xylenes (BTEX), were performed using a HP 5890 capillary gas chromatography (GC) equipped with a flame ionization detector and a HP7673A auto sampler. The GC calibration was checked with standards to verify the validity of the calibration within ± 10%. Dichloromethane (1 mL) was injected in the reactors followed by extraction and analysis as described by (Freitas & Barker (2008)). Tests were conducted in triplicate at time points 1, 8, 15, 26, 40, 56 and 98 days. One replicate was utilized for analysis of pH when required

4.2.4 Isotope analyses

Two 25 mL vials were collected for isotopic analyses and kept in the fridge until they were analyzed. Later, the samples were diluted and prepared in 40 mL vials for the isotopic analyses. Organic compounds were extracted from the vials via a head space solid phase micro extraction (SPME) and then analyzed for both compound specific carbon and hydrogen stable isotopes separately. These isotopic analyses were carried out in the Isotope Tracer Technologies Inc., Waterloo, Canada. GC/TC/IRMS and GC/C/IRMS systems were used to perform the hydrogen and carbon CSIA, respectively. The system consisted of an HP 6890 Series gas chromatograph (Agilent Technologies, Santa Clara, CA, USA) and Delta plus XL Continuous-Flow Isotope Ratio Mass Spectrometer (CF IRMS) (Thermo Finnigan, Bremen, Germany). BTEX compounds were converted to hydrogen gas for the δ^2H analyses and they were converted to CO_2 gas to perform the $\delta^{13}C$ analyses. The δ^2H values were reported relative to Vienna Standard Mean Ocean Water (VSMOW) a water standard from the International Atomic Energy Agency (IAEA, Vienna, Austria), while $\delta^{13}C$ values were reported relative to the Vienna Pee Dee Belemnite (VPDB) international standard reference material. The analytical uncertainties for $\delta^{13}C$ and δ^2H were typically below ± 0.5‰ and ±5.0‰, respectively.

4.3 Results and Discussion

4.3.1 BTEX Oxidation by Persulfate

Figures 4.1 – 4.5 show the change in concentration of BTEXs during the chemical oxidation experiment by non-activated and alkaline-activated PS. Control reactors that contained only BTEX compounds demonstrated insignificant loss of all analyzed gasoline compounds by processes other than the chemical oxidation. Moreover, similar results were obtained when PS was added to the reactors at low temperature 10ºC, while reactors that were kept at 30ºC showed the capability of the PS to oxidize the target contaminants efficiently. The reactivity of PS with the contaminants was considerably higher at the higher temperature. All of BTEX compounds decreased exponentially with time when PS was added. The high-to-low order of oxidation rates was as follows:

ρ-Xylene > Toluene > o-Xylene > Ethylbenzene > Benzene.
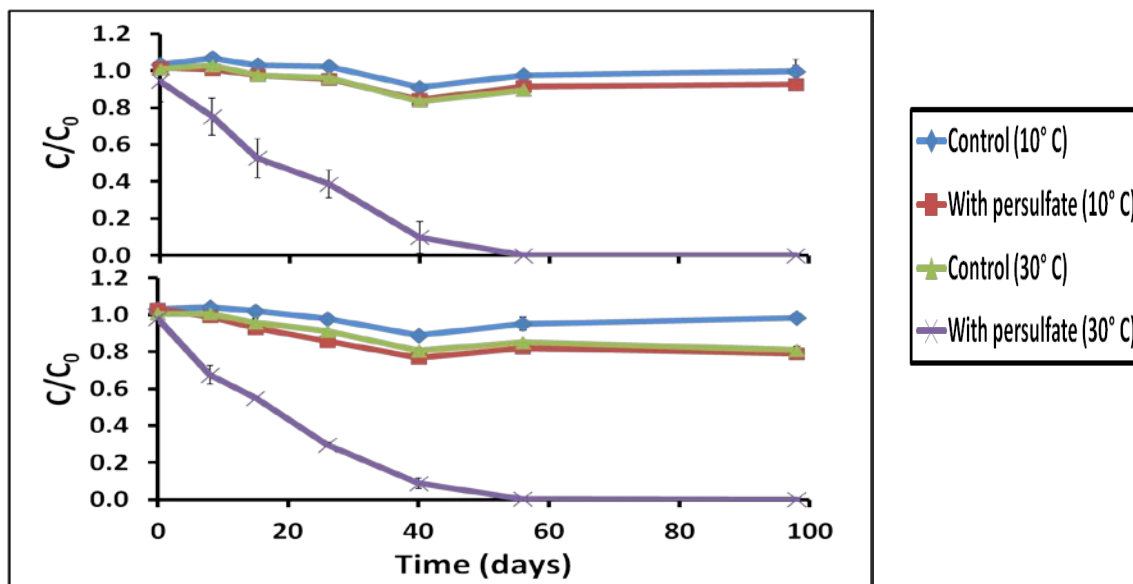
Figure 4.1 The change of concentrations vs. time of Benzene through the 98 days of the oxidation experiments. Non-activated (top) and alkaline-activated (bottom) PS.
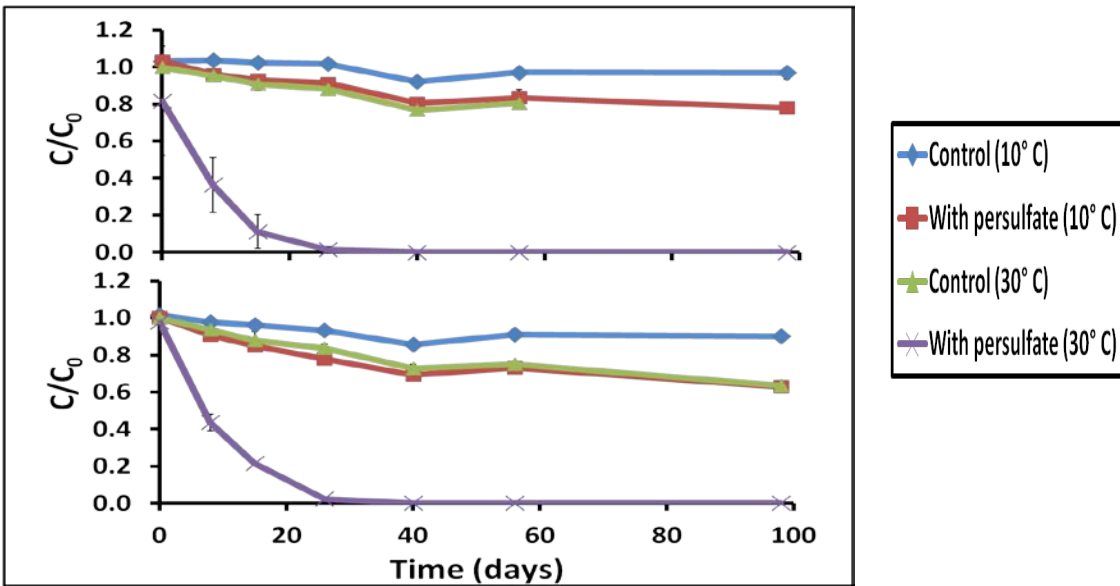
Figure 4.2 The change of concentrations vs. time of Toluene through the 98 days of the oxidation experiments. Non-activated (top) and alkaline-activated (bottom) PS.
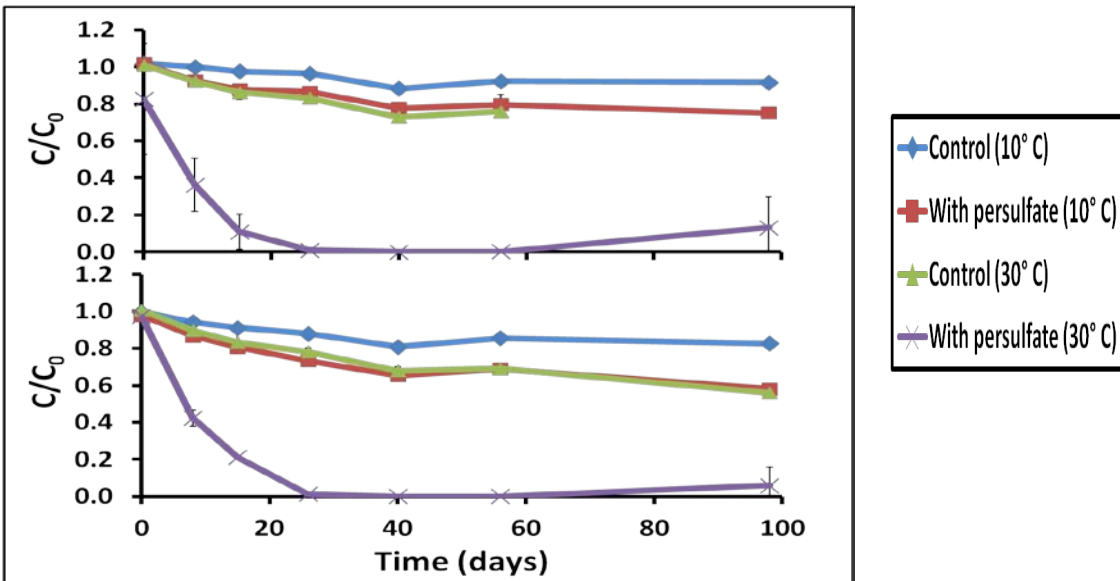
Figure 4.3 The change of concentrations vs. time results of Ethylbenzene over the 98 days of the oxidation experiments. Non-activated (top) and alkaline-activated (bottom) PS.
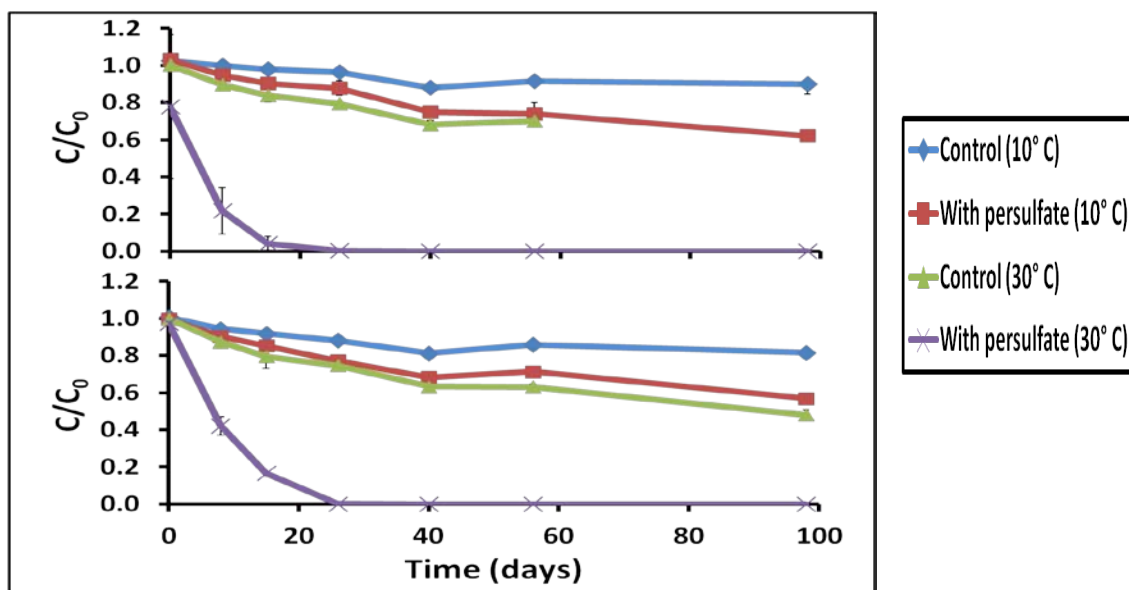
Figure 4.4 The change of concentrations vs. time of ρ-Xylene during the 98 days of the oxidation experiments with non-activated (top) and alkaline-activated (bottom) PS.
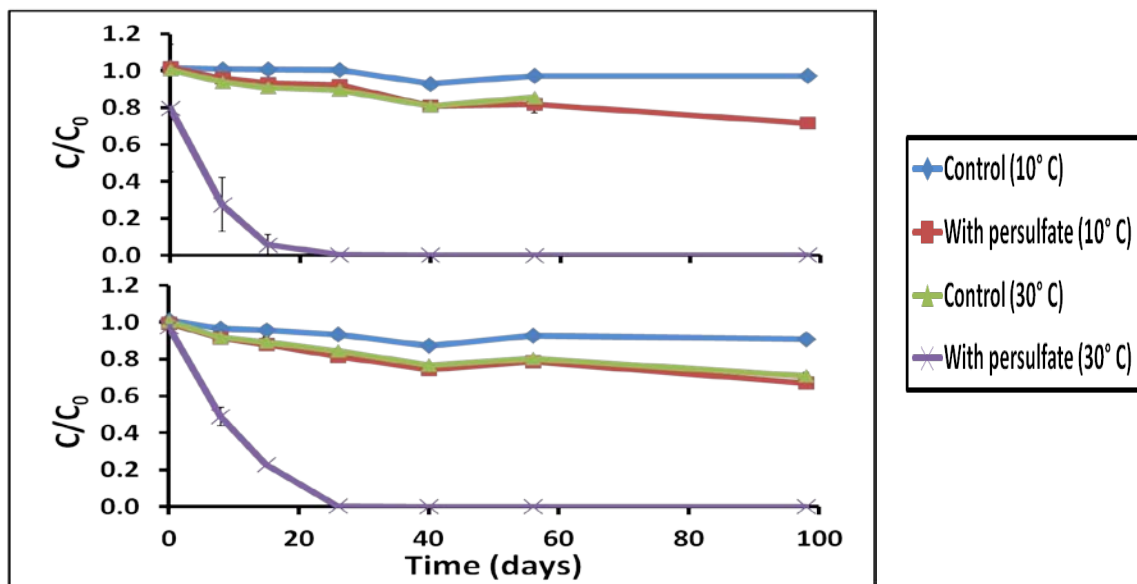
Figure 4.5 The change of concentrations vs. time of o-Xylene over the 98 days of the oxidation experiments with non-activated (top) and alkaline-activated (bottom) PS.

4.3.2 Carbon and Hydrogen Isotope Fractionation during BTEX Oxidation

Carbon isotope fractionation

The decrease of BTEX concentrations at 30°C with time was accompanied by a gradual increase of the $\delta^{13}C$ values (**Figure 4.6**). The strongest $^{13}C/^{12}C$ fractionation was detected when non-activated PS was added for *o*-Xylene with an absolute shift of $\Delta^{13}C = 7.6‰$, followed by Ethylbenzene $\Delta^{13}C = 6.4‰$. A moderate fractionation was found for Toluene $\Delta^{13}C = 5.8‰$, and Benzene $\Delta^{13}C = 5.2‰$. Smallest but still significant fractionation was observed for *p*-Xylene $\Delta^{13}C = 2.9‰$. The $^{13}C/^{12}C$ fractionation with the addition of alkaline-activated PS however was less pronounced and followed the order: Ethylbenzene $\Delta^{13}C = 4.7‰ >$ Toluene $\Delta^{13}C = 4.2‰ >$ Benzene $\Delta^{13}C = 3.3‰ >$ o-Xylene $\Delta^{13}C = 2.0‰ > \rho$-Xylene $\Delta^{13}C = 0.9‰$.

