Pilot-scale Fenton's oxidation of organic contaminants in groundwater using autochthonous iron

John Bergendahl [a,*], Stephanie Hubbard [a], Domenico Grasso [b]

[a] *Department of Civil and Environmental Engineering, Worcester Polytechnic Institute, 100 Institute Road, Worcester, MA 01609, USA*
[b] *Picker Engineering Program, Smith College, Northampton, MA 01063, USA*

Abstract

A pilot-scale study was conducted to evaluate Fenton's oxidation with autochthonous iron for treating extracted groundwater contaminated with organic solvents. Based on a previous bench-scale treatability study, a batch reactor pilot-plant system was designed and operated to evaluate the effects of various parameters including pH, iron concentration, hydrogen peroxide dose, and reaction time. Effective system conditions were found to be pH of 3.5, hydrogen peroxide to iron molar ratio of 75/1, and autochthonous iron at an average concentration of 10 mg/l. The data collected demonstrate the effectiveness of Fenton's oxidation using autochthonous iron for treating this contaminated water, with reductions to below method detection limits for many contaminants. This pilot-scale study provided kinetic rate constants for predicting contaminant disappearance, information necessary for designing a full-scale Fenton's oxidation system.
© 2003 Elsevier Science B.V. All rights reserved.

Keywords: Advanced oxidation processes; Fenton's reagent; Pilot-scale; Contamination; Groundwater

1. Introduction

The Solvent Recovery Service of New England (SRSNE) site located in Southington, Connecticut, operated as a hazardous waste treatment and storage facility from 1955 to 1991. Contamination at the site is found in the non-aqueous phase (NAPL), vapor phase, dissolved in the groundwater, and sorbed to solids. An estimated 500,000 gal of NAPL exists in the subsurface, and are expected to produce a contaminant plume for

* Corresponding author. Tel.: +1-508-831-5772; fax: +1-508-831-5808.
E-mail address: jberg@wpi.edu (J. Bergendahl).

hundreds to thousands of years [1]. The current plume is approximately 14 acres in extent. Contaminants can be found throughout the overburden and into the bedrock and exist as both dense non-aqueous phase liquid (DNAPL) and light non-aqueous phase liquids (LNAPL).

As part of a non-time critical removal action, a treatment system went on-line in 1995, and has been effective in treating organic and inorganic compounds in the extracted groundwater. The treatment scheme comprises influent equalization, metals pretreatment with coagulation/flocculation and filtration, advanced oxidation with ultraviolet light/hydrogen peroxide (UV/H_2O_2), and granular activated carbon prior to discharge. Although the treatment system is effective, the UV/H_2O_2 process is energy and maintenance intensive. As a result, Fenton's reagent oxidation was investigated as an alternative process. Rather than removing autochthonous iron during the metals pretreatment process that precedes oxidation, it was hypothesized that the autochthonous iron concentration was sufficient to serve as the primary catalyst.

Prior to this pilot-scale study, a bench-scale feasibility study [2] had been conducted to evaluate the ability of Fenton's reagent to mineralize compounds in the groundwater at this site. Results from this study indicated significant reductions in contaminant concentrations. This feasibility study concluded that Fenton's oxidation could capitalize on the autochthonous iron, and could be a viable alternative to the current UV/H_2O_2 system on site, possibly resulting in substantial savings in operating costs. A pilot-scale system was designed and constructed to further explore this unique alternative.

A pilot-scale reactor was designed based on results of the previous bench-scale work [2]. The focus of the work presented herein centered on evaluation of the potential, including rate and extent, for Fenton's oxidation of 27 previously identified organic contaminants at the SRS site. A simple kinetic model was developed to represent system performance.

2. Background

Advanced oxidation processes (AOPs) may either completely mineralize organic compounds (i.e. to carbon dioxide and water), or convert complex organic compounds into simpler molecules that can be otherwise treated by conventional methods. AOPs can produce highly reactive hydroxyl radicals through a variety of techniques including ultraviolet radiation/hydrogen peroxide, ozone/hydrogen peroxide, ultraviolet radiation/ozone, Fenton's reagent, and titanium dioxide/ultraviolet radiation [3,4]. The hydroxyl radicals produced by any of these methods are indiscriminant oxidants and can react with a myriad of organic compounds in water [5,6]. Due to their non-selectivity, hydroxyl radicals may also be scavenged by non-target compounds such as carbonate, bicarbonate, phosphates, sulfates, humic material, and other anthropogenic and natural organic compounds.

The hydroxyl radical, a powerful oxidant second only to fluorine in oxidation power [4,7,8], is approximately two times more reactive than chlorine. It can react at near diffusion rates, and has the ability to oxidize a wide range of organic chemicals [6]. AOPs that generate hydroxyl radicals have been found to be very effective for treating drinking water, groundwater, and contaminated soils [3,4,9–12].

