Reductive dechlorination of carbon tetrachloride with elemental iron

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Abstract

Carbon tetrachloride (CCl_4) was abiotically dechlorinated to chloroform ($CHCl_3$) and methylene chloride (CH_2Cl_2) by zero valent iron (Fe^0). Dechlorination of CCl_4 was rapid, and approximately followed first-order kinetics in the range of concentrations tested (CCl_4: 1.5–5.5 μM; Fe^0 powder: 1–10 g per 265 ml distilled water). Initial dechlorination rate coefficients for anoxic batch reactors ($0.290 \pm 0.009\,h^{-1}$ for 1 g Fe^0; $1.723 \pm 0.078\,h^{-1}$ for 10 g Fe^0) increased with iron surface area (initially $2.4 \pm 0.2\,m^2/g$). Rate coefficients also increased with time, probably because of an increase in reactive surface area due to cathodic depolarization and pitting of the iron surface. Dechlorination also occurred under oxic conditions, although the rates were significantly slower (e.g., $0.085 \pm 0.041\,h^{-1}$ for 1 g Fe^0 and initial dissolved oxygen 7.4 mg/l). A rapid pH increase was synchronous to dissolved oxygen consumption, and the pH remained constant after the oxygen was depleted. This was attributed to the proton and oxygen consuming aerobic corrosion of the Fe^0 surface. The potential for developing remediation technology with Fe^0 is discussed.

1. Introduction

Chlorinated aliphatics such as carbon tetrachloride (CCl_4) are common environmental contaminants due to their widespread use as solvents and industrial chemicals [1]. CCl_4 was also widely used as a grain fumigant until 1985 [2]. Annual US production of CCl_4 averaged approximately 590 million pounds during the last 10 years [3]. Although CCl_4 production decreased largely due to the decline of chlorofluorocarbon manufacture, and is scheduled to be banned by 1996 [4], significant amounts of this halocarbon remain in the environment. CCl_4 is an onerous contaminant due to its carcinogenicity, environmental persistence, and relatively high solubility in water (805 mg/l at 20 °C) [5]; it is commonly found in public water

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systems and in groundwater and surface water supplies at concentrations exceeding the maximum contaminant level of 5 μg/l [6].

Current treatment technologies often merely transfer CCl_4 from one phase to another, rather than transforming it into less harmful compounds. Contaminated groundwater, for example, is frequently treated for human consumption by stripping CCl_4 and other volatile halocarbons from the liquid phase into the atmosphere. These compounds diffuse upward through the tropopause and deplete stratospheric ozone and act as greenhouse gasses [7]. Therefore, there is considerable interest in improving current CCl_4 remediation techniques. Research on the biological degradation of chlorinated compounds has received much attention (for reviews, see Refs. [8, 9]). Nevertheless, microbial degradation of CCl_4 can be relatively slow [10], and may be inhibited by the toxicity of CCl_4 or its dechlorinated product, chloroform ($CHCl_3$) [11]. Consequently, abiotic reductive dechlorination with reduced metals has received increased attention recently.

Ferrous iron (Fe^{2+}), either at mineral surfaces [12] or enhanced by chelation with porphyrins or other biomolecules [13, 14], can participate in reductive dechlorination of CCl_4. Dissolved Fe^{2+} can also dechlorinate CCl_4 to $CHCl_3$ [15], although the rates are probably too slow for practical engineered applications. The potential feasibility of zero-valent metals to enhance dechlorination was demonstrated in a full-scale column reactor packed with combinations of Fe^0, Al^0, Cu^0, Zn^0 and sand [16]. Patents exist that are based on dechlorination of pollutants with Fe^0 (e.g., Ref. [17]), and recent work has investigated the role of Fe^0 in abiotic reductive dechlorination of CCl_4 [18]. Nevertheless, the detailed interaction of CCl_4 and Fe^0 under various reaction conditions is not fully understood. This paper addresses the kinetics and reaction mechanisms of the CCl_4/Fe^0 system in oxic and anoxic water to contribute to the rational development of process design.

