Fenton degradation of tetrachloroethylene and hexachloroethane in Fe(II) catalyzed systems

E.H. Jho a,1, N. Singhal a,∗, S. Turner b

a Department of Civil and Environmental Engineering, University of Auckland, Private Bag 92019, Auckland, New Zealand
b School of Biological Science, University of Auckland, Private Bag 92019, Auckland, New Zealand

A R T I C L E   I N F O
Article history:
Received 1 April 2010
Received in revised form 5 August 2010
Accepted 7 August 2010
Available online 17 August 2010

Keywords:
Contaminant degradation
Fenton reagent
Oxidative and reductive pathways
Tetrachloroethylene
Hexachloroethane

A B S T R A C T

The degradation of tetrachloroethene (PCE) and hexachloroethane (HCA) using Fe(II) and Fe(II)–citrate at different H2O2 concentrations was studied to clarify the role of oxidation and reduction pathways in Fenton chemistry. The interactions between oxidative and reductive radicals, and the cyclic nature of the Fe(II)–Fe(III) ions make for a complex system that displays a suppression or enhancement of PCE or HCA degradation as the experimental conditions are varied. PCE degradation decreased, while HCA degradation increased, for larger H2O2 concentration. The degradations of PCE and HCA were slower in vials where they were individually present compared to vials with the PCE–HCA mixture. Using Fe(II)–citrate instead of Fe(II) resulted in slower PCE and insignificant HCA degradation. These observations indicate that degradation efficiency losses arise from interactions between the oxidant and reductant radical moieties, and that the production of reduction radicals is only significant when the hydroxyl radical (OH•) production is rapid.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

The Fenton reagent, a mixture of iron(II) and hydrogen peroxide (H2O2), is frequently used to treat organic contaminants in water and soil[1,2]. The Fenton chemistry is complex, involving a number of interrelated reactions that produce a variety of radical moieties (grouped in Table 1 as primary, secondary, or tertiary based on reactions between the parent chemicals or their daughter products). Of the different radicals produced, the hydroxyl radical, OH• (Reaction (1) in Table 1) is acknowledged as being the most active species, capable of oxidizing several organic compounds at near diffusion-controlled rates with second-order rate constants >10^9 M^-1 s^-1 [3,4]. The reaction rate is primarily influenced by the H2O2 and iron concentrations [5–9] and the Fenton reactions are optimal in the pH range of 3–4 [10]. At low H2O2:Fe(II) ratios the reaction produces OH• [3] associated with the conversion of Fe(II) to Fe(III), but for large H2O2:Fe(II) ratios the production of reductant moieties such as superoxide anion radicals (O2•−) and perhydroxyl radicals (HO••) (Reactions (2)–(4)) has been observed [11–13]. Thus, it is likely that under appropriate conditions the oxidation and reduction of contaminants may simultaneously occur upon addition of the Fenton reagent.

In some studies iron complexes with inorganic or organic chelates have been used to increase iron solubility at near neutral pH condition and to control H2O2 consumption rate [14–16]. Citric acid, an environmentally friendly and biodegradable natural multidentate organic chelate, has been successfully used for this purpose [17]. Various iron–chelate complexes have been shown to produce OH• [18]. Using Fe(III)–citrate the mineralization of 2,4-dichlorophenoxy acetic acid was maintained over several days in comparison to reactions with Fe(III) that only lasted ~4 h [14]. Similarly, Fe(II)–citrate-catalyzed TCE degradation at pH 6–7 [15] and carbon tetrachloride degradation with a 2.5:1 H2O2:Fe(II) ratio by producing O2••− [19].

Tetrachloroethylene (PCE) and hexachloroethane (HCA) are two common groundwater pollutants [20,21] that possess a structural similarity but display different reactivities to the oxidative and reductive species produced by Fenton chemistry. PCE is rapidly degraded by both OH• and reductive moieties [11,22]; HCA, however, being a saturated compound, reacts poorly with OH• and is primarily transformed by reductant radical moieties such as O2•− [11,12]. The PCE degradation is rapid with complete mineralization in only a few hours [20,23] and may proceed through parallel oxidation and reduction reactions [11]. HCA degradation via the reduction pathway, which was confirmed by using chloroform as a reductant scavenger, was shown in previous studies [11,24].
Contaminated soils and groundwater generally involve mixtures of chemicals [25], but the degradation of mixtures of contaminants having different reactivity toward OH\(^{•}\) and O\(_2\)\(^{•}\) has not been explored in previous studies, other than showing the effective treatment of industrial wastewaters using mixtures of reactive moieties [22]. In this study a combination of PCE and HCA, used as representative chemicals exhibiting partially to oxidative or to reductive degradation, is used to explore the effect of concomitant oxidative and reductive moiety production on degradation of defined chemical mixtures. Specifically, the degradation of PCE and HCA individually and as a mixture is investigated using Fe(II) at different concentration of H\(_2\)O\(_2\). In addition, the effect of slowing the radical production on the oxidation and reduction pathways is explored by chelating Fe(II) with citrate.

