



Fenton degradation of tetrachloroethene 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

ARTICLE INFO

Article history:

Received 19 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

Tetrachloroethene

Hexachloroethane

ABSTRACT

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 lower 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 >10⁹ 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 (HO₂[•]) (Reactions (2)–(4)) has been observed [11–13]. Thus, it is likely that under appropriate conditions the oxidation and reduc-

tion 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–citrate 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(II) 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].

* Corresponding author. Tel.: +64 9 373 7599x84512; fax: +64 9 373 7428.

E-mail addresses: ejho001@aucklanduni.ac.nz (E.H. Jho),

n.singhal@auckland.ac.nz (N. Singhal), s.turner@auckland.ac.nz (S. Turner).

¹ Present address: Department of Civil and Environmental Engineering, Seoul National University, Seoul, Korea.

Table 1
Rate constant or equilibrium constant for Fenton's and related reactions.

	Reaction no.	Reactions	Rate constants ($M^{-1} s^{-1}$)	References
Primary	(1)	$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^{\bullet} + OH^{-}$	76	[3]
Secondary	(2)	$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^{\bullet} + H^+$	0.01	[31]
Secondary	(3)	$H_2O_2 + OH^{\bullet} \rightarrow H_2O + HO_2^{\bullet}$	$(1.2-4.5) \times 10^7$	[3]
Equilibrium	(4)	$HO_2^{\bullet} \leftrightarrow H^+ + O_2^{\bullet-}$	$pK^a: 4.8$	[32]
Secondary	(5)	$Fe^{3+} + OH^{\bullet} \rightarrow Fe^{2+} + O_2 + H^+$	3.1×10^5	[33]
Tertiary	(6)	$OH^{\bullet} + HO_2^{\bullet} \rightarrow O_2 + H_2O$	0.71×10^{10}	[34]
Tertiary	(7)	$OH^{\bullet} + O_2^{\bullet-} \rightarrow OH^{-} + O_2$	1.0×10^{10}	[35]
Tertiary	(8)	$HO_2^{\bullet} + H_2O_2 \rightarrow H_2O + O_2 + OH^{\bullet}$	0.50 ± 0.09	[36]
Tertiary	(9)	$Fe^{2+} + O_2^{\bullet-} + H^+ \rightarrow Fe^{3+} + HO_2^{-}$	1×10^7	[37]
Tertiary	(10)	$Fe^{2+} + HO_2^{\bullet} + H^+ \rightarrow Fe^{3+} + H_2O_2$	1.2×10^6	[38]
Tertiary	(11)	$Fe^{2+} + HO^{\bullet} \rightarrow Fe^{3+} + OH^{-}$	3×10^8	[3]
Tertiary	(12)	$Fe^{3+} + O_2^{\bullet-} \rightarrow Fe^{2+} + O_2$	1.5×10^8	[33]
Tertiary	(13)	$Fe^{3+} + HO_2^{\bullet-} \rightarrow Fe^{2+} + H^+ + O_2$	3.1×10^5	[33]
Tertiary	(13)	$HO_2^{\bullet} + HO_2^{\bullet} \rightarrow H_2O_2 + O_2$	8.3×10^5	[30,32]
Tertiary	(14)	$HO_2^{\bullet} + O_2^{\bullet-} \rightarrow HO_2^{-} + O_2$	$8.5-9.7 \times 10^7$	[32]
Tertiary	(15)	$2OH^{\bullet} \rightarrow H_2O_2$	$4.2-5.3 \times 10^9$	[3]

^a The dimensions of equilibrium constant pK depend on the stoichiometry of the reaction.

Contaminated soils and groundwater generally involve mixtures of chemicals [25], but the degradation of mixtures of contaminants having different reactivity toward OH^{\bullet} and $O_2^{\bullet-}$ 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 partiality 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_2O_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_2O_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 deionised water. Exposure to light was minimized by covering the vials with cloth. Water and Fe(II) or Fe(II)-citrate (1:3 molar ratio) solution were added to obtain a concentration of 1 mM Fe(II). The pH in vials was adjusted to $pH 3.1 \pm 0.1$ using 1 M perchloric acid and 1 M potassium hydroxide solution. Fe(II) stock solution (20 mM) was prepared by dissolving $Fe(ClO_4)_2$ in 0.01 M $HClO_4$ solutions and Fe(II)-citrate solutions (20 mM Fe(II)) were prepared by dissolving $Fe(ClO_4)_2$ in 60 mM citrate solutions. A PCE or HCA saturated solution and 30% H_2O_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_2O_2 in vials containing 59.2 \pm 0.8 mL solution for Fe(II) and 59.0 \pm 0.1 mL solution for Fe(II)-citrate. Up to four replicates of each experimental condition were performed with the samples analyzed in duplicate along with controls where H_2O_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 6860A gas chromatograph equipped with a 0.25 mm (I.D.) \times 60 m ZB-624 capillary column (Phenomenex) or a 0.53 mm (I.D.) \times 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 temper-