2. Theory

Hydrogenolysis is an important process by which chlorinated pollutants are reductively dechlorinated to less persistent and (often) less toxic forms. This process involves the reduction of the pollutant with electrons from an external source (e.g., Fe^0). For a two-electron transfer, the net effect is replacement of a chlorine substituent with a hydrogen atom, with the concomitant liberation of a chloride ion [19]. This suggests that the overall surface-controlled hydrogenolysis of alkyl chlorides (R-Cl) by Fe^0 is likely to occur as follows:

$$Fe^0 + R\text{-}Cl + H^+ \rightarrow Fe^{2+} + R\text{-}H + Cl^-. \tag{1}$$
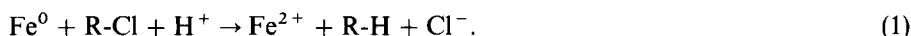
The sequential dechlorination of CCl_4 to $CHCl_3$, CH_2Cl_2, CH_3Cl and CH_4 with Fe^0 as electron donor is thermodynamically very favorable (Table 1). Such reactions are equivalent to iron corrosion with the chlorinated methanes acting as the oxidizing agent. In aqueous systems, however, other iron dissolution reactions can compete

Table 1
Standard potentials for reduction of chlorinated methanes with elemental iron

Reactants		Products	$\Delta E^{\circ\prime}$ (V)[a]
$Fe^0 + CCl_4 + H^+$	$\longrightarrow$	$Fe^{2+} + CHCl_3 + Cl^-$	1.11
$Fe^0 + CHCl_3 + H^+$	$\longrightarrow$	$Fe^{2+} + CH_2Cl_2 + Cl^-$	1.00
$Fe^0 + CH_2Cl_2 + H^+$	$\longrightarrow$	$Fe^{2+} + CH_3Cl + Cl^-$	0.93
$Fe^0 + CH_3Cl + H^+$	$\longrightarrow$	$Fe^{2+} + CH_4 + Cl^-$	0.91

[a] Calculated for dilute aqueous solution, pH 7, 25 °C, Cl^- activity $= 10^{-3}$, equal activities of chlorinated reactants and products, unit activity for Fe^0 and Fe^{2+}, and thermodynamic data from Ref. [20].

with Eq. (1), such as aerobic (Eq. (2)) and anaerobic (Eq. (3)) corrosion:

$$2Fe^0 + O_2 + 4H^+ \rightarrow 2Fe^{2+} + 2H_2O \tag{2}$$
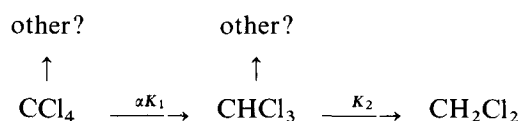
$$Fe^0 + 2H^+ \rightarrow Fe^{2+} + H_2. \tag{3}$$

All three reactions result in increased pH and produce potential reductants for dechlorination (i.e., Fe^{2+} and H_2) (Fig. 1). However, hydrogen gas is not an effective reductant without a catalyst [21], and dechlorination of alkyl halides with dissolved Fe^{2+} is relatively slow [13, 15]. Nevertheless, iron dissolution by cathodic depolarization has a potential beneficial effect: it increases the reactive surface area due to pitting of the iron surface [22]. Aerobic corrosion, however, could also adversely affect dechlorination. Dissolved oxygen (DO) would accelerate the further oxidation of dissolved Fe^{2+} to Fe^{3+}, which could readily precipitate as iron oxides at neutral and basic pH [22]. Such rust could eventually form a surface layer on the metal surface that would inhibit surface-controlled reactions.

Reductive dechlorination of alkyl chlorides is probably initiated by a one-electron transfer, producing an alkyl radical and liberating a chloride ion [23]. The alkyl radical can rapidly uptake a second electron and a proton from solution [19]. Since the formation of the alkyl radical is probably the rate limiting step, the law of mass action suggests that the rate of CCl_4 dechlorination should be directly proportional to the CCl_4 concentration:

$$\frac{d[CCl_4]}{dt} = -K_1 [CCl_4], \tag{4}$$

where brackets denote concentration, and K_1 is the overall pseudo first-order decay coefficient for CCl_4. Further hydrogenolysis involves two elementary first-order reactions in series:

$$
\begin{array}{ccc}
other? & & other? \\
\uparrow & & \uparrow \\
CCl_4 & \xrightarrow{\alpha K_1} CHCl_3 & \xrightarrow{K_2} CH_2Cl_2
\end{array}
$$