2. Materials and methods

Chemicals used were PCE (>99.5%) from Fluka, HCA (99%) and iron(II) perchlorate hydrate (98%) from Aldrich, hexane (95%) and sodium citrate dihydrate from Mallinckrodt Baker, and H\(_2\)O\(_2\) (30%) from LabServ Pronalys. All experiments were conducted at room temperature in intermittently stirred 60 mL borosilicate serum vials sealed with PTFE-lined septa and aluminum caps and all solutions were prepared using distilled and deionized water. Exposure to light was minimized by covering the vials with cloth. Water and Fe(II) or Fe(II)–citrato (1:3 molar ratio) solution were added to obtain a concentration of 1 mM Fe(II). The pH in vials was adjusted to pH 3 ± 0.1 using 1 M perchloric acid and 1 M potassium hydroxide solution. Fe(II) stock solution (20 mM) was prepared by dissolving Fe(CIO\(_4\))\(_2\) in 0.01 M HClO\(_4\) solutions and Fe(II)–citrato solutions (20 mM Fe(II)) were prepared by dissolving Fe(CIO\(_4\))\(_2\) in 60 mM citrate solutions. A PCE or HCA saturated solution and 30% H\(_2\)O\(_2\) were added to obtain concentrations of 0.30 ± 0.17 mM PCE, 0.015 ± 0.007 mM HCA, and 0.01 M – 2 M H\(_2\)O\(_2\) in vials containing 59.2 ± 0.8 mL solution for Fe(II) and 59.0 ± 0.1 mL solution for Fe(II)–citrato. Up to four replicates of each experimental condition were performed with the samples analyzed in duplicate along with controls where H\(_2\)O\(_2\) was substituted with water.

At predetermined time intervals a 6 mL liquid aliquot was collected from a vial and analyzed for PCE or HCA, following extraction using 2 mL hexane, using a Hewlett-Packard 6890A gas chromatograph equipped with a 0.25 mm (I.D.) × 60 m ZB-624 capillary column (Phenomenex) or a 0.53 mm (I.D.) × 30 m AT-624 capillary column (Alltech) and a halogen specific detector (O.I. Analytical). The ZB-624 column was kept at 40 °C for 2 min followed by 10 °C min\(^{-1}\) rise to 225 °C. The injector and the 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 mM for PCE and 0.001 mM for HCA. While the residual amounts of PCE and HCA were monitored, the intermediate products of their degradation were not determined. The GraphPad Prism (CA, USA) software was used to estimate the kinetic parameters and their associated confidence intervals (CI) by fitting an empirical model to observations, as well as to determine the significance of difference in the estimates by performing the extra sum-of-squares test at a P-value of 0.05.

3. Results and discussion

The change in solution pH was 0.13 pH units on average and losses of chemicals from vials via volatilization (estimated via losses of PCE and HCA in controls) were 5.7 ± 3.6% over 24 h for PCE in Fe(II) system and 9.9 ± 4.8% over 25 h for PCE in Fe(II)–citrato system and 6.8 ± 2.7% over 24 h for HCA in Fe(II) system and 7.4 ± 6.7% over 25 h for HCA in Fe(II)–citrato system. Gas formation was observed in all vials except those with 0.01 M and 0.05 M H\(_2\)O\(_2\). Oxygen production via Reactions (5)–(8) and (12)–(14) (Table 1) and decomposition of H\(_2\)O\(_2\) [26] has been reported in the literature. Although carbon dioxide formation from PCE and HCA degradation [20,23] can also occur, the high carbon dioxide solubility in water and the low concentrations of PCE and HCA relative to H\(_2\)O\(_2\) suggest that gas bubbling in vials is associated primarily with oxygen production. Visual observations indicate a more vigorous bubble formation at higher H\(_2\)O\(_2\) concentration consistent with literature [27], suggesting that oxic conditions prevail in vials.