atures were maintained at 150 °C and 1000 °C, respectively. The helium flow rate was set to 1.2 mL min^{-1} with a split ratio of 35:1. The method detection limits for PCE and HCA were 0.010 mM and 0.004 mM, respectively. The AT-624 column 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, maintained for 2 min. 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 (C.I.) 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 $5.7 \pm 3.6\%$ over 24 h for PCE in Fe(II) system and $9.9 \pm 4.8\%$ over 25 h for PCE in Fe(II)-citrate system and $6.8 \pm 2.7\%$ over 24 h for HCA in Fe(II) system and $7.4 \pm 6.7\%$ over 25 h for HCA in Fe(II)-citrate system. Gas formation was observed in all vials except those with 0.01 M and 0.05 M H_2O_2 . Oxygen production via Reactions (5)–(8) and (12)–(14) (Table 1) and decomposition of H_2O_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_2O_2 suggest that gas bubbling in vials is associated primarily with oxygen production. Visual observations indicate a more vigorous bubble formation at higher H_2O_2 concentration consistent with literature [27], suggesting that oxidic 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_2O_2 concentrations (Fig. 1), while in Fe(II)-citrate-catalyzed vials PCE degradation was slower with complete degradation over 24 h. PCE degradation was only observed for low H_2O_2 concentrations and the amount degraded decreased for higher H_2O_2 concentrations (Fig. 2). With Fe(II), HCA was degraded only for $H_2O_2 \geq 0.2$ M and the amount degraded increased for higher H_2O_2 concentrations (Fig. 3); $\sim 90\%$ removal of HCA was achieved for 2 M H_2O_2 after 24 h with the PCE-HCA mixture (Fig. 3b). HCA degradation in the Fe(II)-citrate

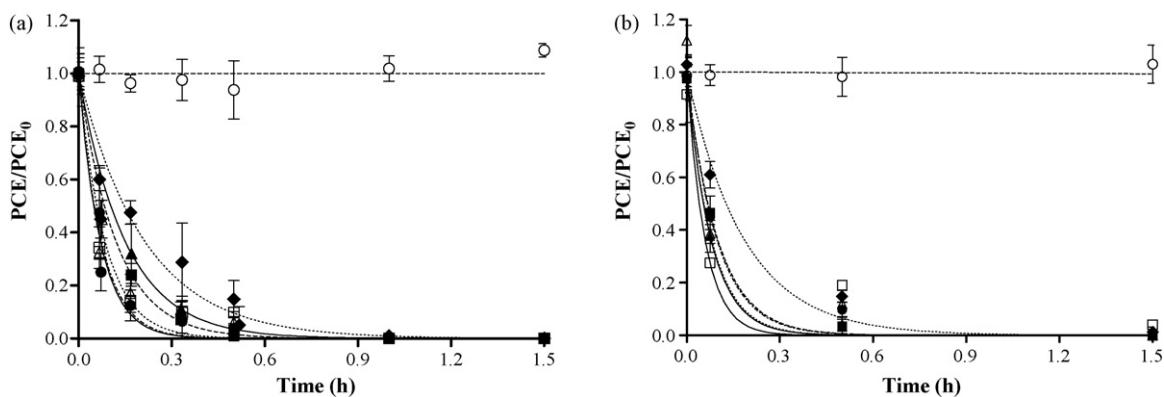


Fig. 1. Effect of H_2O_2 concentration on PCE degradation using Fe(II) in vials containing (a) PCE and (b) PCE–HCA mixture. $[\text{Fe(II)}]_0 = 1 \text{ mM}$, $[\text{PCE}]_0 = 0.30 \pm 0.17 \text{ mM}$, $[\text{HCA}]_0 = 0.015 \pm 0.007 \text{ mM}$, $\text{pH } 3.1 \pm 0.1$. Symbols represent \circ Control, \square 0.01 M, \triangle 0.05 M, \bullet 0.2 M, \blacksquare 0.5 M, \blacktriangle 1 M, and \blacklozenge 2 M. The lines shown are 1st order fits of the data. Data points show mean \pm standard deviation – 2 replicates for 0.5 M and 1 M H_2O_2 in PCE-only vials and for 0.01 M and 0.05 M H_2O_2 in PCE–HCA mixtures, 4 replicates for 0.2 M and 2 M H_2O_2 in PCE–HCA mixtures, 6 replicates for control, 0.5 M and 1 M H_2O_2 in PCE–HCA mixtures, 8 replicates for other H_2O_2 concentrations in PCE-only vials.

system at all H_2O_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_{res} , from the observed concentrations).

