

Hydroxyl radical and non-hydroxyl radical pathways for trichloroethylene and perchloroethylene degradation in catalyzed H_2O_2 propagation systems

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ABSTRACT

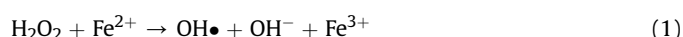
Catalyzed H_2O_2 propagations (CHP) is characterized by the most robust reactivity of any of the in situ chemical oxidation (ISCO) technologies because it generates the strong oxidant hydroxyl radical along with nucleophiles + reductants, such as superoxide radical. The most common groundwater contaminants, trichloroethylene (TCE) and perchloroethylene (PCE), were used as model contaminants in evaluating the effect of hydrogen peroxide (H_2O_2) dosage on contaminant destruction kinetics. Both TCE and PCE degradation rates increased with H_2O_2 dosages up to 0.1 M, and then decreased with higher H_2O_2 dosages. Parallel reactions conducted with the addition of the hydroxyl radical scavenger 2-propanol and the hydroxyl radical-specific probe nitrobenzene confirmed that hydroxyl radical is primarily responsible for TCE and PCE degradation; however, 5–20% of their degradation was attributed to a non-hydroxyl radical mechanism. Reactions conducted with the superoxide probe tetranitromethane showed that superoxide generation rates increased with increasing H_2O_2 dosages. These results were confirmed by electron spin resonance spectroscopy. Therefore, the non-hydroxyl radical pathway for TCE and PCE degradation at $\text{H}_2\text{O}_2 \geq 0.5$ M was likely via nucleophilic attack by superoxide. The results of this research demonstrate that contaminants present in the aqueous phase that are reactive with hydroxyl radical require only low doses of H_2O_2 (≤ 0.1 M), but subsurface systems contaminated with species not reactive with hydroxyl radical (e.g., carbon tetrachloride) require H_2O_2 concentrations ≥ 0.5 M.

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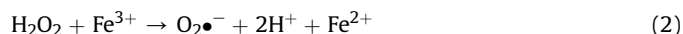
1. Introduction

In situ chemical oxidation (ISCO) has become one of the most commonly used technologies for the remediation of contaminated source zones in surface soils and the subsurface. Three oxidant sources are commonly used for ISCO: sodium persulfate, potassium or sodium permanganate, and hydrogen peroxide (H_2O_2) (Siegrist et al., 2001; Petri et al., 2011a, 2011b). Of the three, H_2O_2 , which is activated to generate catalyzed H_2O_2 propagations (CHP), is characterized by the most robust chemistry for contaminant destruction (Watts and Teel, 2005).

CHP is based on Fenton's reagent, in which decomposition of dilute H_2O_2 is initiated by iron (II) to generate hydroxyl radical ($\text{OH}\bullet$) (Walling, 1975):



Alternatively, a superoxide-driven Fenton reaction can provide a pathway for the generation of iron (II) if iron (III) is present in the system:

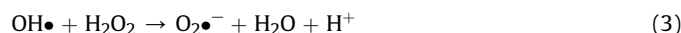


Hydroxyl radical oxidizes most contaminants of concern, including trichloroethylene (TCE), perchloroethylene (PCE), and polychlorinated biphenyls (PCBs), at near diffusion-controlled rates ($k_{\text{OH}\bullet} > 10^9 \text{ M}^{-1} \text{ s}^{-1}$) (Haag and Yao, 1992). Therefore, hydroxyl radical has the potential to rapidly oxidize most contaminants found in surface soils and the subsurface if they are in the aqueous phase and are not sorbed or present as nonaqueous phase liquids (NAPLs) (Sedlak and Andren, 1994). In addition, non-radical pathways can potentially generate ferryl iron (FeO^{2+}); its presence is difficult to differentiate from hydroxyl radical (Deguillaume et al., 2005; Barbusiński, 2009).

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As H_2O_2 concentrations are increased in CHP systems, hydroxyl radical reacts with the excess H_2O_2 to generate superoxide radical anion ($\text{O}_2^{\bullet-}$) (De Laat and Gallard, 1999):



Superoxide is a weak nucleophile and reductant (Frimer, 1988). In deionized water, it is unreactive with highly chlorinated aliphatic compounds, such as carbon tetrachloride, hexachloroethane, and chloroform (Halliwell and Gutteridge, 1985; Pignatello, 1992). However, in the presence of solids or of cosolvents that are less polar than water, including H_2O_2 , superoxide reactivity in water increases (Furman et al., 2009) resulting in effective degradation of halogenated aliphatic compounds via nucleophilic attack. Smith et al. (2004) documented that superoxide is unreactive with chloroaliphatic compounds in deionized water; however, superoxide reactivity increased proportionately with the addition of increasing hydrogen peroxide concentrations. The same increase in superoxide reactivity was found when acetone, ethylene glycol, and other solvents were added to deionized water–superoxide systems. Highly oxidized compounds such as hexachloroethane, carbon tetrachloride, and perfluorooctanoic acid (PFOA) are unreactive with hydroxyl radical but are rapidly degraded in CHP systems by superoxide (Watts et al., 1999; Teel and Watts, 2002; Che and Lee, 2011; Jho et al., 2012; Mitchell et al., 2014; da Silva-Rackov et al., 2016). Furthermore, superoxide has surfactant-like properties and promotes the enhanced desorption of hydrophobic contaminants from solids (Corbin et al., 2007; Do and Kong, 2012; Rosas et al., 2014) and the enhanced dissolution of NAPLs (Watts et al., 2005; Smith et al., 2006); these studies, which used ISCO formulations that generate superoxide but do not generate measurable hydroxyl radical activity, are consistent with a surfactant-like role played by superoxide. These results corroborate field data showing that CHP ISCO injections result in contaminant rebound (Petri et al., 2011a). The mechanism of enhanced desorption of hydrophobic contaminants and enhanced dissolution of NAPLs by superoxide has yet to be determined.

