Tetrachloroethylene and hexachloroethane degradation in Fe(III) and Fe(III)–citrate catalyzed Fenton systems

EunHea Jho,a,c Naresh Singhal*a and Susan Turnerb

Abstract

BACKGROUND: Tetrachloroethylene (PCE) and hexachloroethane (HCA) degradation, individually and in mixture, is investigated by Fe(III) or Fe(III)–citrate initiated Fenton reaction under a range of hydrogen peroxide (H2O2) concentrations to illustrate the applicability and constraints of Fenton chemistry in degrading contaminants in polluted groundwater.

RESULTS: In individual solutions Fe(III) rapidly degraded PCE for all H2O2 concentrations, but HCA at ≥ 0.2 mol L−1 H2O2; the apparent PCE degradation rate initially increased but then decreased with increasing H2O2, while the HCA degradation rate was either unaffected or increased. With Fe(III)-citrate PCE degradation was lower and no HCA degradation occurred. PCE degradation of organic compounds at near diffusion-controlled rates with second-order kinetics is acknowledged, as being the most active and capable of oxidizing many organic compounds at near diffusion-controlled rates with second-order rate constants >109 M−1 s−1.2,17 Probably, as a result of this the degradation of organic compounds by other radicals of Fenton chemistry (e.g. O₂•−) has not been as extensively investigated as their degradation by OH•.

CONCLUSION: Fe(III) catalyzed reactions can potentially degrade chemicals through reductive as well as oxidative pathways. Degradation of chemicals in mixtures occurs at a slower rate due to competition for radical moieties. The Fe(III)-citrate complex further slowed chemical transformation. This study expands on the use of different forms of iron to catalyze the Fenton reaction to degrade chemicals.

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Keywords: contaminant degradation; Fenton reagent; oxidative and reductive pathways; tetrachloroethene; hexachloroethane

INTRODUCTION

The Fenton reagent, consisting of a mixture of iron(II) and hydrogen peroxide (H2O2), is often used to degrade organic contaminants in water and soil. One of its common modifications involves the use of Fe(III), instead of Fe(II), to initiate the reactions, producing oxidative and reductive radical moieties via several interconnected reactions (Table 1). A second modification involves using iron complexed with inorganic or organic chelates, instead of the free Fe(II) or Fe(III), to increase iron solubility at near neutral pH as well as to control the H2O2 consumption rate.2–4 In such applications citric acid, a naturally occurring biodegradable multidentate organic chelate, has often been used as a modifier to extend the reactivity duration.2,5

Upon initiation, Fe(III) forms Fe(III)-hydroperoxy complexes, which are assumed to decompose to Fe(II), and this is accompanied with the production of perhydroxyl radicals (HO₂•) and superoxide anion radicals (O₂•−) (Reactions 1 and 2 in Table 1).8 According to the Fenton chemistry, Fe(II) is oxidized back to Fe(III) via Reactions 3–5, resulting in production of hydroxyl radicals (OH•). The radicals can further react with H2O2 (Reaction 6 and 7) or with each other (Reaction 8). Of the various radicals present, OH• is acknowledged as being the most active and capable of oxidizing many organic compounds at near diffusion-controlled rates with second-order rate constants >109 M−1 s−1.2,17 Probably, as a result of this the degradation of organic compounds by other radicals of Fenton chemistry (e.g. O₂•−) has not been as extensively investigated as their degradation by OH•.
neously degrade PCE and HCA. Additionally, the simultaneous degradation of trichloroethene (TCE) and carbon tetrachloride have been reported for modified Fenton reactions catalyzed by pyrite. However, the degradation of a mixture of PCE and HCA via Fe(III) catalyzed reactions (i.e. $O_2^-$ driven transformations) has not been reported. This study investigates the degradation behavior of PCE and HCA, individually and as PCE–HCA mixture, using Fe(III) or Fe(III)-citrate to catalyze the Fenton reaction. Specifically, the effect of H$_2$O$_2$ concentration on the degradation of PCE and HCA is studied to define the applicability of Fe(III) or Fe(III)–citrate initiated Fenton reaction for remediation of contaminant mixtures.