Fenton's oxidation reactions are initiated by the interaction between hydrogen peroxide and ferrous iron [13]:

$$Fe^{2+} + H_2O_2 \xrightarrow{k\bullet_{OH}} Fe^{3+} + OH^- + \bullet OH \tag{1}$$

Ferric ions produced can be reduced back to ferrous ions in the presence of hydrogen peroxide by the simplified net reaction [14] (stepwise reactions are summarized by Pignatello [15]):

$$2Fe^{3+} + H_2O_2 \longrightarrow 2Fe^{2+} + O_2 + 2H^+ \tag{2}$$
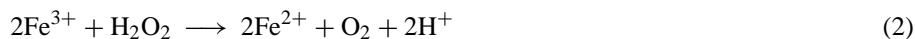
Hydroxyl radicals generated in reaction 1 can react with target organic contaminants [13]:

$$\bullet OH + \text{organic contaminants} \xrightarrow{k_{contam}} \text{products} \tag{3}$$

Alternatively, hydroxyl radicals can react with non-target scavengers, including hydrogen peroxide [6,16], and be eliminated from participating in further chain propagating reactions:

$$\bullet OH + \text{scavengers} \xrightarrow{k_{scav}} \text{products} \tag{4}$$

The rate and extent of the Fenton's reactions are dependent on system parameters including hydrogen peroxide dosage, pH, and iron concentration [9,10,17–22]. The influence of hydrogen peroxide is evident from reactions 1 and 2. Although hydrogen peroxide is a hydroxyl radical scavenger, increasing the hydrogen peroxide concentration will shift both reactions to the right (as written), producing more net hydroxyl radicals. As expected, many studies have reported that higher hydrogen peroxide concentrations result in higher conversions of contaminants [23–25].

Clearly, solution pH also affects reactions 1 and 2. It has been found that Fenton's oxidation is more effective at lower solution pH values. Kang and Hwang [22] reported that COD removal was optimum between pH 3 and 6, with a maximum removal at 3.5. Watts et al. [8] observed the optimum pH for treating pentachlorophenol-contaminated soil to be 2 and 3. Alternately, basic solutions may promote the decomposition of hydrogen peroxide to oxygen [26] before the formation of hydroxyl radicals. Further, removal of the dissolved iron catalyst from solution via the formation of iron hydroxide precipitates is also possible at higher pH values.

Reactions 1 and 2 are also influenced by iron concentration. Although higher iron concentrations may allow for greater mineralization over time [9], the tendency for the production of iron sludge is a mitigating factor.

3. Materials and methods

The project was prosecuted in two phases. The first phase was conducted to screen the system parameters (discussed earlier) critical for Fenton's oxidation of contaminated water at the site. A subsequent phase was designed to evaluate the kinetics of Fenton's oxidation at selected system conditions identified in the screening phase. The pilot-scale system utilized a batch reactor, and received contaminated water from an existing 10,000-gal equalization

tank. The pilot-scale system schematic is shown in Fig. 1. The influent water from the equalization tank drained by gravity through 0.5 in. NPS pipe into a 55-gal tank used as the reaction vessel. Two valves, the influent isolation valve and the tank inlet valve, were opened to allow flow into the reaction tank, and closed when the tank was filled. The solution in the tank was kept well stirred with a mixer (Model 1JTC-0.25, Chemineer Inc., Dayton, OH) at a constant speed of 30 rpm. The addition of hydrogen peroxide and iron was done manually, and solution pH was lowered to pre-designated values and kept constant by the addition of sulfuric acid with the aid of a pH probe (Omega Model #PHE-6510, Omega Engineering Inc., Stamford, CT), pH controller (Omega Model PHM-55) and an acid addition pump (Omega Model PHP-165).

To determine effective system conditions during the screening phase, three parameters were regulated and changed sequentially: pH, H_2O_2 dosage, and ferrous iron ($FeSO_4 \cdot 7H_2O$) concentration (when the autochthonous iron was augmented). The solution pH was adjusted from 3.5 to 4.5, hydrogen peroxide H_2O_2/iron molar ratio dose varied from 20/1 to 75/1, and iron concentration varied from the autochthonous concentration (10 mg/l average) to 30 mg/l.

Samples were acquired from the reaction vessel at different reaction times: 0, 10, 15, 25, 40, 70, 130, and 250 min. These times were chosen to explore extent of reaction. From the kinetic data collected from the previous bench-scale treatability study [2], it was expected that 250 min of reaction time would be sufficient for the reaction to go to completion. An initial sample was taken immediately after the ferrous iron (solid $FeSO_4 \cdot 7H_2O$, certified ACS, Fisher Scientific, Pittsburgh, PA) was added to the system, but before other chemicals were added. Following acquisition of the initial sample, hydrogen peroxide (50% commercial grade) was added and the pH of the system adjusted to the pre-determined values with sulfuric acid (93.2% commercial grade). Samples were collected in 250 ml amber glass bottles that had been washed with detergent (Sparkleen, Fisher Scientific, Pittsburgh, PA), soaked in a sulfuric acid bath (certified ACS, Fisher Scientific, Pittsburgh, PA) and purified water (E-Pure Barnstead Water Purification System; Barnstead, Dubuque, IA), rinsed with hexane (HPLC Grade, Fisher Scientific, Pittsburgh, PA), and dried. Samples were preserved with hydrochloric acid (certified ACS, Fisher Scientific, Pittsburgh, PA), tightly capped, and placed in a cooler to be transported to the laboratory for analysis [27].