With Fe(II), in vials containing PCE or PCE–HCA mixture PCE degradation was complete within 2 h for all H\(_2\)O\(_2\) concentrations (Fig. 1), while in Fe(II)–citrato-catalyzed vials PCE degradation was slower with complete degradation over 24 h. PCE degradation was only observed for low H\(_2\)O\(_2\) concentrations and the amount degraded decreased for higher H\(_2\)O\(_2\) concentrations (Fig. 2). With Fe(II), HCA was degraded only for H\(_2\)O\(_2\) ≥0.2 M and the amount degraded increased for higher H\(_2\)O\(_2\) concentrations (Fig. 2); ~90% removal of HCA was achieved for 2 M H\(_2\)O\(_2\) after 24 h with the PCE–HCA mixture (Fig. 3b). HCA degradation in the Fe(II)–citrato

---

**Table 1**

<table>
<thead>
<tr>
<th>Reaction no.</th>
<th>Reactions</th>
<th>Rate constants (M(^{-1}) s(^{-1}))</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Primary</td>
<td>[1]</td>
<td>Fe(^{2+}) + H(_2)O(_2) → Fe(^{3+}) + OH(^{•}) + OH(^−)</td>
<td>76</td>
</tr>
<tr>
<td>Secondary</td>
<td>[2]</td>
<td>Fe(^{3+}) + H(_2)O(_2) → Fe(^{2+}) + HCO(_3)(^−) + H(^{•})</td>
<td>0.01</td>
</tr>
<tr>
<td>Tertiary</td>
<td>(5)</td>
<td>Fe(^{2+}) + OH(^{•}) → Fe(^{3+}) + H(^{•}) + H(_2)O</td>
<td>3.1 × 10(^{8})</td>
</tr>
<tr>
<td>Tertiary</td>
<td>(6)</td>
<td>OH(^•) + HO(_2)(^•) → O(_2) + H(_2)O</td>
<td>0.71 × 10(^{10})</td>
</tr>
<tr>
<td>Tertiary</td>
<td>(7)</td>
<td>OH(^•) + O(_2) → OH(^−) + O(_2)</td>
<td>1.0 × 10(^{9})</td>
</tr>
<tr>
<td>Tertiary</td>
<td>(8)</td>
<td>HO(^•) + HO(_2) + H(_2) → O(_2) + HO(_2)</td>
<td>5.0 × 0.09</td>
</tr>
<tr>
<td>Tertiary</td>
<td>(9)</td>
<td>Fe(^{2+}) + O(_2) + H(_2)O → Fe(^{3+}) + H(_2)O(_2)</td>
<td>1 × 10(^{5})</td>
</tr>
<tr>
<td>Tertiary</td>
<td>(10)</td>
<td>Fe(^{2+}) + HO(_2)(^•) → Fe(^{3+}) + H(_2)O</td>
<td>1.2 × 10(^{8})</td>
</tr>
<tr>
<td>Tertiary</td>
<td>(11)</td>
<td>Fe(^{2+}) + HO(_2) → Fe(^{3+}) + OH(^•)</td>
<td>3 × 10(^{4})</td>
</tr>
<tr>
<td>Tertiary</td>
<td>(12)</td>
<td>Fe(^{2+}) + O(_2) → Fe(^{3+}) + O(_2)</td>
<td>1.5 × 10(^{4})</td>
</tr>
<tr>
<td>Tertiary</td>
<td>(13)</td>
<td>Fe(^{2+}) + HO(_2)(^•) → Fe(^{3+}) + H(^{•}) + O(_2)</td>
<td>3.1 × 10(^{3})</td>
</tr>
<tr>
<td>Tertiary</td>
<td>(14)</td>
<td>HO(_2) + HO(_2) → HO(_2) + H(_2)O(_2)</td>
<td>8.3 × 10(^{3})</td>
</tr>
<tr>
<td>Tertiary</td>
<td>(15)</td>
<td>HO(_2) + O(_2) → HO(_2) + O(_2)</td>
<td>8.5–9.7 × 10(^{3})</td>
</tr>
</tbody>
</table>

\(^{a}\) The dimensions of equilibrium constant pK depend on the stoichiometry of the reaction.
system at all H\textsubscript{2}O\textsubscript{2} concentrations was negligible, showing losses similar to controls (Fig. 3c and d).