**MATERIALS AND METHODS**

**Chemicals and solution preparation**

All the reagents used in this study were reagent grade. PCE (> 99.5%, Fluka, USA), HCA (99%, Aldrich, USA), iron(III) perchlorate hydrate (< 0.10% chloride, Aldrich, USA), hexane (95%), sodium citrate dihydrate (Mallinckrodt Baker, USA), and H$_2$O$_2$ (30%, LabServ Pronalys, Australia) were used. The experimental procedure followed has previously been reported. Fe(III) stock solution (20 mmol L$^{-1}$) and Fe(III)-citrate solution (20 mmol L$^{-1}$) were prepared by dissolving Fe(ClO$_4$)$_3$ in solutions of 0.01 mol L$^{-1}$ HClO$_4$ and 60 mmol L$^{-1}$ citrate, respectively. All experiments were performed at room temperature in intermittently stirred 60 mL borosilicate vials that were filled with 59.0 ± 0.1 mL solution containing 1 mmol L$^{-1}$ Fe(III), 0.01–2 mol L$^{-1}$ H$_2$O$_2$, 0.30 ± 0.17 mmol L$^{-1}$ PCE and/or 0.015 ± 0.007 mmol L$^{-1}$ HCA. The solution pH was adjusted to 2.87 ± 0.03 using 1 mol L$^{-1}$ perchloric acid or 1 mol L$^{-1}$ potassium hydroxide. Up to six replicates of each experimental condition were performed, along with controls in which deionized water substituted for H$_2$O$_2$, with the samples analyzed in duplicate.

**Residual PCE and HCA analysis**

At specified intervals the residual PCE or HCA was extracted in hexane and analyzed using a Hewlett-Packard 6890A gas chromatograph equipped with a 0.53 mm (ID) × 30 m AT-624 capillary column (Alltech, USA) and a halogen specific detector (O.I. Analytical, USA). The oven temperature was kept at 40 °C for 2 min followed by 10 °C min$^{-1}$ rise to 160 °C and then 20 °C min$^{-1}$ rise to a final temperature of 230 °C, which was maintained for 2 min. The injector and detector temperatures were 250 °C and 1000 °C, respectively, and the helium flow rate was 5.09 mL min$^{-1}$ with a split ratio of 12 : 1. The method detection limits were 0.008 mmol L$^{-1}$ for PCE and 0.001 mmol L$^{-1}$ for HCA. While the residual amounts of PCE and HCA were monitored, the intermediate products of their degradation were not determined. The data obtained were fitted to an empirical model and the kinetic parameters and their associated confidence intervals (CI) were estimated using the GraphPad Prism (CA, USA) software. The significance of difference in the estimates was determined by performing the extra sum-of-squares test at a $P$-value of 0.05.

**PCE and HCA data regression**

The rate constants for PCE and HCA degradation in the Fe(III) and Fe(III)-citrate catalyzed reactions were derived from the degradation data to compare the behavior of PCE and HCA with increasing H$_2$O$_2$ concentration. The degradation of PCE and the degradable portion of HCA (i.e. the amount obtained by deducting the final residual fraction, $C_{res}$, from the observed concentrations normalized with respect to the initial concentration) were modeled using the following first order kinetic relationship,

$$ C = (1 - C_{res})e^{-kt} + C_{res} \tag{1} $$

where $C = $ PCE/PCE$_0$ or HCA/HCA$_0$ (dimensionless), the PCE or HCA concentration at time $t$ (h) normalized with respect to the initial concentration (PCE$_0$ or HCA$_0$), $C_{res} = $ PCE$_{residual}$/PCE$_0$ or HCA$_{residual}$/HCA$_0$ (dimensionless), the residual PCE or HCA concentration normalized to the initial concentration (i.e. the remaining nondegradable fraction of PCE or HCA), and $k =$ apparent first-order rate constant ($h^{-1}$). This formulation differs from the typical expression of PCE and HCA degradation rates as second-order kinetic functions of the concentrations of the chemical and the oxidant or reductant radicals,

$$ \frac{d[C]}{dt} = -k[C][R] \tag{2} $$

where, $C$ represents PCE or HCA and $R$ represents oxidant or reductant radicals. As radical moiety concentrations were not measured in this study, the kinetic rates were expressed using a first-order model (Equation (1)) in which the ‘pseudo’-first-order rate constant, $k$, represents the product of the second-order rate constant $k'$ and the radical moiety concentration $R$. The adoption of an apparent first-order rate constant inherently assumes some ‘averaged’ concentration for the radical moiety. Accordingly, a large variation in the radical moiety concentration over the experiment duration will result in a poor fit to data. Additionally, as a result of this approach the fitted apparent first-order rate