Screening phase analyses were conducted at the Worcester Polytechnic Institute Environmental Engineering Laboratory, using an ambient headspace sampling technique [28] and an Agilent Technologies 6890 gas chromatograph (GC) with a flame ionization detector (FID) and an electron capture detector (ECD), with the following conditions: inlet, 250 °C; FID, 300 °C; ECD, 250 °C; oven, 40 °C for 2 min followed by 12 °C/min ramp to and hold at 240 °C for 5 min. This method was chosen for the screening portion of the study because it could be conducted quickly with a minimum of sample preparation. Compounds listed in Table 1 were historically identified in the extracted groundwater at the site, and found in the samples taken during the batch feasibility study [2]. GC analyses were completed within 24 h after sample collection. Once the effective operating conditions had been determined, experimentation was initiated to validate reactor performance at these conditions. Samples during this phase were collected as specified above, with two additional sampling times added at 2 and 5 min. For this final experimental run, the samples were analyzed with GC mass spectrometry (MS) per EPA methods 8015 and 8260.
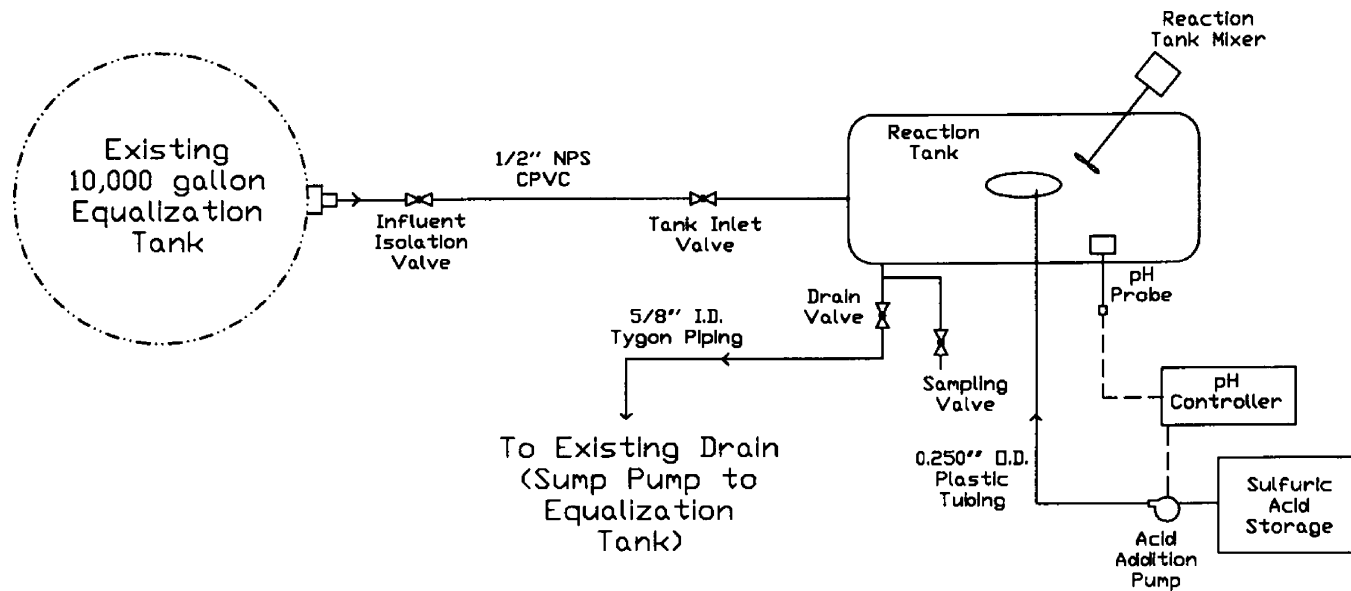
Fig. 1. Schematic of the pilot-scale Fenton's oxidation system.

Table 1
Initial and final concentrations of contaminants quantified, and percent remaining after Fenton's oxidation in the final experimental run

Contaminant	Initial concentration (ppb)[a]	Final concentration (ppb)[a]	Percent remaining[b]
Acetone	ND	320	Indeterminate
Benzene	ND	ND	–
sec-Butylbenzene	ND	ND	–
Chlorobenzene	ND	ND	–
Chloroethane	580	220	37.9
Chloroethene	770	ND	0
1,1-Dichloroethane	310	220	71.0
1,2-Dichloroethane	ND	ND	–
1,1-Dichloroethene	ND	ND	–
cis-1,2-Dichloroethene	2900	9.6	0.3
trans-1,2-Dichloroethene	ND	ND	–
Dichloromethane	ND	ND	–
Ethanol	ND	ND	–
Ethylbenzene	500	ND	0
Isopropanol	ND	ND	–
Methanol	ND	ND	–
Methyl ethyl ketone	230	180	78.3
Methyl isobutyl ketone	ND	ND	–
iso-Propylbenzene	ND	ND	–
n-Propylbenzene	ND	ND	–
Toluene	1700	ND	0
1,1,1-Trichloroethane	520	520	100
Trichloroethene	ND	ND	–
1,2,4-Trimethylbenzene	51	ND	0
m- and *p*-xylene	360	ND	0
o-Xylene	140	ND	0

[a] ND indicates that the compound was not detected above the detection limit of the instrument and method.

[b] The percent remaining is indeterminate when the initial concentration is not detected (assumed to be zero) because of division by zero.

