Chelate-Modified Fenton Reaction for the Degradation of Trichloroethylene in Single and Two-Phase Systems

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Abstract

The Standard Fenton reaction has been used for In-Situ Chemical Oxidation (ISCO) of toxic organics in groundwater. However, it requires low pH operating conditions, and thus has limitations for in situ applications. In addition, hydroxyl radicals are rapidly consumed by hydroxyl scavengers found in the subsurface. These problems are alleviated through the chelate-modified Fenton (hydroxyl radical) reaction, which includes the addition of a nontoxic chelate (L) such as citrate or gluconic acid. This chelate allows the reaction to take place at near neutral pH and control hydrogen peroxide consumption by binding to Fe(II), forming an FeL complex. The chelate also binds to Fe(III), preventing its precipitation as ferric hydroxide and thus prevents problems associated with injection well plugging. The rate of TCE dechlorination in chelate-modified Fenton systems is a function of pH, H₂O₂ concentration, and Fe:L ratio. The primary objective of this research is to model and apply this process to the destruction of trichloroethylene (TCE) present in both the aqueous and organic (in the form of droplets) phases. Experimentation proved the chelate-modified Fenton reaction effectively dechlorinates TCE in both the aqueous and organic phases at near-neutral pH. Other focuses of this work include determining the effect of [L]:[Fe] ratios on H₂O₂ and TCE degradation as well as reusability of the Fe-citrate solution under repeated H₂O₂ injections. Generalized models were developed to predict the concentration of TCE in the aqueous phase and TCE droplet radius as a function of time using established hydroxyl radical kinetics and mass transfer relationships.
Introduction and Background

Groundwater Remediation of TCE

Contamination of groundwater by toxic organic compounds is an issue that deserves much attention. Trichloroethylene (TCE) is a volatile, halogenated organic compound that was once a widely used degreasing agent. Two decades ago, over 200 million pounds of TCE were produced in the United States each year (Vogel et al., 1987). Although the majority of TCE lost to the environment is via volatization, large plumes of TCE have been reported in various groundwater systems (U.S. EPA, 1998). Because concentrations of TCE can be above the solubility limit in water (1000 - 1100 ppm), a majority of the TCE is often present in the form of a dense, non-aqueous phase liquid (DNAPL), particularly at high depth (Russell et al., 1992). Several current remediation techniques successfully treat the dissolved TCE, but are unable to treat the DNAPL itself, eventually resulting in a rebound of TCE in the groundwater. Over the years, much effort has been put into the cleanup of TCE and other contaminants using various remediation technologies. An efficient and cost effective procedure is required for removing toxic organic compounds from groundwater.

Many different strategies have been used for the removal of toxic organic compounds from the subsurface. Pump-and-treat methods have long been used for groundwater remediation, but are very expensive for the amount of contaminant removed and require long periods of time to treat the affected area. In air-stripping operations, TCE is transferred from groundwater to air, but not destroyed. Biological remediation can be performed under both aerobic and anaerobic conditions and is capable of completely mineralizing TCE (Laine and Cheng, 2007; Russell et al., 1992). Due to its reliance on living organisms, these methods have limited applicability. Degrading TCE
through the use of chemicals via oxidative and reductive pathways has been proven to be an effective groundwater remediation technology (Laine and Cheng, 2007).

It was once thought that since TCE is already in an oxidized state, attempting to further oxidize the compound would not be an effective remediation strategy (Russell et al., 1992). However, several powerful oxidants have are able to effectively degrade TCE and many other organic contaminants. Various advanced oxidative processes (AOPs) have been used for in-situ chemical oxidation (ISCO). Currently, the three main oxidants in use for ISCO are permanganate (KMnO₄ NaMnO₄), ozone (O₃), and Fenton’s reagent.

Permanganate, usually in the form of KMnO₄, has the slowest reaction rate of the three oxidants, but also has the highest stability. It has been proven effective from a pH of 3.5 to 12 and, depending on the pH, degrades pollutants by either direct oxidation or hydroxyl radical (OH•) generation (Siegrist and Urynowicz, 2000). Although it can treat a wide variety of pollutants, it has proven ineffective on BTEX, diesel fuel, and gasoline (Amarante, 2000). Ozone (O₃) is also capable of oxidizing pollutants by either direct oxidation or hydroxyl radical generation, but mainly under acidic conditions (Watts and Teel, 2006a). It is very unstable in the subsurface and requires expensive on-site generation (Amarante, 2000).

**Fenton Reaction**

The mechanism for the standard Fenton reaction (Fenton’s reagent) was first proposed by Haber and Weiss in 1934. The reaction of hydrogen peroxide with Fe(II) proceeds as follows (De Laat and Gallard, 1999):

\[
Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH \bullet \quad \text{k}_1 = 63 \text{ M}^{-1}\text{s}^{-1}
\]  

As shown, this reaction generates the hydroxyl radical, an electrophile and strong oxidizing agent (E°=2.73 V) which reacts with most organic contaminants (Haber and
Weiss, 1934). The rate constant of this reaction is widely reported as 63 M$^{-1}$s$^{-1}$, but varies with pH due to Fe(II) speciation (Kwan and Voelker, 1996). Through a series of propagation reactions (Equations 2-10) at acidic pH, ferric iron is reduced to ferrous iron then reacts to form more hydroxyl radicals via reaction 1 (DeLaat and Gallard, 1999; Lin and Gurol, 1998; Pignatello, et al., 2006; Ravikumar and Gurol, 1994; Wang and Lemley, 2001). Iron is said to be catalytic in this respect. It should also be noted that the rate constant for Reaction 8 is four orders of magnitude lower than that of Reaction 1, and therefore is the rate-limiting step in this catalytic cycle.