<table>
<thead>
<tr>
<th>Table 1. Rate constant or equilibrium constant for reactions in Fenton chemistry</th>
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<tbody>
<tr>
<td>Reaction No.</td>
</tr>
<tr>
<td>(1)</td>
</tr>
<tr>
<td>(2)</td>
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<tr>
<td>(3)</td>
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<tr>
<td>(4)</td>
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<td>(5)</td>
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<td>(6)</td>
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<td>(7)</td>
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<td>(8)</td>
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$^1$ The dimensions of equilibrium constant $pK$ depend on the stoichiometry of the reaction.
constants will vary for different experimental conditions.\textsuperscript{10} To further confirm the trends obtained using the above model for data showing partial chemical removal, the obtained rate constant estimates were compared with those from the following model specifically developed for incomplete chemical degradation:\textsuperscript{21}

\[ \frac{C}{C_0} = 1 - \frac{t}{m + bt} \]  

(3)

where \( C_0 \) is the initial chemical concentration, \( 1/m \) represents the initial decay rate (i.e. as \( t \rightarrow 0 \)) and \( 1/b \) represents the maximum degradable fraction of the chemical (i.e. \( 1 - \text{Cres}/C_0 \)).

**RESULTS AND DISCUSSION**

**Effect of H\(_2\)O\(_2\) concentration on PCE and HCA degradation**

Irrespective of the H\(_2\)O\(_2\) concentration the change in solution pH was 0.06 ± 0.01 pH units over 24 h and the volatilization losses of PCE and HCA over 24 h in control vials were 7.5 ± 6.4\% and 4.2 ± 3.3\%, respectively. Consistent with literature\textsuperscript{22} the formation of gas bubbles in vials was more vigorous for higher H\(_2\)O\(_2\) concentrations between 0.2 mol L\(^{-1}\) and 2 mol L\(^{-1}\). The gas formation was attributed to oxygen production (Reactions 6 and 8 in Table 1) and decomposition of H\(_2\)O\(_2\)\textsuperscript{23} rather than carbon dioxide production from PCE and HCA degradation\textsuperscript{19} as carbon dioxide has high solubility in water and the concentrations of PCE and HCA, relative to H\(_2\)O\(_2\), are low. Thus, oxic conditions are expected to prevail in the vials and the possible enhancement of contaminant degradation in the absence of oxygen from the production of organic radicals\textsuperscript{24} was not considered. Furthermore, at H\(_2\)O\(_2\)/Fe(II) ratios greater than 25, a condition that applies to this study except at 0.01 mol L\(^{-1}\) H\(_2\)O\(_2\), the effect of oxygen on the contaminant decomposition rate has been shown to be insignificant.\textsuperscript{25} For both the individual PCE solution and the PCE-HCA mixture, complete PCE degradation was achieved within 2 h in the Fe(III) catalyzed reactions at all H\(_2\)O\(_2\) concentrations (Fig. 1). However, using Fe(III)-citrate it took about 24 h for PCE to completely degrade at H\(_2\)O\(_2\) < 0.2 mol L\(^{-1}\); PCE degradation was lower for H\(_2\)O\(_2\) ≥ 0.2 mol L\(^{-1}\) (Fig. 2). However, no indication of plateauing of PCE degradation was visible in any of the Fe(III)-citrate tests. Therefore, a Cres of zero was used to model PCE degradation in all cases. These observations indicate that PCE can be degraded by the Fe(III) or Fe(III)-citrate catalyzed reactions regardless of the presence or absence of HCA.