4. Results and discussion

4.1. Screening: determining effective conditions

To determine effective system pH, the pilot-scale system was run at three different solution pH values: 3.5, 4.0 and 4.5. It was expected that oxidation by Fenton's reagent would be realized in this pH range while remaining cost effective. Lowering the pH further would result in substantial costs for acid addition, and subsequent base for pH adjustment prior to discharge. Fig. 2 summarizes the percent reduction of contaminants quantified at each of these pH values at the maximum reaction time, 250 min. The ordinate is the percent reduction of the sum of the mass of compounds quantified at 250 min.

Reactions at a solution pH of 3.5 produced significantly greater reduction of contaminants than at pH 4.0 (90.1% versus 73.8%), and slightly less reduction than at pH 4.5 (94.7%). The line plotted with data in Fig. 2 is based on least squares linear regression analysis of
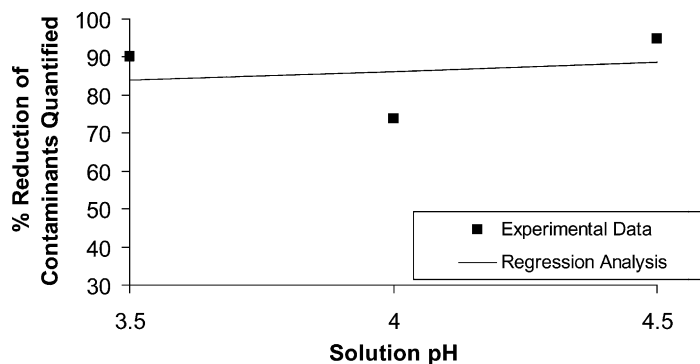
Fig. 2. The percent reduction of contaminants quantified at three different pH after 250 min reaction time (H_2O_2/iron = 20/1, autochthonous iron). The ordinate is the percent reduction of the sum of the mass of compounds quantified in the screening experiments. Each data point indicates the percent reduction of total contaminant mass for one experimental run.

the percent reduction of contaminants quantified as a function of pH (confidence intervals not shown because of the low degree of freedom). The regression shows a slight trend of increasing contaminant reduction with increasing pH, with a scaling ratio of 4.6 (percent reduction/pH).

Iron concentrations entering the equalization tank ranged from 4 to 20 mg/l, with an average of 10 mg/l. The autochthonous iron was augmented by increasing the total iron concentration by adding 10 and 20 mg/l. Fig. 3 summarizes the percent reduction of contaminants quantified with various iron concentrations at 250 min reaction times. The 90% confidence band is also shown [29]. The greatest reduction was observed with an additional 20 mg/l iron added to the solution, resulting in a 99.0% reduction. The reaction with autochthonous iron resulted in 90.1% reduction in contaminant concentrations. The regression
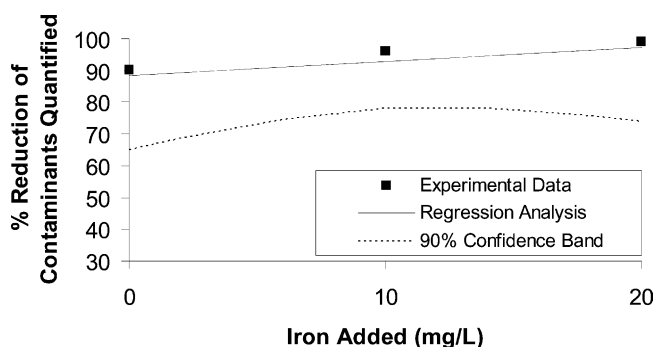

Fig. 3. The percent reduction of contaminants quantified with different iron concentrations after 250 min reaction time (solution pH = 3.5, H_2O_2/iron = 20/1). The ordinate is the percent reduction of the sum of the mass of compounds quantified in the screening experiments. Each data point indicates the percent reduction of total contaminant mass for one experimental run. The dashed line denotes the lower 90% confidence band for the regression analysis.
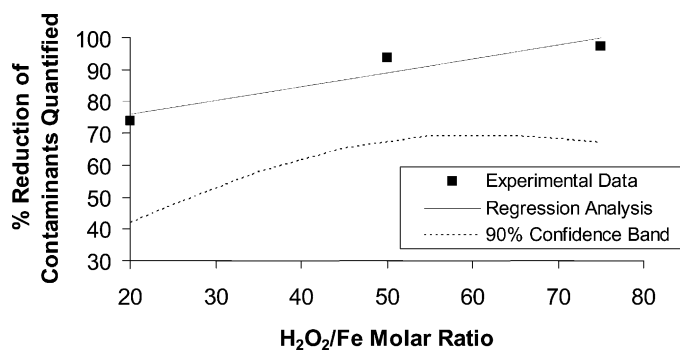
Fig. 4. The percent reduction of contaminants quantified with different hydrogen peroxide doses after 250 min reaction time (solution pH = 4.0, autochthonous iron). The ordinate is the percent reduction of the sum of the mass of compounds quantified in the screening experiments. Each data point indicates the percent reduction of total contaminant mass for one experimental run. The dashed line denotes the lower 90% confidence band for the regression analysis as a function of the hydrogen peroxide/iron molar ratio.

of the percent reduction of contaminants quantified as a function of iron added shows a trend of increasing contaminant reduction with increasing iron dose, with a scaling ratio of 0.45 (percent reduction/(mg l^{-1}) iron added). The iron dose appeared to have little effect on the percent reduction of contaminants quantified.