The generation of both hydroxyl radical and superoxide has distinct advantages for CHP ISCO. When both reactants are generated in CHP systems, they provide a near-universal contaminant destruction matrix in which hydrophobic contaminants that are sorbed or present in NAPLs are released to the aqueous phase and are then oxidized by hydroxyl radical or degraded through nucleophilic attack by superoxide (Quan et al., 2003; Smith et al., 2009, 2015). TCE and PCE are the most common subsurface contaminants resulting from the improper disposal of industrial chemicals (Watts, 1998). These contaminants are alkenes, and therefore react rapidly with hydroxyl radical (k_{OH^\bullet} for TCE = $4.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$; k_{OH^\bullet} for PCE = $2.8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$). TCE and PCE are degraded by hydroxyl radical to dichloroacetic acid during ISCO treatment (Leung et al., 1992). The degradation products are then further degraded in the subsurface by natural attenuation (Watts, 1998). However, these contaminants are highly chlorinated, and may also potentially be degraded by superoxide. The pathways of TCE and PCE transformation in CHP systems have yet to be investigated. Several studies have demonstrated that superoxide generation and reactivity becomes important in CHP systems with H_2O_2 concentrations >0.5% (0.17 M) (Teel and Watts, 2002; Smith et al., 2004, 2006; Ahmad et al., 2011); however, a quantitative assessment of hydroxyl radical generation vs. superoxide generation has not been conducted to date. Therefore, the purpose of this research was to investigate the CHP conditions that effectively degrade the common groundwater contaminants TCE and PCE, to evaluate hydroxyl radical and superoxide generation as a function of H_2O_2 concentration, and to assess their relative contributions to TCE and PCE

degradation.

2. Materials and methods

2.1. Chemicals

H_2O_2 (50%, technical grade), iron (III) perchlorate, TCE, PCE, tetranitromethane, and 2-propanol were purchased from Sigma Aldrich (St. Louis, MO). Nitrobenzene was obtained from J.T. Baker (Phillipsburg, NJ). *n*-Hexane (95%) was obtained from Fisher Scientific (Fair Lawn, NJ). ORBO 32 gas adsorbent tubes were purchased from Supelco (St. Louis). 5,5-Dimethyl-1-pyrroline *N*-oxide (DMPO) ($\geq 99\%$) was purchased from Axxora, LLC (San Diego). DMPO was purified with activated carbon followed by filtration until no extraneous electron spin resonance spectroscopy (ESR) signals were observed. Double-deionized water (>18 M Ω cm) was produced using a Barnstead NANOpure II Ultrapure system.

2.2. Model contaminants, probe compounds, and scavengers

TCE and PCE were used as model contaminants to study degradation kinetics as a function of H_2O_2 concentrations in CHP systems. The initial concentrations of TCE and PCE were 100 μM . These concentrations of TCE and PCE are mid-range in relation to those commonly found in the field, and are above the Maximum Contaminant Levels (MCLs) of 5 $\mu\text{g/L}$ as regulated under the U.S. Safe Drinking Water Act. Groundwater TCE and PCE concentrations at contaminated sites can range from nondetectable to $\sim 10^5 \mu\text{g/L}$. For example, Gross and Termath (1985) documented TCE concentrations up to 10,000 $\mu\text{g/L}$ in groundwater at Wurtsmith Air Force Base, Oscoda, Michigan, U.S., and Boone et al. (1986) reported total chlorinated hydrocarbon concentrations of 160,000 $\mu\text{g/L}$ in groundwater adjacent to a TCE dense nonaqueous phase liquid (DNAPL) underlying the Savannah River Plant, South Carolina, U.S. Nitrobenzene and tetranitromethane were used as reaction-specific probe compounds to identify the generation of reactive oxygen species in CHP systems. The initial concentrations of nitrobenzene and tetranitromethane were 1 mM and 300 μM , respectively. The probe compound concentrations were based on analytical detection limits and the linear range for analysis. Nitrobenzene was used as an oxidant probe to detect hydroxyl radical because it has high reactivity with hydroxyl radical ($k_{\text{OH}^\bullet} = 3.9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) (Buxton et al., 1988) but not with reductants or nucleophiles (Ahmad et al., 2012). Tetranitromethane was used as a superoxide probe because it has high reactivity with superoxide ($k_{\text{O}_2^{\bullet-}} = 1.9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) but not with perhydroxyl radical ($k_{\text{HO}_2^\bullet} < 10^4 \text{ M}^{-1} \text{ s}^{-1}$) (Afanasyev, 1989) or hydroxyl radical ($k_{\text{OH}^\bullet} < 10^6 \text{ M}^{-1} \text{ s}^{-1}$). 2-Propanol was used to scavenge hydroxyl radical ($k_{\text{OH}^\bullet} = 1.9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) (Buxton et al., 1988); the molar ratio of scavenger to probe compound was 1000:1.

2.3. Reaction procedures

CHP systems contained varying concentrations of H_2O_2 (0.01, 0.025, 0.05, 0.1, 0.25, 0.5, 0.75, and 1 M) and 1 mM iron (III)–perchlorate. The reaction systems consisted of H_2O_2 , iron (III), and one of the model contaminants (TCE or PCE) or probe compounds (nitrobenzene or tetranitromethane). The iron (III)–catalyzed system provided a superoxide-driven CHP reaction (Equation (2)). All reactions were conducted in capped 20 mL borosilicate vials; an ORBO-32 gas absorbent tube was inserted into the Teflon cap to capture any volatilized TCE and PCE (Smith et al., 2006). The total aqueous solution was 10 mL. The initial pH in all CHP reactions, ranging from 0.01 M H_2O_2 to 1 M H_2O_2 was 3.1. The consistency of the pH between reactions suggests that the pH of the reactions in

the study was controlled by the iron (III)–perchlorate catalyst, not by H_2O_2 . The pH of the solutions remained constant for 30 min, the maximum duration of the reactions. Hydroxyl radical is generated most effectively at low pH, and superoxide is generated more effectively at high pH. However, the pH of 3.1 used in this study provides sufficient generation of both hydroxyl radical and superoxide (Afanas'ev, 1989; Watts et al., 1999; Smith et al., 2004).

Reaction vials and ORBO tubes were extracted using 5 mL of hexane at selected time points, and TCE, PCE, nitrobenzene, and tetranitromethane concentrations were quantified by gas chromatography (GC). Chromatographic conditions are described in section 2.5. In addition, control experiments were conducted using deionized water in place of H_2O_2 . All reactions were conducted in triplicate at $20 \pm 2^\circ\text{C}$.

2.4. Electron spin resonance (ESR) spectroscopy

DMPO was used as a spin trap agent to detect radicals by ESR spectroscopy. CHP systems prepared for ESR analysis contained 1 mM iron (III)–perchlorate, 50 mM DMPO, and 0.1 M or 1 M H_2O_2 . Reactions were carried out under air-saturated conditions, mixing iron and DMPO solutions together immediately prior to the addition of H_2O_2 . The reaction mixture for ESR spin trapping contained a volume of 2.5 mL and was immediately injected into an aqueous sample cell (Bruker, AquaX high sensitive aqueous sample cell). ESR spectra were obtained using a Bruker 6/1 spectrometer with a resonance frequency of 9.9 GHz, microwave power of 2.0 mW, modulation frequency of 100 kHz, modulation amplitude of 1.0 G, sweep width of 100 G, time constant of 164 ms, sweep time of 168 s, and receiver gain of 2.0×10^5 .