Following earlier studies on PCE degradation in aqueous solution by Fenton reactions [20,28] the following first order kinetic relationship was used to model the degradation of PCE as well as that of the degradable portion of HCA (i.e., the amount obtained by deducting the final residual, \( C_{\text{res}} \), from the observed concentrations).

\[
C = (1 - C_{\text{res}})e^{-kt} + C_{\text{res}}
\]  

(1)

where \( C : \) PCE/PCE\textsubscript{0} or HCA/HCA\textsubscript{0} (dimensionless) is the PCE or HCA concentration at time \( t \) (h) normalized with respect to the initial concentration, \( C_{\text{res}} : \) undegraded concentration (dimensionless) remaining at infinite time/initial concentration, and \( k : \) pseudo first order rate constant (h\textsuperscript{-1}). Theoretically the PCE and HCA degradation rates should be of second-order and expressed as a function of the concentrations of chemical and the oxidant or reductant radicals. As radical moiety concentrations were not measured in this study, the proposed first order model uses a ‘pseudo’ first order rate constant to represent the product of second-order rate constant
Fig. 3. Effect of H$_2$O$_2$ concentration on HCA degradation using 1 mM Fe(II) in vials containing (a) HCA and (b) PCE–HCA mixture, and using 1 mM Fe(II)–citrate (1:3 molar ratio) in vials containing (c) HCA and (d) PCE–HCA mixture. [Fe(II)]$_0$ = 1 mM, [PCE]$_0$ = 0.30 ± 0.17 mM, [HCA]$_0$ = 0.015 ± 0.007 mM, pH 3.1 ± 0.1. Symbols represent ° Control, □ 0.01 M, △ 0.05 M, ● 0.2 M, ■ 0.5 M, ▲ 1 M, and ♦ 2 M. The lines shown are 1st order fits of the data. Data points show mean ± standard deviation – 2 replicates for 0.01 M and 0.05 M H$_2$O$_2$ in PCE–HCA mixtures, 4 replicates for the other H$_2$O$_2$ concentrations in HCA-only vials and for 0.2 M and 2 M H$_2$O$_2$ in PCE–HCA mixtures, 6 replicates for control, 0.2 M and 2 M H$_2$O$_2$ in HCA-only vials and for control, 0.5 M and 1 M H$_2$O$_2$ for PCE–HCA mixtures.

and radical moiety concentration. As a result of this approximation the estimated first order rate ‘constants’ reported in this study are not true constants and vary for different experimental conditions. PCE degradation in the Fe(II) system is complete (Fig. 1) and a $C_{res}$ of zero is used; however, for other cases non-zero $C_{res}$ is used as the degradation of HCA in the Fe(II) system (Fig. 3a and b) and of PCE (Fig. 2) or HCA (Fig. 3c and d) in the Fe(II)–citrate system is incomplete. The estimated values and 95% confidence intervals for the $k$ and $C_{res}$ for PCE in the Fe(II)–citrate system are presented in Table 2 along with the coefficients of correlation ($R^2$) for the fits. Table 3 presents similar information for HCA degradation in the Fe(II) system; the $k$ and $C_{res}$ for HCA degradation in the Fe(II)–citrate system were statistically zero and one, respectively, and have not been presented here. For degradation rates above ∼0.15 h$^{-1}$ the $R^2$ values for the fits are high, ranging between 0.75 and 1.0; however, for smaller rate constant estimates the $R^2$ values are low.