The final parameter studied in the screening phase was the hydrogen peroxide concentration. The hydrogen peroxide dose was based on its molar ratio to iron of 20/1, 50/1 and 75/1. Fig. 4 illustrates the percent reduction of contaminants quantified for the three hydrogen peroxide dosages at 250 min reaction times, and the regression of the percent reduction of contaminants quantified as a function of H_2O_2/Fe molar ratio. The data illustrates that there is a correlation between hydrogen peroxide dose and reduction of contaminant concentrations. With the H_2O_2/iron molar ratios increased from 20/1, to 50/1 and 75/1, we observed an increase in average contaminant removal of 73.8, 93.9 and 97.4%, respectively. The scaling ratio of the regression line is 0.44 (percent reduction/H_2O_2/Fe molar ratio). The greatest reduction occurred with the largest hydrogen peroxide dose, 75/1.

Fig. 5 shows the percent reduction of contaminants quantified as a function of time for different iron doses in the initial time domain of the experiment. While Potter and Roth [9] found that additional iron increased the initial rate of reaction, Fig. 5 shows that additional iron did not affect the initial rate at which contaminant reduction occurred in these experiments. Using only the autochthonous iron, the contaminants were reduced in concentration to near equilibrium values within 10 min.

Toluene was not included in the calculation for percent reduction in the screening phase presented in Figs. 2–4, because it was initially below the method detection limit. Also, methyl ethyl ketone (MEK) could not be quantified with the headspace analytical method used during the screening phase. However, toluene and MEK were included in the final experimental phase using GC/MS quantification.

Based on the results from the screening phase experiments where parameters were varied sequentially, the following system conditions were selected for further exploration: solution
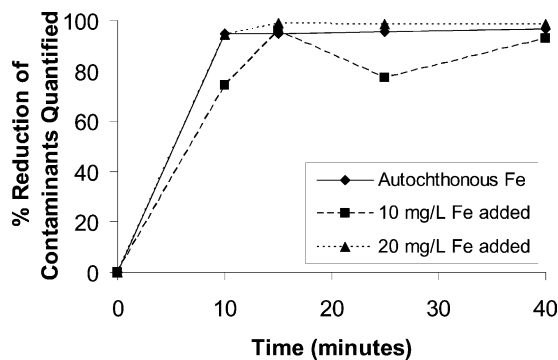
Fig. 5. The percent reduction of contaminants quantified as a function of reaction time for different iron doses (solution pH = 3.5, H_2O_2/iron = 20/1).

pH = 3.5, H_2O_2/iron molar ratio = 75/1, and no allochthonous iron added. The treatment system at this site has historically encountered iron fouling problems even without additional iron added for Fenton's oxidation. These iron fouling problems were in the form of pipe plugging, heavy coatings on mixer blades, and repeated, complete plugging of an existing sand filter. Consequently the autochthonous iron dose was desirable to avoid aggravating the current iron precipitation problem and to minimize operating expenses. The lower solution pH of 3.5 was selected to further assist in keeping the iron in solution.

4.2. Extent and kinetics

A final pilot-scale experiment was designed and conducted at the conditions identified in the screening phase to determine appropriate system reaction kinetic parameters for individual contaminants. Of the 27 contaminants historically identified at the site (as listed in Table 1), only 12 were detected in the influent during this phase of experimentation. This is not surprising as the groundwater extraction wells are operated at variable flow rates dependent on the groundwater level at each individual well. The level of contamination in the influent is a function of which wells are on-line and pumping. The equalization tank in the existing system does provide for flow and concentration equalization, but only over a limited time period.

Seven contaminants (chloroethene, toluene, ethylbenzene, *m*-, *o*- and *p*-xylenes, 1,2,4-trimethylbenzene) were present initially and reduced to below detectable concentrations before 50 min of reaction had elapsed as illustrated in Fig. 6(a), (c) and (d). This is as expected as the rate of disappearance of many of these compounds in the presence of hydroxyl radicals is fast (previously published rate constants for hydroxyl radical oxidation for toluene, *m*-, *o*- and *p*-xylenes are 3.0×10^9, 7.5×10^9, 6.7×10^9, and 7.0×10^9 $l\,mol^{-1}\,s^{-1}$, respectively [6]). This is a significant reduction in contamination level. As displayed in Fig. 6(c), *cis*-1,2-dichloroethene was reduced approximately 99.7% after a 50 min reaction, essentially completely mineralized. *Cis*-1,2-dichloroethene had been identified in the influent at the greatest concentration (2900 ppb). So this large reduction of *cis*-1,2-dichloroethene produced a considerable reduction in overall contamination in the water.
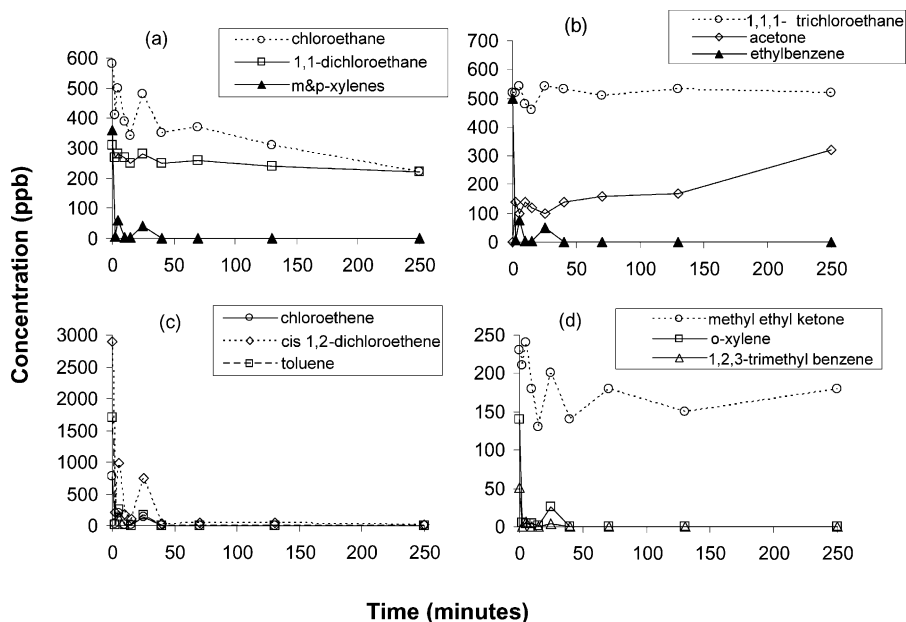
Fig. 6. Reduction in contaminant concentrations with the effective conditions found from screening experiments (solution pH = 3.5, H_2O_2/iron = 75/1, autochthonous iron).