2.5. Analysis

Hexane extracts containing TCE, PCE, or tetranitromethane were analyzed using a Hewlett-Packard 5890 gas chromatograph equipped with a $30\text{ m} \times 0.53\text{ mm}$ Equity-5 capillary column and electron capture detector. The injector and detector temperatures were 220°C and 270°C , the initial and final oven temperatures were 100°C and 160°C , respectively, with a program rate of $30^\circ\text{C}/\text{min}$ for TCE or PCE. The program for tetranitromethane was 50°C and 160°C at a rate of $50^\circ\text{C}/\text{min}$. Nitrobenzene extracts were analyzed using a Hewlett-Packard 5890 gas chromatograph fitted with a $15\text{ m} \times 0.53\text{ mm}$ SPB-5 capillary column and a flame ionization detector. The injector temperature was 200°C , and the detector temperature was 250°C . The initial and final oven temperatures were 60°C and 180°C , respectively, and the program rate was $30^\circ\text{C}/\text{min}$. pH was monitored using a Fisher Accumet pH meter.

Error bars on figures represent the standard error of the mean of three replicates. First order rates were calculated by plotting the natural logarithm of relative concentration as a function of time.

3. Results and discussion

3.1. TCE and PCE degradation by CHP

Loss of TCE in CHP systems dosed with H_2O_2 concentrations ranging from 0.01 M to 1 M, each initiated with 5 mM iron (III), is shown in Fig. 1a–f. Control systems containing deionized water in place of H_2O_2 showed no measurable loss of TCE. TCE was measured in ORBO tubes at the end of each reaction; TCE masses captured in the ORBO tubes were negligible, confirming that volatilization over the course of the reactions was minimal. The loss of TCE after 20 min in systems containing 0.01 M and 0.025 M H_2O_2 was 84% and 97%, respectively. TCE loss was more rapid in systems

containing 0.05 M H_2O_2 (98% loss after 15 min) and 0.1 M H_2O_2 (97% loss after 7.5 min). These results indicate that the rate of TCE loss increased with H_2O_2 concentrations in the range from 0.01 M to 0.1 M, confirming that higher H_2O_2 concentrations increase the generation of reactive species (Watts et al., 2005). However, at higher H_2O_2 concentrations TCE loss decreased with 98% loss after 15 min at 0.5 M H_2O_2 and 95% loss after 20 min at 1 M H_2O_2 . In summary, rates of TCE loss increased as a function of H_2O_2 concentrations up to 0.1 M, but then decreased with increasing H_2O_2 concentrations up to 1 M.

Scavenging of hydroxyl radical with 2-propanol (Fig. 1) resulted in no loss of TCE in systems with $<0.1\text{ M}$ H_2O_2 , but approximately 10% and 20% TCE loss occurred with hydroxyl radical scavenging in CHP systems with 0.5 M H_2O_2 and 1 M H_2O_2 , respectively. These results suggest that a non-hydroxyl radical pathway may be degrading some of the TCE at H_2O_2 concentrations $\geq 0.5\text{ M}$.

The loss of PCE in CHP systems with H_2O_2 concentrations ranging from 0.01 M to 1 M is shown in Fig. 2a–f. Parallel control systems containing deionized water in place of H_2O_2 showed no measurable loss of PCE. As in the TCE systems, analysis of ORBO tubes showed negligible PCE volatilization. PCE loss over 30 min was 87% in the CHP system dosed with 0.01 M H_2O_2 and was 96% in the presence of 0.025 M H_2O_2 . PCE loss increased in CHP systems containing 0.05 M H_2O_2 (96% loss after 25 min) and 0.1 M H_2O_2 (96% loss after 15 min). However, when the H_2O_2 concentration was increased to 0.5 M PCE loss was slower, with 97% loss after 30 min, and in CHP systems containing 1 M H_2O_2 , only 87% of the PCE was oxidized over 30 min. Similar to the TCE results, rates of PCE loss increased as a function of H_2O_2 dosage through 0.1 M, and then decreased with H_2O_2 dosages of 0.5 M and 1 M.

The addition of 2-propanol to scavenge hydroxyl radical (Fig. 2) resulted in no loss of PCE in systems with H_2O_2 concentrations $<1\text{ M}$ H_2O_2 ; however, approximately 5% PCE loss occurred with hydroxyl radical scavenging in CHP systems with 1 M H_2O_2 . Randomized block design analysis of variance (ANOVA) confirmed that the difference between the control and scavenged experiments was statistically significant at $p < 0.05$. These results suggest that a non-hydroxyl radical pathway may contribute a small amount to PCE loss at H_2O_2 concentrations $\geq 1\text{ M}$.

First order rate constants for TCE and PCE loss were derived from the data of Figs. 1 and 2 and from additional data of CHP systems containing 0.25 M and 0.75 M H_2O_2 , and were plotted as a function of H_2O_2 dosage (Fig. 3a and b). First order rate constants for both TCE and PCE loss increased as a function of H_2O_2 dosage, reaching a maximum at 0.1 M H_2O_2 , and then decreased at higher H_2O_2 concentrations. The rate of TCE loss at 1 M H_2O_2 was $2.3 \times$ lower than at 0.1 M H_2O_2 (Fig. 3a), and the rate of PCE loss at 1 M H_2O_2 was $4.0 \times$ lower than in the 0.1 M H_2O_2 system (Fig. 3b).

The results of Fig. 3 are also in agreement with second order rate constants for the attack of hydroxyl radical on TCE and PCE. The second order rate constant for hydroxyl radical attack on TCE is $4.0 \times 10^9\text{ M}^{-1}\text{ s}^{-1}$, which is $1.7 \times$ greater than the rate constant for hydroxyl radical attack on PCE ($k_{\text{OH}\cdot} = 2.4 \times 10^9\text{ M}^{-1}\text{ s}^{-1}$). The mean TCE/PCE ratio of first order rate constants shown in Fig. 3 for the six H_2O_2 dosages is 1.7 ± 0.34 , which is in agreement with hydroxyl radical as the primary transforming species in these CHP systems.