$$Fe^{2+} + OH \cdot \rightarrow Fe^{3+} + OH^-$$  \hspace{1cm} k_2 = 3.2 \times 10^8 \text{ M}^{-1}\text{s}^{-1} \hspace{1cm} (2)

$$H_2O_2 + OH \cdot \rightarrow H_2O + HO_2 \cdot$$  \hspace{1cm} k_3 = 3.3 \times 10^7 \text{ M}^{-1}\text{s}^{-1} \hspace{1cm} (3)

$$OH \cdot + OH \cdot \rightarrow H_2O_2$$  \hspace{1cm} k_4 = 6 \times 10^9 \text{ M}^{-1}\text{s}^{-1} \hspace{1cm} (4)

$$OH \cdot + HO_2 \cdot \rightarrow H_2O + O_2$$  \hspace{1cm} k_5 = 7.1 \times 10^9 \text{ M}^{-1}\text{s}^{-1} \hspace{1cm} (5)

$$HO_2 \cdot + HO_2 \cdot \rightarrow H_2O_2 + O_2$$  \hspace{1cm} k_6 = 8.3 \times 10^5 \text{ M}^{-1}\text{s}^{-1} \hspace{1cm} (6)

$$H_2O_2 + HO_2 \cdot \rightarrow H_2O + O_2 + OH \cdot$$  \hspace{1cm} k_7 = 3.1 \text{ M}^{-1}\text{s}^{-1} \hspace{1cm} (7)

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2 \cdot + H^+$$  \hspace{1cm} k_8 = 2 \times 10^{-3} \text{ M}^{-1}\text{s}^{-1} \hspace{1cm} (8)

$$Fe^{3+} + HO_2 \cdot \rightarrow Fe^{2+} + O_2 + H^+$$  \hspace{1cm} k_9 = 2 \times 10^3 \text{ M}^{-1}\text{s}^{-1} \hspace{1cm} (9)

$$Fe^{2+} + HO_2 \cdot \rightarrow Fe^{3+} + HO_2^-$$  \hspace{1cm} k_{10} = 1.2 \times 10^6 \text{ M}^{-1}\text{s}^{-1} \hspace{1cm} (10)

Several problems arise for application of this process for in-situ. The high buffering capacity of groundwater systems maintains a near-neutral pH, resulting in the precipitation of Fe(III) as Fe(OH)$_3$. Lowering the groundwater pH may be feasible for small treatment areas, but not for larger areas. Fe(OH)$_3$ precipitation not only prevents Fe(III) from reducing to Fe(II), but can also cause injection-well plugging. Other problems include rapid heat generation, limited mobility of the reactants, and the hazards
of transporting highly concentrated hydrogen peroxide. The latter can be alleviated through the enzymatic production of H$_2$O$_2$ on-site (Ahuja et al., 2007). The hydroxyl radical’s reaction rate with most organic contaminants is on the order of $10^8$ – $10^{10}$ M$^{-1}$s$^{-1}$ therefore making its reactivity with these contaminants diffusion limited ($\sim 10^{10}$ M$^{-1}$s$^{-1}$ in water) (Watts and Teel, 2005b).

**Chelate-Modified Fenton Reaction**

The problems related with application of the standard Fenton reaction for ISCO can be alleviated through the use of the chelate-modified Fenton reaction. This involves the addition of a nontoxic chelate (L) such as citrate or gluconic acid, which has the potential to be produced on-site (Ahuja et al., 2007). The chelate is capable of binding ferrous and ferric iron, reducing concentrations of Fe(II) and Fe(III) in solution. This limits the amounts of Fe(II) and Fe(III) available for reaction with H$_2$O$_2$ thus controlling the rate of hydroxyl radical generation. The use of a chelate for remediation in aerobic environments prevents Fe(II) oxidation by O$_2$. Li et al. (2007b) demonstrated that dissolved oxygen has no effect on the degradation of trichlorophenol (TCP) by the chelate-modified Fenton reaction using polyacrylic acid (PAA) as the chelating agent.

**TCE Degradation**

Hydroxyl radical degradation of TCE is second order in nature ($k_{TCE} = 4 \times 10^9$ M$^{-1}$s$^{-1}$) and generally forms intermediates such as di- and trichloroacetic acids (Pignatello et al., 1999; Li et al., 2007a; Watts and Teel, 2005b). These are then oxidized further by hydroxyl radicals and, if run to completion, the final products are harmless organic acids and carbon dioxide. In the subsurface, most hydrophobic organic contaminants present in concentrations higher than their solubility limits are in droplet form (Roy-Perreault et al., 2005; Yaron-Marcovich et al, 2007). These droplets are generally trapped within the
soil, making them very difficult to treat and impeding their dissolution into the aqueous phase (Kennedy and Lennox, 1997). Figure 1 illustrates a possible distribution of TCE in the subsurface.

Watts et al. (1994) showed that hexachlorobenzene sorbed to silica sand surfaces exhibits greater rates of degradation using a Fenton-like system than was lost by desorption. In addition to direct contaminant destruction, Morgan and Watkinson (1992) showed the addition of hydrogen peroxide aids in the bioremediation of groundwater.

Considerable research on Fenton-like reactions for the destruction of organic contaminants present in the aqueous phase has been done. However, in order to effectively treat DNAPLs, information regarding the destruction of contaminants in both aqueous and organic phases is essential. Objectives of this research include: determine the effect of chelate (citrate):Fe(II) ratio on the rate of H\textsubscript{2}O\textsubscript{2} degradation, determine effect of H\textsubscript{2}O\textsubscript{2} dosing on TCE dechlorination, study the destruction of TCE droplets via standard and chelate-modified Fenton reactions, and develop a kinetic model to describe the destruction of TCE in both aqueous and non-aqueous phases.