Other compounds (chloroethane, 1,1-dichloroethane, and MEK) were partially reduced in concentration. Chloroethane was reduced 62.1% after 250 min of reaction. The rate of reduction of chloroethane was slower than the six contaminants listed above, and the trend of reduction in concentration with time was still evident at 250 min as shown in Fig. 6(a). The contaminant 1,1-dichloroethane was only reduced by 29.0% after 250 min of reaction time. The very slow rate of disappearance of 1,1-dichloroethane, illustrated in Fig. 6(a), produced the lowest rate constant found in this experimental run, discussed later. The slow rate of reduction of 1,1-dichloroethane continued at 250 min reaction time, so additional reduction may have been possible with a longer reaction time. MEK was only partially removed, with 21.7% reduction after 250 min reaction time, shown in Fig. 6(d). The concentration of MEK with reaction time appeared variable, most likely due to sampling and analytical variability.

The concentration of 1,1,1-trichloroethane remained constant over time. This is consistent with the feasibility study (see Fig. 1 in [2]). The concentration–time profile for acetone is also shown in Fig. 6(b), and illustrates that acetone increased in concentration over time. This increase was also reported during the feasibility study [2]. While the reduction in concentration of contaminants is described with the reaction listed in Eq. (3) above, the actual observed concentration–time profiles are from net reactions. That is, many organic compounds are products of reactions of other organics with hydroxyl radicals. For example, acetone can be a by-product of methyl *tert*-butyl ether degradation [30], and possibly a by-product of the numerous other compounds present in this contaminated water. The initial

concentration of the acetone was below the method detection limit, so quantification of the initial concentration could not be made. It has been reported that acetone is readily degraded by hydroxyl radicals with a large degradation rate constant, approximately $10^8 \, \text{l} \, \text{mol}^{-1} \, \text{s}^{-1}$ [6]. As acetone was formed overall (net) with time, the rate of formation was faster than the rate of degradation.

The initial and final concentrations of the contaminants after a 250 min reaction time, along with the percent remaining, are listed in Table 1. Concentrations reported as not detectable (ND) were assumed to be zero for the percent remaining calculation. Overall, the percent reduction of total quantified contaminant mass with Fenton's oxidation in the pilot-scale system is 81.8%.

Although it is often easy to assume simple pseudo-first order kinetics, intellectually and scientifically it is more desirable and satisfying to relate a kinetic expression to a plausible mechanism. Hence, referring back to Eq. (3), and assuming an elementary reaction:

$$r_{\text{contam}} = -k_{\text{contam}} C_{\bullet \text{OH}} C_{\text{contam}} \tag{5}$$

where k_{contam} is the rate constant for disappearance of contaminant (ppb^{-1} min^{-1}), $C_{\bullet \text{OH}}$ the hydroxyl radical concentration (ppb), and C_{contam} the contaminant concentration (ppb).

The rate of contaminant removal is dependent on the concentration of hydroxyl radicals, which depends on reactions 1, 3 and 4:

$$r_{\bullet \text{OH}} = (k_{\bullet \text{OH}} C_{\text{Fe}^{2+}} C_{\text{H}_2\text{O}_2}) - (k_{\text{contam}} C_{\bullet \text{OH}} C_{\text{contam}}) - (k_{\text{scav}} C_{\bullet \text{OH}} C_{\text{scav}}) \tag{6}$$

where $k_{\bullet \text{OH}}$ is the rate constant for generation of hydroxyl radicals (ppb^{-1} min^{-1}), $C_{\text{Fe}^{2+}}$ the ferrous iron concentration (ppb), $C_{\text{H}_2\text{O}_2}$ the hydrogen peroxide concentration (ppb), k_{scav} the rate constant for generation of scavengers (ppb^{-1} min^{-1}), and C_{scav} the scavenger concentration (ppb).