3.2. Generation of hydroxyl radical in CHP systems

In order to evaluate the pathways of the reactive oxygen species generated as H_2O_2 dosages are increased in CHP systems, reactions were conducted using the hydroxyl radical-specific probe compound nitrobenzene (Fig. 4). In systems containing 0.05 M and 0.1 M H_2O_2 dosages, $>99\%$ nitrobenzene oxidation was achieved

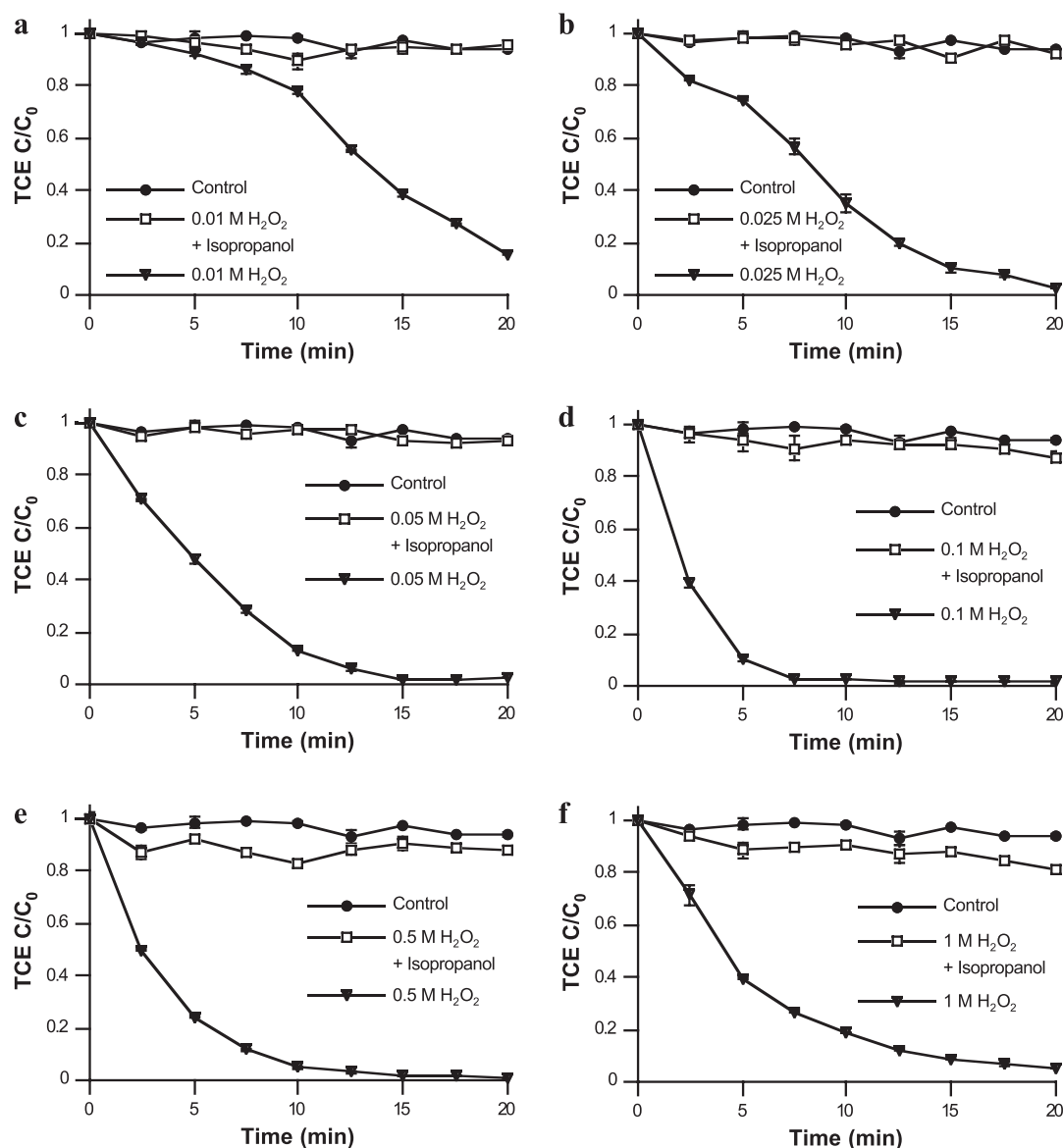


Fig. 1. TCE degradation in CHP systems with and without 2-propanol scavenging of hydroxyl radical. a) 0.01 M H_2O_2 ; b) 0.025 M H_2O_2 ; c) 0.05 M H_2O_2 ; d) 0.1 M H_2O_2 ; e) 0.5 M H_2O_2 ; f) 1 M H_2O_2 . Error bars represent the standard error of the mean of three replicates.

within 10 min. However, with a 0.5 M H_2O_2 dose, nitrobenzene loss was slower with 93% oxidized over 15 min. When the H_2O_2 dose was increased to 1 M, nitrobenzene oxidation decreased further with 69% loss over 15 min. The results of Fig. 4 demonstrate that the maximum nitrobenzene oxidation rate was achieved with a dose of 0.1 M H_2O_2 . These results are similar to the data shown in Figs. 1 and 2 for TCE and PCE destruction, which suggests that hydroxyl radical is the primary reactive oxygen species responsible for TCE and PCE degradation. The results of Figs. 1–4 can be applied to laboratory treatability studies, which are typically conducted to determine appropriate ISCO process field conditions. These results suggest that, for contaminants reactive with hydroxyl radical ($k_{\text{OH}\cdot} > 10^9 \text{ M}^{-1} \text{ s}^{-1}$), treatability studies should be conducted with target concentrations in the subsurface of $\leq 0.1 \text{ M}$ (0.34%) H_2O_2 .

3.3. Generation of superoxide radical anion in CHP systems

Recent studies have shown that oxidized contaminants not

reactive with hydroxyl radical, such as carbon tetrachloride and chloroform, are degraded in CHP systems; the reactive species that has been proposed for the degradation of such oxidized organic contaminants is superoxide (Watts et al., 1999; Smith et al., 2004; Mitchell et al., 2014). To evaluate the role of superoxide in the degradation of TCE and PCE, loss of the superoxide probe tetranitromethane was evaluated in CHP systems with H_2O_2 dosages ranging from 0.05 to 1 M.