Accordingly, the gradual increase in the $\delta^{13}C$ versus time followed almost a linear trend. In general, enrichments in the $\delta^{13}C$ during the transformation of each compound were observed in all experiment conditions. The chemical oxidation of Benzene, Toluene, Ethylbenzene, ρ-Xylene and o-Xylene by non-activated PS at 30⁰C, was accompanied by significant carbon isotope fractionations with isotope enrichment factors of -2.0‰, -1.6‰, -1.6‰, -0.6‰ and -1.4‰, respectively. Similar results were observed when alkaline-activated PS was added with carbon enrichment factors of -2.0‰, -1.2‰, -1.1‰, -0.4‰ and -1.3‰, respectively.

Strong carbon isotope fractionation was also observed during the chemical oxidation of trichloroethylene (TCE), tetrachloroethylene (PCE), and cis-1,2-dichloroethylene (cDCE), when permanganate was used as an oxidant (Poulson & Narakora, 2002; Hunkeler et al., 2003). However, the significant carbon enrichment factor obtained in this study for Toluene is in contrast with the one associated with Fenton-like oxidation where a small carbon isotope enrichment factor (ε) of -0.2‰ was reported (Ahad & Slater, 2008). The differences between the results obtained from this study and the Ahad & Slater (2008) study are most likely due to the different oxidation mechanism involving sulfate radicals versus hydroxyl radicals (which are the dominant oxidants during Fenton-Like oxidation). However, the reaction mechanisms involving sulfate radicals remains uncertain (Tsitonaki et al., 2011).

Hydrogen isotope fractionation

In general, BTEX oxidation by persulfate has shown little hydrogen isotope fractionation (**Figure 4.7**). One reason for this result may be the absence of C-H bond cleavage and the breaking of C-C in the initial step during the chemical oxidation by PS.

During the chemical oxidation by non-activated PS at 30ºC, all BTEX compounds showed only a small $^2H/^1H$ shift of$\leq$ 26.6‰ (**Table 4.2**). Although these fractionations are larger than those observed for the carbon isotopes, they are relatively small when they are compared to the average hydrogen fractionation during transformation by other chemical or biochemical process. Strongest $^2H/^1H$ fractionation was observed for Toluene with an absolute shift Δ ^2H = 26.6‰, followed by Benzene Δ^2H = 18.6‰. Small fractionations were detected for o-Xylene Δ^2H = 8.9‰, and ρ-Xylene Δ^2H = 6.2‰. On the other hand, the smallest fractionation was observed for Ethylbenzene Δ^2H = 1.6‰. Similar $^2H/^1H$ fractionations were observed with the addition of alkaline-activated PS. The high-to-low order of $^2H/^1H$ shifts can be demonstrated as follows: Benzene Δ^2H = 18.7‰ > o-Xylene Δ^2H = 8.9‰ > Toluene Δ^2H = 8.1‰ > ρ-Xylene Δ^2H = 5.7‰ > Ethylbenzene Δ^2H = 1.4‰.

Consequently, the chemical oxidation of Benzene, Toluene, Ethylbenzene, ρ-Xylene and o-Xylene by non-activated PS at 30ºC, was accompanied by insignificant hydrogen isotope fractionations with isotope enrichment factors of -10.9‰, -6.6‰, -2.5‰, -5.6‰ and -9.4‰, respectively. Similar results were observed when alkaline-activated PS was added with hydrogen enrichment factors of -10.6‰, -6.4‰, -2.1‰, -7.4‰ and -7.1‰, respectively.

4.3.3 Two-dimensional Isotope Fractionation Analyses

For the 2D-CSIA approach, lambda (λ) values were calculated as the ratio of hydrogen to carbon enrichment factors ($\Lambda = \Delta\delta^2H / \Delta\delta^{13}C \approx \varepsilon H / \varepsilon C$) (Fischer et al., 2009). The resultant Λ values when non-activated PS was used are 5.5, 4.1, 1.6, 9.3, and 6.7 for Benzene, Toluene, Ethylbenzene, ρ-Xylene and o-Xylene, respectively. Nearly identical results were observed with the alkaline- activated PS and the Λ values for Benzene, Toluene, Ethylbenzene, ρ-Xylene and o-Xylene were 5.3, 5.3, 1.9, 18.5, and 5.5, respectively. In general the Λ values produced by these two different PS addition were

insignificant when compared with the uncertainties of the analytical methodologies for measuring carbon and hydrogen isotopes where (±5.0‰) for hydrogen and (±0.5‰) for carbon analyses. The only compound that showed some significant fractionation in the ∧ values between the different PS additions was ρ-Xylene. The ∧ values during the chemical oxidation of ρ-Xylene by non-activated and alkaline-activated PS at 30°C were calculated based on only one sampling point due to the lack of material (very low concentrations) for this particular compound. Thus, the experiment on this compound needs to be re-conducted on higher concentration samples and in shorter sampling intervals.

The initial step of BTEX oxidation by $SO_4^{\bullet-}$ can be suggested from the result in this study. The aromatic ring in each compound, particularly at the C-C bond, is attacked by $SO_4^{\bullet-}$ causing an electron transfer from the organic compound to the $SO_4^{\bullet-}$ as suggested in Eq. 4 (Snook & Hamilton, 1974; Chawla & Fessenden, 1975; Forsey 2004). Considering this step as the rate-determining of the reaction, large carbon isotope enrichment due to the breaking of the C-C is obtained. In contrast, an insignificant fractionation in the hydrogen enrichment is observed indicating no cleavage on the C-H has occurred in the initial step.

$$\text{(4)}$$
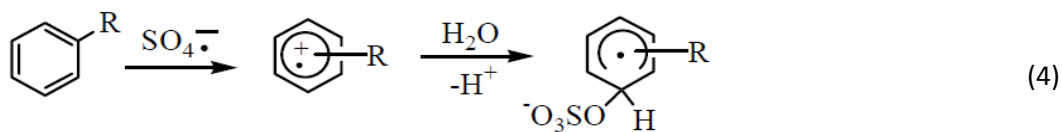
The (2D-CSIA) data obtained in this experiment was compared with other biochemical studies to show the potential of isotope effect to assess the transformation pathways (**Figures 4.8 – 4.10).** Unfortunately, for Ethylbenzene, no two dimensional data was reported in the literature to allow the comparison. In general, the hydrogen and carbon isotope fractionations during the chemical oxidation of BTEXs by PS were smaller than the isotope fractionations during other transformation processes (e.g., sulfate reduction, denitrification). This result demonstrated that chemical oxidation is a very fast process. In general, faster reaction steps show smaller isotopic fractionations than slower steps because the oxidant/organism is not selective (Hunkeler & Morasch, 2010). Moreover, the data

showed the differences and similarities in the kinetic isotope effect when a contaminant undergoes chemical oxidation, aerobic, or anaerobic transformation (**Table 4.3**). For instance, the results show that the initial reactions under chemical oxidation were associated with quite large ε_C and only a small ε_H. This result is quite similar to the isotope fractionation associated with an aromatic ring-monooxygenation (Morasch et al., 2002; Fischer et al., 2008). Moreover, similar ε_C was obtained under sulfate-reducing condition. Yet, the ε_H was observed to spread over a wide range (Ahad et al., 2000; Vogt et al., 2008), which was not observed under the chemical oxidation condition in this study. Thus, combined analyses of carbon and hydrogen isotopes may be a more robustness method to assess the transformation pathways of BTEX than measuring carbon isotopes only.
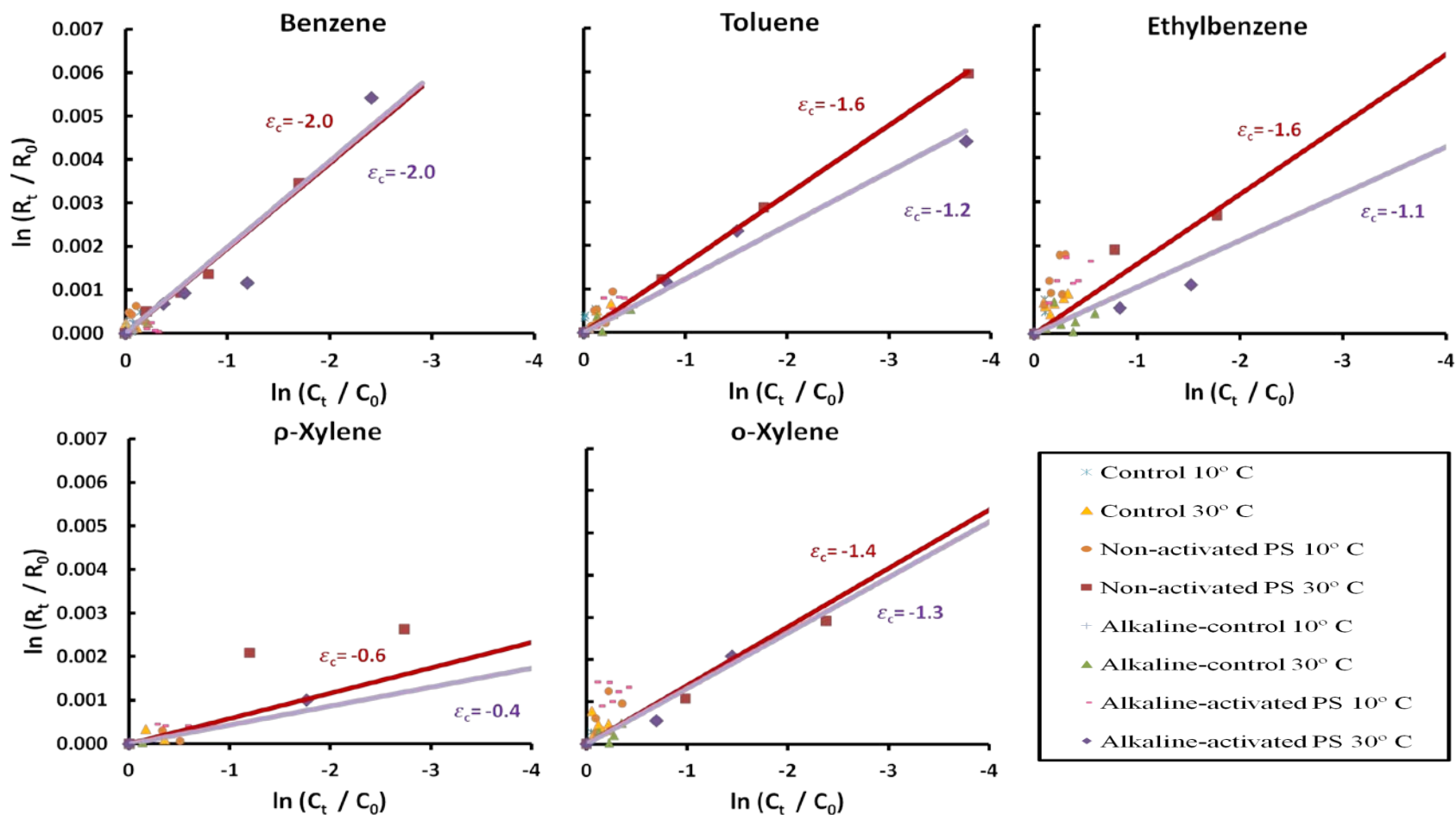
Figure 4.6 Double logarithmic plots of carbon isotopic fractionations according to the Rayleigh equation of the changes in concentrations versus the shifts in the isotopic ratios of Benzene, Toluene, Ethylbenzene, ρ-Xylene and o-Xylene. The slopes represent the calculated isotopic enrichment factors (ε).
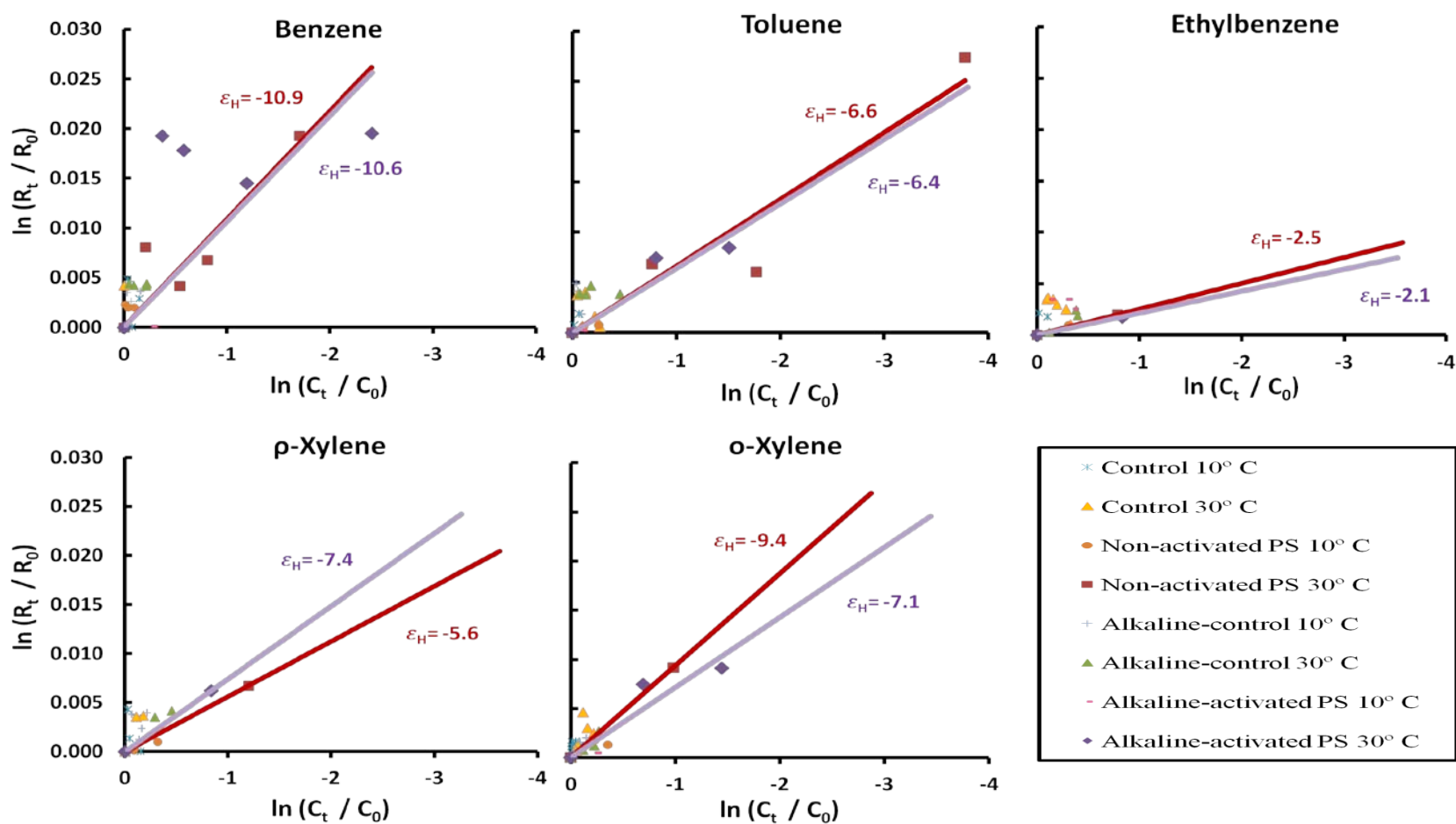
Figure 4.7 Double logarithmic plots of hydrogen isotopic fractionations according to the Rayleigh equation of the changes in concentrations versus the shifts in the isotopic ratios of Benzene, Toluene, Ethylbenzene, ρ-Xylene and o-Xylene. The slopes represent the calculated isotopic enrichment factors (ε).

