

Article

Laboratory Experiments to Evaluate the Effectiveness of Persulfate to Oxidize BTEX in Saline Environment and at Elevated Temperature Using Stable Isotopes

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Abstract: In this study, batch experiments were carried out to investigate the effectiveness of persulfate (PS) as an oxidant agent to remediate benzene, toluene, ethylbenzene, and xylenes (BTEX) in saline environments and at high water temperatures (30 °C). This hydrological setting is quite common in contaminated groundwater aquifers in Middle Eastern countries. In general, increasing the system temperature from 10 to 30 °C greatly enhanced the effectiveness of PS, and resulted in a faster oxidation rate for the target contaminants. When PS was added to the reactor at 30 °C, the targeted contaminants were almost completely oxidized over a 98-day reaction period. During the chemical oxidation of the BTEX, carbon and hydrogen isotope fractionations were monitored and utilized as potential proof of contaminant degradation. The calculated carbon-enrichment values were −1.9‰ for benzene, −1.5‰ for ethylbenzene and toluene, −0.4‰ for *p,m*-xylene, and −1.4‰ for *o*-xylene, while the hydrogen enrichment values were −9.5‰, −6.8‰, −2.1‰, −6.9‰, and −9.1‰, respectively. In comparison with other processes, the hydrogen and carbon isotope fractionations during the chemical oxidation by PS were smaller than the isotope fractionations resulting from sulfate reduction and denitrification. This observation demonstrates the differences in the transformation pathways and isotope fractionations when compounds undergo chemical oxidation or biodegradation. The distinct trend observed on the dual isotope plot ($\Delta\delta^{13}\text{C}$ vs. $\Delta\delta^2\text{H}$) suggests that compound-specific isotope analysis can be utilized to monitor the chemical oxidation of BTEX by PS, and to distinguish treatment zones where PS and biodegradation technologies are applied simultaneously.

Keywords: chemical oxidation; persulfate; gasoline compounds; stable isotopes



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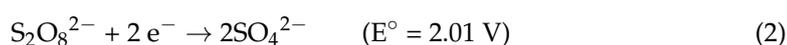


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1. Introduction

In-situ chemical oxidation (ISCO) is a promising methodology for the remediation of petroleum hydrocarbons due to its relative inexpensiveness, simple preparation of treatment solutions, and the ability to degrade contaminants in place [1]. ISCO technology involves the reduction of the contaminant mass by injecting chemical oxidants into the vadose or saturated zone. In the past few decades, several aqueous oxidants (e.g., hydrogen peroxide, permanganate, and ozone) have been employed to remediate petroleum hydrocarbons [2,3]. One oxidant used for ISCO applications is sodium persulfate ($\text{Na}_2\text{S}_2\text{O}_8$), which has been proven to be able to oxidize a wide range of environmentally relevant contaminants [4–7]. In comparison with other chemical oxidants, persulfate (PS) is more stable than peroxide in the presence of aquifer materials [5], more effective for treating contaminants in the saturated zone than ozone due to its higher aqueous solubility [2],

and is capable of treating a wider range of organic compounds than permanganate [8,9]. The use of PS to treat contaminated aquifers has been extensively reviewed in [3] and [10]. When sodium PS salts are added to water, they dissociate to PS anions (Equation (1)), and with an estimated oxidation potential of $E^\circ = 2.01$ V (Equation (2)), the PS anions are capable of efficiently oxidizing most common hydrocarbon compounds. In addition, PS can be activated thermally or under alkaline conditions [10] to generate a suite of energetic species, such as free sulfate radicals ($\text{SO}_4^{\bullet-}$) (Equation (3)). Sulfate radicals have a significant oxidation potential ($E^\circ = 2.60$ V), and can effectively initiate radical chain reactions to oxidize organic compounds [10].



Most of the research on PS applications has been carried out on fresh groundwater aquifers and at low temperatures, which represent typical hydrogeological settings in Northern America and Europe [5–8,11]. In this relatively cold groundwater setting, heating technologies, such as radio frequency heating [12] or electrical resistance heating [13], are applied to a contaminated aquifer to activate PS thermally and thus enhance in-situ chemical oxidation. However, the artificial-heating-activation approach has been reported to be incredibly challenging due to the heterogeneity in the subsurface conditions, and in some cases, maintaining a uniform distribution of the steam cannot be achieved [14]. Furthermore, supplying a heating system at a field site can increase the treatment costs. In the current study, however, batch experiments were carried out to investigate the effectiveness of PS to remediate benzene, toluene, ethylbenzene, and xylene (known as BTEX compounds), in a saline environment, at a relatively elevated groundwater temperature (30 °C). This hydrological setting is quite common in groundwater aquifers in Middle Eastern countries, where water resources are at high risk of contamination due to widespread oil and gas exploitation activities. Noteworthy, the focus in this study was mainly to evaluate the impact of the water temperature and quality within the well itself, rather than to evaluate the impact of the geology, which will be the subject of a future study. In addition, this study assumes that the role of biodegradation on the removal of the target contaminants is insignificant, as inorganic compounds were added to the samples at the beginning of the experiment to inhibit biodegradation. An expected outcome of the current study is to answer the question of whether PS can be activated naturally under the typical groundwater temperature in Middle Eastern countries (i.e., ~30 °C), as this can enhance treatment efficiency by generating more powerful oxidants (e.g., sulfate free radicals) and can also lower the capital costs of the treatment by avoiding the use of artificial heating.