The estimated values and 95\% confidence intervals for the apparent rate constants (\( k \)) for PCE in the Fe(III) system and the Fe(III)–citrate system are presented in Table 2 along with the coefficients of correlation (\( R^2 \)) for the fits. The apparent PCE degradation rate constants increased with increasing H\(_2\)O\(_2\) concentration from 0.01 mol L\(^{-1}\) to 0.2 mol L\(^{-1}\) for Fe(III) catalyzed reactions, but then decreased for higher H\(_2\)O\(_2\) concentrations regardless of the presence or absence of HCA.

For corresponding H\(_2\)O\(_2\) concentrations, the first order degradation rate constants in vials with only PCE were statistically larger than those in the vials with PCE–HCA mixture. In the Fe(III)–citrate system the estimated PCE degradation rate constants were significantly smaller than those for the Fe(III) system. The PCE degradation rate constants and the amount degraded in Fe(III)–citrate catalyzed vials decreased with increasing H\(_2\)O\(_2\) concentration regardless of the presence or absence of HCA.

**Figure 1.** Effect of H\(_2\)O\(_2\) concentration on PCE degradation using Fe(III) in (a) PCE-only vials with control, 0.01 mol L\(^{-1}\), 0.05 mol L\(^{-1}\), 0.2 mol L\(^{-1}\), and 2 mol L\(^{-1}\) H\(_2\)O\(_2\), (b) PCE-only vials with control, 0.5 mol L\(^{-1}\), and 1 mol L\(^{-1}\) H\(_2\)O\(_2\), (c) PCE-HCA mixture with control, 0.01 mol L\(^{-1}\), 0.05 mol L\(^{-1}\), 0.2 mol L\(^{-1}\), and 2 mol L\(^{-1}\) H\(_2\)O\(_2\), and (d) PCE-HCA mixture with control, 0.5 mol L\(^{-1}\) H\(_2\)O\(_2\), Fe(III)\(_0\) = 1 mmol L\(^{-1}\), [PCE]\(_0\) = 0.30 ± 0.17 mmol L\(^{-1}\), [HCA]\(_0\) = 0.015 ± 0.007 mmol L\(^{-1}\), pH 2.87 ± 0.03. Symbols represent -○- Control -○- 0.01 mol L\(^{-1}\) -○- 0.05 mol L\(^{-1}\) -○- 0.2 mol L\(^{-1}\) -○- 2 mol L\(^{-1}\). The lines shown are first-order fits to data. Data points and lines represent mean ± standard deviation with 4 replicates for PCE-only vials and 5 replicates for PCE-HCA mixtures.
OH*, thereby enhancing PCE degradation; at high H$_2$O$_2$ levels, however, two changes result in reversal of this trend for PCE degradation – first, OH* consumption is dominated by its reaction with H$_2$O$_2$ (Reaction (7) in Table 1) and secondly, the bulk of Fe(III) is present as Fe(III)–peroxo complexes, which do not participate in propagation reactions and lower the concentrations of Fe(II) and OH* in solution.\(^{26}\) Fe(III) measurements in the current experiments are consistent with this explanation (data for Fe(III) has not been presented). The final Fe(III) concentrations in reaction vials were lower than those in controls (i.e. vials containing no H$_2$O$_2$); however, this difference decreased for higher H$_2$O$_2$ concentrations, indicating an increase in Fe(III) within the reaction vial. For systems with Fe(III)–citrate, Fe(III) in solution is limited and that exacerbates the consequences of the above reactions. Furthermore, citrate can also act as a sink for OH*.\(^{27}\) As a result the pseudo-decay rate for PCE decreases for larger H$_2$O$_2$. In PCE–HCA mixture the degradation of PCE is lower than the corresponding PCE-only system due to the consumption of O$_2^*$ by HCA, which decreases the O$_2^*$ available for reductive transformation of PCE as well as lowers the formation of OH* by Reaction (6) in Table 1 to decrease the oxidative transformation of PCE.

