



## Degradation of perchloroethylene in cosolvent solutions by zero-valent iron

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### Abstract

Remediation of sites contaminated by chlorinated organic compounds is a significant priority in the environmental field. Subsequently, the addition of cosolvent solutions for in situ flushing of contaminated source zones has been successfully field tested. However, the treatment of effluent fluids in such cleanup efforts is an often overlooked component of this technology implementation. The purpose of this research was to evaluate the effectiveness of zero-valent iron ( $\text{Fe}^0$ ) in treating perchloroethylene (PCE) in an aqueous solution, and how the presence of a cosolvent (ethanol) and modification of the iron surface altered dechlorination. The modified iron surfaces included in this study were nickel-plated iron, acid-treated iron, and untreated iron surfaces. PCE dechlorination in the presence of each of the iron surfaces displayed pseudo first-order kinetics. The highest degradation rate of PCE occurred on the nickel-plated iron surface,  $5.83 \times 10^{-3} \text{ h}^{-1}$ , followed by the acid-treated iron,  $4.92 \times 10^{-3} \text{ h}^{-1}$ , and the untreated iron,  $3.34 \times 10^{-3} \text{ h}^{-1}$ . Dechlorination on each of the surfaces decreased with increasing cosolvent fractions. It was shown that as cosolvent fractions increased, PCE adsorption decreased and resulted in a concomitant decrease in PCE degradation rates. © 2002 Elsevier Science B.V. All rights reserved.

*Keywords:* Zero-valent iron; PCE; Cosolvents; Adsorption; Dechlorination

### 1. Introduction

Remediation of sites contaminated by non-aqueous phase liquids (NAPLs), especially chlorinated organic compounds, is a significant priority in the environmental field because of their widespread use in industrial, military, and commercial applications. Also, their

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detrimental effects to both the environment and human health are well documented [1–3]. Limitations of conventional pump-and-treat technologies [4–6] has led to the development of in situ extraction techniques based on chemical additives such as cosolvents for enhanced cleanup. Lab and field studies have demonstrated success in the removal of NAPLs from subsurface source zones using cosolvents [7–12].

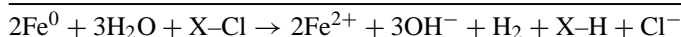
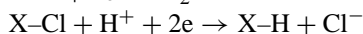
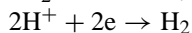
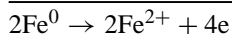
Once extracted from the subsurface by cosolvent flushing, the issue of how to manage the waste effluent containing high concentrations of dissolved NAPLs and alcohols becomes a major concern. Management options include treatment of the waste by separation technologies [13–15] and potential destruction of the harmful contaminants in solution [16–18]. The goals in the implementation of distillation and separation techniques include the reduction in waste volume and potential recycle of cosolvent chemicals; however, the separated and concentrated waste must still be managed. The use of a destructive technique, such as the application of zero-valent iron ( $\text{Fe}^0$ ) or bimetallic solids, could effectively remove or reduce the more harmful contaminants in the waste effluent and allow for recovery of reusable cosolvent.

The use of zero-valent metals, especially iron, has produced success in treatment of chlorinated organic solutions [19–28]. Recently, research into the effects of surfactants and cosolvents on the treatment efficiency of zero-valent iron has also been investigated [26,28,29]. This initial information will be useful in designing systems utilizing iron for treatment of waste effluents produced during innovative cosolvent flushing procedures of dense non-aqueous phase liquid (DNAPL) source zones.

The purpose of this research was to evaluate the effectiveness of zero-valent iron in treating a solution which contained perchloroethylene (PCE), and how addition of various concentrations of cosolvent (ethanol) to this solution would affect treatment efficiency. Modifications to the zero-valent iron, including acid treatment and nickel plating, were also investigated in treating PCE solutions containing the different cosolvent fractions. The experiments provided information about the effectiveness of different forms of iron for treating PCE in the presence of different cosolvent fractions, which would provide useful information in the designing of above-ground treatment systems for chlorinated waste fluids generated from in situ cosolvent flushing at contaminated sites.

## 2. Background

The degradation of the halogenated organic contaminants, especially chlorinated organics, by iron is an abiotic process. There is generally a simultaneous occurrence of two reactions in dechlorination using elemental iron: oxidation of iron by water and reductive dechlorination with the  $\text{Fe}^0$  serving as the source of electrons. The reactions could be depicted by the following equations [30–33]



Carbon in chlorinated compounds is in the oxidized state and thus the compounds tend to be thermodynamically unstable in a reducing environment [34]. This highly reducing environment is provided by the zero-valent iron metal, and other metallic combinations. Gillham and O'Hannesin [30] concluded the rate of degradation declined with decreasing degree of dechlorination.