In most ISCO studies, decreasing pollutant concentrations has been utilized as the only method to prove that contaminants are being eliminated [15]. Under field conditions, however, a decrease in contaminant concentrations may occur from displacement by the injected solution rather than destruction by chemical oxidation. Moreover, continuous dissolution from the remaining source mass can keep the contaminant concentrations at an elevated level, even though some destruction may have occurred [16]. Thus, the interpretation of contaminant destruction based on concentration data only may be ambiguous [17,18]. To avoid this ambiguity, compound-specific isotope analysis (CSIA) has been widely utilized as a potential proof of contaminant degradation [17–28]. This is based on the observation of a gradual enrichment of heavier isotopes (e.g., ^{13}C or ^2H) in the residual contaminant when an organic compound undergoes biotic or abiotic degradation [17]. The measured isotope ratios can be related to the substrate fractions of an analyte by calculating the isotopic enrichment factor (ϵ) using the Rayleigh model (Equation (4)) [29].

$$\ln \frac{R(t)}{R(0)} \approx \epsilon \cdot \ln f_{\text{substrate}}(t) \quad (4)$$

Here, $R(0)$ is the stable isotope ratio of the organic compound at the initial time, $R(t)$ is the isotopic ratio after oxidation has occurred at time t , $f_{\text{substrate}}(t)$ denotes the fraction of the compound remaining at this stage of the experiment (often approximated by the remaining organic compound concentration according to $C(t)/C(0)$ at a time (t) , and ϵ is the isotopic enrichment factor for this particular process and can be derived by a linear regression of the data. Moreover, the transformation pathways during the contaminant degradation can be characterized more precisely by applying a two-dimensional compound-specific isotope analysis (2D-CSIA) [22,24,25,30–32]. Prior to the isotope-sensitive bond change, carbon and hydrogen fractionation are equally influenced by the rate limitations [30], and therefore, any rate limitations that mask the values of the kinetic isotope effect 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 [32]. The notation λ (Λ) is used for the ratio between the isotope enrichment factors for the two elements [32]. For instance, the slope of the linear regression for hydrogen ($\Delta\delta^2\text{H}$) versus carbon ($\Delta\delta^{13}\text{C}$) is given in Equation (5). Alternatively, Λ values can be assessed by the ratio of hydrogen to carbon isotope enrichment factors.

$$(\Lambda_{\text{bulk}}) = \Delta\delta^2\text{H}/\Delta\delta^{13}\text{C} \approx \epsilon_{\text{H}_{\text{bulk}}}/\epsilon_{\text{C}_{\text{bulk}}} \quad (5)$$

The main objectives of this study were: (1) to investigate the effect of temperature (10 °C versus 30 °C) on the efficiency of PS to oxidize the BTEX in a saline environment; (2) to explore the potential of carbon and hydrogen fractionation and 2D-CSIA to investigate the performance of chemical oxidation of the BTEX; and (3) to utilize the isotope fractionation data to suggest a transformation pathway for BTEX during the chemical oxidation by PS.

2. Materials and Methods

2.1. Materials

A field trip was conducted to a contaminated site in Saudi Arabia where an underground storage tank accidentally leaked and released a fuel product which contaminated a shallow groundwater aquifer (<30 m deep). The contaminated site is currently in the monitoring stage. Aspects of site-monitoring protocol include water sampling, data management, screening of different remediation approaches, and feasibility studies. Seven liters of groundwater samples were collected from a designated monitoring well at the contaminated site by using low-flow sampling methods [33]. The contaminated samples were collected about two weeks after the incident was reported from a confidential site in Saudi Arabia. The collected water samples were preserved with a 10% sodium azide solution (v/v) (added 43 mL/4.3L = 1 g/L) to inhibit biodegradation of the organic compounds. The collected samples were stored in coolers with Utek ice packs and were shipped to laboratories in Canada. The samples were analyzed by the ALS laboratory group, Waterloo, Canada, for specific conductance, alkalinity, total dissolved solids, and anion and cation content. The characteristics of the samples are shown in Table 1.

Table 1. Hydrochemical properties of the contaminated water samples.

Ca²⁺	31 mg/L	Alkalinity	1020 mg/L	Br⁻	5.6 mg/L
Mg²⁺	1940 mg/L	SO₄²⁻	<20 mg/L	TDS	5330 mg/L
Na⁺	33.1 mg/L	Cl⁻	3030 mg/L	pH	7.7
EC	10400 $\mu\text{mhos/cm}$	Benzene	22.0 mg/L	Ethylbenzene	3.6 mg/L
$\rho,\text{m-xylene}$	9.8 mg/L	Toluene	41.1 mg/L	o-xylene	6.1 mg/L