Table 2

<table>
<thead>
<tr>
<th>Reactions</th>
<th>Fe(II)-catalyzed reactions</th>
<th>Fe(II)–citrate-catalyzed reactions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solutions</td>
<td>PCE-only solution</td>
<td>PCE–HCA mixture</td>
</tr>
<tr>
<td>[PCE]$_0$ (mM)$^a$</td>
<td>0.23 ± 0.05</td>
<td>0.31 ± 0.06</td>
</tr>
<tr>
<td>[HCA]$_0$ (mM)$^a$</td>
<td>Not Relevant</td>
<td>0.011 ± 0.002</td>
</tr>
<tr>
<td>PCE/HCA Ratio</td>
<td>Not Relevant</td>
<td>20.8 ± 2.6</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$H_2O_2$ (M)</th>
<th>Rate constant (h$^{-1}$)$^b$</th>
<th>Rate constant (h$^{-1}$)$^b$</th>
<th>Rate constant (h$^{-1}$)$^b$</th>
<th>$C_{res}$$^b$</th>
<th>Rate constant (h$^{-1}$)$^b$</th>
<th>Rate constant (h$^{-1}$)$^b$</th>
<th>$C_{res}$$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>14.34 ± 2.06a</td>
<td>0.97</td>
<td>17.17 ± 7.08a</td>
<td>0.94</td>
<td>1.70 ± 0.90a</td>
<td>0.03 ± 0.03A</td>
<td>0.92</td>
</tr>
<tr>
<td>0.05</td>
<td>11.83 ± 1.41a</td>
<td>0.98</td>
<td>12.60 ± 3.13a</td>
<td>0.98</td>
<td>0.35 ± 0.08b</td>
<td>0.04 ± 0.04A</td>
<td>0.93</td>
</tr>
<tr>
<td>0.2</td>
<td>13.71 ± 1.79a</td>
<td>0.98</td>
<td>10.43 ± 1.64a</td>
<td>0.98</td>
<td>0.15 ± 0.06c</td>
<td>0.16 ± 0.13A</td>
<td>0.94</td>
</tr>
<tr>
<td>0.5</td>
<td>8.34 ± 0.40b</td>
<td>1.00</td>
<td>10.14 ± 0.92a</td>
<td>0.99</td>
<td>0.06 ± 0.06c</td>
<td>0.29 ± 0.29AB</td>
<td>0.82</td>
</tr>
<tr>
<td>1</td>
<td>6.70 ± 0.74c</td>
<td>0.99</td>
<td>12.99 ± 1.19a</td>
<td>0.99</td>
<td>0.28 ± 0.26b/c</td>
<td>0.51 ± 0.16B</td>
<td>0.65</td>
</tr>
<tr>
<td>2</td>
<td>4.71 ± 0.64d</td>
<td>0.95</td>
<td>5.46 ± 0.90c</td>
<td>0.98</td>
<td>0.10 ± 0.08c</td>
<td>0.49 ± 0.18B</td>
<td>0.87</td>
</tr>
</tbody>
</table>

$^a$ [PCE]$_0$ and [HCA]$_0$ are presented as mean ± S.D.

$^b$ Values followed by the same letter do not differ significantly (P-value > 0.05) by extra sum-of-squares F test in Prism.
In Fe(II)-catalyzed reactions the PCE degradation rate constants (Table 2) in PCE-only vials were statistically similar for H2O2 concentrations up to 0.2 M, but then decreased for higher H2O2 concentrations. In vials with PCE–HCA mixture the PCE degradation rate constants were statistically similar to those in the PCE-only vials for corresponding H2O2 concentrations, except 0.5 M and 1 M, for which the rate constants were larger. In Fe(II)–citrate-catalyzed vials the estimated PCE degradation rate constants were significantly smaller than the corresponding rate constants in Fe(II) vials, except for the lowest H2O2 concentration of 0.01 M in the PCE–HCA mixture. Additionally, with Fe(II)–citrate the PCE degradation rate constants decreased with increasing H2O2 concentration to 0.5 M, but then were statistically similar for higher H2O2 concentrations regardless of the absence or presence of HCA. With the decreasing rate constants for the 0.01 M to 0.5 M H2O2 concentration range, the amount degraded (i.e., 1 – Cres values) also decreased, but then were statistically similar for higher H2O2 concentrations.

Unlike PCE, HCA was only partially degraded over 24 h in the Fe(II) system (Fig. 3); a few hours after the start of experiment HCA degradation ceased, leaving a residual. Table 3 shows that HCA degradation only occurred above H2O2 concentrations of 0.5 M in HCA-only and of 0.2 M in PCE–HCA mixture vials, and that while the rate constants were similar in both systems for these H2O2 concentrations the amount degraded increased for larger H2O2 concentrations. Although a statistically significant difference in the HCA degradation in HCA-only and PCE–HCA mixture vials could not be established, the estimated mean HCA degradation rate constants for PCE–HCA mixture were consistently higher, or similar to, and the Cres were similarly lower than, or similar to, those for HCA-only vials. HCA degradation was either not observed or negligibly small in the Fe(II)–citrate-catalyzed vials. The cessation of HCA degradation after a finite time indicates the exhaustion of reductant radical moieties in the vial, while the decrease in Cres indicates that the size of this pool of radicals increases at higher H2O2 concentrations.