Table 4.2 Carbon and hydrogen isotope fractionation values as well as enrichment factors (εC, εH) caused by chemical oxidation of BTEXs by PS.

Compounds	Persulfate condition	$\Delta^{13}C$	ε_C	Δ^2H	ε_H
Benzene	Non-activated	5.2	-2.0	18.6	-10.9
Benzene	Alkaline-activated	3.3	-2.0	18.7	-10.6
Toluene	Non-activated	5.8	-1.6	26.6	-6.6
Toluene	Alkaline-activated	4.2	-1.2	8.1	-6.4
Ethylbenzene	Non-activated	6.4	-1.6	1.6	-2.5
Ethylbenzene	Alkaline-activated	4.7	-1.1	1.4	-2.1
ρ-Xylene	Non-activated	2.9	-0.6	6.2	-5.6
ρ-Xylene	Alkaline-activated	0.9	-0.4	5.7	-7.4
o-Xylene	Non-activated	7.6	-1.4	8.9	-9.4
o-Xylene	Alkaline-activated	2.0	-1.3	8.9	-7.1

4.4 Conclusion and Suggestions

In the control reactors (i.e. no addition of PS), BTEX concentrations as well as carbon and hydrogen isotopic signatures remained stable. Similar results were obtained when PS was added to the low temperature system 10ºC, indicating that the reactivity of PS with the objective contaminants was considerably influenced by the change in temperature.

Significant carbon isotope fractionations were observed during the chemical oxidation of BTEX by PS at 30ºC. In contrast, the chemical oxidation of BTEX was accompanied by little or no hydrogen isotope fractionation. This could be due the absence of C-H bond cleavage and the presence of C-C breaking in the initial step during the chemical oxidation by PS

In general, the hydrogen and carbon isotope fractionations associated with the chemical oxidation of BTEXs by PS were smaller than the isotope fractionations during biodegradation demonstrating that chemical oxidation by PS is probably a fast process.

Moreover, the combined analyses of carbon and hydrogen isotopes showed higher potential to assess the transformation pathways of BTEXs than measuring one isotope only.
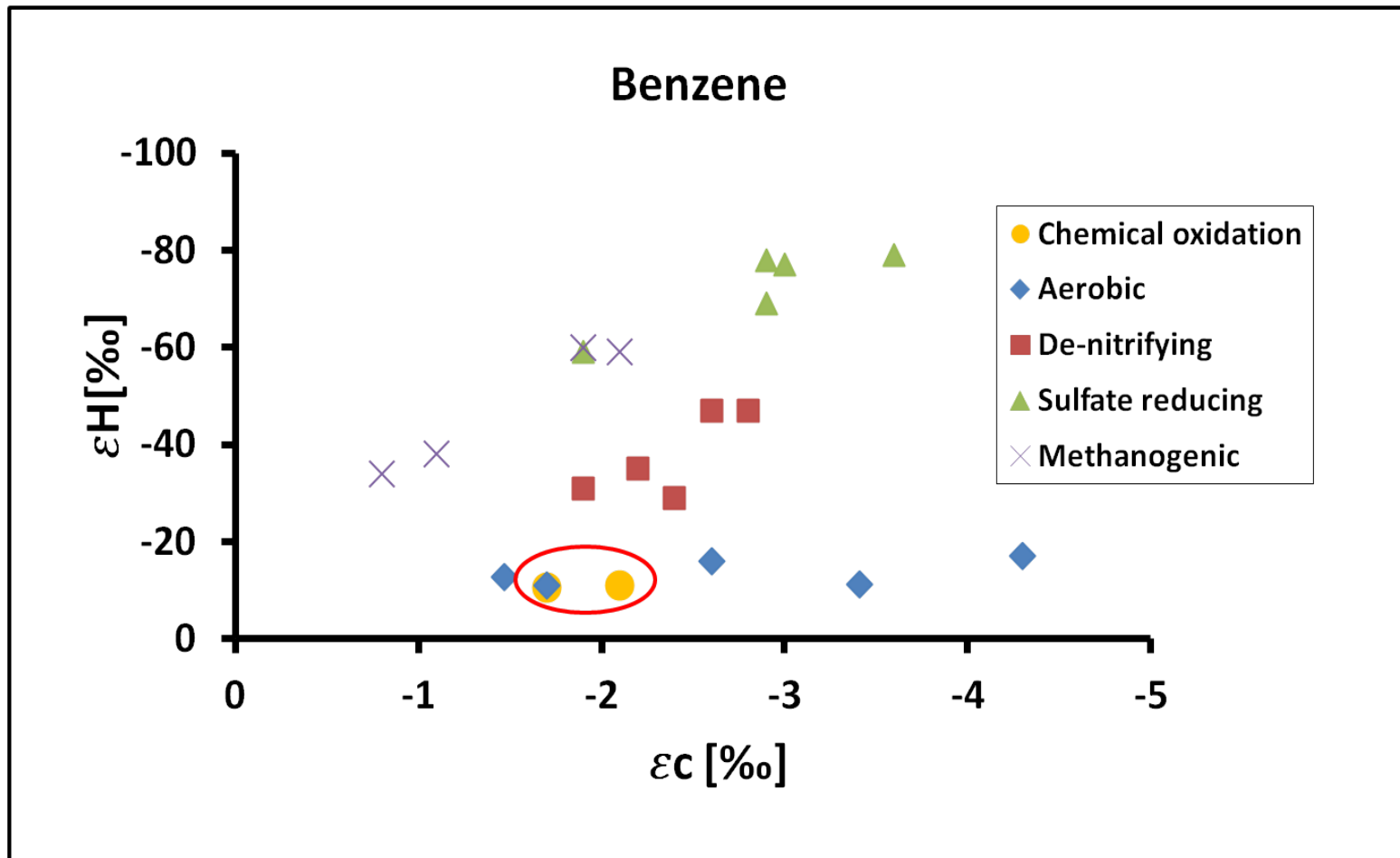
Figure 4.8 Concurrent Carbon and hydrogen enrichment factors (εC, εH) for Benzene during the chemical oxidation by PS compared with recently published values for aerobic and anaerobic degradations of Benzene.
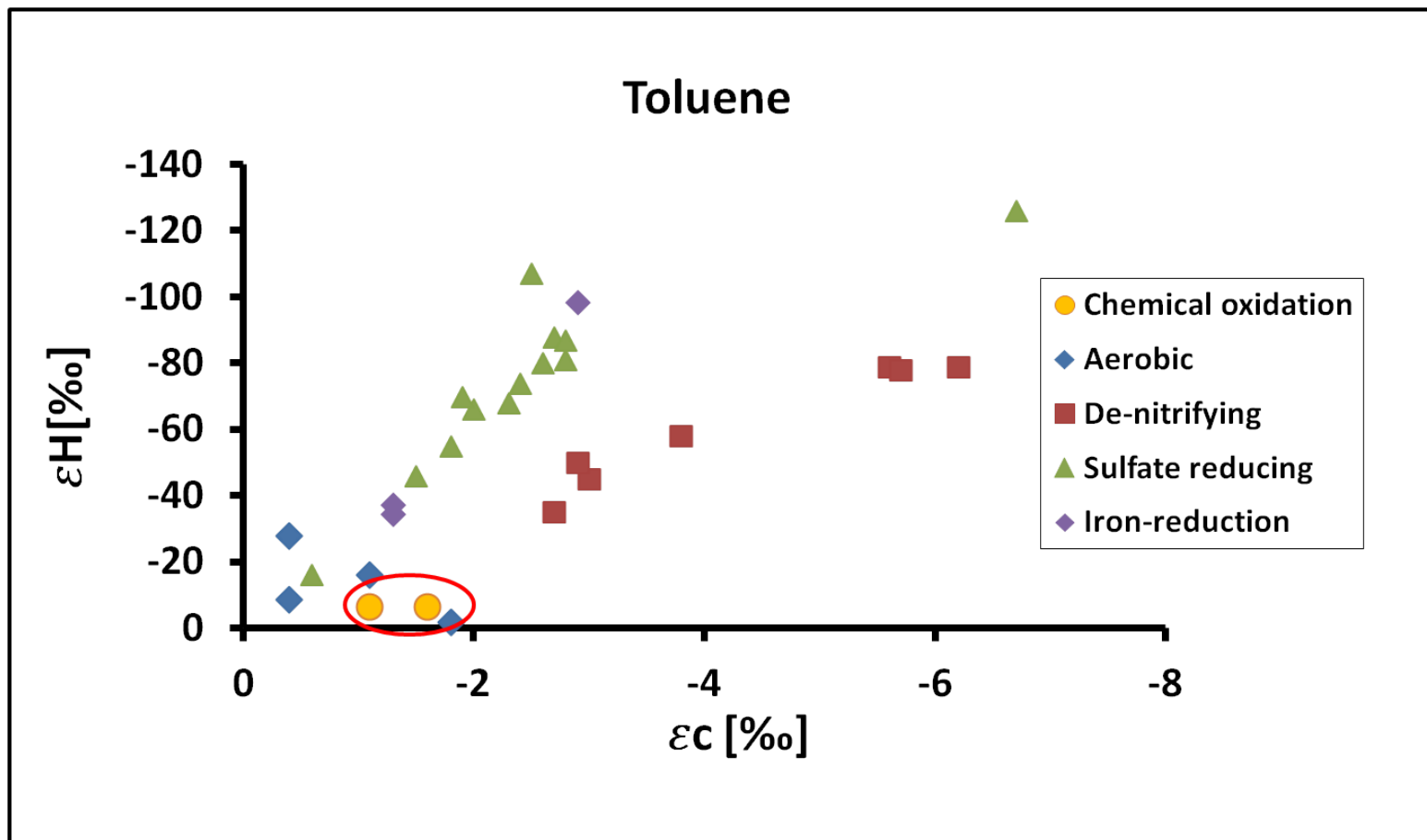
Figure 4.9 Concurrent Carbon and hydrogen enrichment factors (εC, εH) for Toluene during the chemical oxidation by PS compared with recently published values for aerobic and anaerobic degradations of Toluene.
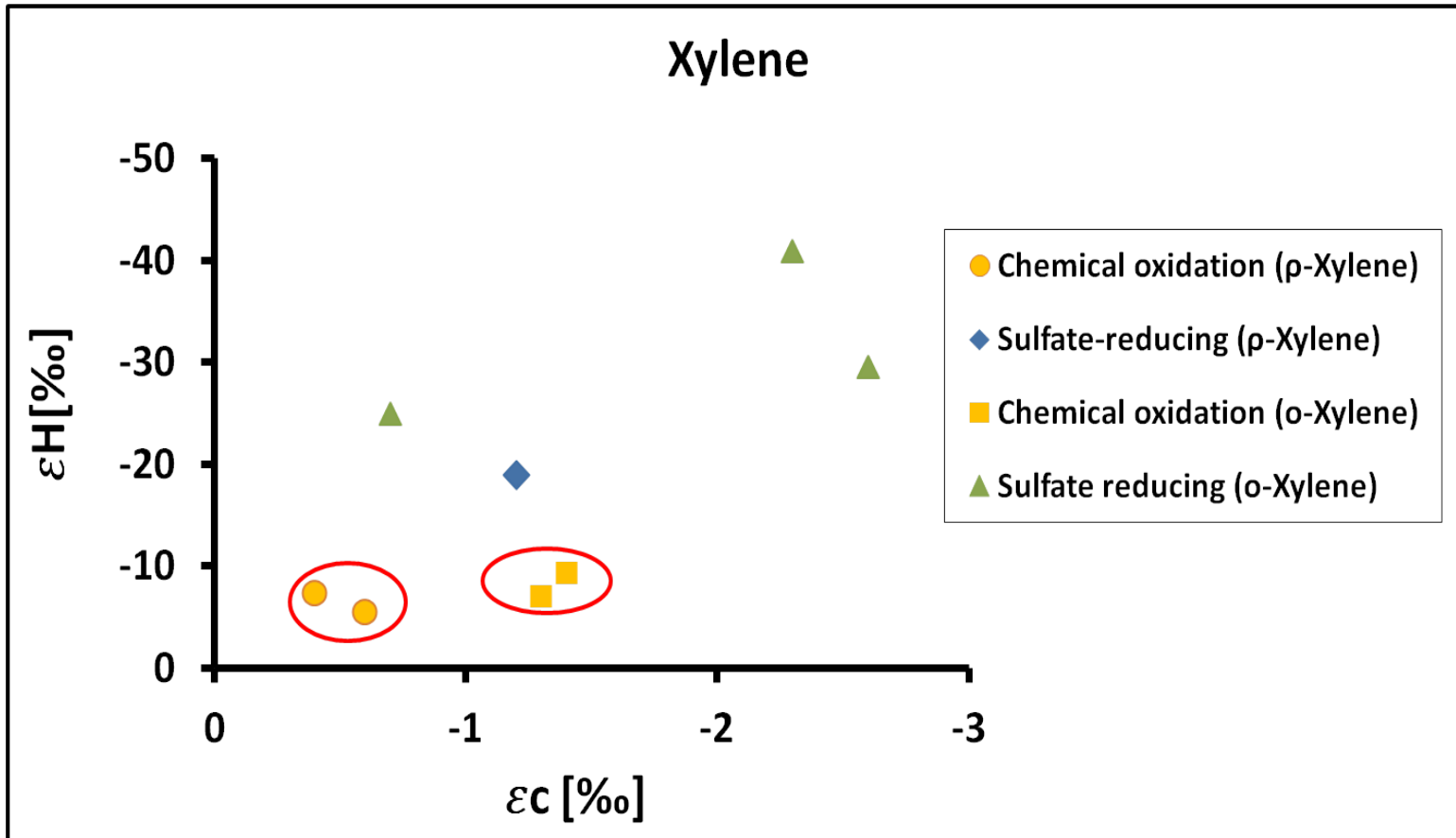
Figure 4.10 Concurrent Carbon and hydrogen enrichment factors (εC, εH) for Xylenes during the chemical oxidation by PS compared with recently published values for aerobic and anaerobic degradations of Xylenes.