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

where C : PCE/PCE_0 or HCA/HCA_0 (dimensionless) is the PCE or HCA concentration at time t (h) normalized with respect to the initial concentration, C_{res} : undegraded concentration (dimensionless) remaining at infinite time/initial concentration, and k : pseudo first order rate constant (h^{-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

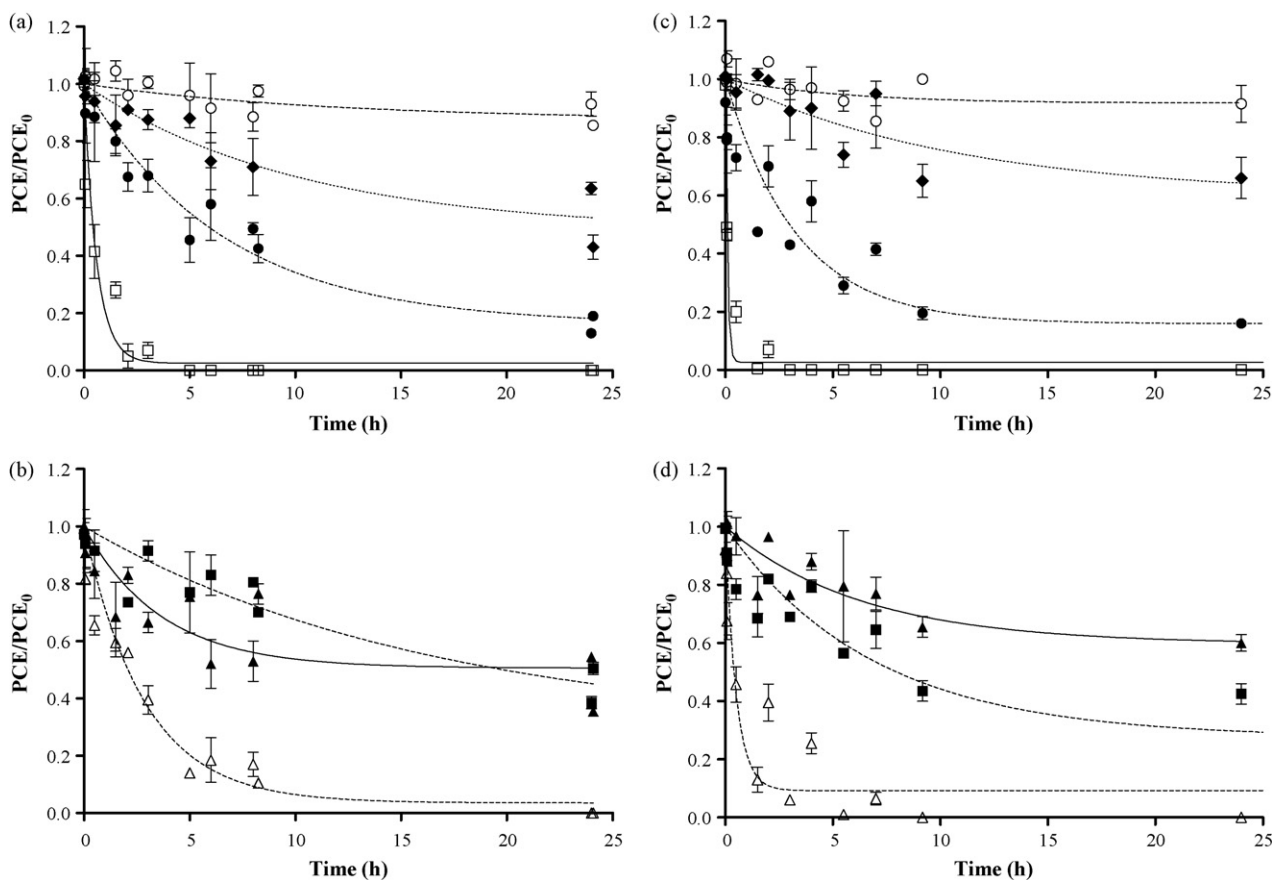


Fig. 2. Effect of H_2O_2 concentration on PCE degradation using Fe(II)–citrate (1:3 molar ratio) in vials containing (a) PCE for control, 0.01 M, 0.2 M, and 2 M H_2O_2 (b) PCE for 0.05 M, 0.5 M, and 1 M H_2O_2 and (c) PCE–HCA mixture for control, 0.01 M, 0.2 M, and 2 M H_2O_2 (d) PCE–HCA mixture for 0.05 M, 0.5 M, and 1 M H_2O_2 . $[\text{Fe(II)}]_0 = 1 \text{ mM}$, $[\text{PCE}]_0 = 0.30 \pm 0.17 \text{ mM}$, $[\text{HCA}]_0 = 0.015 \pm 0.007 \text{ mM}$, $\text{pH } 3.1 \pm 0.1$. Symbols represent \circ Control, \square 0.01 M, \triangle 0.05 M, \bullet 0.2 M, \blacksquare 0.5 M, \blacktriangle 1 M, and \blacklozenge 2 M. The lines shown are 1st order fits of the data. Data points show mean \pm standard deviation – 4 replicates for all H_2O_2 concentrations in PCE-only vials and in PCE–HCA mixtures.