**Experimental Methods**

**Chemicals**

All chemicals used were of reagent grade. TCE, ferrous sulfate, sodium citrate, sodium phosphate, hydrogen peroxide (30 wt%), pentane, sodium hydroxide, sulfuric acid, and deionized ultrafiltered (DIUF) water were all purchase from Fisher Scientific. Copper(II) Sulfate was purchased from EM Science. 2,9-Dimethyl-1,10-phenanthroline (DMP) and 1,2-dibromoethane (EDB) were purchased from Sigma-Aldrich. Chloride
reference solution (1000 ppm) was purchased from Thermo Electron Corporation.
Sodium nitrate was purchased from LabChem Inc.

**Experimental Procedure**

For standard Fenton reactions, ferrous sulfate was added to deoxygenated DIUF water and the pH was adjusted to ~3. For chelate-modified Fenton reactions, sodium citrate was added to deoxygenated DIUF water, the pH was adjusted to ~3, followed by the addition of ferrous salt and adjustment of the pH to neutral. TCE was added to these solutions, which were then sealed and allowed to mix for certain reaction times. For experiments with TCE present in both aqueous and organic (droplet) phases, saturated solutions of TCE were prepared overnight and excess TCE constituting the organic phase was added before initiating the reaction. For batch experimentation, reactions were conducted in 500 mL flasks with continuous mixing and N₂ in the headspace at room temperature (22-25°C). H₂O₂ was injected through a septum to initiate the reaction in either one dose for lower concentrations or six doses over 10 minutes for higher concentrations. Adjustments to pH were made using H₂SO₄ and NaOH. As part of this study, site-specific RGA aquifer materials were collected from a location identified by Sexton (2005) as an outcrop of the Regional Gravel Aquifer (RGA). Groundwater samples for experiments using natural water were collected from a local residential well outside of the TCE contaminant plumes from areas surrounding the Paducah Gaseous Diffusion Plant (PGDP) and supplied by the Kentucky Research Consortium for Energy and Environment (KRCEE) in cooperation with the Kentucky Water Resources Research Institute (KWRRI). When received, this water contained no TCE.

**H₂O₂ Measurement**
Hydrogen peroxide concentrations were measured using the method described by Kosaka et al. (1998). One mL each of 0.01 M copper(II) sulfate, 2,9-Dimethyl-1,10-phenanthroline (DMP) solution, and 0.1 M phosphate buffer (pH 7) were added to 3mL of diluted sample. DMP solution was prepared by dissolving one gram DMP in 100 mL ethanol. The absorbance of the solution was measured at 454 nm using a Varian Cary 300 Spectrophotometer. The calibration curve was created using 12 concentrations ranging from 10 to 300 µM with $R^2 = 0.9997$ and average analytical error of 2.0%.

**GC/MS Analysis**

After a sample from the reaction vessel was taken, TCE was extracted with pentane previously spiked with an internal standard of 100 ppm EDB. TCE concentrations were measured using a 60 m $\times$ 0.25 mm $\times$ 1.4 µm film thickness Supelco SPB-624 fused silica capillary column installed in a Hewlett Packard 5890 Series II Gas Chromatography and Mass Spectrometer, model number 5971. The calibration curve was created using 7 concentrations ranging from 4.55 to 364 ppm TCE with $R^2 = 0.9982$ and average analytical error of 5.3%.

**Cl$^-$ Analysis**

Either a Thermo Orion ion-selective electrode or an Accumet Chloride Combination Electrode was used for measuring Cl$^-$ concentrations. The calibration curve was created using 6 concentrations ranging from 5 to 200 ppm Cl$^-$. In agreement with previous Cl$^-$ analysis by our group, multiple calibrations were produced with different concentrations of citrate to account for citrate interference (Li et al., 2005). $R^2$ values ranged from 0.9933 to 0.9987 with average analytical error from 3.8% to 8.6%.

Calibration curves were checked with standards before measuring samples.

**Results and Discussion**
This section focuses on the destruction of TCE droplets using the standard Fenton reaction. Then, the chelate’s effect on Fe(II) concentration in solution is quantified using equilibrium values reported from the literature. The effects of the resulting Fe-chelate equilibria and of iron speciation on hydrogen peroxide degradation are then discussed. The applicability of the chelate-modified Fenton reaction to groundwater systems is tested using natural water and, separately, a packed column for simulated groundwater flow. A model for the degradation of TCE in both the aqueous and non-aqueous phases is developed.

**TCE Droplet Degradation with Standard Fenton Reaction**

The standard Fenton reaction operates most efficiently at pH below 3 (Pignatello 2006). However, as discussed earlier, application of Fenton processes at low pH in large groundwater systems is highly impractical. The standard Fenton reaction occurs rapidly, reaching completion in a relatively short amount of time. A series of experiments using a 1:1 TCE:Fe(II) molar ratio were conducted in order to determine the optimum amount of hydrogen peroxide for complete dechlorination of both TCE droplets and TCE in the aqueous phase. These experiments were conducted at a low initial pH of approximately 2.5 and allowed to continue without pH adjustment as the pH did not vary significantly as the reaction proceeded. Twenty hours after adding the hydrogen peroxide, the quantities of TCE and Cl\(^-\) were analyzed, as shown in Figure 2. The 1:1 \(\text{H}_2\text{O}_2:\text{Fe(II)}\) molar ratio resulted in the formation of 47% of the maximum possible Cl\(^-\) concentration and an 81% reduction in the amount of TCE present. The higher \(\text{H}_2\text{O}_2:\text{Fe(II)}\) ratios degraded almost 100% of the available TCE and formed approximately 82% of the maximum possible Cl\(^-\). In the control, in which no \(\text{H}_2\text{O}_2\) was added, a 29% loss of TCE was observed. This loss is the largest contributor to the deviations between the actual and theoretical chloride
formation. Another contributing factor is the presence of chlorinated organic intermediates. This data indicates the optimum H₂O₂:Fe(II) molar ratio for dechlorination of TCE in both droplet and dissolved form at pH 2.5 is between 1:1 and 2:1. Teel et al. (2001) found the optimum H₂O₂:Fe(II) molar ratio to be 1:1 for TCE degradation in the aqueous phase. H₂O₂ in excess of this 1:1 ratio is required to degrade the TCE present in droplet form.