Table 4.3 Concurrent Carbon and hydrogen enrichment factors (ε_C, ε_H) and calculated (Λ) values for BTEXs during the chemical oxidation by PS compared with recently published values for aerobic and anaerobic degradations of BTEX.

Compound	Transformation Type	Isotope Enrichment		$\Lambda = \Delta\delta^2H/\Delta\delta13C$ $\approx \varepsilon H/\varepsilon C$	Reference
		ε_C	ε_H		
Benzene	Chemical oxidation, alkaline-activated persulfate, 30^{0}C	-2.0	-10.9	5.5	This study
Benzene	Chemical oxidation, Non-activated persulfate, 30^{0}C	-2.0	-10.6	5.3	This study
Benzene	Aerobic	-1.47	-12.8	8.7	(Hunkeler et al., 2001)
Benzene	Aerobic	-3.41	-11.2	3.3	(Hunkeler et al., 2001)
Benzene	Aerobic	-1.7	-11	6.5	(Fischer et al., 2008)
Benzene	Aerobic	-4.3	-17	4.0	(Fischer et al., 2008)
Benzene	Aerobic	-2.6	-16	6.2	(Fischer et al., 2008)
Benzene	Denitrifying	-2.4	-29.0	12.1	(Mancini et al., 2003)
Benzene	Denitrifying	-2.2	-35.0	15.9	(Mancini et al., 2003)
Benzene	Denitrifying	-2.6	-47.0	18.1	(Mancini et al., 2008)
Benzene	Denitrifying	-2.8	-47.0	16.8	(Mancini et al., 2008)
Benzene	Denitrifying	-1.9	-31.0	16.3	(Mancini et al., 2008)
Benzene	Sulfate-reducing	-3.6	-79.0	21.9	(Mancini et al., 2003)
Benzene	Sulfate-reducing	-1.9	-59.0	31.1	(Fischer et al., 2008)

Benzene	Sulfate-reducing	-2.9	-78.0	26.9	(Fischer et al., 2009)
Benzene	Sulfate-reducing	-2.9	-69.0	23.8	(Fischer et al., 2009)
Benzene	Sulfate-reducing	-3	-77.0	25.7	(Fischer et al., 2009)
Benzene	Methanogenic	-1.9	-60.0	31.6	(Mancini et al., 2003)
Benzene	Methanogenic	-2.1	-59.0	28.1	(Mancini et al., 2003)
Benzene	Methanogenic	-0.8	-34.0	42.5	(Mancini et al., 2008)
Benzene	Methanogenic	-1.1	-38.0	34.5	(Mancini et al., 2008)
Toluene	Chemical oxidation, alkaline-activated persulfate, 30°C	-1.6	-6.6	4.1	This study
Toluene	Chemical oxidation, Non-activated persulfate, 30°C	-1.2	-6.4	5.3	This study
Toluene	Aerobic	-1.1	-16.0	14.5	(Morasch et al., 2002)
Toluene	Aerobic	-0.4	-28.0	70.0	(Morasch et al., 2002)
Toluene	Aerobic	-0.4	-8.6	21.5	(Vogt et al., 2008)
Toluene	Aerobic	-1.8	-2.0	1.1	(Vogt et al., 2008)
Toluene	Denitrifying	-2.7	-35.0	13.0	(Vogt et al., 2008)
Toluene	Denitrifying	-5.6	-79.0	14.1	(Vogt et al., 2008)
Toluene	Denitrifying	-6.2	-79.0	12.7	(Vogt et al., 2008)
Toluene	Denitrifying	-5.7	-78.0	13.7	(Vogt et al., 2008)
Toluene	Denitrifying	-3	-45.0	15.0	(Vogt et al., 2008)
Toluene	Denitrifying	-3.8	-58.0	15.3	(Vogt et al., 2008)
Toluene	Denitrifying	-2.9	-50.0	17.2	(Vogt et al., 2008)

Toluene	Anoxygenic phototrophic	-4.0	-23.0	5.8	(Vogt et al., 2008)
Toluene	Fe(III)-reducing	-1.3	-34.6	26.6	(Tobler et al., 2008)
Toluene	Fe(III)-reducing	-1.3	-37.2	28.6	(Tobler et al., 2008)
Toluene	Fe(III)-reducing	-2.9	-98.4	33.9	(Tobler et al., 2008)
Toluene	Sulfate-reducing	-2	-66.0	33.0	(Vogt et al., 2008)
Toluene	Sulfate-reducing	-2.6	-80.0	30.8	(Vogt et al., 2008)
Toluene	Sulfate-reducing	-2.3	-68.0	29.6	(Vogt et al., 2008)
Toluene	Sulfate-reducing	-2.4	-74.0	30.8	(Vogt et al., 2008)
Toluene	Sulfate-reducing	-2.7	-88.0	32.6	(Vogt et al., 2008)
Toluene	Sulfate-reducing	-2.8	-81.0	28.9	(Vogt et al., 2008)
Toluene	Sulfate-reducing	-2.8	-87.0	31.1	(Vogt et al., 2008)
Toluene	Sulfate-reducing	-1.5	-46.0	30.7	(Fischer et al., 2009)
Toluene	Sulfate-reducing	-1.8	-55.0	30.6	(Fischer et al., 2009)
Toluene	Sulfate-reducing	-1.9	-70.0	36.8	(Fischer et al., 2009)
Toluene	Sulfate-reducing	-0.6	-16.0	26.7	(Fischer et al., 2009)
Toluene	Sulfate-reducing	-2.5	-107.0	42.8	(Herrmann., et al 2009)
Toluene	Sulfate-reducing	-6.7	-126.0	18.8	(Herrmann., et al 2009)
Ethylbenzene	Chemical oxidation, alkaline-activated persulfate, 30°C	-1.6	-2.5	1.6	This study
Ethylbenzene	Chemical oxidation, Non-activated persulfate, 30°C	-1.1	-2.1	1.9	This study
p-Xylene	Chemical oxidation, alkaline-activated persulfate, 30°C	-0.6	-5.6	9.3	This study

p-Xylene	Chemical oxidation, Non-activated persulfate, 30^{0}C	-0.4	-7.4	18.5	This study
p-Xylene	Sulfate-reducing	-1.2	-19	15.8	(Herrmann., et al 2009)
o-Xylene	Chemical oxidation, alkaline-activated persulfate, 30^{0}C	-1.4	-9.4	6.7	This study
o-Xylene	Chemical oxidation, Non-activated persulfate, 30^{0}C	-1.3	-7.1	5.5	This study
o-Xylene	Sulfate-reducing	-2.6	-29.6	11.4	(Steinbach et al., 2004)
o-Xylene	Sulfate-reducing	-2.3	-41.0	17.8	(Herrmann., et al 2009)
o-Xylene	Sulfate-reducing	-0.7	-25.0	35.7	(Herrmann., et al 2009)

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Appendix A: Total petroleum hydrocarbons (TPH) and persulfate analyses

Total Petroleum Hydrocarbons Analysis (TPH)

Total Petroleum Hydrocarbons Analysis (TPH)

LEGEND

0.0 = NOT DETECTED = < MDL

GC= Gas Chromatographic Repeat

All results are dilution corrected

Start Date 20-Oct-10

Sample Identification	Date	Temperature (ºC)	Day	TPH (Total) µg/L	Persulfate g/L
Non-Activated Persulfate Experiment					
1-Con-1	21-Oct-10	10C	1	100964.6415	
1-Con-2	21-Oct-10	10C	1	105970.4803	
1-Con-3	21-Oct-10	10C	1	105100.6422	
2-Con-1	28-Oct-10	10C	8	104701.5615	
2-Con-2	28-Oct-10	10C	8	104470.2746	
2-Con-3	28-Oct-10	10C	8	104276.4664	
3-Con-1	4-Nov-10	10C	15	107296.0166	
3-Con-2	4-Nov-10	10C	15	102831.9666	
3-Con-3	4-Nov-10	10C	15	102404.7866	
4-CON-1	15-Nov-10	10C	26	101337.5334	
4-CON-2	15-Nov-10	10C	26	101289.9454	
4-CON-3	15-Nov-10	10C	26	101301.6699	
5-Con-1	29-Nov-10	10C	40	92013.97173	
5-Con-2	29-Nov-10	10C	40	88802.1729	
5-Con-3	29-Nov-10	10C	40	91281.33257	
6-Con-1	15-Dec-10	10C	56	95412.04772	
6-Con-2	15-Dec-10	10C	56	97039.53577	
6-Con-3	15-Dec-10	10C	56	98019.74647	
7-Con-1	26-Jan-11	10C	98	98164.31741	
7-Con-2	26-Jan-11	10C	98	100018.6599	
7-Con-3	26-Jan-11	10C	98	97986.88258	

1 PER-1 (20g)	21-Oct-10	10C	1	103486.499	18.6
1 PER-2 (20g)	21-Oct-10	10C	1	104191.1975	18.4
1 PER-3 (20g)	21-Oct-10	10C	1	104719.5287	18.8
2 PER-1 (20g)	28-Oct-10	10C	8	99387.67926	16.1
2 PER-2 (20g)	28-Oct-10	10C	8	98670.20118	16.4
2 PER-3 (20g)	28-Oct-10	10C	8	96986.08762	19.9
3 PER-1 (20g)	4-Nov-10	10C	15	94927.09798	13.9
3 PER-2 (20g)	4-Nov-10	10C	15	86760.30281	17.9
3 PER-3 (20g)	4-Nov-10	10C	15	97861.29807	17.9
4-PER-1(20g)	15-Nov-10	10C	26	91835.65083	14.8
4-PER-2(20g)	15-Nov-10	10C	26	95177.94105	14.4
4-PER-3(20g)	15-Nov-10	10C	26	97110.81535	14.4
5 PER-1 (20g)	29-Nov-10	10C	40	82992.51503	16.3
5 PER-2 (20g)	29-Nov-10	10C	40	84876.60752	15.8
5 PER-3 (20g)	29-Nov-10	10C	40	82984.60128	17.4
6 PER-1 (20g)	15-Dec-10	10C	56	85885.81718	15.8
6 PER-2 (20g)	15-Dec-10	10C	56	91299.01989	15.8
6 PER-3 (20g)	15-Dec-10	10C	56	#DIV/0!	17.5
7 PER-1 (20g)	26-Jan-11	10C	98	85799.4395	15.7
7 PER-2 (20g)	26-Jan-11	10C	98	86817.27709	17.5
7 PER-3 (20g)	26-Jan-11	10C	98	85375.37913	15.2

Samples diluted 1:5 in H2O for analytical analysis (due to very high concentration of persulfate)- values are dilution corrected

1 PER-1 (100g)	21-Oct-10	10C	1	90433.65214	99.9
1 PER-2 (100g)	21-Oct-10	10C	1	94753.91937	105.8
1 PER-3 (100g)	21-Oct-10	10C	1	94077.90362	108.7
2 PER-1 (100g)	28-Oct-10	10C	8	80193.33511	135.6
2 PER-2 (100g)	28-Oct-10	10C	8	76881.17259	99.3
2 PER-3 (100g)	28-Oct-10	10C	8	79188.07578	103.3
3 PER-1 (100g)	4-Nov-10	10C	15	73193.29631	104.4
3 PER-2 (100g)	4-Nov-10	10C	15	75600.28561	110.1
3 PER-3 (100g)	4-Nov-10	10C	15	72221.16574	96.0
4-PER-1 (100g)	15-Nov-10	10C	26	64668.47822	94.5
4-PER-2 (100g)	15-Nov-10	10C	26	65380.07497	105.3
4-PER-3 (100g)	15-Nov-10	10C	26	64869.41835	115.2

5 PER-1 (100g)	29-Nov-10	10C	40	52557.21342	113.1
5 PER-2 (100g)	29-Nov-10	10C	40	50924.15063	101.4
5 PER-3 (100g)	29-Nov-10	10C	40	52784.49908	105.3
6 PER-1 (100g)	15-Dec-10	10C	56	47244.39908	97.2
6 PER-2 (100g)	15-Dec-10	10C	56	49358.88893	107.2
6 PER-3 (100g)	15-Dec-10	10C	56	50080.51823	109.8
7 PER-1 (100g)	26-Jan-11	10C	98	33402.48733	97.4
7 PER-2 (100g)	26-Jan-11	10C	98	36566.05865	99.4
7 PER-3 (100g)	26-Jan-11	10C	98	35616.12461	92.5
1-Con-1	21-Oct-10	30C	1	105043.4257	
1-Con-2	21-Oct-10	30C	1	106222.6956	
1-Con-3	21-Oct-10	30C	1	104332.2632	
2-Con-1	28-Oct-10	30C	8	100174.8823	
2-Con-2	28-Oct-10	30C	8	100668.3335	
2-Con-3	28-Oct-10	30C	8	100336.5719	
3-Con-1	4-Nov-10	30C	15	98644.433	
3-Con-2	4-Nov-10	30C	15	97295.37791	
3-Con-3	4-Nov-10	30C	15	93217.92266	
4-CON-1	15-Nov-10	30C	26	92884.91331	
4-CON-2	15-Nov-10	30C	26	94626.23561	
4-CON-3	15-Nov-10	30C	26	93545.40718	
5-Con-1	29-Nov-10	30C	40	80893.09816	
5-Con-2	29-Nov-10	30C	40	81762.81612	
5-Con-3	29-Nov-10	30C	40	82970.5514	
6-Con-1	15-Dec-10	30C	56	86856.96115	
6-Con-2	15-Dec-10	30C	56	86083.31771	
6-Con-3	15-Dec-10	30C	56	85993.98214	
7-Con-1	26-Jan-11	30C	98	104051.224	
7-Con-1	26-Jan-11	30C	98	104188.5791	
7-Con-2	26-Jan-11	30C	98	100470.6083	
7-Con-3	26-Jan-11	30C	98 GC	98620.27929	
1 PER-1 (20g)	21-Oct-10	30C	1	103850.5429	19.2
1 PER-2 (20g)	21-Oct-10	30C	1	105427.5838	19.2
1 PER-3 (20g)	21-Oct-10	30C	1	104092.2004	18.8
2 PER-1 (20g)	28-Oct-10	30C	8	61302.00638	16.1