2.2. Experimental Procedure

Laboratory batch experiments were carried out to evaluate the effectiveness of PS in oxidizing the BTEX over time. Twenty-five mL borosilicate VOA vials with PTFE septa

and screw caps were employed as reaction systems. The batch reactor experiments were designed with a 5 mL headspace of air to accommodate the expected gas production from the reactions. Temperatures were maintained at either 10 °C or 30 °C by using constant-temperature incubators. Vials containing only contaminated groundwater were prepared and used as control samples for the experiments and to measure the initial concentration of BTEX. For the oxidation experiments, reagent-grade sodium persulfate ($\text{Na}_2\text{S}_2\text{O}_8 > 98\%$, Sigma Aldrich) was diluted with ultra-pure water and added, via syringe, to the water samples. The added oxidant concentrations were calculated to achieve a final concentration of 20 g/L in the reaction vials. The reactors were then capped, shaken to completely mix the solutions, and incubated at 10 °C and 30 °C. During sampling, 19.0 mL was extracted from the reactors for organic compound analyses, and 0.5 mL samples were extracted to measure the remaining concentrations of PS. A ground-glass syringe with a stainless-steel tip was utilized for the purpose of sample extractions. Analyses of the BTEX concentrations were performed at the Organic Chemistry Laboratory, Department of Earth and Environmental Sciences, University of Waterloo, Canada. The analyses were performed using an HP 5890 capillary gas chromatography (GC) unit equipped with a flame ionization detector and an HP7673A autosampler. The GC calibration was checked with appropriate standards to verify that the calibration was within $\pm 10\%$. Dichloromethane (1 mL) was injected into the reactors followed by extraction and analysis, as described by [34]. The bulk petroleum hydrocarbon (PHC) fractions F1 (C_6 to C_{10}) included integration of all the area counts on a PHC chromatogram from the beginning of the hexane (nC_6) peak to the apex of the decane (nC_{10}) peak, whereas the PHC fraction F2 (C_{10} to C_{16}) included integration from the apex of the decane peak to the apex of the hexadecane (nC_{16}) peak. Total petroleum hydrocarbon (TPH) was estimated as the sum of the PHC F1 and F2 fractions. Organic analyses were conducted in triplicate at time points 0, 8, 15, 26, 40, 56, and 98 days. In addition, one replicant was utilized to measure the residual oxidant by using the spectrophotometric method [35]. One sample was kept for pH analysis. An Orion pH meter (Model 290A) was used to measure pH.

2.3. Isotope Analyses

For the isotope analyses, two 25-mL vials of the contaminated water samples were collected from a designated monitoring well at the contaminated site by using low-flow sampling methods (Puls and Barcelona, 1996). The samples were diluted and prepared in 40 mL vials. Organic compounds were extracted from the vials via headspace-solid-phase microextraction (SPME), and the extracted compounds were analyzed for carbon and hydrogen isotopes. The isotopic analyses were carried out at Isotope Tracer Technologies Inc., Waterloo, Canada, with GC/TC/IRMS and GC/C/IRMS systems being used to perform the hydrogen and carbon isotope analyses, respectively. The system consisted of an HP 6890 series gas chromatograph (Agilent Technologies, Santa Clara, CA, USA) and a Delta plus XL Continuous-Flow Isotope Ratio Mass Spectrometer (CF-IRMS) (Thermo Finnigan, Bremen, Germany). The BTEX were converted to hydrogen gas for the $\delta^2\text{H}$ analyses, and converted to CO_2 gas to perform the $\delta^{13}\text{C}$ analyses. The $\delta^2\text{H}$ values were reported relative to the international Vienna Standard Mean Ocean Water (VSMOW), while the $\delta^{13}\text{C}$ values were reported relative to the international standard Vienna Pee Dee Belemnite (VPDB). The analytical uncertainties for the $\delta^{13}\text{C}$ and $\delta^2\text{H}$ were typically better than $\pm 0.5\%$ and $\pm 5.0\%$, respectively.

3. Results and Discussion

3.1. BTEX Oxidation by Persulfate

The Initial volatile organic compounds (VOCs) analyses showed that the water samples contain 82.6 mg/L of BTEX, 2.9 mg/L of Trimethylbenzenes, and 0.3 mg/L of naphthalene. This data indicates that the TPH concentration in this site is considerably high, when compared with a typical concentration encountered in groundwater originating from gasoline-contaminated source zones, which is in the range of ~ 25 mg/L. In addition, this

data indicates that BTEX accounts for about 96% of the total petroleum hydrocarbons and thus were chosen as representative compounds. The initial concentrations of benzene, toluene, ethylbenzene, *p,m*-xylene, and *o*-xylene were 22.0, 41.1, 3.6, 9.8, and 6.1 mg/l, respectively. Figure 1 shows the change in the BTEX concentrations during the 98-day treatment period. Data from the control reactors at 10 °C indicated that the concentration of each compound was stable over the experiment period. Similarly, insignificant losses of the target contaminants were observed in the control reactors at 30 °C. These results reveal the inefficiency of thermal treatment alone to remove the organic compounds from the water samples. Similar results were also obtained when PS was added to the contaminated samples at the lower temperature (10 °C), where insignificant oxidations of benzene (<7%), toluene (<25%), ethylbenzene (<26%), and xylene (<36%) were observed. This observation was utilized to establish the similarity between the thermal treatment at 30 °C without PS and the chemical oxidation by PS at the lower temperature (10 °C). The low oxidation rate of the target contaminants by PS at 10 °C is mainly attributed to the low reactivity of the PS anions at this temperature. In contrast, benzene, toluene, *p,m*-xylene, and *o*-xylene were completely oxidized (100%), and almost complete oxidation of ethylbenzene (>91%) was observed when PS was added to the reactor at 30 °C. This enhancement in the oxidation rate of the BTEX was mainly attributed to the thermal activation of PS at 30 °C (Equation (3)). These data show that the natural groundwater temperature (30 °C) in Middle Eastern countries is sufficient to activate PS thermally. This will ultimately enhance treatment efficiency by generating powerful oxidants (e.g., sulfate free radicals) and lower the capital costs of the treatment by avoiding the use of costly artificial heating technologies.