The degradation of tetranitromethane in CHP systems over 5 min is shown in Fig. 5. With 0.05 M and 0.1 M H_2O_2 dosages, tetranitromethane degradation was 69% and 78%, respectively. When the H_2O_2 dosage was increased to 0.5 M and 1 M, tetranitromethane degradation increased to 81% and 83%, respectively. Unlike the findings of nitrobenzene oxidation rates, tetranitromethane degradation increased with increasing concentrations of H_2O_2 , even above 0.1 M H_2O_2 . Similar results were documented by Smith et al. (2004); as H_2O_2 concentrations in CHP systems increased from 0.1 M to 1 M, greater carbon tetrachloride

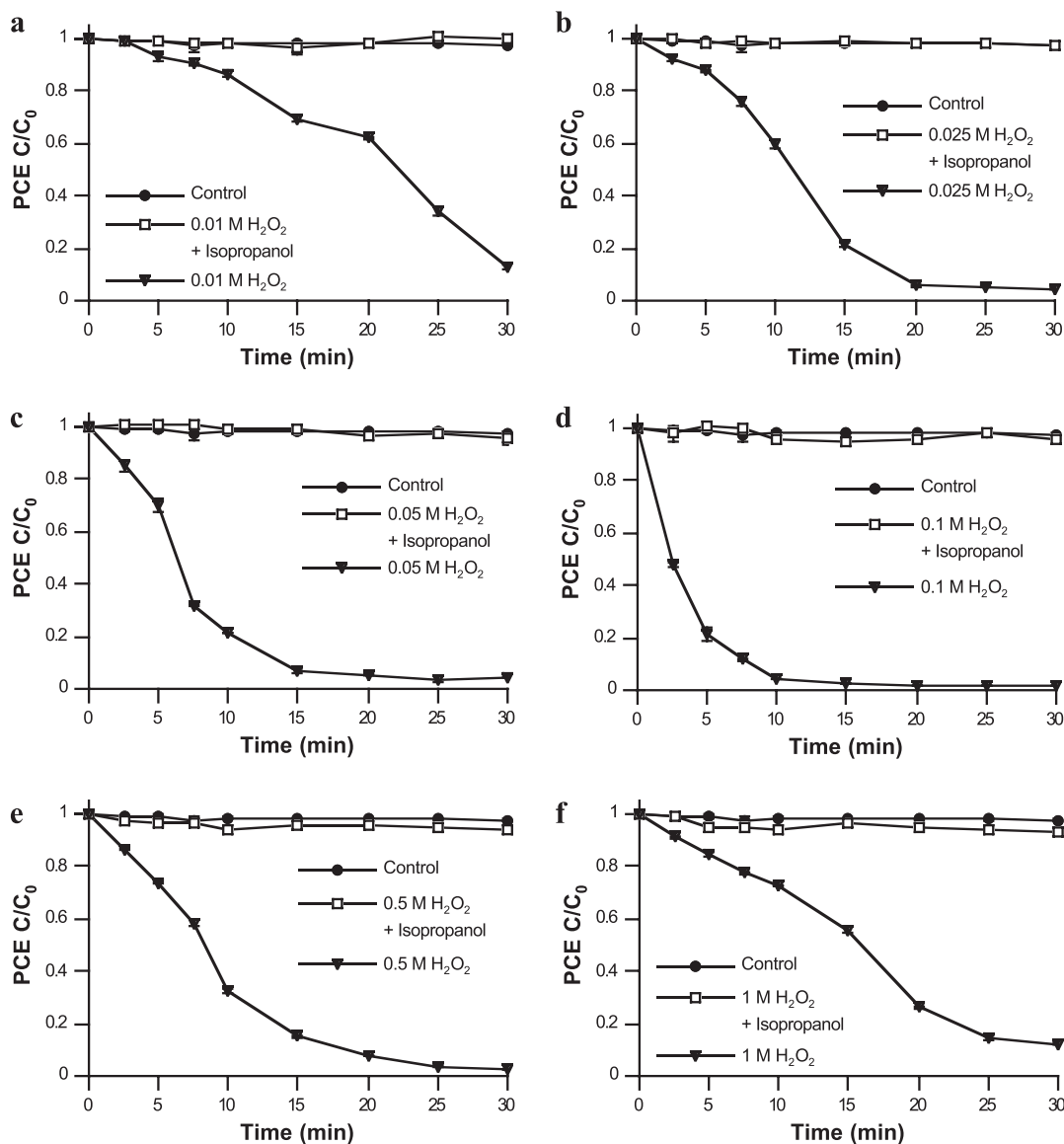


Fig. 2. PCE degradation in CHP systems with and without 2-propanol scavenging of hydroxyl radical. a) 0.01 M H₂O₂; b) 0.025 M H₂O₂; c) 0.05 M H₂O₂; d) 0.1 M H₂O₂; e) 0.5 M H₂O₂; f) 1 M H₂O₂. Error bars represent the standard error of the mean of three replicates.

transformation was observed and was proposed to be due to increased superoxide generation. The results of Fig. 5 suggest that, because superoxide is very effective at H₂O₂ concentrations >0.1 M (0.34%), laboratory treatability studies should provide >0.1 M H₂O₂ to the subsurface if the contaminants are not reactive with hydroxyl radical but are degraded by superoxide (e.g. carbon tetrachloride, polyfluorinated compounds) (Teel and Watts, 2002; Smith et al., 2004; Mitchell et al., 2014).

3.4. Kinetic analysis

First order rate constants for nitrobenzene oxidation and tetranitromethane degradation were derived from the data of Figs. 4 and 5 and from additional data of CHP systems containing 0.25 M and 0.75 M H₂O₂, and plotted as a function of H₂O₂ dosage (Fig. 6). Nitrobenzene oxidation rates, which are proportional to hydroxyl radical generation rates, reached a maximum at 0.1 M H₂O₂ (Fig. 6a); these results are similar to the results of Fig. 3a and b for TCE and PCE degradation rate constants. In contrast, the results of

Fig. 6b demonstrate that relative superoxide generation rates, as measured by tetranitromethane degradation, continued to increase with increasing H₂O₂ concentrations. These results are in agreement with the formation of superoxide through the propagation reaction shown in equation (2): as the H₂O₂ concentration increases, H₂O₂ reacts with hydroxyl radical to generate superoxide, which then degrades tetranitromethane.