Assuming a steady-state concentration for the hydroxyl radicals [31], Eq. (6) can be solved for the hydroxyl radical concentration and substituted into Eq. (5):

$$r_{\text{contam}} = -k_{\text{contam}} \left[\frac{k_{\bullet \text{OH}} C_{\text{Fe}^{2+}} C_{\text{H}_2\text{O}_2}}{(k_{\text{contam}} C_{\text{contam}}) + (k_{\text{scav}} C_{\text{scav}})} \right] C_{\text{contam}} \tag{7}$$

It can be shown that Eq. (7) can be simplified to a pseudo-first order rate expression:

$$r_{\text{contam}} = -k' C_{\text{contam}} = \frac{dC_{\text{contam}}}{dt} \tag{8}$$

where

$$k' = \frac{k_{\bullet \text{OH}} C_{\text{Fe}^{2+}} C_{\text{H}_2\text{O}_2}}{(k_{\text{contam}} C_{\text{contam}}) + (k_{\text{scav}} C_{\text{scav}})}$$

the pseudo-first order rate constant for the disappearance of contaminant.

Integrating the pseudo-first order rate expression Eq. (8), yields:

$$\frac{C_{\text{contam}}}{C_{\text{contam},0}} = e^{-k't} \tag{9}$$

where $C_{\text{contam}, 0}$ is the initial contaminant concentration (ppb).

Table 2
Kinetic analysis of Fenton's oxidation of extracted groundwater in the pilot-scale reactor (conditions: pH = 3.5; H_2O_2/iron = 75/1 molar ratio, autochthonous iron)

Contaminant	Initial concentration (ppb)	Final concentration (ppb)[a]	Percent remaining	Pseudo-first order rate constant (min^{-1})	r^2
Chloroethane	580	220	37.9	3×10^{-3}	0.61
1,1-Dichloroethane	310	220	71.0	1×10^{-3}	0.63
cis-1,2-Dichloroethene	2900	9.6	0.3	1	0.79
Toluene	1700	ND	0	2	0.96
Ethylbenzene	500	ND	0	2	0.96
m- and *p*-xylenes	360	ND	0	2	0.95
o-Xylene	140	ND	0	2	0.96

[a] ND indicates that the compound was not detected above the detection limit of the instrument and method.

For each compound with detectable concentrations, the pseudo-first order rate constants, k' were found from least squares non-linear regression. Eight of the 27 compounds had sufficient data for kinetic analysis, and were used to predict the performance of a full-scale Fenton's oxidation system. The results for all compounds are listed in Table 2. Table 2 lists the rate constants (k') for the compounds where kinetic data could be obtained, and r^2 to indicate goodness-of-fit.

The oxidation rate constants were found so that a full-scale Fenton's oxidation system could be designed to treat the extracted groundwater at the site. Toluene, ethylbenzene, *m*-, *o*-, and *p*-xylene were reduced in concentration with the greatest rate constant: $2 \, min^{-1}$. However, the reduction in concentration of 1,1-dichloroethane was found to be the slowest, disappearing according to the rate constant $1 \times 10^{-3} \, min^{-1}$. This is not surprising due to the inductive effect of the electronegative chlorine atoms on the reactivity of the compound [32].

5. Conclusions

A pilot-scale system was designed and operated to investigate an advanced oxidation process using Fenton's reagent as an alternative to the current UV/H_2O_2 system used for the treatment of organic compounds in extracted groundwater. From the data collected during the operation of this pilot-scale system, it was determined that Fenton's oxidation using autochthonous iron is an excellent alternative for treating the contaminated water at this site. Fenton's oxidation was able to reduce the concentrations of many organic contaminants to non-detectable levels with proper system conditions, and reduce the concentrations of many other contaminants significantly. Effective system conditions were found to be pH of 3.5, a hydrogen peroxide to iron molar ratio of 75/1, and autochthonous iron at an average concentration of 10 mg/l. Kinetic rate constants for a pseudo-first order rate expression were found from the data and used to determine the reactor size for a full-scale Fenton's oxidation system at the site.

Acknowledgements

References

[1] Blasland, Bouck and Lee Inc., Non-Time Critical Removal Action 100% Ground-Water Containment and Treatment System Design Report, Solvent Recovery Services of New England Site, Southington, Connecticut, 1994, Syracuse, NY.

[2] D. Grasso, J. Bergendahl, M. Engwall, SRSNE Non-Time Critical Removal Action Treatment System: Fenton's Oxidation, The University of Connecticut, Storrs, CT, 1999.

[3] S. Chiron, A. Fernandez-Alba, A. Rodriguez, E. Garcia-Calvo, Pesticide chemical oxidation: state of the art, Water Res. 34 (2) (2000) 366–377.

[4] R. Venkatadri, R.W. Peters, Chemical oxidation technologies: ultraviolet light/hydrogen peroxide, Fenton's reagent, and titanium dioxide-assisted photocatalysis, Hazard. Waste Hazard. Mater. 10 (2) (1993) 107–149.

[5] W.R. Haag, C.C.D. Yao, Rate constants for reaction of hydroxyl radicals with several drinking water contaminants, Environ. Sci. Technol. 26 (5) (1992) 1005–1013.

[6] 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 ($OH^{\bullet}/O^{\bullet-}$) in aqueous solution, J. Phys. Chem. Ref. Data 17 (2) (1988) 513–759.

[7] R.J. Bigda, Consider Fenton's chemistry for wastewater treatment, Chem. Eng. Progress 91 (1995) 62–66.