2 PER-2 (20g)	28-Oct-10	30C	8	59525.19632	15.6
2 PER-3 (20g)	28-Oct-10	30C	8	59803.65361	15.6
3 PER-1 (20g)	4-Nov-10	30C	15	42998.63854	15.4
3 PER-2 (20g)	4-Nov-10	30C	15	44577.19853	16.5
3 PER-3 (20g)	4-Nov-10	30C	15	35342.39459	15.2
4-PER-1 (20g)	15-Nov-10	30C	26	31169.41943	13.8
4-PER-2 (20g)	15-Nov-10	30C	26	29571.11877	14.6
4-PER-3 (20g)	15-Nov-10	30C	26	28716.57855	14.2
5 PER-1 (20g)	29-Nov-10	30C	40	20567.99379	15.8
5 PER-2 (20g)	29-Nov-10	30C	40	15683.83132	12.4
5 PER-3 (20g)	29-Nov-10	30C	40	8908.732818	14.8
6 PER-1 (20g)	15-Dec-10	30C	56	9732.646612	12.0
6 PER-2 (20g)	15-Dec-10	30C	56	5374.698254	15.1
6 PER-3 (20g)	15-Dec-10	30C	56	4408.372247	14.9
7 PER-1 (20g)	26-Jan-11	30C	98	2325.853299	10.4
7 PER-2 (20g)	26-Jan-11	30C	98	4832.948672	9.6
7 PER-3 (20g)	26-Jan-11	30C	98	2384.506113	8.7

Samples diluted 1:5 in H2O for analytical analysis (due to very high concentration of persulfate)- values are dilution corrected

1 PER-1 (100g)	21-Oct-10	30C	1	95709.50044	102.9
1 PER-2 (100g)	21-Oct-10	30C	1	95538.80134	103.8
1 PER-3 (100g)	21-Oct-10	30C	1	95461.20713	116.6
2 PER-1 (100g)	28-Oct-10	30C	8	5182.906991	93.5
2 PER-2 (100g)	28-Oct-10	30C	8	#DIV/0!	NS
2 PER-3 (100g)	28-Oct-10	30C	8	5091.009805	105.8
3 PER-1 (100g)	4-Nov-10	30C	15	15506.42105	106.3
3 PER-2 (100g)	4-Nov-10	30C	15	15056.1113	107.2
3 PER-3 (100g)	4-Nov-10	30C	15	15287.978	99.8
4-PER-1 (100g)	15-Nov-10	30C	26	21093.1187	86.6
4-PER-2 (100g)	15-Nov-10	30C	26	20334.18972	86.6
4-PER-3 (100g)	15-Nov-10	30C	26	23545.12032	87.6
5 PER-1 (100g)	29-Nov-10	30C	40	22528.34623	72.8
5 PER-2 (100g)	29-Nov-10	30C	40	22280.9103	72.8
5 PER-3 (100g)	29-Nov-10	30C	40	23536.15297	72.8
6 PER-1 (100g)	15-Dec-10	30C	56	17568.85481	51.6
6 PER-2 (100g)	15-Dec-10	30C	56	18212.79941	50.4
6 PER-3 (100g)	15-Dec-10	30C	56	17484.55625	48.0

7 PER-1 (100g)	26-Jan-11	30C	98	2942.613097	23.6
7 PER-2 (100g)	26-Jan-11	30C	98	12718.24563	23.6
7 PER-3 (100g)	26-Jan-11	30C	98	14019.48079	23.6

NaOH Activated Persulfate Experiment

1-CON-NaOH-1	21-Oct-10	10C	1	104357.9325	
1-CON-NaOH-2	21-Oct-10	10C	1	106681.944	
1-CON-NaOH-3	21-Oct-10	10C	1	107637.1831	
2-CON-NaOH-1	28-Oct-10	10C	8	102728.1321	
2-CON-NaOH-2	28-Oct-10	10C	8	102981.2468	
2-CON-NaOH-3	28-Oct-10	10C	8	102797.6559	
3-CON-NaOH-1	4-Nov-10	10C	15	100171.4112	
3-CON-NaOH-2	4-Nov-10	10C	15	101366.6328	
3-CON-NaOH-3	4-Nov-10	10C	15	102054.699	
4-CON-NaOH-1	15-Nov-10	10C	26	97762.73293	
4-CON-NaOH-2	15-Nov-10	10C	26	97496.507	
4-CON-NaOH-3	15-Nov-10	10C	26	97412.26001	
5-CON-NaOH-1	29-Nov-10	10C	40	88385.68493	
5-CON-NaOH-2	29-Nov-10	10C	40	90185.41939	
5-CON-NaOH-3	29-Nov-10	10C	40	90604.30135	
6-CON-NaOH-1	15-Dec-10	10C	56	92577.16963	
6-CON-NaOH-2	15-Dec-10	10C	56	94405.42185	
6-CON-NaOH-3	15-Dec-10	10C	56	98715.00061	
7-CON-NaOH-1	26-Jan-11	10C	98	96512.76102	
7-CON-NaOH-2	26-Jan-11	10C	98	96981.91441	
7-CON-NaOH-3	26-Jan-11	10C	98	97280.49547	
1-PER-(20g)-NaOH-1	21-Oct-10	10C	1	105095.5621	19.0
1-PER (20g)-NaOH-2	21-Oct-10	10C	1	106274.0817	18.0
1-PER (20g)-NaOH-3	21-Oct-10	10C	1	104800.6478	17.4
2-PER-(20g)-NaOH-1	28-Oct-10	10C	8	96315.05678	16.1
2-PER (20g)-NaOH-2	28-Oct-10	10C	8	97176.95043	18.1
2-PER (20g)-NaOH-3	28-Oct-10	10C	8	97048.8857	16.1
3-PER-(20g)-NaOH-1	4-Nov-10	10C	15	92613.38955	16.2
3-PER (20g)-NaOH-2	4-Nov-10	10C	15	93060.7039	15.6

3-PER (20g)-NaOH-3	4-Nov-10	10C	15	93888.58182	14.8
4-PER-(20g) NaOH-1	15-Nov-10	10C	26	85954.48901	15.6
4-PER-(20g) NaOH-2	15-Nov-10	10C	26	85980.17071	15.4
4-PER-(20g) NaOH-3	15-Nov-10	10C	26	85332.66584	16.5
5-PER-(20g)-NaOH-1	29-Nov-10	10C	40	78159.84952	14.4
5-PER (20g)-NaOH-2	29-Nov-10	10C	40	76438.85013	15.8
5-PER (20g)-NaOH-3	29-Nov-10	10C	40	77565.45194	14.0
6-PER-(20g)-NaOH-1	15-Dec-10	10C	56	79315.2926	15.4
6-PER (20g)-NaOH-2	15-Dec-10	10C	56	85263.93306	16.0
6-PER (20g)-NaOH-3	15-Dec-10	10C	56	83199.5189	15.8
7-PER-(20g)-NaOH-1	26-Jan-11	10C	98	74189.67874	15.2
7-PER (20g)-NaOH-2	26-Jan-11	10C	98	75825.16786	15.9
7-PER (20g)-NaOH-3	26-Jan-11	10C	98	74628.12975	14.2

Samples diluted 1:5 in H2O for analytical analysis (due to very high concentration of persulfate)- values are dilution corrected

1-PER-(100g)-NaOH-1	21-Oct-10	10C	1	86345.00496	96.0
1-PER (100g)-NaOH-2	21-Oct-10	10C	1	96014.40009	96.0
1-PER (100g)-NaOH-3	21-Oct-10	10C	1	96051.5432	85.9
2-PER-(100g)-NaOH-1	28-Oct-10	10C	8	69460.18304	108.3
2-PER (100g)-NaOH-2	28-Oct-10	10C	8	45594.81274	109.1
2-PER (100g)-NaOH-3	28-Oct-10	10C	8	30309.63231	102.5
3-PER-(100g)-NaOH-1	4-Nov-10	10C	15	56605.62807	103.4
3-PER (100g)-NaOH-2	4-Nov-10	10C	15	63888.76961	106.3
3-PER (100g)-NaOH-3	4-Nov-10	10C	15	66707.51039	109.1
4-PER-(100g) NaOH-1	15-Nov-10	10C	26	47959.10679	101.4
4-PER-(100g) NaOH-2	15-Nov-10	10C	26	55178.49158	97.4
4-PER-(100g) NaOH-3	15-Nov-10	10C	26	52722.06455	107.3
5-PER-(100g)-NaOH-1	29-Nov-10	10C	40	14078.5879	101.4
5-PER (100g)-NaOH-2	29-Nov-10	10C	40	20338.26785	93.7
5-PER (100g)-NaOH-3	29-Nov-10	10C	40	5930.476973	98.5
6-PER-(100g)-NaOH-1	15-Dec-10	10C	56	11124.54166	99.6
6-PER (100g)-NaOH-2	15-Dec-10	10C	56	1621.788121	96.0
6-PER (100g)-NaOH-3	15-Dec-10	10C	56	13214.14159	106.1
7-PER-(100g)-NaOH-1	26-Jan-11	10C	98	6508.978499	105.3
7-PER (100g)-NaOH-2	26-Jan-11	10C	98	3226.571747	92.5
7-PER (100g)-NaOH-3	26-Jan-11	10C	98	2865.042512	100.4

1-CON-NaOH-1	21-Oct-10	30C	1	106639.9214	
1-CON-NaOH-2	21-Oct-10	30C	1	106863.6093	
1-CON-NaOH-3	21-Oct-10	30C	1	106595.3688	
2-CON-NaOH-1	28-Oct-10	30C	8	100121.26	
2-CON-NaOH-2	28-Oct-10	30C	8	98244.17259	
2-CON-NaOH-3	28-Oct-10	30C	8	100284.8664	
3-CON-NaOH-1	4-Nov-10	30C	15	96229.05892	
3-CON-NaOH-2	4-Nov-10	30C	15	90682.89637	
3-CON-NaOH-3	4-Nov-10	30C	15	97994.61141	
4-CON-NaOH-1	15-Nov-10	30C	26	92090.54323	
4-CON-NaOH-2	15-Nov-10	30C	26	88466.78309	
4-CON-NaOH-3	15-Nov-10	30C	26	90145.94359	
5-CON-NaOH-1	29-Nov-10	30C	40	78041.94761	
5-CON-NaOH-2	29-Nov-10	30C	40	79601.9023	
5-CON-NaOH-3	29-Nov-10	30C	40	82306.12525	
6-CON-NaOH-1	15-Dec-10	30C	56	81634.45458	
6-CON-NaOH-2	15-Dec-10	30C	56	84042.51743	
6-CON-NaOH-3	15-Dec-10	30C	56	82691.12339	
7-CON-NaOH-1	26-Jan-11	30C	98	75775.5372	
7-CON-NaOH-2	26-Jan-11	30C	98	77637.50706	
7-CON-NaOH-3	26-Jan-11	30C	98	72935.03747	
1-PER(20g)-NaOH-1	21-Oct-10	30C	1	103834.0887	17.8
1-PER(20g)-NaOH-2	21-Oct-10	30C	1	105075.8702	17.8
1-PER(20g)-NaOH-3	21-Oct-10	30C	1	103664.2377	19.4
2-PER(20g)-NaOH-1	28-Oct-10	30C	8	60499.9847	14.2
2-PER(20g)-NaOH-2	28-Oct-10	30C	8	51040.11102	15.4
2-PER(20g)-NaOH-3	28-Oct-10	30C	8	49941.98904	14.7
3-PER(20g)-NaOH-1	4-Nov-10	30C	15	44181.05217	16.2
3-PER(20g)-NaOH-2	4-Nov-10	30C	15	43746.4809	15.6
3-PER(20g)-NaOH-3	4-Nov-10	30C	15	42879.41161	16.2
4-PER-(20g) NaOH-1	15-Nov-10	30C	26	21621.60707	13.2
4-PER-(20g) NaOH-2	15-Nov-10	30C	26	19508.77555	13.2
4-PER-(20g) NaOH-3	15-Nov-10	30C	26	19597.5123	12.4
5-PER(20g)-NaOH-1	29-Nov-10	30C	40	7550.807752	12.6
5-PER(20g)-NaOH-2	29-Nov-10	30C	40	5571.994401	12.0
5-PER(20g)-NaOH-3	29-Nov-10	30C	40	5380.711815	12.8

6-PER(20g)-NaOH-1	15-Dec-10	30C	56	901.2213649	13.2
6-PER(20g)-NaOH-2	15-Dec-10	30C	56	932.9114833	13.0
6-PER(20g)-NaOH-3	15-Dec-10	30C	56	1113.492591	10.1
7-PER(20g)-NaOH-1	26-Jan-11	30C	98	1152.1865	9.1
7-PER(20g)-NaOH-2	26-Jan-11	30C	98	958.4009118	10.0
7-PER(20g)-NaOH-3	26-Jan-11	30C	98	3050.363906	9.6

Samples diluted 1:5 in H2O for analytical analysis (due to very high concentration of persulfate)- values are dilution corrected

Used mininert valve tops instead of scew cap septa tops - Waleed added in NaOH through valve

1-PER(100g)-NaOH-1	21-Oct-10	30C	1	94045.00683	88.9
1-PER(100g)-NaOH-2	21-Oct-10	30C	1	86983.55144	98.5
1-PER(100g)-NaOH-3	21-Oct-10	30C	1	91097.91197	94.0
2-PER(100g)-NaOH-1	28-Oct-10	30C	8	1938.987173	96.0
2-PER(100g)-NaOH-2	28-Oct-10	30C	8	1601.539193	109.1
2-PER(100g)-NaOH-3	28-Oct-10	30C	8	1479.649206	91.9
3-PER(100g)-NaOH-1	4-Nov-10	30C	15	12456.97958	100.6
3-PER(100g)-NaOH-2	4-Nov-10	30C	15	650.5653168	104.4
3-PER(100g)-NaOH-3	4-Nov-10	30C	15	386.6443097	104.4
4-PER-(100g) NaOH-1	15-Nov-10	30C	26	356.2456979	100.4
4-PER-(100g) NaOH-2	15-Nov-10	30C	26	291.168421	94.5
4-PER-(100g) NaOH-3	15-Nov-10	30C	26	321.5534678	103.3
5-PER(100g)-NaOH-1	29-Nov-10	30C	40	435.1293205	88.6
5-PER(100g)-NaOH-2	29-Nov-10	30C	40	370.4513519	95.5
5-PER(100g)-NaOH-3	29-Nov-10	30C	40	455.1273234	101.4
6-PER(100g)-NaOH-1	15-Dec-10	30C	56	1370.38092	96.0
6-PER(100g)-NaOH-2	15-Dec-10	30C	56	336.0411908	106.1
6-PER(100g)-NaOH-3	15-Dec-10	30C	56	217.8557987	92.4
7-PER(100g)-NaOH-1	26-Jan-11	30C	98	13506.83226	74.8
7-PER(100g)-NaOH-2	26-Jan-11	30C	98	14378.56098	76.8
7-PER(100g)-NaOH-3	26-Jan-11	30C	98	#DIV/0!	N/A