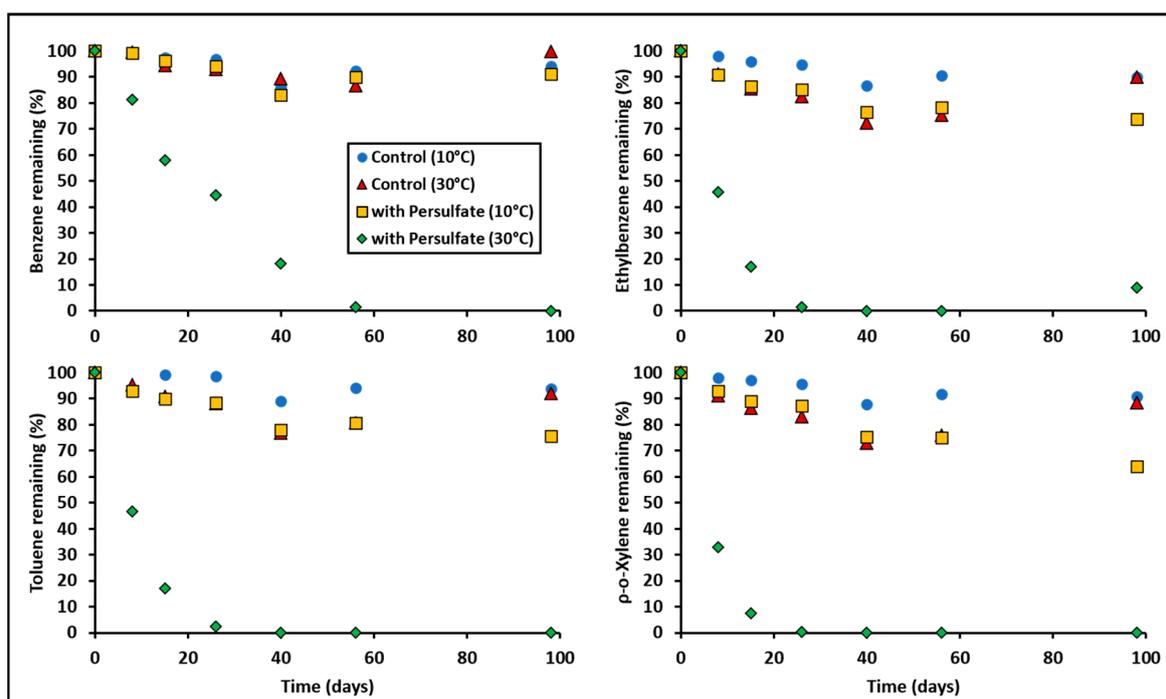


Figure 1. Changes in BTEX concentrations vs. time during the oxidation experiments with persulfate.

Notably, the increase in the oxidation rate for all the BTEX was accompanied by a significant decrease in the solution pH < 3. Accordingly, it is suggested that decreasing system pH may play a major role in oxidizing organic compounds. A plausible explanation for the observed enhancement in the oxidation potential of PS at an acidic pH might be related to the generation of peroxymonosulfuric acids (H_2SO_5) through acid-catalyzed oxidation of PS, as given in Equation (6) [36].



Although the oxidation rate of the organic compounds was enhanced by increasing the system temperature from 10 to 30 °C in the current study, elevating the system temperature in some other cases was observed to reduce the mineralization efficiency of the organic carbons [37]. This was attributed to the extremely quick release of reactive sulfate radicals. Too many generations of sulfate radicals may favour radical–radical reactions over radical–organic reactions, which would ultimately reduce the degradation efficiency of the oxidant. Hydrochemical analyses of the water samples (Table 1) confirmed the presence of several well-known radical scavengers (e.g., chloride, bromide, CaCO₃), yet no adverse effect on the oxidation rate of the organic compounds by the presence of these species was observed in the current study, in contrast to the study by [37]. A plausible explanation for the difference between the two studies is attributed to the significant drop in the system pH (<3) in this study. This may minimize the scavenging potential of free radicals by the carbonate species, which can be highly active at neutral and alkaline pHs. Moreover, it is possible that free halogen radicals may contribute to the oxidation of the organic compounds, as illustrated in Equations (7) and (8) [37]. These results demonstrate the complexity of PS chemistry and show that numerous reactions may be involved in the transformation process.



The experimental data were fitted using a pseudo first-order kinetic model [38]. This model was extremely good at describing the observed data for all compounds ($R^2 > 0.94$). In general, the data showed a significant increase in the pseudo-first-order-rate coefficient (K_{obs}) for all compounds when the system temperature was elevated from 10 °C to 30 °C (Table 2).

Table 2. First-order oxidation-rate coefficients (k_{obs}) of the BTEX after the 98-day oxidation experiment with persulfate at 10 to 30 °C.