HCA degradation by Fe(III) (Fig. 3(a), (b)) was modeled using a non-zero $C_{HCA}$ in Equation (1) to account for non-degradable residual chemical; HCA degradation in Fe(III)–citrate system was insignificant and was not modeled (data not presented here). Table 3 presents $k$ and $C_{HCA}$ for HCA degradation in the Fe(III) system. The $R^2$ values for HCA degradation range between 0.70 and 1.00 for fits to data that yielded statistically significant (i.e. non-zero) degradation rates; for rate constant estimates that were statistically insignificant (i.e. they were zero), the $R^2$ values were low ($R^2 < 0.37$). HCA degradation in the Fe(III) catalyzed reactions was observed only for H$_2$O$_2 \geq 0.2$ mol L$^{-1}$ and the rate constants and the amount degraded (i.e. 1–$C_{res}$ values) increased for higher H$_2$O$_2$ concentrations between 0.2 mol L$^{-1}$ and 2 mol L$^{-1}$ in vials with only HCA in solution (Fig. 3(a)–(b) and Table 3). For vials with a PCE–HCA mixture, the rate constants were unaffected by the H$_2$O$_2$ concentration but the amount of HCA degraded increased for higher H$_2$O$_2$ concentrations between 0.2 mol L$^{-1}$ and 2 mol L$^{-1}$ (Table 3). At 2 mol L$^{-1}$ H$_2$O$_2$, complete HCA degradation was achieved within 2 h in the HCA-only vials (Fig. 3(a)), but required about 24 h in the PCE–HCA mixture (Fig. 3(b)). The parameters $1/m$ and $1/b$ (Equation (3)) show similar trends as $k$ and $(1 - C_{res})$, respectively, for increasing H$_2$O$_2$ concentrations (data not presented).

Simulations of Fe(III) initiated Fenton reaction show rapid formation and peaking of HO$_2^*/O_2^*$, and an increase in their concentration for higher levels of H$_2$O$_2$.\(^{26}\) These findings indicate that the O$_2^*$ pool will increase for larger H$_2$O$_2$, but because the pool is finite, reaction with HCA will result in depleting it. Thus, with an increase in H$_2$O$_2$ concentration the rate as well as the amount of HCA degraded can be expected to rise. The degradation of carbon tetrachloride, a compound bearing similarity to HCA in its structure and degradation mechanism, by a Fe(III) initiated Fenton reaction has also similarly shown an increase with H$_2$O$_2$.\(^{16}\) The amount of HCA degraded was similar in vials with the individual chemical and those with the PCE–HCA mixture (Fig. 4(b) and 4(c)), indicating that the O$_2^*$ pool in the two systems was similar. However, HCA degradation in PCE–HCA mixture was slower than that in the HCA-only system for large H$_2$O$_2$ concentration, but the reason for this kinetic limitation is unclear.

The apparent PCE degradation rate constants, HCA degradation rate constants, and HCA residuals show correlation with the log H$_2$O$_2$ concentration ($R^2 \geq 0.91$) (Fig. 4). In this figure a negative
slope represents a decrease in the PCE degradation rate constant or the HCA residual for larger H2O2 concentrations, while a positive slope shows the converse. A horizontal line was fitted when values were statistically similar, indicating their non-dependence on H2O2 concentration. Figure 4 shows that the increase in PCE degradation for H2O2 concentrations up to 0.2 mol L\(^{-1}\) in the PCE-only vials, and up to 0.5 mol L\(^{-1}\) in the PCE-HCA mixtures, is accompanied by negligible HCA degradation, and that the decrease in the PCE degradation at higher H2O2 concentrations is accompanied by greater HCA degradation (i.e. an increase in either the rate constant or the amount of HCA degraded). These observations show that the reactive moieties available at H2O2 < 0.5 mol L\(^{-1}\) in the PCE-HCA mixture are unable to cause significant HCA degradation, while the reactive moieties produced at H2O2 > 0.2 mol L\(^{-1}\) in the HCA-only vial can degrade HCA.