Appendix B: Petroleum hydrocarbon analysis

ORGANIC GEOCHEMISTRY
LABORATORY

LEGEND

0.0 = NOT DETECTED = < MDL

GC repeat = Gas Chromatographic Repeat

Petroleum Hydrocarbon
Analysis

All results are dilution corrected

Report Date: Feb 3, 2011

Units are µg/L (ppb)

Start Date 20-Oct-10

Sample Identification	Date	Temperature (°C)	Day	*F1 Fraction* (nC6 to nC10)	*F2 Fraction* (nC10 to nC16)
Non-Activated Persulfate Experiment					
1-Con-1	21-Oct-10	10C	1	95996.7	4967.9
1-Con-2	21-Oct-10	10C	1	100539.7	5430.8
1-Con-3	21-Oct-10	10C	1	99646.6	5454.0
2-Con-1	28-Oct-10	10C	8	99425.7	5275.9
2-Con-2	28-Oct-10	10C	8	99213.1	5257.2
2-Con-3	28-Oct-10	10C	8	98950.2	5326.2
3-Con-1	4-Nov-10	10C	15	102571.4	4724.6
3-Con-2	4-Nov-10	10C	15	98344.3	4487.7
3-Con-3	4-Nov-10	10C	15	97957.5	4447.3
4-CON-1	15-Nov-10	10C	26	97084.2	4253.4
4-CON-2	15-Nov-10	10C	26	97052.0	4237.9
4-CON-3	15-Nov-10	10C	26	97048.6	4253.1
5-Con-1	29-Nov-10	10C	40	88280.9	3733.1
5-Con-2	29-Nov-10	10C	40	85235.5	3566.6
5-Con-3	29-Nov-10	10C	40	87600.9	3680.4
6-Con-1	15-Dec-10	10C	56	91631.6	3780.4
6-Con-2	15-Dec-10	10C	56	93160.5	3879.0
6-Con-3	15-Dec-10	10C	56	94135.3	3884.4
7-Con-1	26-Jan-11	10C	98	93957.8	4206.5
7-Con-2	26-Jan-11	10C	98	95552.7	4465.9
7-Con-3	26-Jan-11	10C	98	93655.3	4331.6

1 PER-1 (20g)	21-Oct-10	10C	1	98148.0	5338.5
1 PER-2 (20g)	21-Oct-10	10C	1	98707.9	5483.3
1 PER-3 (20g)	21-Oct-10	10C	1	99335.5	5384.1
2 PER-1 (20g)	28-Oct-10	10C	8	94293.6	5094.1
2 PER-2 (20g)	28-Oct-10	10C	8	93609.2	5061.0
2 PER-3 (20g)	28-Oct-10	10C	8	94155.2	2830.9
3 PER-1 (20g)	4-Nov-10	10C	15	90675.9	4251.2
3 PER-2 (20g)	4-Nov-10	10C	15	82437.6	4322.7
3 PER-3 (20g)	4-Nov-10	10C	15	93544.2	4317.1
4-PER-1(20g)	15-Nov-10	10C	26	87805.6	4030.1
4-PER-2(20g)	15-Nov-10	10C	26	91080.7	4097.3
4-PER-3(20g)	15-Nov-10	10C	26	92898.5	4212.3
5 PER-1 (20g)	29-Nov-10	10C	40	79412.5	3580.0
5 PER-2 (20g)	29-Nov-10	10C	40	81131.5	3745.1
5 PER-3 (20g)	29-Nov-10	10C	40	79304.9	3679.7
6 PER-1 (20g)	15-Dec-10	10C	56	81127.7	4758.1
6 PER-2 (20g)	15-Dec-10	10C	56	86297.1	5001.9
6 PER-3 (20g)	15-Dec-10	10C	56	#DIV/0!	#DIV/0!
7 PER-1 (20g)	26-Jan-11	10C	98	80091.9	5707.6
7 PER-2 (20g)	26-Jan-11	10C	98	81170.0	5647.2
7 PER-3 (20g)	26-Jan-11	10C	98	79688.1	5687.3

Samples diluted 1:5 in H2O for analytical analysis (due to very high concentration of persulfate)-values are dilution corrected

1 PER-1 (100g)	21-Oct-10	10C	1	87470.8	2962.8
1 PER-2 (100g)	21-Oct-10	10C	1	91700.1	3053.8
1 PER-3 (100g)	21-Oct-10	10C	1	90928.6	3149.3
2 PER-1 (100g)	28-Oct-10	10C	8	76850.9	3342.4
2 PER-2 (100g)	28-Oct-10	10C	8	72240.6	4640.5
2 PER-3 (100g)	28-Oct-10	10C	8	74631.7	4556.3
3 PER-1 (100g)	4-Nov-10	10C	15	68393.4	4799.9
3 PER-2 (100g)	4-Nov-10	10C	15	69964.7	5635.6
3 PER-3 (100g)	4-Nov-10	10C	15	66741.6	5479.6
4-PER-1 (100g)	15-Nov-10	10C	26	59723.9	4944.6
4-PER-2 (100g)	15-Nov-10	10C	26	60037.4	5342.7
4-PER-3 (100g)	15-Nov-10	10C	26	59568.2	5301.2
5 PER-1 (100g)	29-Nov-10	10C	40	46884.5	5672.7
5 PER-2 (100g)	29-Nov-10	10C	40	45351.0	5573.1

5 PER-3 (100g)	29-Nov-10	10C	40	46821.1	5963.4
6 PER-1 (100g)	15-Dec-10	10C	56	40848.4	6396.0
6 PER-2 (100g)	15-Dec-10	10C	56	42018.9	7340.0
6 PER-3 (100g)	15-Dec-10	10C	56	42832.5	7248.0
7 PER-1 (100g)	26-Jan-11	10C	98	28874.9	4527.6
7 PER-2 (100g)	26-Jan-11	10C	98	31377.1	5189.0
7 PER-3 (100g)	26-Jan-11	10C	98	30773.2	4842.9
1-Con-1	21-Oct-10	30C	1	99561.1	5482.3
1-Con-2	21-Oct-10	30C	1	100638.2	5584.5
1-Con-3	21-Oct-10	30C	1	98900.1	5432.2
2-Con-1	28-Oct-10	30C	8	95277.2	4897.6
2-Con-2	28-Oct-10	30C	8	95742.8	4925.6
2-Con-3	28-Oct-10	30C	8	95409.4	4927.2
3-Con-1	4-Nov-10	30C	15	94529.8	4114.6
3-Con-2	4-Nov-10	30C	15	93196.3	4099.1
3-Con-3	4-Nov-10	30C	15	89200.8	4017.1
4-CON-1	15-Nov-10	30C	26	89223.9	3661.0
4-CON-2	15-Nov-10	30C	26	90875.1	3751.2
4-CON-3	15-Nov-10	30C	26	89806.7	3738.7
5-Con-1	29-Nov-10	30C	40	77748.1	3145.0
5-Con-2	29-Nov-10	30C	40	78585.1	3177.7
5-Con-3	29-Nov-10	30C	40	79721.1	3249.5
6-Con-1	15-Dec-10	30C	56	83554.1	3302.9
6-Con-2	15-Dec-10	30C	56	82802.3	3281.0
6-Con-3	15-Dec-10	30C	56	82725.5	3268.5
7-Con-1	26-Jan-11	30C	98	101311.5	2739.7
7-Con-1	26-Jan-11	30C	98	101517.9	2670.7
7-Con-2	26-Jan-11	30C	98	97871.3	2599.4
7-Con-3	26-Jan-11	30C	98 GC	95941.3	2679.0
1 PER-1 (20g)	21-Oct-10	30C	1	98526.8	5323.7
1 PER-2 (20g)	21-Oct-10	30C	1	99983.0	5444.6
1 PER-3 (20g)	21-Oct-10	30C	1	98842.2	5250.0
2 PER-1 (20g)	28-Oct-10	30C	8	55878.3	5423.7
2 PER-2 (20g)	28-Oct-10	30C	8	53416.5	6108.7
2 PER-3 (20g)	28-Oct-10	30C	8	53611.3	6192.3

3 PER-1 (20g)	4-Nov-10	30C	15	37659.5	5339.2
3 PER-2 (20g)	4-Nov-10	30C	15	39157.3	5419.9
3 PER-3 (20g)	4-Nov-10	30C	15	29437.7	5904.7
4-PER-1 (20g)	15-Nov-10	30C	26	25985.2	5184.2
4-PER-2 (20g)	15-Nov-10	30C	26	24978.0	4593.2
4-PER-3 (20g)	15-Nov-10	30C	26	24243.8	4472.7
5 PER-1 (20g)	29-Nov-10	30C	40	18070.5	2497.5
5 PER-2 (20g)	29-Nov-10	30C	40	13977.3	1706.5
5 PER-3 (20g)	29-Nov-10	30C	40	7990.1	918.6
6 PER-1 (20g)	15-Dec-10	30C	56	7978.5	1754.1
6 PER-2 (20g)	15-Dec-10	30C	56	3833.2	1541.5
6 PER-3 (20g)	15-Dec-10	30C	56	3097.0	1311.4
7 PER-1 (20g)	26-Jan-11	30C	98	2060.2	265.7
7 PER-2 (20g)	26-Jan-11	30C	98	4544.0	289.0
7 PER-3 (20g)	26-Jan-11	30C	98	2120.4	264.1

Samples diluted 1:5 in H2O for analytical analysis (due to very high concentration of persulfate)-values are dilution corrected

1 PER-1 (100g)	21-Oct-10	30C	1	92533.8	3175.7
1 PER-2 (100g)	21-Oct-10	30C	1	92427.2	3111.6
1 PER-3 (100g)	21-Oct-10	30C	1	92230.7	3230.5
2 PER-1 (100g)	28-Oct-10	30C	8	3031.8	2151.1
2 PER-2 (100g)	28-Oct-10	30C	8	#DIV/0!	#DIV/0!
2 PER-3 (100g)	28-Oct-10	30C	8	2861.4	2229.6
3 PER-1 (100g)	4-Nov-10	30C	15	14834.3	672.1
3 PER-2 (100g)	4-Nov-10	30C	15	14365.3	690.8
3 PER-3 (100g)	4-Nov-10	30C	15	14573.2	714.8
4-PER-1 (100g)	15-Nov-10	30C	26	20013.4	1079.7
4-PER-2 (100g)	15-Nov-10	30C	26	19326.0	1008.2
4-PER-3 (100g)	15-Nov-10	30C	26	22162.5	1382.6
5 PER-1 (100g)	29-Nov-10	30C	40	21154.4	1373.9
5 PER-2 (100g)	29-Nov-10	30C	40	21011.6	1269.3
5 PER-3 (100g)	29-Nov-10	30C	40	22166.2	1369.9
6 PER-1 (100g)	15-Dec-10	30C	56	16709.6	859.2
6 PER-2 (100g)	15-Dec-10	30C	56	17253.2	959.6
6 PER-3 (100g)	15-Dec-10	30C	56	16596.4	888.2
7 PER-1 (100g)	26-Jan-11	30C	98	2667.5	275.2
7 PER-2 (100g)	26-Jan-11	30C	98	12358.4	359.9

7 PER-3 (100g)	**26-Jan-11**	**30C**	**98**	13370.6	648.9

**NaOH Activated
Persulfate Experiment**

1-CON-NaOH-1	**21-Oct-10**	**10C**	**1**	98942.2	5415.7
1-CON-NaOH-2	**21-Oct-10**	**10C**	**1**	101081.8	5600.1
1-CON-NaOH-3	**21-Oct-10**	**10C**	**1**	102044.0	5593.2
2-CON-NaOH-1	**28-Oct-10**	**10C**	**8**	97568.8	5159.3
2-CON-NaOH-2	**28-Oct-10**	**10C**	**8**	97832.5	5148.7
2-CON-NaOH-3	**28-Oct-10**	**10C**	**8**	97588.4	5209.2
3-CON-NaOH-1	**4-Nov-10**	**10C**	**15**	95747.4	4424.0
3-CON-NaOH-2	**4-Nov-10**	**10C**	**15**	96957.1	4409.6
3-CON-NaOH-3	**4-Nov-10**	**10C**	**15**	97551.2	4503.5
4-CON-NaOH-1	**15-Nov-10**	**10C**	**26**	93592.6	4170.1
4-CON-NaOH-2	**15-Nov-10**	**10C**	**26**	93372.2	4124.3
4-CON-NaOH-3	**15-Nov-10**	**10C**	**26**	93311.5	4100.8
5-CON-NaOH-1	**29-Nov-10**	**10C**	**40**	84723.4	3662.2
5-CON-NaOH-2	**29-Nov-10**	**10C**	**40**	86414.1	3771.3
5-CON-NaOH-3	**29-Nov-10**	**10C**	**40**	86854.4	3749.9
6-CON-NaOH-1	**15-Dec-10**	**10C**	**56**	88849.2	3728.0
6-CON-NaOH-2	**15-Dec-10**	**10C**	**56**	90249.8	4155.6
6-CON-NaOH-3	**15-Dec-10**	**10C**	**56**	94333.7	4381.3
7-CON-NaOH-1	**26-Jan-11**	**10C**	**98**	93881.4	2631.3
7-CON-NaOH-2	**26-Jan-11**	**10C**	**98**	94370.4	2611.5
7-CON-NaOH-3	**26-Jan-11**	**10C**	**98**	94699.5	2581.0
1-PER-(20g)-NaOH-1	**21-Oct-10**	**10C**	**1**	99747.4	5348.1
1-PER (20g)-NaOH-2	**21-Oct-10**	**10C**	**1**	100930.8	5343.2
1-PER (20g)-NaOH-3	**21-Oct-10**	**10C**	**1**	99516.0	5284.6
2-PER-(20g)-NaOH-1	**28-Oct-10**	**10C**	**8**	91346.9	4968.1
2-PER (20g)-NaOH-2	**28-Oct-10**	**10C**	**8**	92294.0	4882.9
2-PER (20g)-NaOH-3	**28-Oct-10**	**10C**	**8**	94271.0	2777.9
3-PER-(20g)-NaOH-1	**4-Nov-10**	**10C**	**15**	88358.8	4254.6
3-PER (20g)-NaOH-2	**4-Nov-10**	**10C**	**15**	88897.5	4163.3
3-PER (20g)-NaOH-3	**4-Nov-10**	**10C**	**15**	89658.2	4230.4
4-PER-(20g) NaOH-1	**15-Nov-10**	**10C**	**26**	82193.3	3761.2
4-PER-(20g) NaOH-2	**15-Nov-10**	**10C**	**26**	82192.8	3787.4