Compounds	Temperature (°C)	k_{obs} [10^2 h^{-1}]	(r^2)
Benzene	10	4.6	0.96
Benzene	30	236.4	0.96
Toluene	10	6.5	0.96
Toluene	30	226.6	0.99
Ethylbenzene	10	6.72	0.94
Ethylbenzene	30	312.7	0.99
ρ,m -Xylene	10	12.24	0.99
ρ,m -Xylene	30	377.0	0.99

This provides further evidence of the high efficiency of thermal activation in enhancing the oxidation potential of PS. The k_{obs} for ρ,m -xylene were the largest ($\sim 377 \times 10^{-2} \text{ h}^{-1}$), followed by ethylbenzene ($\sim 312 \times 10^{-2} \text{ h}^{-1}$), benzene ($\sim 236 \times 10^{-2} \text{ h}^{-1}$), toluene ($\sim 266 \times 10^{-2} \text{ h}^{-1}$), and o-xylene ($\sim 150 \times 10^{-2} \text{ h}^{-1}$). However, this trend might be influenced by the initial concentration of the organic compound, rather than the oxidation potential of PS. For the same organic compound, a lower oxidation rate would most likely be associated with higher concentrations [3]. In comparison, the k_{ob} data in this study were ~2-to-6 times higher than the k_{ob} data for the PS system used by [5]. The difference in the k_{ob} values between the two studies is probably due to the slightly lower temperature (20 °C) in [5] as opposed to the 30 °C in this experiment.

3.2. Persistence of Persulfate

In the current work, the persistence of PS during the oxidational experiment was examined (Figure 2). Examining the persistence of PS is crucial for viable and cost-effective ISCO applications. In the 10 °C system, only 13% of the initial PS concentration was decomposed. These data were utilized as an indication of a low reaction rate between the

sulfate anions and the organic contaminants at a low temperature. In the 30 °C system, however, the PS concentration declined by ~50% by the end of the experiment. These data indicate that although increasing the system temperature from 10 °C to 30 °C improved the oxidation rate of the BTEX, it compromises the persistence of PS. Three reactions may have contributed to the rapid decomposition of PS in the relatively higher temperature system (30 °C). These include: PS decomposition through a homolytic cleavage of PS to produce hydrogen sulfate and oxygen; acid-catalyzed reaction to yield Caro's acid; and free-radical-oxidation processes [5,36].

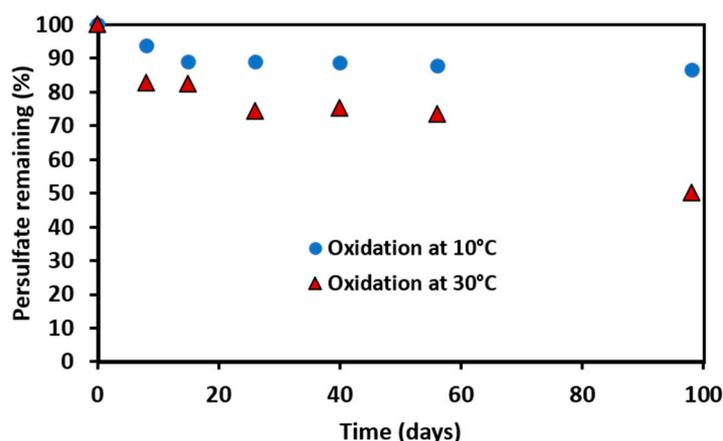


Figure 2. Concentrations of residual persulfate during and after the oxidation of the BTEX at 10 °C and 30 °C.

3.3. Isotopic Enrichment Factors for Carbon and Hydrogen during BTEX Oxidation

Throughout the experiments, the results from the control reactors and when PS was added at 10 °C showed no significant changes in the $\delta^{13}\text{C}$ and $\delta^2\text{H}$ values. The average values for benzene, toluene, ethylbenzene, ρ , m -xylene, and o -xylene were -30.5‰ , -29.7‰ , -28.3‰ , -28.6‰ , and -28.3‰ for $\delta^{13}\text{C}$, and -42.2‰ , -39.8‰ , -173.7‰ , 76.8‰ , and -23.1‰ for $\delta^2\text{H}$, respectively. These values were utilized to represent the initial isotopic composition and to estimate the fractionation factors. As expected, the decline in the BTEX concentrations by PS at 30 °C was associated with increases in the $\delta^{13}\text{C}$ and $\delta^2\text{H}$ values. The chemical oxidation of the target contaminants by PS was unexpectedly and significantly rapid. Accordingly, the concentration of most of the organic compounds was too low to measure the isotope values (below detection limit) after 26 days of running the experiment. The $\delta^{13}\text{C}$ fractionation value for o -xylene was the largest (7.7‰), followed by ethylbenzene (6.5‰), toluene (5.8‰), benzene (3.4‰), and ρ , m -xylenes (3.0‰). The $\delta^2\text{H}$ value increased by 18.6‰ for benzene, 26.6‰ for toluene, 1.6‰ for ethylbenzene, 6.2‰ for ρ , m -xylene, and 8.9‰ for o -xylene. These enrichments in the $\delta^{13}\text{C}$ and $\delta^2\text{H}$ values strongly confirm that both isotopes can provide chemical oxidation to the target contaminants. For the majority of the samples, the good fit ($R^2 > 0.98$) between $\ln(C_{(t)}/C_{(0)})$ and the isotopic shift for carbon and hydrogen suggest that the isotopic enrichment factors for both isotopes can be obtained by using the simplified form of the Rayleigh distillation equation (Equation (3) and Figure 3). The calculated carbon enrichment (ϵC) for benzene, toluene, ethylbenzene, ρ , m -xylene and o -xylene was -1.9‰ , -1.5‰ , -1.5‰ , -0.4‰ and -1.4‰ , respectively. Smaller ϵC values were reported by [11] during the chemical oxidation of benzene, toluene, and o -xylene by PS at 20 °C (Table S1, Supporting Information). The relatively larger carbon-enrichment factors obtained in this study are probably due to the rise in the system temperature (30 °C), which may enhance the oxidation potential of PS by the generation of more powerful oxidants (e.g., sulfate free radicals).