The iron degradation reactions with respect to chlorinated organic solvents have been reported to follow pseudo first-order kinetics by several researchers [30–32,35]. Additionally, the use of elemental iron in dechlorination has been noted to achieve passive treatment of dissolved solvent plumes in groundwater, i.e. as buried walls, over long periods of time [20,22,30]. Burris et al. [36] concluded that reduction of PCE and TCE on zero-valent iron is a complex reaction involving a series of interconnected processes (non-reactive sites, competition between sorbing chemicals). However, Burris et al. [36] did state that in accounting for the sorption to non-reactive sites in a site balance analysis that the loss of PCE and TCE was, in effect, shown to be a pseudo first-order process. Both Alessi and Li [26] and Loraine [29] reported that PCE degraded by zero-valent iron displayed a pseudo first-order relationship.

Reductive dechlorination can occur abiotically under strongly reducing conditions, especially in the presence of galvanized steel, stainless steel, aluminum, and iron. Due to its low cost and non-toxicity, iron was proposed for in situ remediation of contaminated groundwaters [30,31]. Other metals, especially zinc, tin, nickel, and palladium, have been reported to transform halogenated organic compounds more rapidly than iron [34,37,38]. These metals, when combined with iron to form bimetallic surfaces, act as a catalyst to accelerate the disassociation of the chlorinated hydrocarbons, by preventing formation of iron oxides and by their own highly reducing nature [33,39,40]. Iron is still used as the basic substrate for possible industrial uses due to its moderate effectiveness and, more importantly, its low cost for the large quantities that would be required at a field site [30].

Arnold and Roberts [25] and Helland et al. [32] described hydrogenolysis as a minor process by which chlorinated hydrocarbons are reductively dechlorinated to less persistent, and often less toxic, forms. Arnold and Roberts [24,25] go on to report that reductive elimination and hydrogenation are also plausible schemes for reduction of chlorinated ethylenes by zero-valent iron, and for many compounds, more than one reaction may exist. Further, Arnold and Roberts [25] report that the dominant mechanism for PCE reduction by zero-valent iron is reductive elimination.

There has been minimal literature to date that explores the effect of alcohol cosolvents on iron-catalyzed degradation of chlorinated hydrocarbons [29]. Perhaps this is due to the belief that sorption of contaminants onto the iron is the controlling factor in the degradation of the chlorinated organic compounds. There has been some research into the sorption of chlorinated organics onto iron surfaces [36,41,42]. This factor cannot be ignored because the major impact of cosolvents is to enhance the aqueous solubility of NAPLs, like chlorinated compounds, thereby decreasing their sorption to solid matrices [43,44]. Therefore, increasing cosolvent fraction is expected to decrease degradation of PCE by reducing the ability of the compound to adsorb to the iron surface. The level to which these cosolvent fractions will affect not only the sorption of PCE to the iron, but also its degradation by the iron will be explored in this research.

### 3. Materials and methods

Individual batch reactor systems, analyzed over a 2-week period, were used to evaluate the degradation kinetics in aqueous solutions containing PCE at different concentrations and at various cosolvent ethanol fractions. The iron-catalyzed degradation of PCE at initial concentration levels of  $\sim 2$  and  $\sim 55$   $\mu\text{g/ml}$  were investigated at ethanol fractions of 0, 10, 30, and 50%.

Each batch reaction took place in a 5 ml glass vial fitted with a teflon-lined septa screw-top cap. The vial was initially weighed empty, then iron (approximately 1.25 g) was added, and the vial was weighed again. The vials were then filled to the top with solutions containing PCE at various ethanol fractions, allowing no headspace, and re-weighed. This generally provided a 4:1 volume/mass ratio, the same as that used by Gillham and O'Hannesin [30] and Muftikian et al. [33]. The vials were then placed on a rotator (15 rpm), and samples were taken off the rotator at the desired sampling times. Aqueous-phase samples were transferred to 0.5 ml vial inserts (without headspace) for GC analysis. The remaining supernatant solution was removed and the vial re-weighed to aid in estimation of mass sorbed to iron surfaces.