**Applicability of Fe(III) and Fe(III)–citrate catalyzed reaction for degradation of PCE–HCA mixtures**

For both the Fe(III) and the Fe(III)–citrate systems, the PCE degradation rates in the PCE-HCA mixtures were lower than the rates in the PCE-only vials. Similarly, the estimated mean HCA degradation rate constants for the HCA-only vials were consistently higher than or similar to, and the C\textsubscript{res} values were similarly lower than or similar to, those for the PCE-HCA mixture. In the HCA-only vials, the plateauing of the HCA degradation begins about 2 h into the reaction (Fig. 3(a)), within which the PCE degradation is generally completed in the PCE-only vials (Fig. 1(a)–(b)); however, in the PCE-HCA mixtures, the plateauing of the HCA degradation begins after more than 2 h of reaction (Fig. 3(b)). This suggests that appropriate reactive moieties are present for a longer duration in a mixture of PCE and HCA. However, in the beginning of the reactions when both PCE and HCA are present, the PCE and HCA degradation were lower in the mixtures than in the individual solutions. This could simply be a consequence of competition for radicals due to the increase in the total concentration of contaminants; however, in our previous study with Fe(II) and the Fe(II)–citrate systems the opposite trend was observed, suggesting that the increase in the total concentration of contaminants was not the likely reason for this behavior.

As HCA can only be degraded by O\(^{2-}\), the negligible degradation of HCA at H2O2 < 0.2 mol L\(^{-1}\) indicates that at low H2O2 concentrations the O\(^{2-}\) pool is small, and the increase in the HCA degradation at H2O2 > 0.2 mol L\(^{-1}\) is indicative of an enlargement of this pool (e.g. via Reactions 1 and 2). The cessation of HCA

### Table 2. PCE degradation rate constant (best-fit value ± 95% CI) for different H2O2 concentrations in the Fe(III) catalyzed and Fe(III)–citrate catalyzed reactions at pH 3 (C\textsubscript{res} = 0)

<table>
<thead>
<tr>
<th>Reactions</th>
<th>Fe(III) catalyzed reactions</th>
<th>Fe(III) – citrate catalyzed reactions</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Solutions</strong></td>
<td><strong>PCE-only solution</strong></td>
<td><strong>PCE-HCA mixture</strong></td>
</tr>
<tr>
<td>[PCE(_0)] (mmol L(^{-1}))</td>
<td>0.21 ± 0.18</td>
<td>0.17 ± 0.00</td>
</tr>
<tr>
<td>[HCA(_0)] (mmol L(^{-1}))</td>
<td>Not relevant</td>
<td>0.017 ± 0.005</td>
</tr>
<tr>
<td>PCE/HCA ratio</td>
<td>Not relevant</td>
<td>7.2 ± 2.2</td>
</tr>
<tr>
<td>H2O2 (M)</td>
<td>Rate constant (h(^{-1}))</td>
<td>R(^2)</td>
</tr>
<tr>
<td>0.01</td>
<td>6.04 ± 1.10</td>
<td>0.97</td>
</tr>
<tr>
<td>0.05</td>
<td>15.76 ± 1.78b</td>
<td>0.99</td>
</tr>
<tr>
<td>0.2</td>
<td>40.54 ± 5.81c</td>
<td>1.00</td>
</tr>
<tr>
<td>0.5</td>
<td>24.68 ± 1.99d</td>
<td>1.00</td>
</tr>
<tr>
<td>1</td>
<td>18.88 ± 0.69e</td>
<td>1.00</td>
</tr>
<tr>
<td>2</td>
<td>14.20 ± 1.15f</td>
<td>0.99</td>
</tr>
</tbody>
</table>

† [PCE\(_0\)] and [HCA\(_0\)] are presented as mean ± S.D.
‡ Values followed by the same letter do not differ significantly (P-value > 0.05) by extra sum-of-squares F test in Prism.