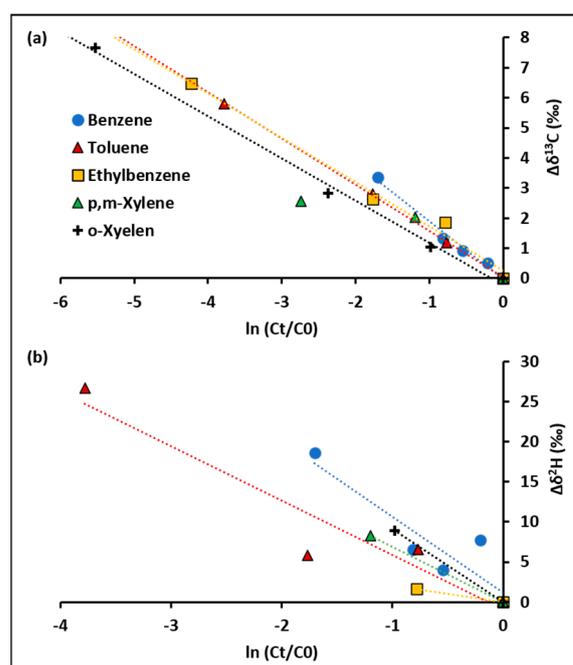


Figure 3. Linearized plot of (a) $\Delta\delta^{13}\text{C}$ vs. normalized concentrations of BTEX and (b) Linearized plot of $\Delta\delta^2\text{H}$ enrichment vs. normalized concentrations of BTEX during chemical oxidation by PS at 30 °C. The slopes represent the calculated isotopic enrichment factors (ϵ) according to the Rayleigh equation.

In comparison with other chemical oxidants, the significant ϵC obtained in this study for toluene is much larger than the one associated with the Fenton-like oxidation experiment ($\epsilon\text{C} = -0.2\text{‰}$) [39]. The difference between the two values is probably related to a different oxidation mechanism involving sulfate radicals in this experiment, as against hydroxyl radicals, the dominant oxidants during the oxidation by the Fenton-like process. The hydrogen enrichment (ϵH) values obtained during the chemical oxidation of benzene, toluene, ethylbenzene, ρ,m -xylene, and o -xylene by PS were -9.5‰ , -6.8‰ , -2.1‰ , -6.9‰ , and -9.1‰ , respectively. Although these enrichment factors are larger than those observed for the carbon isotopes, they are relatively small when compared to the average ϵH values during the BTEX degradation by other chemical or biochemical processes (Table S1, Supporting Information). For instance, the ϵH obtained in this study is much smaller than those reported from biological degradations under denitrification and sulfate-reducing conditions [19,22,23] and (Table S1, Supporting Information). Since the enrichment factors are generally specific to the reaction mechanism, it is expected that distinct degradation processes produce distinct values. The enrichment factors presented in this research should therefore be regarded as relevant only for the chemical oxidation by PS at 30 °C.

3.4. Two-Dimensional Isotope Fractionation Analyses

For the 2D-CSIA approach, the lambda (Λ) values were calculated as the ratio of hydrogen to carbon-enrichment factors ($\Lambda \approx \epsilon\text{H}/\epsilon\text{C}$). The resultant Λ values during the chemical oxidation by PS at 30 °C were 5.0, 4.5, 1.4, 17.3, and 6.5 for benzene, toluene, ethylbenzene, ρ,m -xylene, and o -xylene, respectively. Based on these data, the initial step of BTEX oxidation by free sulfate radicals ($\text{SO}_4^{\bullet-}$) was proposed. As illustrated in Figure 4, the aromatic ring in each compound, particularly at the C-C bond, is attacked by $\text{SO}_4^{\bullet-}$, causing an electron transfer from the organic compound to the $\text{SO}_4^{\bullet-}$ [40].

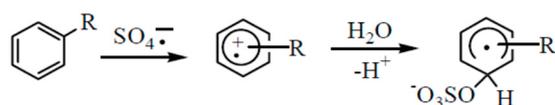


Figure 4. Proposal of the oxidation route of benzene during the chemical oxidation by free sulfate radicals.