#### 3.1. Desorption

To determine the mass of the PCE sorbed to the iron, the PCE was desorbed from the iron and analyzed separately. For the 55  $\mu\text{g/ml}$  PCE concentration samples, PCE was desorbed by adding methanol (MeOH) to the vial with the remaining iron. After equilibrium was reached, the methanol extract was transferred to a 0.5 ml vial insert for analysis. This procedure, for both aqueous and sorbed phase sampling, was followed for each experiment, except for the 2  $\mu\text{g/ml}$  PCE analysis. For low-concentration analysis ( $\sim 2$   $\mu\text{g/ml}$ ), the solutions were extracted with hexane and analyzed by gas chromatograph/electron capture detector (GC/ECD). Both the aqueous and sorbed phase 2  $\mu\text{g/ml}$  samples were extracted with a 1:1 ratio of hexane.

Analysis of methanol extracts was conducted on a Shimadzu-10A High Performance Liquid Chromatograph (HPLC) System fitted with a Supelco PAH-C18 Column, and a UV-VIS Detector set at a wavelength of 230 nm. The mobile phase (65% methanol and 35% HPLC water) flow rate was set at 2 ml/min.

Hexane extracts were analyzed using a Shimadzu GC-17A System equipped with a J&W Scientific DB-624 Column (30 m  $\times$  0.53 mm  $\times$  3  $\mu\text{m}$ ), a  $^{63}\text{Ni}$  electron capture detector with nitrogen as the carrier gas.

#### 3.2. Types of iron filings

Three types of iron were evaluated in this research. Iron filings purchased from Fisher Scientific, nickel-plated iron, and pretreated (acid-washed) iron. The nickel-plated iron filings provided by Stephanie O'Hannesin (Environmental Technologies Inc., Guelph, Ont.) were industrially produced. Zero-valent iron filings were pretreated to remove possible impurities that may hinder surface catalysis. Matheson and Tratnyek [31] noted that increasing the clean surface of iron greatly increases dehalogenation. Acid pretreatment of the filings

was done similar to the methods reported by Matheson and Tratnyek [31], Muftikian et al. [33] and Liang et al. [38].

#### 4. Results and discussion

The disappearance of PCE from solution was determined by conducting a PCE mass balance including the aqueous and adsorbed phases based on the equation:

$$\frac{dM_T}{dt} = \frac{d(V_w C_w + a_s \Gamma_s)}{dt} = -k a_s \Gamma_s \quad (1)$$

where  $M_T$  is the total mass of PCE ( $\mu\text{g}$ ) degraded over time  $t$  (h);  $V_w$  the volume of the aqueous phase (ml);  $C_w$  the PCE concentration in the aqueous phase ( $\mu\text{g}/\text{ml}$ );  $a_s$  the surface area of the iron ( $\text{cm}^2$ );  $k$  the rate constant for PCE degradation on the iron surface ( $\text{h}^{-1}$ ) and  $\Gamma_s$  is the surface excess quantity of PCE on the iron ( $\mu\text{g}/\text{cm}^2$ ). It was expected that the change in mass over time ( $dM_T/dt$ ) would be equal to  $-k a_s \Gamma_s$  based on the assumption that degradation on the solid phase would dominate when compared to that in the aqueous phase. Assuming that PCE sorption can be approximated by a linear isotherm [45]

$$\Gamma_s = K_i C_w \quad (2)$$

and substituting the value for  $\Gamma_s$  into Eq. (1) mass balance and integrating, the resulting equation was linear with respect to  $\ln(C_w/C_w^0)$  versus time with a slope of  $-k'$ . This pseudo first-order relationship is represented in Eq. (3).

$$\ln\left(\frac{C_w}{C_w^0}\right) = -k' t \quad (3)$$

The slopes of  $\ln(C_w/C_w^0)$  versus time,  $k'$  ( $\text{h}^{-1}$ ), were generally linear and known as PCE loss or disappearance rates in the batch reactor vials and are displayed in Table 1. The slope of the pseudo first-order relationship was defined by the following equation:

$$k' = \frac{k K_i}{(V_w/a_s) + K_i} \quad (4)$$

where  $K_i$  is the adsorption coefficient ( $\text{cm}^3/\text{cm}^2$ ).