When similar reactions are performed (without chelate) at near-neutral or high pH, the amount of TCE degraded drops dramatically. Thus, this process must be modified to perform efficiently at near-neutral pH.

**Iron-Chelate Equilibria**

The use of a chelate reduces the amount of free Fe(II) and Fe(III) in solution, but is pH dependent. The equilibrium reactions associated with citrate as well as the complexation of Fe species with citrate are given in Equations 11-20, where \( L = L^{4-} \) (Inczedy, 1976; Brady and Humiston, 1982).

\[
\begin{align*}
Fe^{2+} + L & \rightleftharpoons Fe(II)L & K_{11} = 10^{15.5} \\
Fe^{2+} + H^+ + L & \rightleftharpoons Fe(II)HL & K_{12} = 10^{19.1} \\
Fe^{2+} + 2H^+ + L & \rightleftharpoons Fe(II)H_2L & K_{13} = 10^{24.2} \\
Fe^{3+} + L & \rightleftharpoons Fe(III)L & K_{14} = 10^{25} \\
Fe^{3+} + H^+ + L & \rightleftharpoons Fe(III)HL & K_{15} = 10^{27.8} \\
Fe^{3+} + 2H^+ + L & \rightleftharpoons Fe(III)H_2L & K_{16} = 10^{28.4} \\
H^+ + L & \rightleftharpoons HL & K_{17} = 10^{16} \\
H^+ + HL & \rightleftharpoons H_2L & K_{18} = 10^{5.1} \\
H^+ + H_2L & \rightleftharpoons H_3L & K_{19} = 10^{5.4}
\end{align*}
\]
Using Equations 12-20 and those associated with the hydrolysis of Fe$^{2+}$ and Fe$^{3+}$ (Equations 21-27), the speciation of virtually any Fe-citrate solution can be computed for a given pH (Baes and Mesmer, 1976). The speciation of ferrous iron is shown in Figure 3. As pH approaches neutral, only a small amount of Fe is in an uncomplexed form. As pH decreases, more iron is released from this complex, which results in an increase in the overall rate of reaction. Similar calculations for ferric iron have been made, but are not shown here.

$$H^+ + H_3L \rightleftharpoons H_4L \quad K_{20} = 10^{3.0} \quad (20)$$

Adjusting the [L]:[Fe] ratio allows one to control the amount of Fe(II) and Fe(III) in solution and alter the generation of hydroxyl radicals as desired. In order to correctly determine the rates of free radical generation, quantification of the equilibrium distribution of iron is necessary.

**Effect of L:Fe Ratio and Fe Speciation on H$_2$O$_2$ Decomposition**

The initial reaction rate of Fe(II) with H$_2$O$_2$ is very rapid, but as more Fe(II) is oxidized to Fe(III), the decomposition of H$_2$O$_2$ slows significantly. Figures 4 and 5 illustrate the decomposition of H$_2$O$_2$ in the presence of ferrous and ferric iron,
respectively, with varying [L]:[Fe] molar ratios (L = citrate). When ferrous iron is used, the initial rate of H$_2$O$_2$ decomposition is very rapid. However, when ferric iron is used, the decomposition is much slower and almost linear, indicating a zero-order reaction. As expected, the rate limiting step in the reactions between ferrous/ferric iron and H$_2$O$_2$ is Reaction 8 and thus confirms the rate of the reaction depends mostly on the concentration of Fe(II). In addition to the speciation of iron, the [L]:[Fe] ratio plays an important role in determining the rate of H$_2$O$_2$ degradation. This rate decreases as this ratio increases and, in conjunction with other findings, indicates Fe-citrate complexes are nonreactive with H$_2$O$_2$ when compared to uncomplexed iron (Li et al., 2007b). Increasing the L:Fe ratio increases the efficiency of H$_2$O$_2$ consumption by reducing the rate of hydroxyl radical production. This reduces the quantities of H$_2$O$_2$ and hydroxyl radicals consumed in Reactions 3-5, and 7, leaving more hydroxyl radicals available for reaction with TCE. Depending on the conditions present at a given groundwater site, the [L]:[Fe] and [Fe(II)]:[Fe(III)] ratios can be adjusted to allow for the optimization of H$_2$O$_2$ consumption and TCE degradation.

**TCE Degradation with Chelate-Modified Fenton Reaction in Natural Water**

At near-neutral pH, both Fe(II) and Fe(III) are almost entirely complexed with citrate. Due to this chelation, H$_2$O$_2$ decomposition and TCE degradation take place at much lower rates than without a chelate. Regardless, these chelate-modified Fenton reactions are still capable of degrading significant quantities of TCE in natural water, as shown in **Figure 6**. These experiments were conducted in order to quantify the degradation of TCE in the water containing a representative chemical background for the contaminated area. These chelate-modified Fenton reaction experiments ([L]:[Fe] = 1:1) were spiked with 1.1 mM TCE and conducted at an initial pH of 7 and allowed to
continue without pH adjustment, reaching a final pH of approximately 5. The 4:1
H₂O₂:Fe(II) molar ratio resulted in the formation of 33% of the maximum possible Cl⁻
concentration and an 52% reduction in the amount of TCE present. Doubling the
quantity of H₂O₂ resulted in the degradation of 87% of the available TCE and formed
59% of the maximum possible Cl⁻. A 13% loss of TCE was observed in the control.
Although doubling the amount of H₂O₂ increased the amount of TCE degraded, it did not
do so proportionately. Thus, the same amount of H₂O₂ applied periodically over a longer
time should increase the efficiency of this process.