Considering this step as the rate-determining point of the reaction, the observed large carbon isotope fractionation in the current experiment probably resulted from the break in the C-C bond, whereas the insignificant fractionation in the hydrogen isotopes may indicate that no cleavage of the C-H bond had occurred in the initial step. The 2D-CSIA data obtained in this experiment were compared with other biochemical studies (Figure 5, Figure 6, Figure 7 and Table S1, Supporting Information), and 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 suggests that the chemical oxidation by PS is an extremely fast process. In general, faster reaction processes show smaller isotopic fractionations because the oxidant/organism is not selective [29]. The data also illustrate the differences and similarities in the transformation pathways when a contaminant undergoes chemical oxidation or aerobic or anaerobic degradations. For instance, the data show that the initial step during the chemical oxidation by PS is associated with a quite large isotopic enrichment for carbon but only a small enrichment for hydrogen. This seems to be quite like the transformation pathways associated with an aromatic ring-mono-oxygenation [17,22]. Although a similar fractionation trend for the carbon isotopes was observed when the organic compounds were degraded by sulfate-reducing organism, the isotopic fractionation of hydrogen was observed to spread over a wider range [41,42]. This clearly demonstrates that combined analyses of carbon and hydrogen isotopes may be a more robust method of assessing the transformation pathways during the degradation of organic compounds, especially when multiple remediation technologies are applied simultaneously.

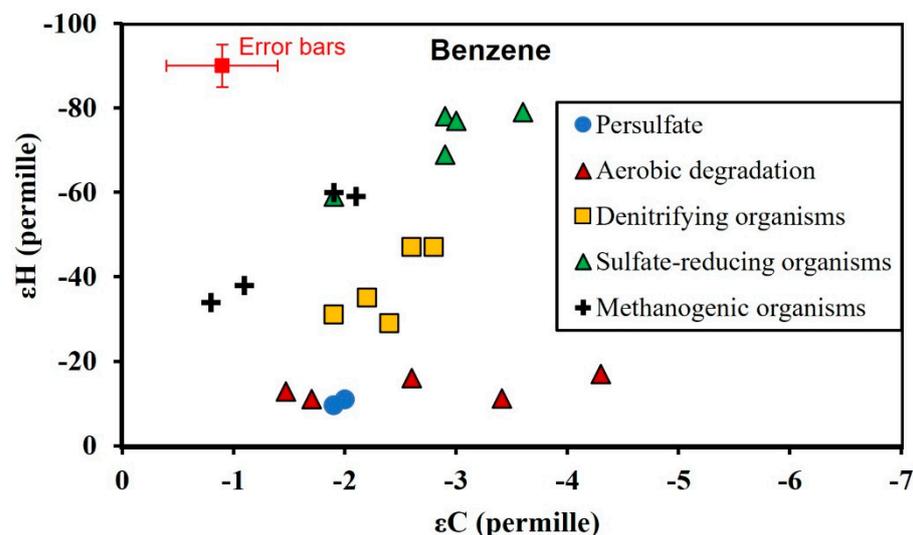


Figure 5. Concurrent carbon and hydrogen enrichment factors (ϵ_C , ϵ_H) for benzene during chemical oxidation by PS compared with recently published values for aerobic and anaerobic degradations derived from [19,22–24,43].

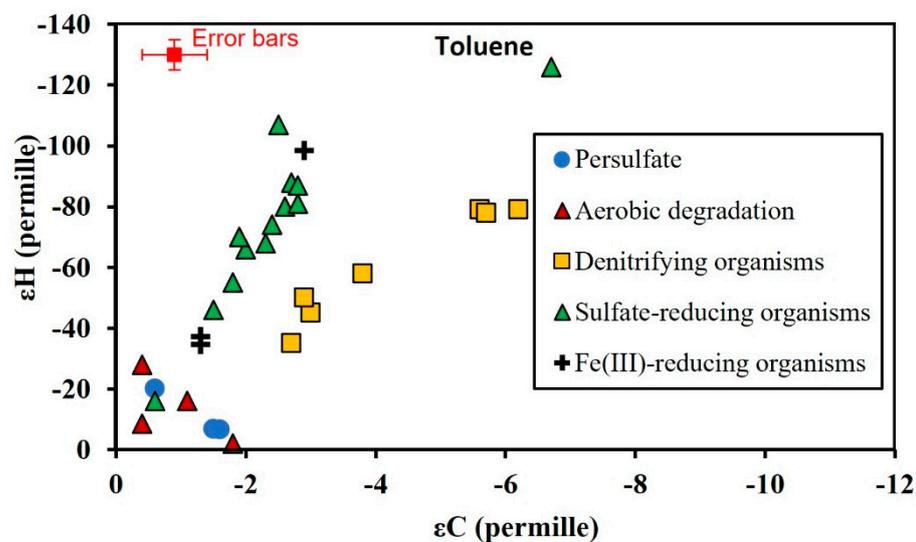


Figure 6. Concurrent carbon and hydrogen enrichment factors (ϵC , ϵH) for toluene during chemical oxidation by PS compared with recently published values for aerobic and anaerobic degradations derived from [11,17,24,32,42,44].