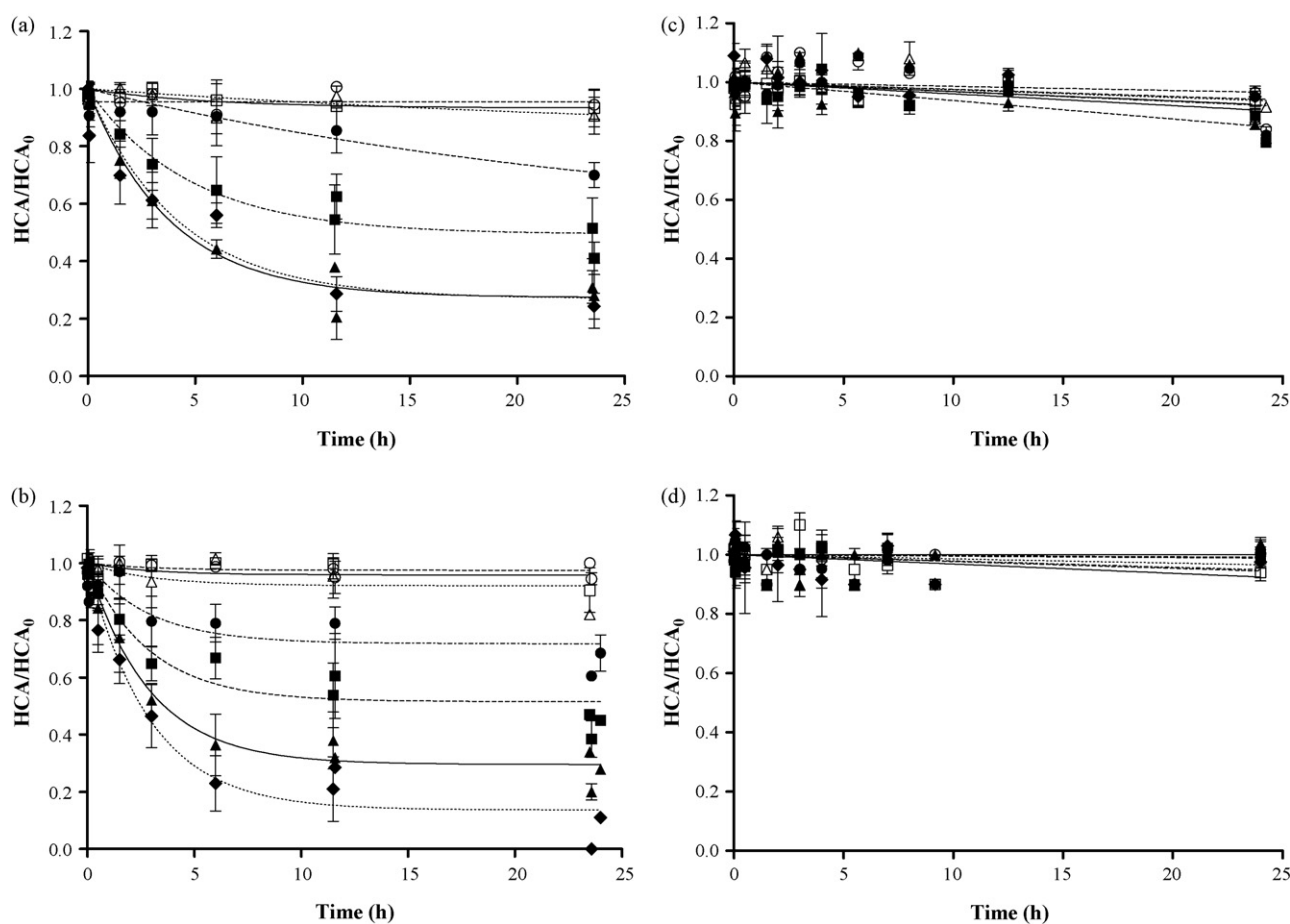


Fig. 3. Effect of H_2O_2 concentration on HCA degradation using 1 mM Fe(II) in vials containing (a) HCA and (b) PCE–HCA mixture, and using 1 mM Fe(II)–citrate (1:3 molar ratio) in vials containing (c) HCA and (d) PCE–HCA mixture. $[\text{Fe(II)}]_0 = 1 \text{ mM}$, $[\text{PCE}]_0 = 0.30 \pm 0.17 \text{ mM}$, $[\text{HCA}]_0 = 0.015 \pm 0.007 \text{ mM}$, $\text{pH } 3.1 \pm 0.1$. Symbols represent \circ Control, \square 0.01 M, \triangle 0.05 M, \bullet 0.2 M, \blacksquare 0.5 M, \blacktriangle 1 M, and \blacklozenge 2 M. The lines shown are 1st order fits of the data. Data points show mean \pm standard deviation – 2 replicates for 0.01 M and 0.05 M H_2O_2 in PCE–HCA mixtures, 4 replicates for the other H_2O_2 concentrations in HCA-only vials and for 0.2 M and 2 M H_2O_2 in PCE–HCA mixtures, 6 replicates for control, 0.2 M and 2 M H_2O_2 in HCA-only vials and for control, 0.5 M and 1 M H_2O_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 for PCE in the Fe(II) system and 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 $\sim 0.15 \text{ h}^{-1}$ 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

PCE degradation rate constants (best-fit value \pm 95% C.I.) for different H_2O_2 concentrations in the Fe(II)-catalyzed ($C_{\text{res}} = 0$) and Fe(II)–citrate-catalyzed reactions at pH 3.