3.5. Scavenging experiments

The results of the scavenging experiments in Figs. 1 and 2 suggest that at H₂O₂ concentrations ≥0.5 M, TCE and PCE are partially degraded by a non-hydroxyl radical mechanism. Superoxide reactivity, as measured by tetranitromethane degradation (Fig. 5), was also highest at H₂O₂ concentrations ≥0.5 M. The most common pathway described for the degradation of chloroaliphatic compounds by superoxide is through nucleophilic attack (Roberts and Sawyer, 1981). TCE and PCE are susceptible to nucleophilic attack, but at relatively slow rates: first order rate constants for

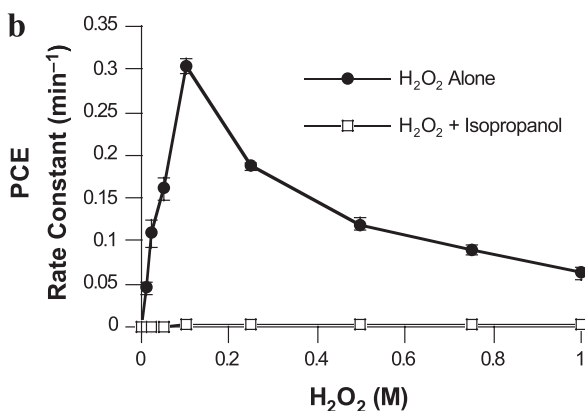
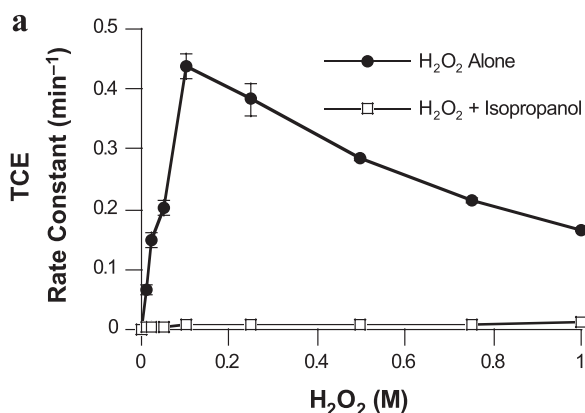


Fig. 3. First order rate constants for the degradation of a) TCE and b) PCE in CHP systems with increasing H₂O₂ dosages, with and without 2-propanol scavenging.

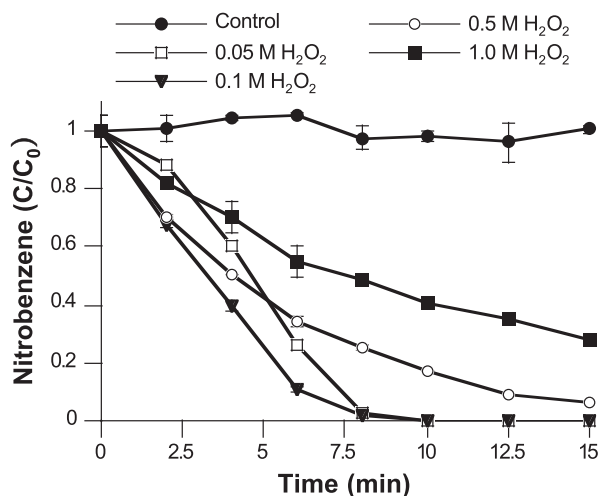


Fig. 4. Oxidation of the hydroxyl radical probe nitrobenzene with increasing H₂O₂ dosages. Error bars represent the standard error of the mean of three replicates.

nucleophilic attack via hydrolysis are $1.07 \times 10^{-12} \text{ min}^{-1}$ for TCE and $1.37 \times 10^{-15} \text{ min}^{-1}$ for PCE (Jeffers et al., 1989). The increase in non-hydroxyl radical degradation of TCE and PCE with increasing superoxide concentrations is consistent with an S_N2 mechanism in

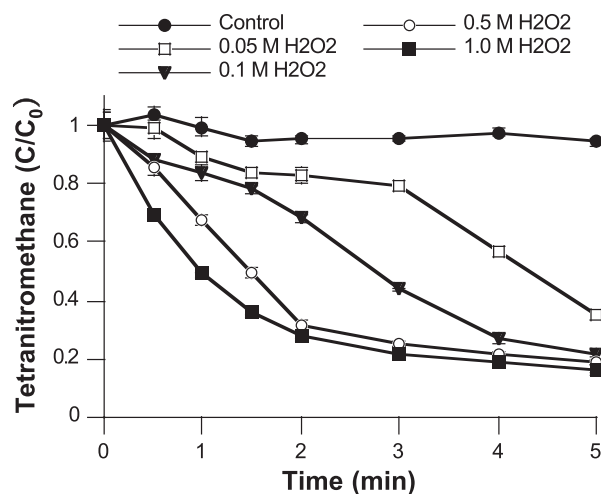


Fig. 5. Loss of the superoxide probe tetranitromethane with increasing H₂O₂ dosages. Error bars represent the standard error of the mean of three replicates.

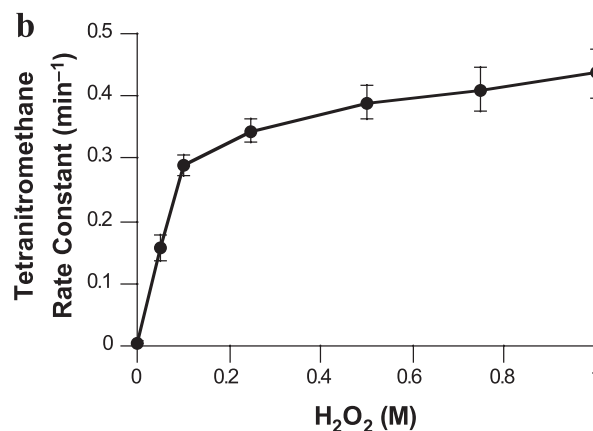
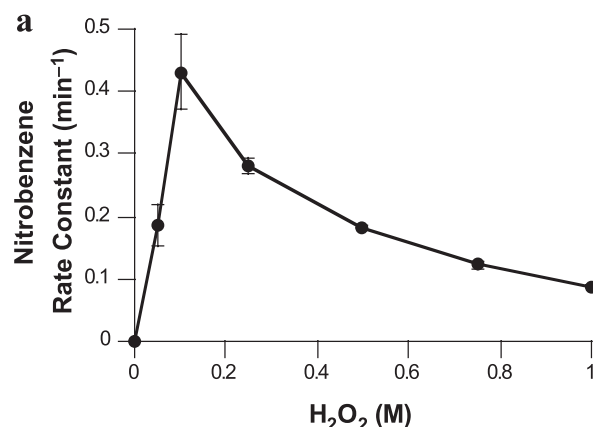


Fig. 6. First order rate constants for degradation of a) the hydroxyl radical probe nitrobenzene and b) the superoxide probe tetranitromethane in CHP systems with increasing H₂O₂ dosages.

which the degradation rate is dependent on the concentrations of both superoxide and TCE or PCE. Furthermore, an S_N2 mechanism is consistent with the results shown in Figs. 1 and 2 because TCE degradation by superoxide was greater than PCE degradation, which is consistent with a more crowded transition state for PCE relative to TCE (Larsen and Weber, 1994).