**Single-Phase Kinetic Modeling of TCE Degradation**

The governing rate law for the second-order reaction of TCE with OH• is shown
in Equation 28, where [TCE]₀ₐ₉ is the concentration of TCE in the aqueous phase
(mmol/L) and [OH•] is the concentration of hydroxyl radicals (mmol/L).

\[
\frac{dTCE}{dt} = -k_{TCE}[TCE]_0[OH•] \quad (28)
\]

If [OH•] is assumed to be constant and small, this reaction becomes pseudo-first-order.
Substituting the observed rate constant, \(k'_{TCE} = -k_{TCE} \times [OH•]\) into Equation 28 and

\[
[TCE]_0 = [TCE]_0 \times \exp(-k'_{TCE} \times t) \quad (29)
\]

For the kinetic data in **Figure 7**, \(k'_{TCE} = 0.614 \text{ hr}^{-1} (R^2 = 0.916)\). The steady-state value
of [OH•] = \(4.26 \times 10^{-14} \text{ M}\) was obtained by dividing the observed rate constant by the
intrinsic rate constant reported in literature. Li *et al.* (2005) calculated a steady-state
[OH•] = \((1.68 \pm 0.10) \times 10^{-13} \text{ M}\) for pH = 6 in the presence of trichlorophenol (TCP)
\((k_{TCP} = 5.48 \times 10^9 \text{ M}^{-1}\text{s}^{-1})\) (Li 2005). Although the reaction conditions for these studies
are not identical, similar concentrations of reactants were used, yielding comparable
results. Li et al. noted that their reported value of [OH•] is greater than the actual value due to intermediate compounds competing for hydroxyl radicals.

Although this assumption is effective, it fails to consider the dependence of [OH•] on hydrogen peroxide concentration. For instance, after the addition of hydrogen peroxide to a system containing mostly Fe(II), there will be a large drop in [H₂O₂] due to its rapid reaction with Fe²⁺. The result is a large increase in [OH•] and a corresponding drop in pollutant concentration followed by a reduction in the rate of reaction, given the appropriate conditions. A first-order model will also predict continuous contaminant degradation even after there is no hydrogen peroxide remaining. Under circumstances such as these, as well as others, improvements to the constant [OH•] model can be made by assuming the quantity of OH• formed is proportional to the rate of hydrogen peroxide decomposition. Substituting Equations 30 and 31 into Equation 28 and solving for [TCE] yields Equation 32.

\[
[OH•] = \alpha \times \left(-\frac{d[H₂O₂]}{dt}\right)
\]

\[
k''_{TCE} = k_{TCE} \times \alpha \times [H₂O₂]₀
\]

\[
[TCE]_{aq} = [TCE]_{aq,0} \times \exp(-k''_{TCE} \times (1 - [H₂O₂]/[H₂O₂]₀))
\]

This model, shown in Figure 7, yields \( k''_{TCE} = 4.30 \) (\( R^2 = 0.965 \)). The experimental \( H₂O₂ \) values and calculated [OH•] for this model are shown in Figure 8.

TCE degradation is accompanied by Cl⁻ formation, with a maximum (mmol Cl⁻ formed) / (mmol of TCE degraded) = 3. However, due to the formation of chlorinated intermediates which compete with TCE for hydroxyl radicals, this amount of chloride is not always formed. Figure 9 shows the kinetic data for Cl⁻ formation as well as the theoretical quantities of Cl⁻ produced for the model based on Equation 32 with (mmol Cl⁻)
formed) / (mmol TCE reacted) = 2 and 3. Analysis of the kinetic data indicates the actual (mmol Cl\textsuperscript{-} formed) / (mmol TCE reacted) = 2.8 ± 0.3, signifying almost complete degradation of TCE. It should be noted that this result indicates there is a possibility of forming more than 3 mmol Cl\textsuperscript{-} per mmol TCE degraded, but this is due to analytical error.

**Two-Phase Kinetic Modeling of TCE Degradation**

In this section, a model for the degradation of TCE in two-phase systems, as seen in Figure 10, will be presented. In this system, n droplets of radius R (m) are present in a sealed reactor vessel of volume V (L). The vessel is stirred at a specific rate in order to maintain the organic-phase TCE in the form of droplets, which maintain a velocity of U (m/s) relative to the surrounding fluid. A mass-transfer boundary layer of thickness \( \delta \) (m) is formed around the droplet, creating a TCE concentration gradient.

The governing equations for this model consist of balances on the radius of the TCE droplets (Equation 33) and the concentration of TCE in the bulk phase, \([\text{TCE}]_{aq}\), (Equation 34) both varying with respect to time, where \( W_r \) (mmol s\(^{-1}\) m\(^{-2}\)) is the mass flux of TCE from the droplet surface to the bulk phase, \( S \) is the surface area of one droplet (m\(^2\)), \( \rho_{\text{TCE}} \) is the density of TCE (g/cm\(^3\)), and \( M_{\text{TCE}} \) is the molecular weight of TCE (g/mol). Because \([\text{H}_2\text{O}_2]\) > 0 for the majority of the experiment, the proposed constant \([\text{OH}\textbullet]\) model is used to calculate the degradation of TCE in the aqueous phase. Using the model assumptions listed below, these equations can be solved simultaneously to yield a dynamic profile for \([\text{TCE}]_{aq}\) and R.

\[
V \frac{d[\text{TCE}]_{aq}}{dt} = -k'_{\text{TCE}} \times V \times [\text{TCE}]_{aq} + W_r \times S \times n \tag{33}
\]

\[
\frac{4\pi R^2 \rho_{\text{TCE}}}{M_{\text{TCE}}} \frac{dR}{dt} = -W_r \times S \tag{34}
\]
In order to calculate $W_r$ (mol s$^{-1}$ m$^{-2}$), **Equation 35** is used, where $k_c$ is the mass transfer coefficient (m/s) and $[\text{TCE}]_{\text{sat}}$ is the maximum dissolved concentration of TCE in the aqueous phase (mmol/L).