Reactions	Fe(II)-catalyzed reactions						Fe(II)–citrate-catalyzed reactions				
	PCE-only solution			PCE–HCA mixture			PCE-only solution		PCE–HCA mixture		
$[\text{PCE}]_0$ (mM) ^a	0.23 \pm 0.05			0.31 \pm 0.06			0.54 \pm 0.06		0.35 \pm 0.11		
$[\text{HCA}]_0$ (mM) ^a	Not Relevant			0.011 \pm 0.002			Not Relevant		0.019 \pm 0.008		
PCE/HCA Ratio	Not Relevant			20.8 \pm 2.6			Not Relevant		13.3 \pm 1.9		
H_2O_2 (M)	Rate constant (h^{-1}) ^b	R^2	Rate constant (h^{-1}) ^b	R^2	Rate constant (h^{-1}) ^b	C_{res}^b	R^2	Rate constant (h^{-1}) ^b	C_{res}^b	R^2	
0.01	14.34 \pm 2.06a	0.97	17.17 \pm 7.08a	0.94	1.70 \pm 0.90a'	0.03 \pm 0.03A	0.92	11.00 \pm 3.00d'	0.03 \pm 0.03A	0.97	
0.05	11.83 \pm 1.41a	0.98	12.60 \pm 3.13a	0.98	0.35 \pm 0.08b'	0.04 \pm 0.04A	0.93	2.00 \pm 1.60a'	0.11 \pm 0.11A	0.86	
0.2	13.71 \pm 1.79a	0.98	10.43 \pm 1.64a	0.98	0.15 \pm 0.06c'	0.16 \pm 0.13A	0.94	0.30 \pm 0.20a'b'c'	0.16 \pm 0.16A	0.75	
0.5	8.34 \pm 0.40b	1.00	10.14 \pm 0.92a	0.99	0.06 \pm 0.06c'	0.29 \pm 0.29AB	0.82	0.15 \pm 0.10c'	0.27 \pm 0.22AB	0.78	
1	6.70 \pm 0.74c	0.99	12.99 \pm 1.19a	0.99	0.28 \pm 0.26b'c'	0.51 \pm 0.16B	0.65	0.16 \pm 0.15c'	0.60 \pm 0.19B	0.75	
2	4.71 \pm 0.64d	0.95	5.46 \pm 0.90cd	0.98	0.10 \pm 0.08c'	0.49 \pm 0.18B	0.87	0.08 \pm 0.17c'	0.57 \pm 0.53AB	0.66	

^a $[\text{PCE}]_0$ and $[\text{HCA}]_0$ are presented as mean \pm 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.

Table 3
HCA degradation rate constants (best-fit value \pm 95% C.I.) for different H₂O₂ concentrations in the Fe(II)-catalyzed reactions at pH 3.

Reactions		Fe(II)-catalyzed reactions				
Solutions		HCA-only solution			PCE–HCA mixture	
[PCE ₀] (mM) ^a		Not Relevant			0.31 \pm 0.06	
[HCA ₀] (mM) ^a		0.009 \pm 0.001			0.011 \pm 0.002	
PCE/HCA Ratio		Not Relevant			20.8 \pm 2.6	
H ₂ O ₂ (M)	Rate constant (h ⁻¹) ^b	C _{res} ^b	R ²	Rate constant (h ⁻¹) ^b	C _{res} ^b	R ²
0	23.0 \pm 23.0 (\approx 0)a	0.96 \pm 0.03 (\approx 1)A	0.02	0.23 \pm 0.23 (\approx 0)a	0.98 \pm 0.04 (\approx 1)A	0.02
0.01	0.18 \pm 0.18 (\approx 0)a	0.93 \pm 0.08 (\approx 1)A	-0.16	23.9 \pm 23.9 (\approx 0)a	0.99 \pm 0.02 (\approx 1)A	-0.08
0.05	0.29 \pm 0.29 (\approx 0)a	0.96 \pm 0.05 (\approx 1)A	-0.39	0.28 \pm 0.28 (\approx 0)a	0.98 \pm 0.05 (\approx 1)A	0.55
0.2	0.08 \pm 0.07ab	0.66 \pm 0.17ABCD	0.65	0.17 \pm 0.13b	0.66 \pm 0.10B	0.52
0.5	0.21 \pm 0.10b	0.49 \pm 0.09B	0.80	0.32 \pm 0.12b	0.51 \pm 0.06B	0.84
1	0.26 \pm 0.06b	0.27 \pm 0.06C	0.95	0.37 \pm 0.10b	0.31 \pm 0.06C	0.90
2	0.24 \pm 0.09b	0.27 \pm 0.11CD	0.85	0.35 \pm 0.10b	0.14 \pm 0.07D	0.93

^a [PCE₀] and [HCA₀] are presented as mean \pm S.D.