Table 1  
Pseudo first-order rate constants for PCE disappearance in cosolvent solutions in contact with various types of modified iron surfaces

Type of iron ( $C_0 \approx 55 \mu\text{g}/\text{ml}$ PCE)	Ethanol			
	0%	10%	30%	50%
Nickel iron	$5.83 \pm 0.30$	$4.48 \pm 0.23$	$3.90 \pm 0.18$	$0.54 \pm 0.04$
Treated iron	$4.92 \pm 0.45$	$4.20 \pm 0.23$	$3.23 \pm 0.14$	$0.47 \pm 0.08$
Untreated iron	$3.34 \pm 0.23$	$2.67 \pm 0.24$	$1.03 \pm 0.14$	$0.14 \pm 0.01$
Untreated iron ( $\sim 2 \mu\text{g}/\text{ml}$ )	$3.74 \pm 0.91$	$3.52 \pm 0.23$	$1.36 \pm 0.08$	$0.29 \pm 0.03$

Degradation rate constant,  $k' \times 10^3$  ( $\text{h}^{-1}$ ).

Batch tests measuring degradation of PCE in the presence of  $\text{Fe}^0$  were conducted for both relatively high ( $\sim 55 \mu\text{g/ml}$ ) and low ( $\sim 2 \mu\text{g/ml}$ ) PCE concentrations, and with different forms of modified zero-valent iron. The different zero-valent iron types included acid-treated iron (TreatFe) and nickel-plated iron (NiFe). These experiments enabled an assessment of the effectiveness of PCE degradation as a function of concentration and iron modification. Additionally, various cosolvent (ethanol) fractions in the solutions containing PCE were evaluated as well. These experiments provided data to establish the relationship between adsorption and degradation.

#### 4.1. Degradation of PCE

PCE degradation reactions were found to follow pseudo first-order kinetics, similar to previous findings [25,29–32,35]. The pseudo first-order rate constants ( $k'$ ) estimated from the slopes of  $\ln(C_w/C_w^0)$  versus time are displayed in Table 1.

In comparing the different concentration levels, the degradation of the higher concentration of PCE ( $\sim 55 \mu\text{g/ml}$ ) with untreated iron occurred more slowly than that of the lower ( $\sim 2 \mu\text{g/ml}$ ) PCE concentration (Table 1). This trend agreed with what was reported by both Wüst et al. [23] and Arnold and Roberts [25]. This seemed to indicate that the PCE molecules compete for a limited number of sorption sites on the iron surface. This competition results from the fact that the solution with fewer PCE molecules ( $\sim 2 \mu\text{g/ml}$ ) could find a greater number of uninhabited sorption sites faster, and, therefore, be degraded at a faster rate than the solution with more PCE molecules present and the same relative number of sorption sites. This relationship was found to be consistent throughout the PCE solutions containing various ethanol fractions (Table 1).

The pseudo first-order degradation rates reported in this research compare favorably to data gathered by previous researchers. Loraine [29] reported a pseudo first-order degradation rate of  $0.47 \times 10^{-7} \text{ s}^{-1} \text{ m}^{-2}$  for PCE treated with zero-valent iron with an initial concentration between 35 and 40 mg/l in an aqueous solution containing 57% ethanol. For this research, the closest comparison can be seen in the aqueous solution containing 50% ethanol with an initial PCE concentration of 55 mg/l treated with untreated iron which had a  $k'$  value of  $0.14 \times 10^{-3} \text{ h}^{-1}$  (Table 1). To compare these values, Eq. (4) transforms the data to a  $k'$  value of  $0.27 \times 10^{-7} \text{ s}^{-1} \text{ m}^{-2}$ . The difference in the values gathered in this research and that of Loraine [29] can be attributed to the solution to iron ratio employed by the two different research experiments. Loraine [29] had a solution to iron ratio of 2.8:1 and a slightly higher ethanol fraction in solution, compared to the 4.0:1 ratio employed by this research. This research had a ratio of solution to iron almost twice that of Loraine [29], which resulted in a pseudo first-order degradation rate almost half of that seen in the work of Loraine [29]. Not only does this data show the similarity between results of this research to previous research, it also implies a direct correlation between the degradation rate and the volume of solution per reactive sites in a given mass of iron as alluded to previously. The more PCE in solution compared to the reactive sites on a given mass of iron, the slower the degradation rate due to competition for these sites.