Net first order rate constants for hydroxyl radical-only degradation of TCE and PCE were calculated from the data of Fig. 3 by subtracting rates of reactions scavenged with 2-propanol from rates of reactions without scavenger. The net first order rate constants for TCE and PCE degradation vs. first order rate constants for oxidation of the hydroxyl radical probe nitrobenzene (from Fig. 6a) at all hydrogen peroxide doses are shown in Fig. 7. The relationships are linear with a slope of 1.17 for TCE vs. nitrobenzene (Figs. 7a) and 0.70 for PCE vs. nitrobenzene (Fig. 7b). The slope of these lines is consistent with the known first order reaction rate constants with hydroxyl radical for nitrobenzene ($k_{\text{OH}\cdot} = 3.9 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$), TCE ($k_{\text{OH}\cdot} = 4.0 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$), and PCE ($k_{\text{OH}\cdot} = 2.8 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$) (Buxton et al., 1988); the ratio of the rate constants is 1.03 for TCE to nitrobenzene and 0.72 for PCE to nitrobenzene. The linear fit of nitrobenzene oxidation rates vs. the net hydroxyl radical-only TCE and PCE degradation rates provides further evidence that hydroxyl radical is the primary species for TCE and PCE degradation.

First order rate constants for TCE and PCE degradation in reactions scavenged with 2-propanol, in which degradation was the result of a non-hydroxyl radical pathway (shown in Fig. 3), were plotted against the first order rate constants for tetranitromethane degradation (shown in Fig. 6b). The result, shown in Fig. 8, is a linear relationship with a slope of 0.022 for TCE (Figs. 8a) and 0.0058 for PCE (Fig. 8b). The results of Fig. 8 provide further evidence that superoxide is the non-hydroxyl radical species

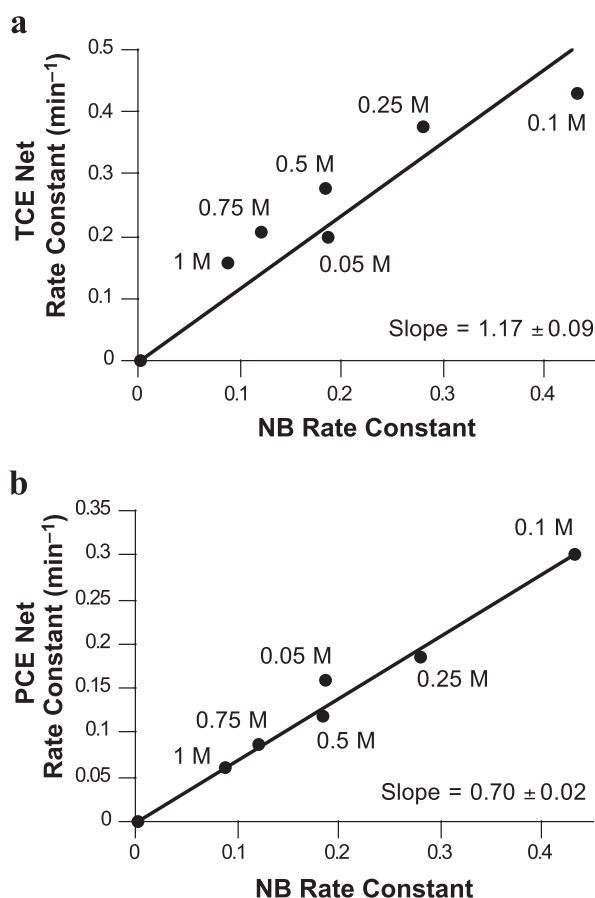


Fig. 7. Net first order rate constants for a) TCE and b) PCE vs. nitrobenzene first order rate constants in CHP systems with increasing H₂O₂ dosages. Rate constants for 2-propanol scavenged reactions were subtracted from non-scavenged experiments to calculate net rate constants for TCE and PCE resulting from hydroxyl radical activity alone. Data points are labeled with their H₂O₂ concentration.

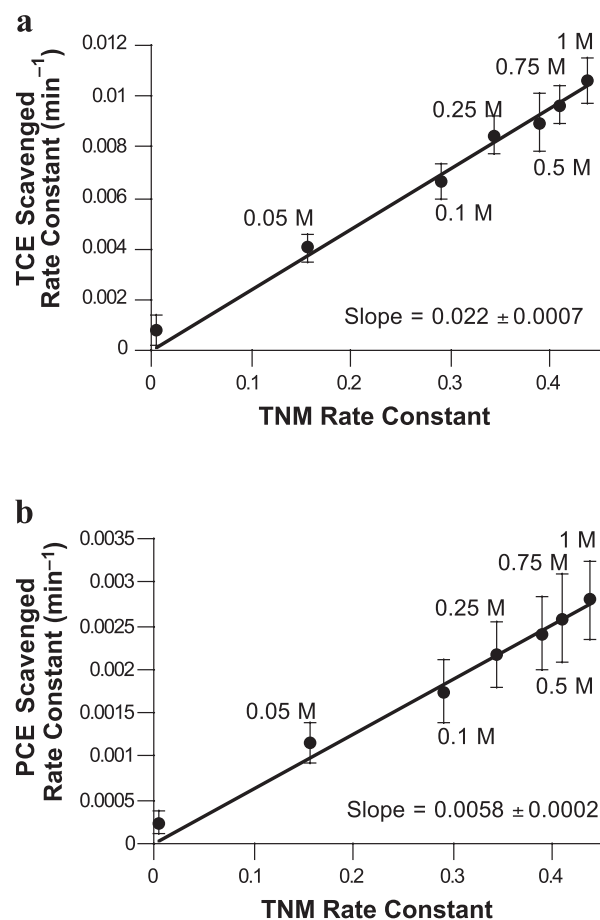


Fig. 8. Scavenged first order rate constants for a) TCE and b) PCE degradation in reactions containing 2-propanol vs. tetranitromethane rate constants in CHP systems with increasing H₂O₂ dosages. Data points are labeled with their H₂O₂ concentration.

responsible for a small portion of TCE and PCE degradation in CHP systems.