^b Values followed by the same letter do not differ significantly (P -value $>$ 0.05) by extra sum-of-squares F test. R^2 will be negative when the best-fit curve fits the data even worse than does a horizontal line.

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., $1 - C_{res}$ 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 than, or similar to, and the C_{res} 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 C_{res} 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 ($R^2 \geq 0.95$) 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^{•-} ($k = 15.0 \pm 4.5 \text{ M}^{-1} \text{ s}^{-1}$ in dimethylformamide) compared to its degradation by OH[•] ($k = 3.9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) [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 ($k = (1.2\text{--}4.5) \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$) 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 C_{res} 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

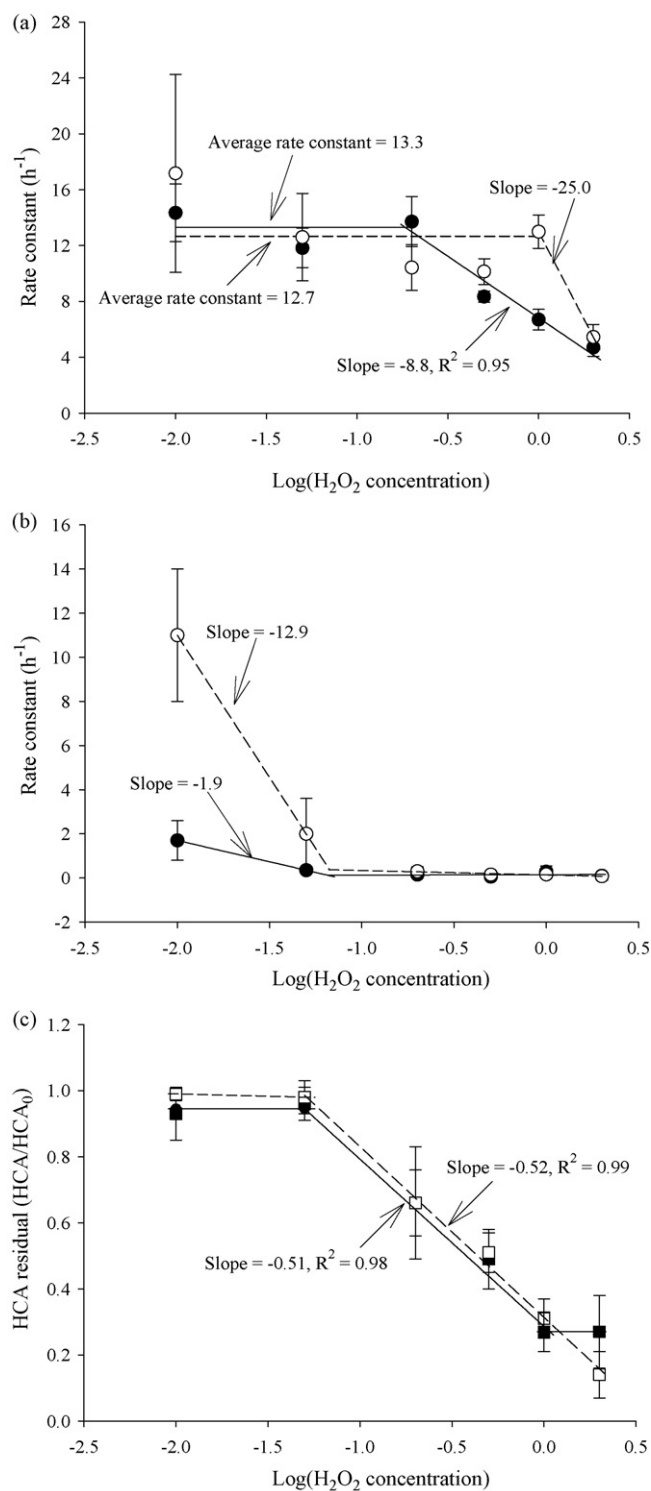


Fig. 4. Relationship between PCE degradation rate constants and H_2O_2 concentrations in the (a) Fe(II) and (b) Fe(II)-citrate (1:3 molar ratio) systems and (c) between HCA residual amount and H_2O_2 concentrations in the Fe(II) system. $[\text{Fe}(\text{II})]_0 = 1 \text{ mM}$, $[\text{PCE}]_0 = 0.30 \pm 0.17 \text{ mM}$, $[\text{HCA}]_0 = 0.015 \pm 0.007 \text{ mM}$, $\text{pH } 3.1 \pm 0.1$. ● PCE-only, ○ PCE in PCE-HCA mixture, ■ HCA-only, □ HCA in PCE-HCA mixture, — PCE-only/HCA-only, -- PCE-HCA mixture. Data points show mean \pm standard deviation. The tables in the figures show the slope and R^2 values for the non-stable part of the data.