Data from experiments using the modified iron (acid-treated and nickel-plated) also followed pseudo first-order degradation reaction rates (Table 1). Comparing the different types of iron employed in this research showed that the NiFe was the most effective, followed

by TreatFe, and, finally, the untreated  $\text{Fe}^0$  was the least effective in degrading the PCE at 55  $\mu\text{g/ml}$  (Table 1). This trend was observed for PCE degradation for all of the ethanol fractions examined in this study. Comparing the two non-bimetallic irons, PCE degradation by the treated iron occurred more rapidly than the untreated iron. This was attributed to the increased number of sorption sites on the treated iron resulting from acid treatment. Our results are consistent with data from similar experiments conducted by Matheson and Tratnyek [31] and Burris et al. [36] which reported that acid washing of the iron provided faster dechlorination rates. This was stated to be a result of the acid dissolving the surface layer of the iron grains which may contain unreactive oxide or organic coatings. The clean, reduced metal surface in conjunction with greater surface area due to corrosion pits is credited with greater reactivity on the acid-washed iron. Also, there was no evidence of residual acidity, so the observed dehalogenation rate could not be attributed to the effect of pH [31].

The bimetallic NiFe was found to degrade PCE faster than the other forms of iron (Table 1). Similar to other reductive metals in bimetallic complexes, the effectiveness of the nickel-plated iron was most likely due to the ability of nickel to facilitate electron transfer, so reduction could proceed more rapidly [46]. It has also been stated that the nickel-plating reduces the formation of oxides on the iron surface, thereby, increasing the relative number of sorption sites when compared to the non-bimetallic iron [39]. The faster degradation rate of PCE with NiFe was also consistent over the range of ethanol fractions investigated (Table 1).

#### 4.2. Cosolvent effects

The degradation of PCE by iron was observed at four different volume fractions of ethanol cosolvent (0, 10, 30, and 50%) to determine how cosolvents would affect the PCE degradation rate. The data in Table 1 shows that increasing the ethanol fraction in the PCE solutions decreased the PCE degradation rates regardless of iron type or PCE concentration level. This was attributed to ethanol suppressing PCE sorption on the iron surfaces. Similar cosolvent effects on PAHs (polycyclic aromatic hydrocarbons) have also been reported by Rao et al. [47] and Wood et al. [48]. Cosolvents have been noted to increase organic solubility in aqueous solutions, which leads to their success in subsurface remedial efforts. However, this increase in aqueous solubility due to cosolvent presence also leads to a reduction in organic sorption, which is important for the treatment of the effluent from remedial processes.

Sorption of PCE onto the iron surfaces in the presence of cosolvent was also investigated in this research. In aqueous solutions containing no ethanol, PCE was found to adsorb to the iron surfaces in a manner best described by the Langmuir sorption isotherm relationship, consistent with data reported by Loraine [29] and Burris et al. [36]. For the aqueous solutions which contained ethanol at a volume fraction of 10% and greater, linear sorption isotherm relationships were found and the results are summarized in Table 2. The following equation was used to describe these isotherms [49]:

$$S = K_d C$$

where  $S$  is the micrograms of PCE sorbed per gram of Fe sorbent;  $C$  the micrograms of PCE in solution per milliliter of bulk solution; and  $K_d$  is the milliliters of PCE solution per

Table 2  
Partition coefficients ( $K_d$ ) for PCE in contact with different types of modified iron and various ethanol fractions

Type of iron	Ethanol		
	10%	30%	50%
Nickel iron	$0.613 \pm 0.015$	$0.405 \pm 0.004$	$0.265 \pm 0.006$
Treated iron	$0.365 \pm 0.014$	$0.313 \pm 0.010$	$0.260 \pm 0.005$
Untreated iron	$0.295 \pm 0.006$	$0.263 \pm 0.006$	$0.235 \pm 0.003$

Partition coefficient,  $K_d$  (ml PCE solution/g of iron).

gram of Fe sorbent and is known as the sorption coefficient. Larger  $K_d$  values (Table 2) indicate a greater tendency of PCE to adsorb to the surface of the solid particles. The experimental results in Table 2 and Fig. 1 show that the bimetallic nickel–iron displayed the greatest adsorption of PCE, followed by the acid-treated iron, and, lastly, the untreated iron. Further, it was shown that the partitioning of PCE to each of the iron types is reduced with increasing ethanol volume fractions. Each of the iron types displayed a log-linear relationship of PCE partitioning as a function of ethanol volume fraction (Fig. 1). This relationship and similar conclusions were also reported by Rao et al. [47] and Wood et al. [48] in the research of sorption of PAHs on soils in the presence of cosolvents.

Initially, it was expected that as more PCE sorbed onto the iron surfaces, more of the chemical would be degraded. In Fig. 1, the log-linear relationship between  $K_d$  and ethanol fraction for the experimentally gathered data was used to estimate data for ethanol fractions not explored in this research. The results indicated that NiFe was the best sorbent for PCE, and that adsorption was most hindered by increasing ethanol fractions.