$$W_r = k_c ([\text{TCE}]_{\text{sat}} - [\text{TCE}]_{\text{aq}})$$ (35)

The boundary layer thickness can be calculated from $k_c$, a function of the Sherwood number ($Sh$). To calculate this coefficient, **Equations 36-39** are used, where

Re is the Reynolds number, $Sc$ is the Schmidt number, $\nu$ is the dynamic viscosity of water, and $D_{\text{TCE-water}}$ is the binary diffusion coefficient of TCE in water ($9.4 \times 10^{-10}$ m$^2$/s) (Fogler, 2006; Reichert *et al.*, 2004; Montgomery, 2000).

$$Re = \frac{U \times (2R)}{\nu}$$ (36)

$$Sc = \frac{\nu}{D_{\text{TCE-water}}}$$ (37)

$$Sh = 2 + 0.6 \times Re^{1/2} \times Sc^{1/3}$$ (38)

$$k_c = \frac{D_{\text{TCE-water}} \times Sh}{2R}$$ (39)

Because $U$ is the velocity of the particle relative to the surrounding fluid, it is very difficult to measure. However, using the theory of stationary slip velocity, the minimum relative velocity can be estimated by calculating the settling velocity of the droplet in a stationary media (Harriott, 1962; Reichert *et al.*, 2004). Since $R$ changes with time, the drag coefficient, $C_D$, will also change with time, therefore changing $U$. Because in-depth fluid dynamics calculations are beyond the scope of this research, a simple correlation between $U$ and $R$ is required. Using **Equation 40** is to estimate $C_D$ from Re and the equations for calculating settling velocity, a linear relationship between $U$ and $R$ was
formulated for values of R ranging from 0 to 0.0015 m, as seen in Equation 41 (R^2 = 0.995) (Brown and Lawler, 2003; Munson, 2002).

\[
C_D = \frac{24}{Re} (1 + 0.150 Re^{0.681}) + \frac{0.407}{1 + \frac{8710}{Re}} \quad (40)
\]

\[
U = 126.4 \times R \quad (41)
\]

For the chelate-modified Fenton reaction, it can be safely assumed that no Fe or citrate species are present in the TCE droplets since they will be ionized at near-neutral pH. Additional model assumptions include:

- Reactions only occur in the bulk aqueous phase
- OH• is the only species that reacts with TCE
- Liquid phase is uniformly mixed and isothermal
- Uniform droplet size, distribution, and relative velocity of droplets
- n = 100 (based on visual approximation)
- Droplets are spherical and have smooth surfaces
- Negligible TCE loss due to volatility
- \([\text{TCE}]_{\text{sat}} = 8 \text{ mmol/L}\)

Solving for \([\text{TCE}]_{\text{aq}}\) and R yields Figures 11 and 12, respectively. Because the value of \(k_c\) is theoretical, calculations were performed using values of \(k_c / 2\), \(k_c\), and \(2 \times k_c\) to show its effect on \([\text{TCE}]_{\text{aq}}\) and R. As expected, the rate of dissolution of the droplets is directly proportional to the value of \(k_c\). The minimum and maximum calculated values for \(k_c\) are 4.6 \times 10^{-5} \text{ m/s} and 9.9 \times 10^{-4} \text{ m/s}, respectively.

The predicted model values indicate no droplets should be present after 18 hours and that TCE degradation should be complete after 22 hours. According to visual observation, the
droplets did not disappear until approximately 28 hours. Thus, the value of $k'$ and/or $k_c$ is likely overestimated.

The $\text{H}_2\text{O}_2$ degradation profile for a chelate-modified Fenton reaction system in the presence of excess TCE in droplet form is shown in Figure 13. Because the dechlorination of TCE is the main focus of this study, it was measured solely by $\text{Cl}^-$ production. In the control run, TCE droplets were visible after a period of several days, indicating minimal loss due to volatility. After complete reaction of the initial addition of $\text{H}_2\text{O}_2$ (12 hours), a second spike of equal quantity was made. The second addition leads to an increase in $\text{Cl}^-$ formation, proving that multiple injections of $\text{H}_2\text{O}_2$ can be used repeatedly in these systems to further degrade contaminants. The initial spike of $\text{H}_2\text{O}_2$ resulted in the production of 10.9 mmol $\text{Cl}^-$, whereas the second spike produced only 5.9 mmol. This significant difference and occurs for two reasons: 1) More $\text{Fe}^{2+}$ is available in the initial stages of the reaction and 2) when TCE concentrations are lower, less hydroxyl radicals are consumed from reaction with TCE, increasing the rates of Reaction 3-5 and 7. The result is a higher rate of $\text{H}_2\text{O}_2$ degradation, which explains why $\text{H}_2\text{O}_2$ is consumed faster after the second injection than the first. Figure 14 shows the actual and model-predicted amounts of $\text{Cl}^-$ formed.

After the first hour of the reaction, $\text{Cl}^-$ production is relatively constant and correspond closely to the model-predicted values (Equations 33 and 34) for $(\text{mmol } \text{Cl}^- \text{ formed}) / (\text{mmol } \text{TCE reacted}) = 1$. This is significantly less $\text{Cl}^-$ formation than in the single-phase TCE experiments despite the larger $(\text{mmol } \text{Cl}^- \text{ formed}) / (\text{mmol } \text{H}_2\text{O}_2 \text{ consumed})$ for the system with droplets. Even though the initial $[\text{H}_2\text{O}_2]:[\text{Fe}]$ ratios are the same, some of this disparity can be explained by the different $[\text{TCE}]_{\text{aq}}:[\text{Fe}]$ ratios,
which are ~1:1 for the system with no droplets and ~2:1 for the for the system containing droplets. Other contributing factors include the overestimation of k’ and/or kc.