**Figure 3.** Effect of H2O2 concentration on HCA degradation using Fe(III) in (a) HCA-only vials and (b) PCE–HCA mixture. [Fe(III)]\(_0\) = 1 mmol L\(^{-1}\), [PCE\(_0\)] = 0.30 ± 0.17 mmol L\(^{-1}\), [HCA\(_0\)] = 0.015 ± 0.007 mmol L\(^{-1}\), pH 2.87 ± 0.03. Symbols represent •− Control □− 0.01 mol L\(^{-1}\) △− 0.05 mol L\(^{-1}\)
•− 0.2 mol L\(^{-1}\) □− 0.5 mol L\(^{-1}\) △− 1 mol L\(^{-1}\) △− 2 mol L\(^{-1}\). The lines shown are first-order fits to data. Data points and lines represent mean ± standard deviation based on 3 replicates for HCA-only vials and 5 replicates for PCE–HCA mixtures.
Figure 4. Relationship between (a) PCE degradation rate constant and H₂O₂ concentration; (b) HCA degradation rate constant and H₂O₂ concentration; (c) HCA residual amount and H₂O₂ concentration in the Fe(III) system; and (d) PCE degradation rate constant and H₂O₂ concentration in the Fe(III)–citrate (1:3 molar ratio) system. [Fe(III)]₀ = 1 mmol L⁻¹, [PCE]₀ = 0.30 ± 0.17 mmol L⁻¹, [HCA]₀ = 0.015 ± 0.007 mmol L⁻¹, pH 2.87 ± 0.03. ○ PCE-only, ◦ PCE in PCE–HCA mixture, ■ HCA-only, □ HCA in PCE–HCA mixture, – PCE-only/HCA-only, - - - - PCE–HCA mixture. Data points and lines represent mean ± standard deviation.

| Table 3. HCA degradation rate constant (best-fit value ± 95% C.I.) for different H₂O₂ concentrations in the Fe(III) catalyzed reactions at pH 3 |
|-----------------|-----------------|-----------------|
| Solutions       | HCA-only solution | Fe(III) catalyzed reactions |
| [PCE₀] (mmol L⁻¹) | Not relevant     | PCE–HCA mixture |
| [HCA₀] (mmol L⁻¹) | 0.022 ± 0.003     | 0.17 ± 0.00 |
| PCE/HCA Ratio   | Not relevant     | 7.2 ± 2.2 |
| H₂O₂ (M)        | Rate constant (h⁻¹) † | C₉₀ ‡ | R² | Rate constant (h⁻¹) † | C₉₀ ‡ | R² |
| 0               | 0.84 ± 0.84 (± 0) a | 0.97 ± 0.02 (± 1) A | 0.09 | 0.56 ± 0.56 (± 0) a | 0.98 ± 0.02 (± 1) A | -0.09 |
| 0.01            | 0.51 ± 0.51 (± 0) a | 0.96 ± 0.04 (± 1) A | 0.17 | 0.05 ± 0.05 (± 0) a | 0.98 ± 0.08 (± 1) A | 0.00 |
| 0.05            | 0.07 ± 0.07 (± 0) a | 0.88 ± 0.11 (± 1) A | 0.70 | 0.17 ± 0.17 (± 0) a | 0.91 ± 0.05 (± 1) A | 0.37 |
| 0.2             | 0.69 ± 0.46bc | 0.75 ± 0.04AB | 0.79 | 0.80 ± 0.49bc | 0.68 ± 0.04AB | 0.70 |
| 0.5             | 1.27 ± 0.55cd | 0.47 ± 0.04C | 0.94 | 0.52 ± 0.28bc | 0.57 ± 0.06F | 0.80 |
| 1               | 2.10 ± 0.56de | 0.23 ± 0.03D | 0.98 | 0.62 ± 0.16bc | 0.36 ± 0.04G | 0.94 |
| 2               | 2.56 ± 0.28e | 0.01 ± 0.01 (± 0) E | 1.00 | 0.65 ± 0.15bc | 0.11 ± 0.05H | 0.96 |