4-PER-(20g) NaOH-3	15-Nov-10	10C	26	81646.2	3686.5
5-PER-(20g)-NaOH-1	29-Nov-10	10C	40	74728.7	3431.1
5-PER (20g)-NaOH-2	29-Nov-10	10C	40	73107.4	3331.4
5-PER (20g)-NaOH-3	29-Nov-10	10C	40	74160.5	3405.0
6-PER-(20g)-NaOH-1	15-Dec-10	10C	56	75480.4	3834.9
6-PER (20g)-NaOH-2	15-Dec-10	10C	56	80887.1	4376.8
6-PER (20g)-NaOH-3	15-Dec-10	10C	56	78960.0	4239.5
7-PER-(20g)-NaOH-1	26-Jan-11	10C	98	71748.9	2440.8
7-PER (20g)-NaOH-2	26-Jan-11	10C	98	73419.6	2405.5
7-PER (20g)-NaOH-3	26-Jan-11	10C	98	72263.4	2364.7

Samples diluted 1:5 in H2O for analytical analysis (due to very high concentration of persulfate)-values are dilution corrected

1-PER-(100g)-NaOH-1	21-Oct-10	10C	1	83620.4	2724.6
1-PER (100g)-NaOH-2	21-Oct-10	10C	1	92785.2	3229.2
1-PER (100g)-NaOH-3	21-Oct-10	10C	1	93032.5	3019.0
2-PER-(100g)-NaOH-1	28-Oct-10	10C	8	67048.9	2411.3
2-PER (100g)-NaOH-2	28-Oct-10	10C	8	43609.2	1985.6
2-PER (100g)-NaOH-3	28-Oct-10	10C	8	28635.4	1674.2
3-PER-(100g)-NaOH-1	4-Nov-10	10C	15	53747.6	2858.0
3-PER (100g)-NaOH-2	4-Nov-10	10C	15	60745.1	3143.6
3-PER (100g)-NaOH-3	4-Nov-10	10C	15	63234.2	3473.3
4-PER-(100g) NaOH-1	15-Nov-10	10C	26	46379.7	1579.4
4-PER-(100g) NaOH-2	15-Nov-10	10C	26	52490.1	2688.4
4-PER-(100g) NaOH-3	15-Nov-10	10C	26	50174.9	2547.1
5-PER-(100g)-NaOH-1	29-Nov-10	10C	40	13433.8	644.8
5-PER (100g)-NaOH-2	29-Nov-10	10C	40	19526.3	812.0
5-PER (100g)-NaOH-3	29-Nov-10	10C	40	5686.0	244.5
6-PER-(100g)-NaOH-1	15-Dec-10	10C	56	9431.9	1692.6
6-PER (100g)-NaOH-2	15-Dec-10	10C	56	1447.0	174.7
6-PER (100g)-NaOH-3	15-Dec-10	10C	56	12803.2	411.0
7-PER-(100g)-NaOH-1	26-Jan-11	10C	98	6024.5	484.5
7-PER (100g)-NaOH-2	26-Jan-11	10C	98	2906.8	319.8
7-PER (100g)-NaOH-3	26-Jan-11	10C	98	2530.3	334.7
1-CON-NaOH-1	21-Oct-10	30C	1	101066.8	5573.1
1-CON-NaOH-2	21-Oct-10	30C	1	101313.4	5550.3
1-CON-NaOH-3	21-Oct-10	30C	1	101114.9	5480.5

2-CON-NaOH-1	28-Oct-10	30C	8	95233.9	4887.3
2-CON-NaOH-2	28-Oct-10	30C	8	93453.0	4791.1
2-CON-NaOH-3	28-Oct-10	30C	8	95403.2	4881.6
3-CON-NaOH-1	4-Nov-10	30C	15	92116.0	4113.0
3-CON-NaOH-2	4-Nov-10	30C	15	86729.6	3953.3
3-CON-NaOH-3	4-Nov-10	30C	15	93883.4	4111.2
4-CON-NaOH-1	15-Nov-10	30C	26	88346.9	3743.6
4-CON-NaOH-2	15-Nov-10	30C	26	86335.0	2131.7
4-CON-NaOH-3	15-Nov-10	30C	26	86437.0	3709.0
5-CON-NaOH-1	29-Nov-10	30C	40	74911.0	3130.9
5-CON-NaOH-2	29-Nov-10	30C	40	76407.2	3194.7
5-CON-NaOH-3	29-Nov-10	30C	40	78983.9	3322.2
6-CON-NaOH-1	15-Dec-10	30C	56	78455.3	3179.2
6-CON-NaOH-2	15-Dec-10	30C	56	80525.4	3517.1
6-CON-NaOH-3	15-Dec-10	30C	56	79114.1	3577.0
7-CON-NaOH-1	26-Jan-11	30C	98	73656.2	2119.4
7-CON-NaOH-2	26-Jan-11	30C	98	75431.7	2205.8
7-CON-NaOH-3	26-Jan-11	30C	98	70820.1	2114.9
1-PER(20g)-NaOH-1	21-Oct-10	30C	1	98588.8	5245.3
1-PER(20g)-NaOH-2	21-Oct-10	30C	1	99825.3	5250.6
1-PER(20g)-NaOH-3	21-Oct-10	30C	1	98466.9	5197.3
2-PER(20g)-NaOH-1	28-Oct-10	30C	8	56961.9	3538.1
2-PER(20g)-NaOH-2	28-Oct-10	30C	8	47771.8	3268.4
2-PER(20g)-NaOH-3	28-Oct-10	30C	8	46779.0	3162.9
3-PER(20g)-NaOH-1	4-Nov-10	30C	15	39494.1	4686.9
3-PER(20g)-NaOH-2	4-Nov-10	30C	15	39041.2	4705.2
3-PER(20g)-NaOH-3	4-Nov-10	30C	15	38526.7	4352.7
4-PER-(20g) NaOH-1	15-Nov-10	30C	26	18985.8	2635.8
4-PER-(20g) NaOH-2	15-Nov-10	30C	26	17378.1	2130.6
4-PER-(20g) NaOH-3	15-Nov-10	30C	26	17499.9	2097.6
5-PER(20g)-NaOH-1	29-Nov-10	30C	40	6588.0	962.8
5-PER(20g)-NaOH-2	29-Nov-10	30C	40	4802.7	769.3
5-PER(20g)-NaOH-3	29-Nov-10	30C	40	4726.1	654.6
6-PER(20g)-NaOH-1	15-Dec-10	30C	56	629.3	271.9
6-PER(20g)-NaOH-2	15-Dec-10	30C	56	795.9	137.0
6-PER(20g)-NaOH-3	15-Dec-10	30C	56	830.5	283.0

7-PER(20g)-NaOH-1	26-Jan-11	30C	98	1058.2	94.0
7-PER(20g)-NaOH-2	26-Jan-11	30C	98	856.4	102.0
7-PER(20g)-NaOH-3	26-Jan-11	30C	98	2839.7	210.6

Samples diluted 1:5 in H2O for analytical analysis (due to very high concentration of persulfate)-values are dilution corrected

Used mininert valve tops instead of scew cap septa tops - Waleed added in NaOH through valve

1-PER(100g)-NaOH-1	21-Oct-10	30C	1	91015.7	3029.3
1-PER(100g)-NaOH-2	21-Oct-10	30C	1	84143.3	2840.3
1-PER(100g)-NaOH-3	21-Oct-10	30C	1	88072.8	3025.1
2-PER(100g)-NaOH-1	28-Oct-10	30C	8	978.1	960.9
2-PER(100g)-NaOH-2	28-Oct-10	30C	8	838.6	762.9
2-PER(100g)-NaOH-3	28-Oct-10	30C	8	772.6	707.1
3-PER(100g)-NaOH-1	4-Nov-10	30C	15	11880.0	577.0
3-PER(100g)-NaOH-2	4-Nov-10	30C	15	570.0	80.5
3-PER(100g)-NaOH-3	4-Nov-10	30C	15	341.4	45.2
4-PER-(100g) NaOH-1	15-Nov-10	30C	26	282.5	73.8
4-PER-(100g) NaOH-2	15-Nov-10	30C	26	238.6	52.5
4-PER-(100g) NaOH-3	15-Nov-10	30C	26	279.1	42.4
5-PER(100g)-NaOH-1	29-Nov-10	30C	40	407.8	27.4
5-PER(100g)-NaOH-2	29-Nov-10	30C	40	268.4	102.1
5-PER(100g)-NaOH-3	29-Nov-10	30C	40	266.4	188.8
6-PER(100g)-NaOH-1	15-Dec-10	30C	56	272.6	1097.8
6-PER(100g)-NaOH-2	15-Dec-10	30C	56	256.2	79.9
6-PER(100g)-NaOH-3	15-Dec-10	30C	56	127.4	90.4
7-PER(100g)-NaOH-1	26-Jan-11	30C	98	13070.3	436.5
7-PER(100g)-NaOH-2	26-Jan-11	30C	98	13838.1	540.5
7-PER(100g)-NaOH-3	26-Jan-11	30C	98	#DIV/0!	#DIV/0!

Appendix C: Concentration vs. isotope analysis of Benzene

Time	Sample Identification	Concentration mg/L	δ 13C ‰	δ2H ‰
0	1-Control 10°C	23.2810	-30.77	-41.91
8	2-Control 10°C	23.4498	-30.30	-43.27
15	3-Control 10°C	22.6661	-31.22	-41.97
26	4-Control 10°C	22.5402	-30.36	-37.24
40	5-Control 10°C	20.0108	-30.29	-39.12
56	6-Control 10°C	21.4737	-30.53	-41.87
98	7-Control 10°C	21.9449	-30.73	-37.89
0	1-per (20g) 10°C	22.3385	-30.68	-38.38
8	2-per (20g) 10°C	22.1339	-30.70	-36.17
15	3-per (20g) 10°C	21.4844	-30.21	-36.45
26	4-per (20g) 10°C	21.0310	-30.26	-41.84
40	5-per (20g) 10°C	18.5902	-30.41	-39.61
56	6-per (20g) 10°C	20.1158	-30.06	-36.46
98	7-per (20g) 10°C	20.3699	-30.61	-41.4
0	1-Control 30°C	23.0732	-30.42	-43.55
8	2-Control 30°C	22.9481	-30.43	-46.72
15	3-Control 30°C	21.7761	-30.52	-45.15
26	4-Control 30°C	21.4495	-30.48	-44.56
40	5-Control 30°C	20.6184	-30.28	-43.95
56	6-Control 30°C	19.9741	-30.50	-44.22
98	7-Control 30°C	23.0011	-30.18	-39.49
0	1-per (20g) 30°C	22.3364	-30.18	-44.72
8	2-per (20g) 30°C	18.1261	-29.68	-36.96
15	3-per (20g) 30°C	12.9656	-29.26	-40.70
26	4-per (20g) 30°C	9.9185	-28.85	-38.20
40	5-per (20g) 30°C	4.0759	-26.82	-26.09
56	6-per (20g) 30°C	0.3566	BQL	B.D.L
98	7-per (20g) 30°C	0.0023	BQL	B.D.L

Sample Identification	Concentration mg/L	δ 13C ‰	δ2H ‰
1-con-NaOH 10°C	23.1	-30.02	-42.02
2-con-NaOH 10°C	22.9	-29.80	-44.3
3-con-NaOH 10°C	22.4	-30.08	-38.63
4-con-NaOH 10°C	21.6	-29.74	-39.51
5-con-NaOH 10°C	19.6	-29.75	-38.48
6-con-NaOH 10°C	20.9	-29.96	-43.38
7-con-NaOH 10°C	21.6	-30.01	-37.56
1-per-NaOH (20g) 10°C	22.8	-29.37	-34.25
2-per-NaOH (20g) 10°C	21.8	-29.63	-40.41
3-per-NaOH (20g) 10°C	20.4	-29.10	-36.71
4-per-NaOH (20g) 10°C	18.9	-29.27	-36.63
5-per-NaOH (20g) 10°C	16.9	-29.32	-40.72
6-per-NaOH (20g) 10°C	18.1	-29.13	-40.42
7-per-NaOH (20g) 10°C	17.4	-29.30	-34.15
1-Control-NaOH 30°C	22.7	-30.18	-44.17
2-Control-NaOH 30°C	22.7	-30.76	-44.77
3-Control-NaOH 30°C	21.6	-30.29	-39.96
4-Control-NaOH 30°C	20.6	-30.25	-40.1
5-Control-NaOH 30°C	18.2	-29.95	-39.93
6-Control-NaOH 30°C	19.2	-30.22	-45.75
7-Control-NaOH 30°C	18.3	-30.35	-40.16
1-per-NaOH (20g) 30°C	22.2	-29.70	-48.60
2-per-NaOH (20g) 30°C	15.3	-29.04	-30.06
3-per-NaOH (20g) 30°C	12.4	-28.80	-31.50
4-per-NaOH (20g) 30°C	6.7	-28.56	-34.69
5-per-NaOH (20g) 30°C	2.0	-24.42	-29.81
6-per-NaOH (20g) 30°C	0.1	BDL	B.D.L
7-per-NaOH (20g) 30°C	0.0	BDL	B.D.L

Appendix D: Concentration vs. isotope analysis of Toluene

TTime	Sample Identification	Concentration mg/L	δ 13C ‰	δ2H ‰
0	1-Control 10°C	42.4172	-30.21	-35.43
8	2-Control 10°C	42.5814	-29.86	-30.59
15	3-Control 10°C	42.0595	-29.88	-35.35
26	4-Control 10°C	41.8378	-29.82	-34.7
40	5-Control 10°C	37.8457	-29.67	-37.45
56	6-Control 10°C	39.9453	-30.12	-36.91
98	7-Control 10°C	39.8429	-30.56	-33.62
0	1-per (20g) 10°C	42.4874	-29.90	-37.36
8	2-per (20g) 10°C	39.5527	-29.75	-38.61
15	3-per (20g) 10°C	38.2837	-29.40	-36.7
26	4-per (20g) 10°C	37.5320	-29.38	-42.18
40	5-per (20g) 10°C	33.1182	-29.53	-36.64
56	6-per (20g) 10°C	34.3505	-29.68	-42.18
98	7-per (20g) 10°C	32.0726	-28.97	-39.06
0	1-Control 30°C	43.1405	-29.64	-45.7
8	2-Control 30°C	41.1991	-29.55	-42.1
15	3-Control 30°C	39.2350	-29.45	-45.06
26	4-Control 30°C	38.0885	-29.15	-41.81
40	5-Control 30°C	33.1536	-28.99	-45.13
56	6-Control 30°C	34.7869	-29.65	-44.15
98	7-Control 30°C	39.7144	-29.84	-49.39
0	1-per (20g) 30°C	42.6278	-29.17	-39.33
8	2-per (20g) 30°C	19.8291	-27.98	-32.75
15	3-per (20g) 30°C	7.2813	-26.36	-33.50
26	4-per (20g) 30°C	0.9737	-23.36	-12.67
40	5-per (20g) 30°C	0.0087	BDL	B.D.L
56	6-per (20g) 30°C	0.0142	BDL	B.D.L
98	7-per (20g) 30°C	0.0038	BDL	B.D.L