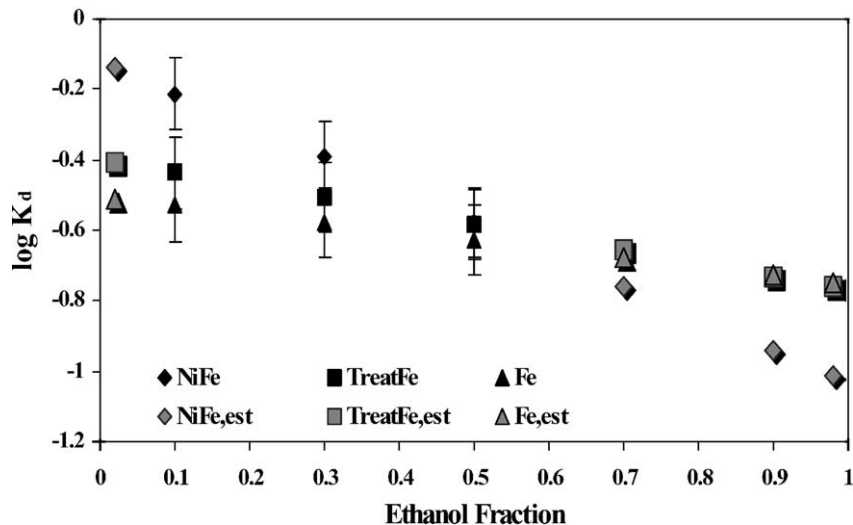


Fig. 1. Estimated (est) and experimentally derived sorption coefficients ( $K_d$ ) of PCE onto modified iron surfaces as functions of ethanol fraction. Modified iron surfaces: nickel-plated iron (NiFe), acid-treated iron (TreatFe), and untreated iron (Fe).



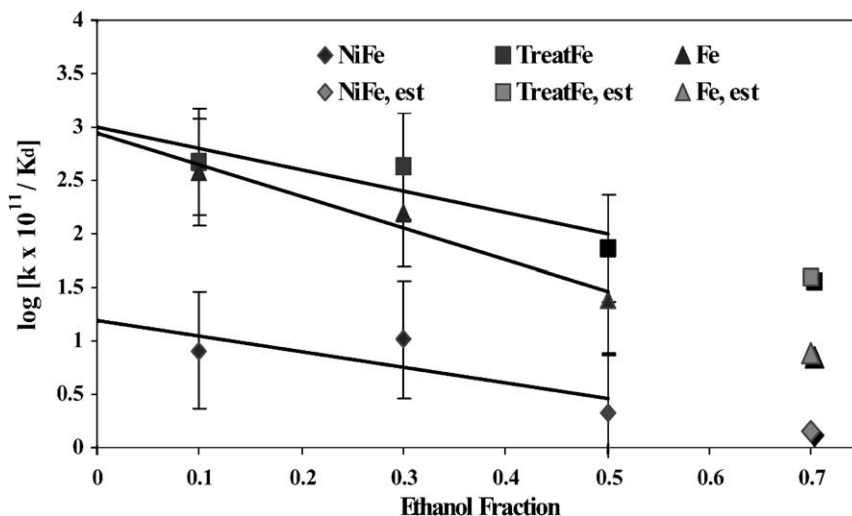


Fig. 2. Ratio of reaction rate ( $k$ ) to sorption ( $K_d$ ) as functions of ethanol fraction.

The ratios of the degradation rate constants to the sorption coefficients were plotted as functions of ethanol fractions in solution (Fig. 2). This figure displays how the increase in ethanol fractions resulted in decreased ratios of degradation to sorption of PCE for the various modified iron surfaces. So, although sorption has been shown to decrease with increasing ethanol (Fig. 1), further data (Fig. 2) indicates that the degradation rate also decreases relative to the sorption rate as ethanol increases. This seems to suggest that sorption to the iron surface is the major and limiting factor for the degradation of PCE contaminant. Increasing the ethanol fraction in an aqueous solution essentially decreases the rate of degradation in large effect by decreasing the rate of sorption to the degradation sites on the iron surfaces, a conclusion also drawn by Alessi and Li [26] and Loraine [29]. Although it has been shown that modification of the iron surface improves PCE dechlorination, these improvements are also greatly diminished by the presence of cosolvents in solution. In applying this information to possible field use, Tratnyek et al. [21] stated that PCE/iron contact time is one of the most critical issues in using dechlorination as a treatment technique. The ex situ design must provide a sufficient contact time of iron with contaminated solution to ensure sufficient degradation of the pollutants. Solutions with increasing cosolvent fractions would require larger treatment containers or slower flow rates through them. These requirements could be minimized if the increased degradation rate constants, provided by bimetallic treatment, are large enough to compensate for the decrease in the sorption rate experienced by alcohol addition.