the iron-citrate complexes [16], and the amount of OH^\bullet production via Reaction (1) is lower [19]. As a result the PCE degradation rate constant is small, similar to observations in other studies involving chelated iron [14]. A consequence of slowing the OH^\bullet formation rate with Fe(II)-citrate is that no significant HCA degradation occurred

in any of the systems studied, indicating the presence of low concentrations of $\text{O}_2^{\bullet-}$ 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 $\text{O}_2^{\bullet-}$ and OH^\bullet 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

- [1] A. Lopez, M. Pagano, A. Volpe, A.C. Di Pinto, Fenton's pre-treatment of mature landfill leachate, *Chemosphere* 54 (2004) 1005–1010.
- [2] J. Beltran de Heredia, J.R. Dominguez, E. Partido, Physico-chemical treatment for the depuration of wine distillery wastewaters (vinasses), *Water Science and Technology* 51 (2005) 159–166.
- [3] C. Walling, Fenton's reagent revisited, *Accounts of Chemical Research* 8 (1975) 125–131.
- [4] C. Walling, R.A. Johnson, Fenton's reagent. V. Hydroxylation and side-chain cleavage of aromatics, *Journal of the American Chemical Society* 97 (1975) 363–367.
- [5] R.J. Bigda, Consider Fenton chemistry for wastewater treatment, *Chemical Engineering Progress* 91 (1995) 62–66.
- [6] R. Stanforth, M.C. McCartney, Using a dense oxidizing agent to remediate a DNAPL, in: *Proceedings of the Annual Madison Waste Conference*, University of Wisconsin-Madison, USA, 1995, pp. 14–21.
- [7] E. Chamarro, A. Marco, S. Esplugas, Use of Fenton reagent to improve organic chemical biodegradability, *Water Research* 35 (2001) 1047–1051.
- [8] N.B. Abderrazik, F. Al Momani, C. Sans, S. Esplugas, Combined advanced oxidation with biological treatment, *Afinidad* 59 (2002) 141–146.
- [9] M.P. Ormad, S. Ratia, M. del Mar Garcia, J. Saras, J.L. Ovelleiro, Degradation of trichloroethylene by Fenton technology, *Tecnologia del Agua* 24 (2004) 48–55.
- [10] R.J. Watts, A.L. Teel, Chemistry of modified Fenton's reagent (catalyzed H_2O_2 propagations-CHP) for in situ soil and groundwater remediation, *Journal of Environmental Engineering* 131 (2005) 612–622.
- [11] R.J. Watts, B.C. Bottenberg, M.D. Jensen, A.L. Teel, T.F. Hess, Role of reductants in the enhanced desorption and transformation of chloroaliphatic compounds by modified Fenton's reactions, *Environmental Science and Technology* 33 (1999) 3432–3437.
- [12] B.A. Smith, A.L. Teel, R.J. Watts, Identification of the reactive oxygen species responsible for carbon tetrachloride degradation in modified Fenton's systems, *Environmental Science and Technology* 38 (2004) 5465–5469.
- [13] R.J. Watts, J. Howsawkung, A.L. Teel, Destruction of a carbon tetrachloride dense nonaqueous phase liquid by modified Fenton's reagent, *Journal of Environmental Engineering* 131 (2005) 1114–1119.
- [14] Y. Sun, J.J. Pignatello, Chemical treatment of pesticide wastes. Evaluation of iron(III) chelates for catalytic hydrogen peroxide oxidation of 2,4-D at circumneutral pH, *Journal of Agricultural and Food Chemistry* 40 (1992) 332–337.
- [15] S. Lewis, A. Lynch, L. Bachas, S. Hampson, L. Ormsbee, D. Bhattacharyya, Chelate-modified fenton reaction for the degradation of trichloroethylene in aqueous and two-phase systems, *Environmental Engineering Science* 26 (2009) 849–859.