Sample Identification	Concentration mg/L	δ 13C ‰	δ2H ‰
1-con-NaOH 10°C	43.5612	-29.13	-40.31
2-con-NaOH 10°C	42.0145	-29.83	-35.59
3-con-NaOH 10°C	41.3355	-30.18	-36.32
4-con-NaOH 10°C	40.0614	-29.74	-38.53
5-con-NaOH 10°C	36.7289	-29.69	-40.95
6-con-NaOH 10°C	39.0751	-29.71	-43.11
7-con-NaOH 10°C	38.6026	-29.15	-41.66
1-per-NaOH (20g) 10°C	43.0966	-28.18	-39.34
2-per-NaOH (20g) 10°C	38.8850	-28.06	-39.16
3-per-NaOH (20g) 10°C	36.5027	-27.40	-44.55
4-per-NaOH (20g) 10°C	33.4002	-27.64	-37.67
5-per-NaOH (20g) 10°C	29.6634	-27.40	-42.26
6-per-NaOH (20g) 10°C	31.3750	-27.39	-41.49
7-per-NaOH (20g) 10°C	26.9847	-27.60	-39.35
1-Control-NaOH 30°C	43.7402	-29.72	-47.29
2-Control-NaOH 30°C	40.9246	-29.75	-43.55
3-Control-NaOH 30°C	38.4192	-29.35	-43.67
4-Control-NaOH 30°C	36.6236	-29.70	-42.83
5-Control-NaOH 30°C	31.8739	-29.25	-48.56
6-Control-NaOH 30°C	32.7714	-29.31	-50.95
7-Control-NaOH 30°C	27.7459	-29.20	-43.61
1-per-NaOH (20g) 30°C	42.7289	-28.92	-38.27
2-per-NaOH (20g) 30°C	19.1317	-27.78	-31.11
3-per-NaOH (20g) 30°C	9.4728	-26.65	-30.10
4-per-NaOH (20g) 30°C	0.9980	-24.64	B.D.L
5-per-NaOH (20g) 30°C	0.0088	BDL	B.D.L
6-per-NaOH (20g) 30°C	0.0040	BDL	B.D.L
7-per-NaOH (20g) 30°C	0.0045	BDL	B.D.L

Appendix E: Concentration vs. isotope analysis of Ethylbenzene

Time	Sample Identification	Concentration mg/L	δ 13C ‰	δ2H ‰
0	1-Control 10°C	3.6689	-28.32	-171.32
8	2-Control 10°C	3.6015	-28.97	-169.53
15	3-Control 10°C	3.5163	-29.10	-172.03
26	4-Control 10°C	3.4704	-29.61	-171.71
40	5-Control 10°C	3.1792	-30.12	-171.66
56	6-Control 10°C	3.3223	-27.57	-169.84
98	7-Control 10°C	3.3014	-27.85	-172.90
0	1-per (20g) 10°C	3.6627	-29.25	-167.11
8	2-per (20g) 10°C	3.3266	-28.62	-168.72
15	3-per (20g) 10°C	3.1645	-28.08	-168.72
26	4-per (20g) 10°C	3.1147	-28.35	-169.91
40	5-per (20g) 10°C	2.7968	-28.38	-168.64
56	6-per (20g) 10°C	2.8666	-27.51	-167.37
98	7-per (20g) 10°C	2.7050	-27.50	-166.34
0	1-Control 30°C	3.7344	-28.38	-178.05
8	2-Control 30°C	3.4082	-27.70	-175.21
15	3-Control 30°C	3.1897	-27.95	-175.2
26	4-Control 30°C	3.0760	-27.72	-175.65
40	5-Control 30°C	2.6977	-27.50	-177.19
56	6-Control 30°C	2.8100	-27.60	-175.99
98	7-Control 30°C	3.3615	-27.78	-175.07
0	1-per (20g) 30°C	3.6881	-28.26	-170.50
8	2-per (20g) 30°C	1.6893	-26.39	-168.87
15	3-per (20g) 30°C	0.6269	-25.63	B.D.L
26	4-per (20g) 30°C	0.0539	-21.78	B.D.L
40	5-per (20g) 30°C	0.0004	BDL	B.D.L
56	6-per (20g) 30°C	0.0028	BDL	B.D.L
98	7-per (20g) 30°C	0.3281	BDL	B.D.L

Sample Identification	Concentration mg/L	δ 13C ‰	δ2H ‰
1-con-NaOH 10°C	3.7954	-26.27	-164.65
2-con-NaOH 10°C	3.5831	-27.35	-164.68
3-con-NaOH 10°C	3.4666	-27.42	-167.13
4-con-NaOH 10°C	3.3447	-27.36	-166.85
5-con-NaOH 10°C	3.0759	-27.56	-166.21
6-con-NaOH 10°C	3.2517	-27.47	-166.48
7-con-NaOH 10°C	3.1432	-27.63	-167.33
1-per-NaOH (20g) 10°C	3.7220	-27.71	-177.89
2-per-NaOH (20g) 10°C	3.2974	-27.04	-175.01
3-per-NaOH (20g) 10°C	3.0621	-26.54	-180.81
4-per-NaOH (20g) 10°C	2.7897	-26.03	-175.03
5-per-NaOH (20g) 10°C	2.4869	-26.55	-179.05
6-per-NaOH (20g) 10°C	2.6216	-26.61	-175.8
7-per-NaOH (20g) 10°C	2.2102	-26.11	-179.84
1-Control-NaOH 30°C	3.8325	-27.29	-193.46
2-Control-NaOH 30°C	3.4123	-27.17	-193.27
3-Control-NaOH 30°C	3.1663	-26.60	-196.38
4-Control-NaOH 30°C	2.9719	-27.08	-194.79
5-Control-NaOH 30°C	2.5818	-27.03	-191.94
6-Control-NaOH 30°C	2.6229	-27.25	-191.48
7-Control-NaOH 30°C	2.1305	-26.85	-195.93
1-per-NaOH (20g) 30°C	3.7013	-27.38	-172.70
2-per-NaOH (20g) 30°C	1.6121	-26.82	-171.24
3-per-NaOH (20g) 30°C	0.8074	-26.31	B.D.L
4-per-NaOH (20g) 30°C	0.0481	-22.66	B.D.L
5-per-NaOH (20g) 30°C	0.0026	BDL	B.D.L
6-per-NaOH (20g) 30°C	0.0000	BDL	B.D.L
7-per-NaOH (20g) 30°C	0.2234	BDL	B.D.L

Appendix F: Concentration vs. isotope analysis of p-Xylene

Time	Sample Identification	Concentration mg/L	δ 13C ‰	δ2H ‰
0	1-Control 10°C	10.0385	-28.19	-72.72
8	2-Control 10°C	9.7843	-29.40	-68.75
15	3-Control 10°C	9.6106	-29.23	-71.49
26	4-Control 10°C	9.4383	-29.75	-72.73
40	5-Control 10°C	8.6180	-29.48	-72.69
56	6-Control 10°C	8.9899	-28.22	-69.58
98	7-Control 10°C	8.8296	-28.28	-76.11
0	1-per (20g) 10°C	10.1118	-28.01	-85.4
8	2-per (20g) 10°C	9.2977	-28.83	-85.27
15	3-per (20g) 10°C	8.8648	-28.56	-87.92
26	4-per (20g) 10°C	8.6124	-28.58	-90.32
40	5-per (20g) 10°C	7.3489	-28.73	-84.5
56	6-per (20g) 10°C	7.2572	-27.72	-89.88
98	7-per (20g) 10°C	6.0851	-27.96	-90.6
0	1-Control 30°C	10.2151	-28.16	-80.82
8	2-Control 30°C	9.1623	-28.58	-77.57
15	3-Control 30°C	8.5649	-28.89	-77.45
26	4-Control 30°C	8.0842	-28.56	-82.99
40	5-Control 30°C	6.9639	-28.44	-82.21
56	6-Control 30°C	7.1666	-28.07	-85.27
98	7-Control 30°C	8.6471	-27.83	-85.13
0	1-per (20g) 30°C	10.1805	-28.94	-74.94
8	2-per (20g) 30°C	3.0790	-26.91	-66.68
15	3-per (20g) 30°C	0.6594	-26.39	B.D.L
26	4-per (20g) 30°C	0.0164	-25.99	B.D.L
40	5-per (20g) 30°C	0.0055	BDL	B.D.L
56	6-per (20g) 30°C	0.0015	BDL	B.D.L
98	7-per (20g) 30°C	0.0000	BDL	B.D.L

Sample Identification	Concentration mg/L	δ 13C ‰	δ2H ‰
1-con-NaOH 10°C	10.3719	-26.54	-85.28
2-con-NaOH 10°C	9.7279	-27.57	-81.78
3-con-NaOH 10°C	9.4514	-28.06	-86.75
4-con-NaOH 10°C	9.0774	-27.73	-84.17
5-con-NaOH 10°C	8.3616	-28.18	-81.65
6-con-NaOH 10°C	8.8435	-28.04	-83.14
7-con-NaOH 10°C	8.4069	-28.11	-88.11
1-per-NaOH (20g) 10°C	10.2701	-26.71	-83
2-per-NaOH (20g) 10°C	9.2948	-26.89	-84.73
3-per-NaOH (20g) 10°C	8.7872	-26.86	-90.8
4-per-NaOH (20g) 10°C	7.9643	-26.28	-89.99
5-per-NaOH (20g) 10°C	7.0400	-26.73	-84.76
6-per-NaOH (20g) 10°C	7.3463	-26.31	-88.17
7-per-NaOH (20g) 10°C	5.8556	-26.31	-89.09
1-Control-NaOH 30°C	10.4758	-27.04	-109.91
2-Control-NaOH 30°C	9.1710	-27.01	-113.02
3-Control-NaOH 30°C	8.3503	-27.40	-111.84
4-Control-NaOH 30°C	7.8351	-27.77	-106.78
5-Control-NaOH 30°C	6.6533	-27.39	-106.22
6-Control-NaOH 30°C	6.6244	-27.59	-110.86
7-Control-NaOH 30°C	5.0445	-27.16	-114.35
1-per-NaOH (20g) 30°C	10.2235	-27.41	-73.47
2-per-NaOH (20g) 30°C	4.4222	-27.54	-67.70
3-per-NaOH (20g) 30°C	1.7515	-26.44	B.D.L
4-per-NaOH (20g) 30°C	0.0177	BDL	B.D.L
5-per-NaOH (20g) 30°C	0.0028	BDL	B.D.L
6-per-NaOH (20g) 30°C	0.0018	BDL	B.D.L
7-per-NaOH (20g) 30°C	0.0015	BDL	B.D.L

Appendix G: Concentration vs. isotope analysis of o-Xylene

Time	Sample Identification	Concentration mg/L	δ 13C ‰	δ2H ‰
0	1-Control 10°C	6.2112	-28.55	-22.96
8	2-Control 10°C	6.1618	-29.14	-22.19
15	3-Control 10°C	6.1519	-28.77	-21.82
26	4-Control 10°C	6.1260	-30.48	-21.37
40	5-Control 10°C	5.6693	-29.52	-21.74
56	6-Control 10°C	5.9369	-28.46	-21.59
98	7-Control 10°C	5.9316	-28.28	-21.34
0	1-per (20g) 10°C	6.2076	-28.08	-23.69
8	2-per (20g) 10°C	5.8565	-28.35	-25.72
15	3-per (20g) 10°C	5.6925	-27.49	-28.89
26	4-per (20g) 10°C	5.6331	-27.81	-24.23
40	5-per (20g) 10°C	4.9389	-27.78	-21.94
56	6-per (20g) 10°C	4.9979	-26.86	-24.94
98	7-per (20g) 10°C	4.3712	-27.15	-22.42
0	1-Control 30°C	6.3283	-27.98	-25.81
8	2-Control 30°C	5.9201	-27.78	-24.6
15	3-Control 30°C	5.7283	-27.73	-27.24
26	4-Control 30°C	5.6462	-27.54	-21.31
40	5-Control 30°C	5.0957	-27.51	-23.42
56	6-Control 30°C	5.3909	-27.69	-22.9
98	7-Control 30°C	6.0143	-27.23	-25.14
0	1-per (20g) 30°C	6.2600	-28.21	-31.39
8	2-per (20g) 30°C	2.3470	-27.17	-22.46
15	3-per (20g) 30°C	0.5826	-25.38	
26	4-per (20g) 30°C	0.0249	-20.54	B.D.L
40	5-per (20g) 30°C	0.0083	BDL	B.D.L
56	6-per (20g) 30°C	0.0059	BDL	B.D.L
98	7-per (20g) 30°C	0.0108	BDL	B.D.L

BDL: Below Detection Limit

BQL: Below Quantification Limit

Sample Identification	Concentration mg/L	δ 13C ‰	δ2H ‰
1-con-NaOH 10°C	6.3679	-26.18	-20.53
2-con-NaOH 10°C	6.0802	-27.19	-20.67
3-con-NaOH 10°C	6.0184	-27.51	-19.79
4-con-NaOH 10°C	5.8788	-27.48	-20.81
5-con-NaOH 10°C	5.4975	-27.93	-18.58
6-con-NaOH 10°C	5.8314	-28.29	-19.01
7-con-NaOH 10°C	5.7235	-28.38	-22.89
1-per-NaOH (20g) 10°C	6.2593	-27.81	-20.55
2-per-NaOH (20g) 10°C	5.7604	-26.38	-23.53
3-per-NaOH (20g) 10°C	5.5287	-26.94	-22.19
4-per-NaOH (20g) 10°C	5.1327	-26.39	-25.38
5-per-NaOH (20g) 10°C	4.6879	-26.60	-29.75
6-per-NaOH (20g) 10°C	4.9586	-26.83	-20.07
7-per-NaOH (20g) 10°C	4.2240	-26.50	-26.47
1-Control-NaOH 30°C	6.4239	-27.31	-27.43
2-Control-NaOH 30°C	5.8688	-27.80	-29.22
3-Control-NaOH 30°C	5.7093	-27.04	-26.7
4-Control-NaOH 30°C	5.3969	-27.45	-27.61
5-Control-NaOH 30°C	4.9133	-27.11	-24.77
6-Control-NaOH 30°C	5.1373	-27.29	-26.24
7-Control-NaOH 30°C	4.5439	-26.83	-27.81
1-per-NaOH (20g) 30°C	6.2353	-28.27	-23.56
2-per-NaOH (20g) 30°C	3.1255	-27.74	-16.26
3-per-NaOH (20g) 30°C	1.4711	-26.26	-14.65
4-per-NaOH (20g) 30°C	0.0374	BDL	B.D.L
5-per-NaOH (20g) 30°C	0.0058	BDL	B.D.L
6-per-NaOH (20g) 30°C	0.0034	BDL	B.D.L
7-per-NaOH (20g) 30°C	0.0066	BDL	B.D.L