[8] R.J. Watts, M.D. Udell, P.A. Rauch, S.W. Leung, Treatment of pentachlorophenol-contaminated soils using Fenton's reagent, Hazard. Waste Hazard. Mater. 7 (4) (1990) 335–345.

[9] F.J. Potter, J.A. Roth, Oxidation of chlorinated phenols using Fenton's reagent, Hazard. Waste Hazard. Mater. 10 (2) (1993) 151–170.

[10] N.R. Mohanty, I.W. Wei, Oxidation of 2,4-dinitrotoluene using Fenton's reagent: reaction mechanisms and their practical applications, Hazard. Waste Hazard. Mater. 10 (2) (1993) 171–183.

[11] S.G. Huling, R.G. Arnold, R.A. Sierka, P.K. Jones, D.D. Fine, Contaminant adsorption and oxidation via Fenton reaction, J. Environ. Eng. 126 (7) (2000) 595–600.

[12] M.A. Engwall, J.J. Pignatello, D. Grasso, Degradation and detoxification of the wood preservatives creosote and pentachlorophenol in water by the photo-Fenton reaction, Water Res. 33 (5) (1999) 1151–1158.

[13] C. Walling, Fenton's reagent revisted, Acc. Chem. Res. 8 (4) (1975) 125–131.

[14] J.J. Pignatello, G. Chapa, Degradation of PCBs by ferric ion, hydrogen peroxide and UV light, Environ. Toxicol. Chem. 13 (3) (1994) 423–427.

[15] J.J. Pignatello, Dark and photo-assisted Fe^{3+}-catalyzed degradation of chlorophenoxy herbicides by hydrogen peroxide, Environ. Sci. Technol. 26 (5) (1992) 944–951.

[16] S.G. Huling, R.G. Arnold, P.K. Jones, R.A. Sierka, Predicting Fenton-driven degradation using contaminant analog, J. Environ. Eng. 126 (4) (2000) 348–353.

[17] F.J. Rivas, F.J. Beltran, J. Frades, P. Buxeda, Oxidation of *P*-hydroxybenzoic acid by Fenton's reagent, Water Res. 35 (2) (2001) 387–396.

[18] K. Zoh, M.K. Stenstrom, Fenton oxidation of hexahydro-1,3,5,7-trinitro-1,3,5-triazine (RDX) and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX), Water Res. 36 (5) (2002) 1331–1341.

[19] J.C. Lou, S.S. Lee, Chemical oxidation of BTX using Fenton's reagent, Hazard. Waste Hazard. Mater. 12 (2) (1995) 185–193.

[20] L. Lunar, D. Sicilia, S. Rubio, D. Perez-Bendito, U. Nickel, Degradation of photographic developers by Fenton's reagent: condition optimization and kinetics for metal oxidation, Water Res. 34 (6) (2000) 1791–1802.

[21] H. Gallard, J. De Laat, Kinetic modeling of $Fe(III)/H_2O_2$ oxidation reactions in dilute aqueous solution using atrazine as a model organic compound, Water Res. 34 (12) (2000) 3107–3116.

[22] Y.W. Kang, K.Y. Hwang, Effects of reaction conditions on the oxidation efficiency in the Fenton process, Water Res. 34 (10) (2000) 2786–2790.

[23] C.H. Liao, M.C. Lu, Y.H. Yang, I.C. Lu, UV-catalyzed hydrogen peroxide treatment of textile wastewater, Environ. Eng. Sci. 17 (1) (2000) 9–18.

[24] S.H. Lin, C.M. Lin, H.G. Leu, Operating characteristics and kinetic studies of surfactant wastewater treatment by Fenton oxidation, Water Res. 33 (7) (1999) 1735–1741.

[25] B.G. Kwon, D.S. Lee, N. Kang, J. Yoon, Characteristics of *P*-chlorophenol oxidation by Fenton's reagent, Water Res. 33 (9) (1999) 2110–2118.

[26] M. Pourbaix, Atlas of Electrochemical Equilibria in Aqueous Solutions, Pergamon Press, Oxford, 1966.

[27] EPA, US, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, EPA Publication SW-846, United States EPA, 1986.

[28] T.M. Cummings, G.A. Robbins, B.J. Henebry, C.R. Goad, E.J. Gilbert, M.E. Miller, J.D. Stuart, A water extraction, static headspace sampling, gas chromatographic method to determine MTBE in heating oil and diesel fuel, Environ. Sci. Technol. 35 (6) (2001) 1202–1208.

[29] R.L. Ott, An Introduction to Statistical Methods and Data Analysis, Fourth ed., Wadsworth, Belmont, CA, 1993.

[30] M.I. Stefan, J. Mack, J.R. Bolton, Degradation pathways during the treatment of methyl *tert*-butyl ether by the UV/H_2O_2 process, Environ. Sci. Technol. 34 (4) (2000) 650–658.

[31] W.H. Glaze, Y. Lay, J.W. Kang, Advanced oxidation processes. A kinetic model for the oxidation of 1,2-dibromo-3-chloropropane in water by the combination of hydrogen peroxide and UV radiation, Ind. Eng. Chem. Res. 34 (7) (1995) 2314–2323.

[32] D.S. Kemp, F. Vellaccio, Organic Chemistry, Worth, New York, 1980.