#### 4.3. Degradation by-products

The focus of this research was not to study PCE by-products; however, TCE, which is reported to be a major by-product of PCE degradation [24,25,50], and DCE were monitored.

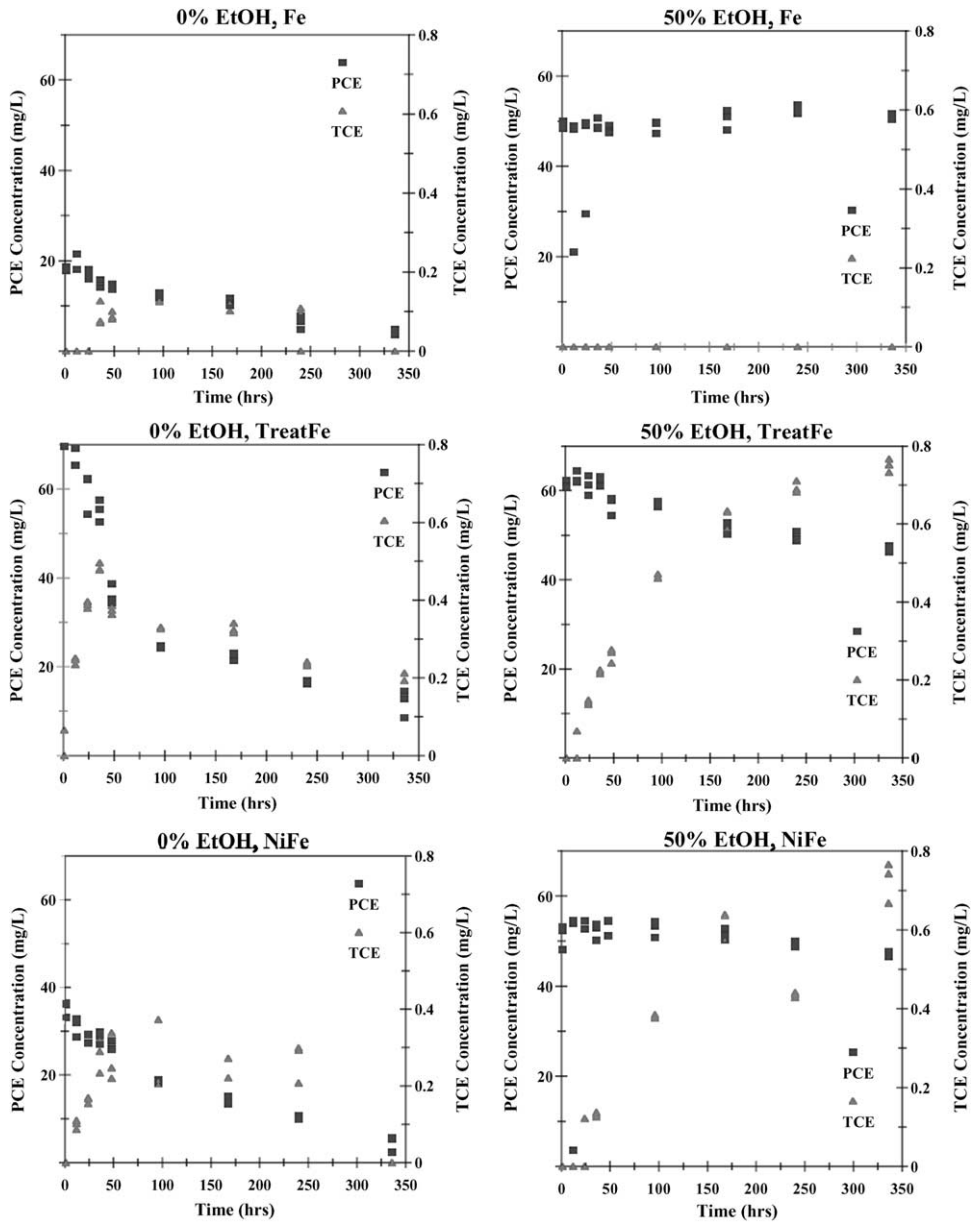


Fig. 3. Concentrations of PCE and TCE in aqueous solution as functions of time in the presence of different iron surfaces with 0 and 50% ethanol present.