The relationships between the fitted PCE degradation rate constants or HCA residuals and the H2O2 concentrations are shown on Fig. 4. The rate constants as well as the residuals show good log-linear fits (R² > 0.95) to the H2O2 concentration. On this figure, statistically similar groups of values were fitted with a horizontal line to illustrate their non-dependence on the H2O2 concentration. As expected from previous analysis the fits display a negative slope, corresponding to a decrease in PCE degradation rate constants and smaller HCA residuals with increases in H2O2 concentration.

The increase in HCA degradation is accompanied by a lowering of PCE degradation at higher H2O2 concentrations. As HCA can only be degraded by reductant radicals the implication is that the concentration of reductant moieties is small at low H2O2 concentrations and at higher H2O2 concentrations larger concentrations of reductant moieties are produced (e.g., via Reaction (4)). Furthermore, as PCE can be degraded by oxidant as well as reductant radicals, the lowering of the PCE degradation rate constant at larger H2O2 concentrations indicates that the concentration of oxidant radicals is smaller (for example, due to losses via Reaction (3), (6) or (7)) and that the reductant radicals are either less effective than the oxidant radicals in degrading PCE or that they have a preference for HCA over PCE. An additional hypothesis is that the lowering of the PCE degradation rate constant results from interactions between the reductant and oxidant radical moieties (e.g., Reaction (6) involving O2•− and OH•). The former hypothesis involving different preferences by radical moieties for PCE is supported by the reportedly smaller rate constant for PCE degradation by O2•− (k = 15.0 ± 4.5 M−1 s−1 in dimethylformamide) compared to its degradation by OH• (k = 3.9 × 109 M−1 s−1) [29,30], while the latter hypothesis involving the loss in PCE degradation efficiency due to interactions between the radical moieties is supported by deduced formation of a larger pool of reductant moieties at higher H2O2 concentrations.

The lowering of PCE degradation is greater at higher H2O2 concentrations as H2O2 dependent reactions, such as the one between OH• and H2O2 (Reaction (3)) while having a smaller rate constant (k = (1.2−4.5) × 107 M−1 s−1) than the reaction between PCE and OH• become increasingly significant when the H2O2 concentration is raised. The observation that high PCE degradation rate constants are maintained in vials with the PCE–HCA mixture for H2O2 concentrations up to 1 M as opposed to 0.2 M in the PCE-only vials is supportive of the hypothesis involving interaction between the radical moieties, as the reactions with PCE and HCA lower the concentrations of reductant as well as oxidant radicals. Even though statistical significance for the differences could not be established due to the large variations in estimated values, a comparison of HCA degradation in vials with PCE–HCA mixture and those with HCA shows that the mean degradation rate constants are higher, or similar, and that the Cres values are lower, or similar, in the mixture, further supporting the hypothesized interaction between the radical moieties. While the observations do not confirm any of the proposed hypotheses, they indicate that interactions between the reductant and oxidant radical moieties are likely contributors to the observed differences in PCE and HCA degradation in vials with the mixture and the sole chemicals.

When Fe(II)–citrate is used of Fe(II), the free Fe(II) concentration in solution is limited by the equilibrium of Fe(II) and citrate with...
in any of the systems studied, indicating the presence of low concentrations of $O_2^{•−}$ in the system. As a citrate is susceptible to degradation by the radicals [10], it is possible that it contributed to the lowering of the PCE or HCA degradation rate.

4. Conclusions

The variety of interactions occurring in the Fe(II)–$H_2O_2$ system and the cyclic nature of the Fe(II)–Fe(III) redox chemistry make for complex system dynamics with different effects on the PCE and HCA degradation rate constants when these chemicals are present in solution individually or as a combination. By using PCE and HCA degradations as measures of the concentrations of $O_2^{•−}$ and OH$^{•−}$ moieties the current study presents evidence indicating that interactions between the radical moieties have a significant effect on chemical degradation. Results show that the presence of chemicals susceptible to degradation by oxidative and reductive moieties can promote chemical degradation by decreasing the interaction between the radical moieties. The use of chelants to enhance Fe(II) solubility can result in decreasing chemical degradation, particularly of chemicals susceptible to degradation solely by the reductant moieties. Thus, the Fenton reagent may be more effective in degrading a mixture of contaminants and the use of chelants may not result in the expected benefit of sustaining the degradation of all chemicals over longer time interval.

Acknowledgements

EJ acknowledges financial support provided by the New Zealand Foundation for Research, Science and Technology. Research funding was provided by Pattle Delamore Partners and the University of Auckland.

References