† [PCE₀] and [HCA₀] are presented as mean ± S.D.
‡ Values followed by the same letter do not differ significantly (P-value > 0.05) by extra sum-of-squares F test. R² will be negative when the best-fit curve fits the data even worse than does a horizontal line.
degradation during the 24 h of reaction indicates that the pool of \( \text{O}_2^- \) is exhausted after some time. Support for this observation is provided by other studies with \( \text{O}_2^- \) generating system using \( \text{K}_2\text{O}_2 \) and \( \text{H}_2\text{O}_2 \) that have shown larger \( \text{O}_2^- \) production with an increase in \( \text{H}_2\text{O}_2 \) concentration.\(^{11,15,16}\) Raising the \( \text{H}_2\text{O}_2 \) concentration from 0.5 mol L\(^{-1}\) to 2 mol L\(^{-1}\) resulted in a larger amount of HCA degradation over the same duration supporting the suggestion of a larger \( \text{O}_2^- \) pool. The decrease in the apparent PCE degradation rate constant at \( \text{H}_2\text{O}_2 > 0.2 \text{ mol L}^{-1} \) is attributed to a reduction in the amount of \( \text{OH}^- \) (for example, due to losses via Reactions 7 and 8); conceivably, for large \( \text{H}_2\text{O}_2 \) concentrations the reaction between \( \text{OH}^- \) and \( \text{H}_2\text{O}_2 \) (Reaction 7) becomes more significant than the reaction between \( \text{OH}^- \) and PCE, leading to a decrease in \( \text{OH}^- \) available for reaction. As PCE is also degraded by \( \text{O}_2^- \), the observed decrease in the PCE degradation rate constant at \( \text{H}_2\text{O}_2 > 0.2 \text{ mol L}^{-1} \) suggests that: (i) the increase in \( \text{O}_2^- \) at the higher \( \text{H}_2\text{O}_2 \) concentrations is either smaller than the decrease in \( \text{OH}^- \); (ii) \( \text{O}_2^- \) are either less effective than \( \text{OH}^- \) in degrading PCE, or (iii) \( \text{O}_2^- \) preferentially degrades HCA over PCE. Although these hypotheses cannot be assessed using our observations, reports of a smaller rate constant for PCE degradation by \( \text{O}_2^- \) \( (k = 15.0 \pm 4.5 \text{ M}^{-1} \text{s}^{-1} \text{ in dimethylformamide}) \) compared to that for degradation by \( \text{OH}^- \) \( (k = 3.9 \times 10^5 \text{ M}^{-1} \text{s}^{-1}) \) indicate that if the decrease in \( \text{OH}^- \) is replaced by equimolar concentration of \( \text{O}_2^- \), the apparent PCE degradation rate would be lower.\(^{13,14}\)

With Fe(III)–citrate only PCE degradation occurred (i.e. no HCA degradation was observed). The degradation rate was slower; however, the degradation continued to occur over the entire 24 h reaction duration. In such systems PCE and HCA degradation can be expected to be lower as the \( \text{O}_2^- \) and \( \text{OH}^- \) formation rates in this system are limited by the small Fe(III) concentration in equilibrium with citrate and the iron–citrate complex.\(^4\) The slowdown can also be partly attributed to enhanced quenching of \( \text{OH}^- \) with Fe(III) in the presence of iron complexes.\(^{28}\) In addition, citrate degradation by radicals can also potentially contribute to a lowering of the degradation rates.\(^{29}\) Remediation systems based on the use of Fe(III)–citrate should take the above limitations into consideration.

CONCLUSIONS

PCE and HCA show complex patterns of degradation in the Fe(III)–\( \text{H}_2\text{O}_2 \) system. The degradation of individual chemicals is faster than when they are present as a combination in solution; however, the HCA concentration remaining undegraded in vials with the individual chemical or the mixture was similar. The form of iron as well as the \( \text{H}_2\text{O}_2 \) concentration had a significant effect on the individual reductants in the enhanced desorption and transformation of chloroaliphatic compounds by modified Fenton’s reactions.\(^\text{[26]}\) Raising the \( \text{H}_2\text{O}_2 \) loading will need to be controlled as an excessive loading can result in lower chemical degradation. The enhancement in Fe(III) solubility via chelation with citric acid led to a significant lowering in the degradation of chemicals; HCA was not degraded and PCE degradation occurred at significantly lower rates compared to the Fe(III) system. As the PCE degradation rate in this system was highest for the lowest \( \text{H}_2\text{O}_2 \) concentration used, in practice chelation may serve a useful purpose by slowing down the \( \text{H}_2\text{O}_2 \) consumption rate and would be most effective at low \( \text{H}_2\text{O}_2 \) concentrations. These findings identify some of the opportunities along with some of the potential pitfalls in the application of Fenton chemistry to degrade contaminants in the field.

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REFERENCES