3.6. Electron spin resonance spectroscopy

The presence of both hydroxyl radical and superoxide in the CHP systems was investigated by the addition of the spin trapping agent DMPO followed by ESR spectroscopy analysis. In the 0.1 M H₂O₂ CHP system, a distinct signal was seen for the hydroxyl radical adduct (DMPO–OH) (hyperfine splitting constants of $A_N = 14.6 \text{ G}$ and $A_H = 14.6 \text{ G}$), confirming the presence of hydroxyl radical in the system (Fig. 9a). When the H₂O₂ concentration was increased to 1 M, the intensity of the DMPO–OH hydroxyl radical adduct decreased significantly and a superoxide adduct (DMPO–OOH) was present (hyperfine splitting constants of $A_N = 14.4 \text{ G}$, $A_H^\beta = 11.3 \text{ G}$, and $A_H^\alpha = 1.1 \text{ G}$), confirming a decrease in hydroxyl radical generation and an increase in superoxide generation in CHP systems at higher H₂O₂ concentrations. The ESR results from the two CHP systems are consistent with ESR spectra and hyperfine splitting constants obtained for superoxide and hydroxyl radical in other studies (Finkelstein et al., 1980; Yim et al., 1990; Zhao et al., 2001).

The results documented herein are based on conditions not generally applicable to full-scale ISCO injections. For example, iron (III) perchlorate was used as a catalyst because perchlorate does not quench hydroxyl radical, but would not be used in the field because perchlorate is a groundwater pollutant (Watts, 1998). Most

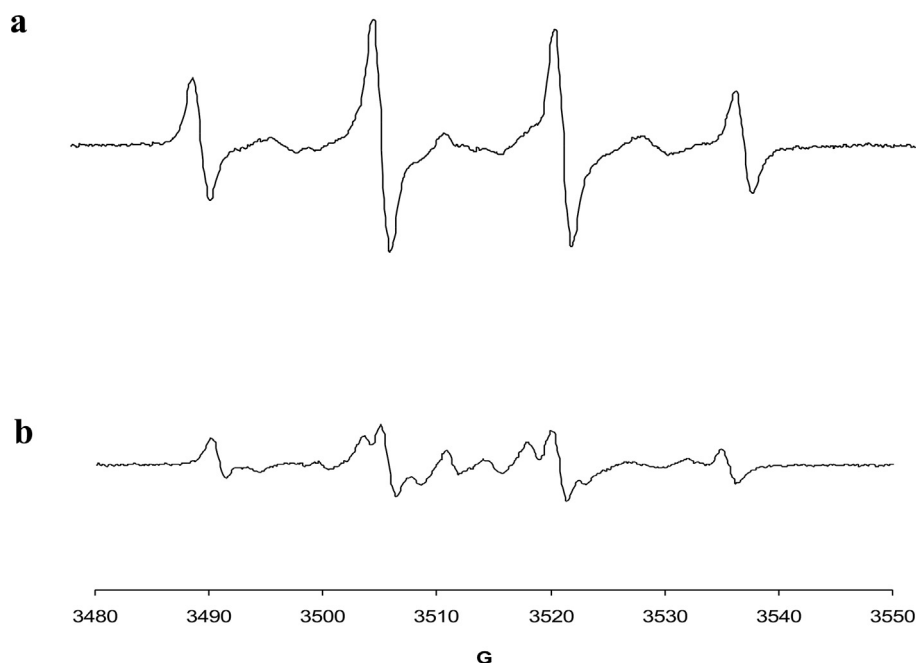


Fig. 9. ESR spectra of hydroxyl radical and superoxide DMPO adducts in CHP systems dosed with a) 0.1 M H_2O_2 ; b) 1 M H_2O_2 .

groundwaters do not contain soluble iron in mM concentrations; however, the subsurface is rich in iron and manganese oxides and oxyhydroxides, which are effective CHP catalysts (Tyre et al., 1991; Leung et al., 1992; Teel et al., 2001, 2007). Because of the significant range of subsurface mineral contents, soil organic matter, and porosity, laboratory treatability studies are always conducted to provide dosing criteria prior to conducting full-scale ISCO injections. The fundamental approach presented in this paper provides a rational basis for conducting such treatability studies, interpreting their results, and troubleshooting in the field. Treatability studies on groundwater containing contaminants reactive with hydroxyl radical would potentially investigate several doses of H_2O_2 at concentrations ≤ 0.1 M. In contrast, these results can be applied to treatability studies of contaminants not reactive with hydroxyl radical by applying several hydrogen peroxide doses of >0.1 M.

3.7. Practical applications

The results of this research demonstrate that if a contaminant reacts rapidly with hydroxyl radical and it is not sorbed or present in a NAPL phase, relatively low concentrations of H_2O_2 are effective in its destruction. Examples of such contaminants include TCE, PCE, 1,4-dioxane, and methyl *tert*-butyl ether (MTBE). Because hydroxyl radical reacts rapidly with most contaminants of concern, contaminant destruction to $<\text{MCLs}$ ($5 \mu\text{g/L}$) is theoretically possible. However, if the contaminant exhibits low reactivity with hydroxyl radical but is degraded by superoxide in the presence of cosolvents or solids (Smith et al., 2004; Furman et al., 2009), then higher H_2O_2 concentrations (>0.1 M) are necessary to promote superoxide generation, and also to provide sufficient cosolvent in the system to enhance superoxide reactivity (Smith et al., 2004). For example, groundwater contaminated with carbon tetrachloride or chloroform, which are unreactive with hydroxyl radical, would require higher H_2O_2 concentrations that generate superoxide and increase its reactivity. Because superoxide lifetime and generation rates are greater at high pH (Afanasyev, 1989), the superoxide degradation pathway is minimized under the pH conditions used in this study.

More alkaline conditions could be used if the superoxide pathway is to be optimized, such as in the degradation of PFOA described by Mitchell et al. (2014). In addition, any contaminant that is sorbed or present as a NAPL will require higher H_2O_2 concentrations to generate superoxide to promote the enhanced desorption of hydrophobic contaminants and the enhanced dissolution of NAPLs (Corbin et al., 2007; Smith et al., 2006, 2009, 2015). Enhanced desorption and dissolution of contaminants increases their concentration in the aqueous phase, where they can then be destroyed by hydroxyl radical, superoxide, or both. Hydrogen peroxide represents the primary cost of CHP ISCO for soil and groundwater remediation. The findings of this research provide guidelines for injecting the doses that provide the most effective and efficient use of hydrogen peroxide.

4. Conclusions

- TCE and PCE oxidation rates in CHP systems increased to a maximum at 0.1 M H_2O_2 , and then decreased at higher H_2O_2 concentrations
- Hydroxyl radical is the reactive species primarily responsible for TCE and PCE degradation at H_2O_2 dosages ≤ 0.1 M
- Superoxide generation increased with increasing hydrogen peroxide concentrations
- Superoxide was partially responsible for TCE and PCE degradation at H_2O_2 concentrations >0.1 M

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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