- [16] Y. Li, D. Bhattacharyya, L.G. Bachas, Kinetics studies of trichlorophenol destruction by chelate-based Fenton reaction, *Environmental Engineering Science* 22 (2005) 756–771.
- [17] C. Liang, C.J. Bruell, M.C. Marley, K.L. Sperry, Persulfate oxidation for in situ remediation of TCE. II. Activated by chelated ferrous ion, *Chemosphere* 55 (2004) 1225–1233.
- [18] I. Gautier-Luneau, P. Bertet, A. Jeunet, G. Serratrice, J.L. Pierre, Iron-citrate complexes and free radicals generation: is citric acid an innocent additive in foods and drinks? *BioMetals* 20 (2007) 793–796.
- [19] L. Li, Y. Abe, K. Kanagawa, T. Shoji, T. Mashino, M. Mochizuki, M. Tanaka, N. Miyata, Iron-chelating agents never suppress Fenton reaction but participate in quenching spin-trapped radicals, *Analytica Chimica Acta* 599 (2007) 315–319.
- [20] M. Yoshida, B.D. Lee, M. Hosomi, Decomposition of aqueous tetrachloroethylene by Fenton oxidation treatment, *Water Science and Technology* 42 (2000) 203–208.
- [21] F. Aulenta, M. Majone, P. Verbo, V. Tandoi, Complete dechlorination of tetrachloroethene to ethene in presence of methanogenesis and acetogenesis by an anaerobic sediment microcosm, *Biodegradation* 13 (2002) 411–424.
- [22] R.J. Watts, F.J. Loge, A.L. Teel, J. Sarasa, Oxidative and reductive pathways in manganese-catalyzed Fenton's reactions, *Journal of Environmental Engineering* 131 (2005) 158–164.
- [23] S.W. Leung, R.J. Watts, G.C. Miller, Degradation of perchloroethylene by Fenton's reagent: speciation and pathway, *Journal of Environmental Quality* 21 (1992) 377–381.
- [24] A.L. Teel, R.J. Watts, Degradation of carbon tetrachloride by modified Fenton's reagent, *Journal of Hazardous Materials* 94 (2002) 179–189.
- [25] S.G. Huling, B.E. Pivetz, In-Situ Chemical Oxidation, in: Engineering Issue, U.S. Environmental Protection Agency, Washington DC, 2006.
- [26] J.H. Merz, W.A. Waters, A. Electron-transfer reactions. The mechanism of oxidation of alcohols with Fenton's reagent, *Discussions of the Faraday Society* 2 (1947) 179–188.
- [27] A. Aris, P.N. Sharratt, Influence of initial dissolved oxygen concentration on Fenton's reagent degradation, *Environmental Technology* 27 (2006) 1153–1161.
- [28] W.Z. Tang, C.P. Huang, An oxidation kinetic model of unsaturated chlorinated aliphatic compounds by Fenton's reagent, *Journal of Environmental Science and Health Part A Environmental Science and Engineering: Toxic and Hazardous Substance Control* 31 (1996) 2755–2775.
- [29] T.S. Calderwood, R.C. Neuman Jr., D.T. Sawyer, Oxygenation of chloroalkenes by superoxide in aprotic media, *Journal of the American Chemical Society* 105 (1983) 3337–3339.
- [30] G.V. Buxton, C.L. Greenstock, W.P. Helman, A.B. Ross, Critical review of rate constants for reactions of hydrated electrons, hydrogen atoms and hydroxyl radicals (OH/O^-) in aqueous solution, *Journal of Physical and Chemical Reference Data* 17 (1988) 513.
- [31] C. Walling, A. Goosen, Mechanism of the ferric ion catalyzed decomposition of hydrogen peroxide. Effect of organic substrates, *Journal of the American Chemical Society* 95 (1973) 2987–2991.
- [32] B.H.J. Bielski, D.E. Cabelli, R.L. Arudi, A.B. Ross, Reactivity of HO_2/O_2^- radicals in aqueous solution, *Journal of Physical and Chemical Reference Data* 14 (1985) 1041–1100.
- [33] J.D. Rush, B.H.J. Bielski, Pulse radiolytic studies of the reaction of perhydroxyl/superoxide O_2^- with iron(II)/iron(III) ions. The reactivity of HO_2/O_2^- with ferric ions and its implication on the occurrence of the Haber-Weiss reaction, *Journal of Physical Chemistry* 89 (1985) 5062–5066.
- [34] K. Sehested, O.L. Rasmussen, H. Fricke, Rate constants of OH with HO_2 , O_2^- , and H_2O_2^+ from hydrogen peroxide formation in pulse-irradiated oxygenated water, *Journal of Physical Chemistry* 72 (1968) 626–631.
- [35] K. Sehested, E. Bjergbakke, O.L. Rasmussen, H. Fricke, Reactions of H_2O_3 in the pulse-irradiated $\text{Fe(II)}-\text{O}_2$ system, *The Journal of Chemical Physics* 51 (1969) 3159–3166.
- [36] I.B. Afanas'ev, Superoxide Ion: Chemistry and Biological Implications, CRC Press, Boca Raton, FL, 1989.
- [37] J.J. Pignatello, E. Oliveros, A. MacKay, Advanced oxidation processes for organic contaminant destruction based on the Fenton reaction and related chemistry, *Critical Reviews in Environmental Science and Technology* 36 (2006) 1–84.
- [38] G.G. Jayson, J.P. Keene, D.A. Stirling, A.J. Swallow, Pulse-radiolysis study of some unstable complexes of iron, *Transaction of the Faraday Society* 65 (1969) 2453–2464.