Although most TCE degradation is thought to occur via oxidation by hydroxyl radicals, it has been proven that other species formed during Fenton reaction propagations are capable of degrading toxic organics. Watts et al. (2005a) used an iron-catalyzed modified Fenton reaction with chelate at pH 3 with a high H2O2:Fe ratio to destroy DNAPLs of carbon tetrachloride and chloroform. These contaminants were chosen because of their resistance to oxidation via hydroxyl radicals (kOH• on the order of 10^6 M^-1s^-1) (Haag and Yao, 1992). The main species responsible for this is superoxide radical anion (O2•^-) (Watts and Teel, 2006b). Other oxidants include perhydroxy radical (HO2•), hydroperoxide anion (HO2^-), which are present in Reactions 3 and 5-10 (DeLaat and Gallard, 1999; Lin and Gurol, 1998; Pignatello, et al., 2006; Ravikumar and Gurol, 1994; Wang and Lemley, 2001). Superoxide radical anion, the conjugate base of perhydroxy radical (Equation 42), could also play a role in the destruction of TCE DNAPLs.

\[ HO_2^- \Leftrightarrow O_2^- + H^+ \quad K_{42} = 1.58 \times 10^{-5} \text{ M} \]  

Li et al. (2007) showed that superoxide radical anion concentrations were two orders of magnitude higher for a chelate-modified Fenton reaction system ([L]:[Fe] = 1:1) than for a standard Fenton reaction system (no chelate), both containing [Fe] = 0.2mM and [H2O2] = 0.5 mM.

**Efficiency of Chelate-Modified Fenton Reaction**

One way to determine the efficiency of H2O2 use for TCE degradation is to compare the quantity of Cl^- formed to the quantity of H2O2 reacted. For the chelate-modified Fenton reaction data in Figures 9 (no TCE droplet) and 10 (with TCE droplets),
the time-averaged (mmol Cl\(^{-}\) formed) / (mmol H\(_2\)O\(_2\) reacted) values are given in **Figure 15**. Overall, this ratio is larger in the presence of TCE droplets since there is more TCE available to be degraded, but for these reaction conditions, between 0.2 and 0.5 mmol of Cl\(^{-}\) are formed per mmol H\(_2\)O\(_2\) reacted. In order to completely degrade 1 mmol TCE, approximately 6 to 15 mmol H\(_2\)O\(_2\) are required. This is in contrast to the efficiency of the standard Fenton reaction (**Figure 2**), which yields (mmol Cl\(^{-}\) formed) / (mmol H\(_2\)O\(_2\) reacted) = 1.2 to 1.5, meaning 2 to 2.5 mmol H\(_2\)O\(_2\) are needed to completely degrade 1 mmol TCE. Considering the standard Fenton reaction takes place at optimum operating conditions, the results for the chelate-modified Fenton reaction are very reasonable and can be increased by injecting H\(_2\)O\(_2\) in small doses over a longer period of time, increasing the L:Fe ratio, and/or other methods.

**Packed Column Studies for Simulated Groundwater Injection**

The possibility exists to use the naturally occurring iron found in the subsurface to catalyze Fenton-like reaction; however, this would only be applicable to a limited number of remediation sites due to the high concentrations of naturally occurring iron required for significant contaminant destruction. The rate of hydroxyl radical generation must also be great enough to overcome hydroxyl radical scavenging that takes place in the subsurface. Ravikumar and Gurol (1994) found that the addition of a small amount of soluble iron to sand containing bound iron results in a dramatic increase in hydrogen peroxide decomposition. For practical applications, the chelate-modified Fenton reaction was used to degrade TCE in a simulated gravel aquifer. A column packed with RGA gravel was filled with 2.25 L of DIUF water containing 0.41 mM TCE, 1.5 mM Fe(II), and 1.5 mM citrate at near-neutral pH, as seen in **Figure 16**. The circulation rate was adjusted to give an equivalent groundwater velocity of 2.5 ft/day. At 0 hr and 24 hr,
H$_2$O$_2$ was injected into the top of the column so as to yield a 2:1 [H$_2$O$_2$]:[Fe] molar ratio. TCE dechlorination results are shown in Figure 17 with (mmol Cl$^-$ formed) / (mmol TCE degraded) $\approx 3$.

After a period of 24 hr, approximately 40% of the TCE had been degraded up to a depth of at least 2 ft. No degradation was observed at a depth of 3 ft given the reactants had not had sufficient time to traverse that distance. After 48 hr, TCE degradation at a depth of 3 ft had reached approximately 40%. The chelate-modified Fenton reaction is capable of degrading significant quantities of TCE in the presence of RGA gravel under simulated groundwater flow.

**Conclusions**

These studies prove that the chelate-modified Fenton reaction effectively degrades TCE in both the aqueous and organic (present as droplet) phases at near-neutral pH. This chelate allows the reaction to take place at near neutral pH and control hydrogen peroxide consumption by binding to Fe(II), forming an FeL complex. The chelate also binds to Fe(III), preventing its precipitation as ferric hydroxide. For the standard Fenton reaction at low pH, an optimum H$_2$O$_2$:Fe(II) ratio was found. Experimentation suggests multiple doses of H$_2$O$_2$ yield greater contaminant degradation than an equivalent single dose. The extent of dechlorination for the chelate-modified Fenton reaction is limited by the amount of H$_2$O$_2$ present. Thus, Fe-citrate complexes can be used repeatedly for dechlorination over long periods of time in the presence of H$_2$O$_2$. Generalized models were developed to predict the concentration of TCE in the aqueous phase and TCE droplet radius as a function of time using established hydroxyl radical kinetics and mass transfer relationships. Destruction of TCE in aqueous and droplet phases has been accomplished in natural water. Simulation of the application of
the chelate-modified Fenton reaction to an aquifer has been achieved through packed column studies with successful TCE degradation.