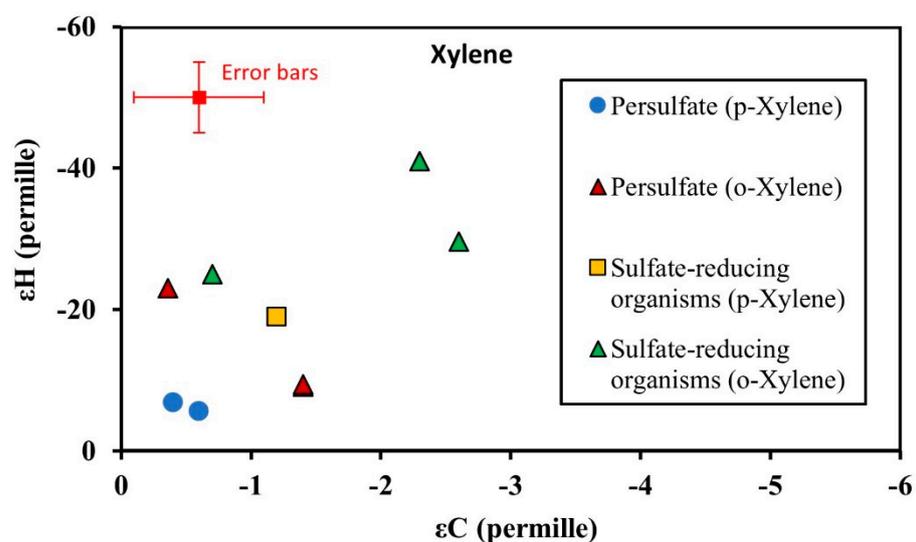


Figure 7. Concurrent carbon and hydrogen enrichment factors (ϵC , ϵH) for xylenes during chemical oxidation by PS compared with recently published values for biodegradation by sulfate-reducing organisms derived from [32,45].

4. Conclusions

Most of the research on persulfate (PS) applications, as a chemical oxidant to remediate gasoline compounds, has been carried out on fresh groundwater aquifers and at low temperatures, which represent typical hydrogeological settings in Northern America and Europe. In this study, however, batch experiments were carried out to investigate the effectiveness of PS to remediate benzene, toluene, ethylbenzene, and xylene (known as BTEX compounds) in a saline environment at a relatively elevated groundwater temperature (30 °C). This hydrological setting is quite common in groundwater aquifers in Middle Eastern countries, where water resources are at high risk of contamination due to widespread oil and gas activities. When PS was added to the reactors at 10 °C, at least 83% of benzene, 75% of toluene, 74% of ethylbenzene, and 64% of xylene remained in the reactors at the end of the 98-day experimental period. In contrast, all the target contaminants were almost completely oxidized within the treatment period when PS was activated thermally by elevating the system temperature to 30 °C. The outcome of the

current study shows that the natural groundwater temperature (30 °C) in Middle Eastern countries is sufficient to activate PS. This will ultimately enhance the treatment efficiency in this hydrogeological setting by activating PS thermally and lowering the capital costs of the treatment by avoiding the use of subsurface heating activation technologies. Additionally, the result from this study shows that the chemical oxidation by PS can provide a rapid and extensive removal of the BTEX as compared to bioremediation technologies which require longer time spans. The pseudo-first-order rate coefficient (k_{obs}) for ρ , m -xylene degradation was the largest, followed by ethylbenzene, benzene, toluene, and o -xylene. However, this trend might be influenced by the initial concentrations of the organic compounds rather than the potential of PS to oxidize a compound. In the 10 °C system, the PS concentration decreased by ~13% compared with ~50% in the 30 °C system. This indicates that although the oxidation coefficients were at least 31 times higher at 30 °C than the one at 10 °C, it compromises the persistence of PS.

Isotopically, the chemical oxidation of the BTEX by PS at 30 °C was accompanied by enrichments in heavier isotopes (^{13}C and ^2H) in the residual contaminants. This observation was utilized as further proof of contaminant degradation rather than removal by other physical processes such as volatile organic compound evaporation. Calculated carbon-enrichment values (ϵC) of -1.9‰ for benzene, -1.5‰ for ethylbenzene and toluene, -0.4‰ for ρ , m -xylene, and -1.4‰ for o -xylene were obtained, while hydrogen enrichment values (ϵH) after the chemical oxidation of benzene, toluene, ethylbenzene, ρ , m -xylene, and o -xylene were -9.5‰ , -6.8‰ , -2.1‰ , -6.9‰ and -9.1‰ , respectively. The observed large carbon isotope fractionation indicates a break in the C–C bond, whereas the insignificant fractionation in the hydrogen isotopes may suggest that no cleavage of the C–H bond occurred in the initial step of the chemical oxidation. In comparison, the hydrogen and carbon isotope fractionations associated with the chemical oxidation of the BTEX by PS were smaller than the ones resulted from biodegradation (e.g., sulfate reduction, denitrification). This indicates that chemical oxidation by PS is probably a fast process and does not allow for the oxidant to be isotopically selective. Combined analyses of the carbon and hydrogen isotopes and the generated isotope plot ($\Delta\delta^{13}\text{C}$ vs. $\Delta\delta^2\text{H}$) has proven to be a more robust method of assessing the transformation pathways during the chemical oxidation of the BTEX by PS, and to distinguish treatment zones where PS and biodegradation technologies are applied simultaneously. Future work will evaluate and compare different approaches including other chemical oxidants (e.g., hydrogen peroxide) as well as biodegradation on the effectiveness of in-situ remediation of the BTEX.

Supplementary Materials: The following are available online at <https://www.mdpi.com/article/10.3390/hydrology8030139/s1>, Table S1: Concurrent Carbon and hydrogen enrichment factors (ϵC , ϵH) and calculated (Λ) values for BTEX during the chemical oxidation by PS compared with recently published values for aerobic and anaerobic degradations.

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