The degradation process is generally accepted to be electrochemical in nature including a simple dechlorination process, with  $\text{Fe}^0$  serving as the source of electrons where oxidation of the iron and reductive chlorination of the organic compounds takes place [31–33,35]. Arnold and Roberts [25] did state that reductive  $\beta$ -elimination accounted for over 87% of PCE reduction by zero-valent iron, while the residual amount of PCE degradation can be attributed to hydrogenolysis and hydrogenation.

In this research, DCE quantities were below detectable limits, however, production of TCE was detected in small amounts. Fig. 3 shows that TCE was found to be produced as PCE degraded, suggesting a logical correlation between the PCE dechlorination and TCE presence in the systems. It was also noted that as time continued, the TCE itself was also seen to decrease or degrade, especially in systems where no ethanol was present (0% EtOH plots in Fig. 3).

As previously shown, when higher ethanol fractions were combined with untreated iron, minimal amounts of PCE was degraded (Table 1). In those cases where lower amounts of PCE was degraded, as depicted in the 50% ethanol fraction for untreated iron plot in Fig. 3, very little TCE was detected. Furthermore, for the high ethanol fraction solutions treated iron surfaces, PCE was seen to degrade minimally and TCE was seen to form. However, for these cases, TCE was not seen to degrade as in the cases where no ethanol was present (50% EtOH plots in Fig. 3). This raises concerns that TCE formed during degradation competes for sorption reaction sites on the limited iron surface area with PCE which may affect degradation, as suggested by Arnold and Roberts [25] and Burris et al. [36]. However, a more exhaustive by-product study of dechlorination reactions would need to be conducted before this question could be answered for certain.

Consistent with the observation of previous research [27,30,33], a headspace was observed to form in the reactor vials over time. Although not quantified, based on the above references, the major components of the headspace were expected to be hydrogen and nitrogen. Slight formation of iron oxides (rust) was also noted to appear on the iron surface over the duration of the experiment, as also reported by Chen et al. [27]. Generally, the longer the rotation time, the more dark brown oxides were observed on the iron surface. It was also noted in the results of this study that at higher ethanol fractions, less headspace and smaller amounts of iron oxides were produced. These observations support the findings that at lower cosolvent fractions, more degradation and more adsorption which increases degradation occurs, seen by the higher amounts of by-product gas and iron oxides produced.

## 5. Summary and conclusions

The purpose of this research was to evaluate the effectiveness of ex situ zero-valent iron in treating an aqueous waste solution which contained perchloroethylene. Modifications to the iron and different fractions of a cosolvent, ethanol, added to the solution were included in the investigation to observe how these variations would affect the PCE degradation.

The experimental batch tests results showed that PCE was found to degrade in the presence of zero-valent iron. These degradation reactions were found to be pseudo first-order

with respect to PCE loss over time, which agreed with results reported from previous research.

Different iron surfaces were studied to determine their effect on PCE degradation. In degrading PCE, the results showed that a bimetallic composite of nickel-plated iron was the most effective, followed by the acid pretreated zero-valent iron and, finally, the untreated zero-valent iron.

Linear sorption isotherms were displayed for solutions in which ethanol cosolvent was present. A relationship between degradation rate and adsorption showed that as adsorption to the iron surface increased, so did the degradation rates. Experimental results showed that increased ethanol fractions resulted in decreased adsorption of PCE to the iron surface which, consequently, led to the decreased rates of PCE degradation. For solutions with no ethanol cosolvent present, Langmuir sorption isotherms described PCE adsorption to the iron surfaces.

By-product formation was not a focus in this study, but TCE was observed to be produced as PCE degraded, which paralleled what was seen in previous research. Increasing ethanol fractions and decreasing PCE degradation rates reduced TCE produced to negligible amounts. By-product TCE was also seen to degrade, except in cases where higher ethanol fractions were present in solution. This implied that TCE might compete with PCE for reactive sites on the iron surface for degradation.

Overall, it was concluded that although cosolvent fractions increase the removal of PCE and other NAPLs from the subsurface, their presence would reduce the effectiveness of dechlorination by zero-valent iron, even if the iron surface was modified. However, due to the potential economic feasibility of this method for potential recycle of cosolvent solutions, increased residence times and improvement in treated iron sorptive capacity could still make this method a viable option for on-site waste treatment.

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