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**Nomenclature**

- $C_D$: drag coefficient
- $D_{TCE-water}$: diffusion coefficient (m$^2$/s)
- $Fe$: total quantity of all iron species (mmol)
- $(H_2O_2)_0$: initial total quantity of hydrogen peroxide (mmol)
- $[H_2O_2]$: hydrogen peroxide concentration (mmol/L)
- $k_e$: mass transfer coefficient (m/s)
- $k'_{TCE}$: fitted first-order rate constant for constant [OH•] model (s$^{-1}$)
- $k''_{TCE}$: fitted constant for varying [OH•] model
- $M_{TCE}$: molecular weight of TCE (g/mol)
- $n$: number of TCE droplets
- $[OH•]$: hydroxyl radical concentration (mmol/L)
- $R$: droplet radius (m)
- $Re$: Reynolds number
- $S$: surface area of single droplet (m$^2$)
Sc  Schmidt number
Sh  Sherwood number
$TCE_0$  initial total quantity of TCE (mmol)
$[TCE]_{aq}$  aqueous-phase TCE concentration (mmol/L)
$[TCE]_{sat}$  TCE saturation concentration (mmol/L)
U  velocity of droplet relative to surrounding fluid (m/s)
V  reactor volume (L)
$W_r$  mass flux in radial direction

$\alpha$  proportionality constant relating $[\text{OH}^\cdot]$ and $d[H_2O_2]/dt$
$\delta$  droplet boundary layer thickness (m)
$\nu$  kinematic viscosity of water (m$^2$/s)
$\rho_{TCE}$  density of TCE (g/cm$^3$)

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Figure 1. Illustrative example of DNAPL distribution in aquifer (adapted from Kennedy and Lennox, 1997).

Figure 2. TCE reacted and Cl⁻ formed at 20 hr for varying TCE:Fe(II):H₂O₂ molar ratios with equivalent initial TCE concentration of 15.2 mM and TCE:Fe(II) molar ratio of 1:1. TCE present in both aqueous and organic phases. Control experiment conducted with no addition of H₂O₂.
Figure 3. (a) Fe(II) species distribution as a function of pH. Total [Fe(II)] = 0.01 M, L/[Fe(II)] = 1, L = citrate. (b) Fe(II) species distribution for pH = 5 to 8.
Figure 4. (a) Role of ferrous iron (Fe(II)) on H$_2$O$_2$ decomposition with varying [L]:[Fe] molar ratio. L = citrate. (b) H$_2$O$_2$ decomposition for t = 0 to 3 hr.

Figure 5. Role of ferric iron (Fe(III)) on H$_2$O$_2$ decomposition with varying [L]:[Fe] molar ratio. L = citrate.
Figure 6. TCE reacted and Cl⁻ formed for varying Fe(II):L:H₂O₂: molar ratio with initial TCE concentration of 1.1 mM, where L is citrate. Conducted in natural water obtained from DOE site. Control experiment conducted with no addition of H₂O₂. Initial pH = 7.

[TCE]₀ = 1.1 mM
[Fe] = 1.5 mM
Figure 7. TCE degradation and proposed kinetic models using constant [OH•] (Equation 29) and varying [OH•] (Equation 32). Control experiment conducted with no addition of H₂O₂.

- TCE Reaction
- TCE Control
- Kinetic Model for Constant [OH•]
- Kinetic Model for Varying [OH•]

TCE₀ ≈ 2.2 mmol
Fe = 4 mmol
[L]:[Fe] = 1:1
(H₂O₂)₀ = 32 mmol
V = 0.5 L
pH = 6
Figure 8. \( \text{H}_2\text{O}_2 \) consumption and \([\text{OH}^\bullet]\) for proposed kinetic model using varying \([\text{OH}^\bullet]\) (Equation 32).
Figure 9. Cl⁻ formation for proposed kinetic model using varying [OH•] (Equation 32) for (mmol Cl⁻ formed) / (mmol TCE reacted) = 2 and 3.

Figure 10. Schematic of TCE droplet dissolution into aqueous solution.
Figure 11. Model-predicted values of $[\text{TCE}]_{\text{aq}}$ for varying values of $k_c$ using Equations 33 and 34.

Figure 12. Model-predicted values of $R$ for varying values of $k_c$ using Equations 33 and 34.
Figure 13. H₂O₂ degradation profile for chelate-modified Fenton reaction in two-phase TCE system. H₂O₂ injected at time = 0 hr and 12 hr.
Figure 14. Cl⁻ formation profile for chelate-modified Fenton reaction in two-phase TCE system. Experimental results for H₂O₂ injected at time = 0 hr and 12 hr. Model-predicted results for (mmol Cl⁻ formed) / (mmol TCE reacted) = 1 and 2 using Equations 33 and 34.

Figure 15. (mmol Cl⁻ formed) / (mmol H₂O₂ reacted) for one system containing no TCE droplets (TCE₀ ≈ 4 mmol) and one with TCE droplets (TCE₀ ≈ 16 mmol).
Figure 16. Column packed with RGA gravel for simulation of TCE degradation in groundwater systems using chelate-modified Fenton reaction. Void volume = 2.25 L.
Figure 17. TCE dechlorination results for packed column. $[\text{TCE}]_0 = 0.41 \text{ mM, } [\text{Fe}] = 1.5 \text{ mM, } [\text{L}]:[\text{Fe}] = 1:1$. $\text{H}_2\text{O}_2$ injections at 0 and 24 hr for 2:1 $[\text{H}_2\text{O}_2]$:[$\text{Fe}$] molar ratio. Column flowrate = 2.5 ft/day. $(\text{mol Cl}^- \text{ formed}) / (\text{mol TCE reacted}) \approx 3.$