$$2H_2 + 2CCl_4 \rightarrow 2CHCl_3 + 2H^+ + 2Cl^-$$

$$2Fe^{2+} + CCl_4 + H^+ \rightarrow 2Fe^{3+} + CHCl_3 + Cl^-$$

$$4e^- \leftarrow 4H^+ + 2OH^- \leftrightarrow 2H_2O$$

Corrosion

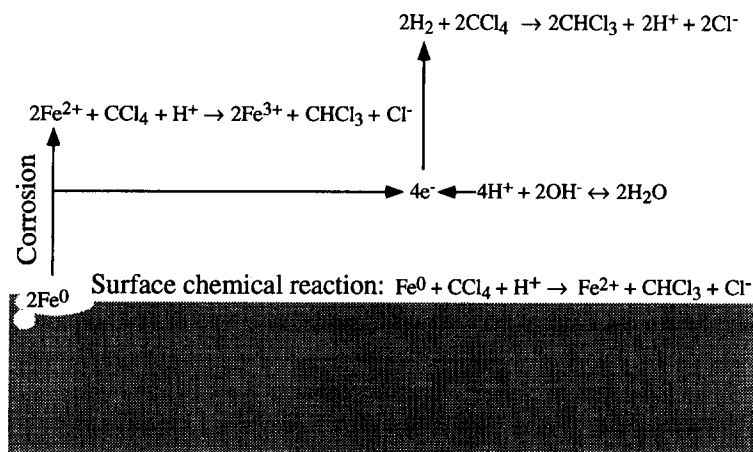$2Fe^0$ Surface chemical reaction: $Fe^0 + CCl_4 + H^+ \rightarrow Fe^{2+} + CHCl_3 + Cl^-$

Fig. 1. Reduction of carbon tetrachloride to chloroform by cathodic depolarization of an iron surface.

where α is the fraction of CCl_4 that is transformed to $CHCl_3$ rather than to other compounds such as formate, which is the hydrolysis byproduct of a dichlorocarbene intermediate (i.e., $:CCl_2$)[24], and K_2 is the hydrogenolysis rate coefficient for $CHCl_3$. Thus, the rate of change in $CHCl_3$ concentration should obey the following expression:

$$\frac{d[CHCl_3]}{dt} = \alpha K_1[CCl_4] - K_2[CHCl_3]. \tag{5}$$

Eqs. (4) and (5) can be integrated to yield expressions that characterize the dynamic transformation of CCl_4 and $CHCl_3$ in completely mixed batch systems (based on Ref. [25]):

$$[CCl_4] = [CCl_4]_0 e^{-K_1 t} \tag{6}$$

and

$$[CHCl_3] = \frac{\alpha K_1[CCl_4]_0}{K_2 - K_1} (e^{-K_1 t} - e^{-K_2 t}), \tag{7}$$

where $[CCl_4]_0$ is the initial CCl_4 concentration. The rate coefficients (K_1 and K_2) are system specific, and should depend on iron surface area and morphology, pH, temperature, redox potential, and mass transfer limitations from bulk solution to the iron surface, which in turn might be affected by other variables such as competitive adsorption and mixing intensity.

3. Methodology

3.1. Experimental approach

A completely mixed batch reactor was constructed to investigate reductive de-chlorination of CCl_4 with Fe^0 in initially oxic (DO = 7.4 mg/l) and anoxic

(DO < 0.5 mg/l) distilled deionized water (Barnstead NANOpure[R]). Oxygen was removed by sparging the water with N_2 gas for 20 min. Headspace was eliminated from the reactor to preclude potential confounding effects associated with the kinetics of liquid–gas-phase equilibrium for CCl_4 and other volatile compounds. The reactor consisted of a 250 ml round-bottom flask modified with gas-tight glass fittings for a dissolved oxygen (DO) probe, a pH probe, a thermometer, and a Mininert[R] sampling valve. This apparatus permitted continuous monitoring of critical process variables, including aqueous concentrations of CCl_4 and its dechlorinated homologues, pH, and DO. Fe^0 powder (1 or 10 g) was weighed and placed in the reactor, and all headspace was displaced with water (total volume 265 ± 3 ml). Continuous mixing was provided at a constant rate by a magnetic mixer in all batch reactors. A small aliquot of a saturated aqueous solution of CCl_4 (stored at 28 ± 2 °C) was then injected into the reactor with a gas-tight 500 µl syringe (Hamilton no. 1750LT) while displaced water was allowed to escape from the reactor through the sampling port. Initial CCl_4 concentrations (230–840 µg/1 or 1.5–5.5 µM) were representative of concentrations commonly detected in contaminated groundwater [6]. Control runs were prepared similarly, except that Fe^0 was omitted to discern CCl_4 degradation from potential volatilization or sorption losses. Data for DO, pH, and temperature were recorded on line. All batch reactors were maintained at a temperature of 28 ± 3 °C. For chlorinated methanes analysis, aqueous (10 µl) samples were removed through the sampling port with a syringe (Hamilton no. 701N), and transferred to 10 ml crimp-cap vials (Hewlett Packard) prior to gas chromatography (GC) analysis.

3.2. Analytical procedures

CCl_4 and its dechlorinated homologues were measured by static headspace GC using a Hewlett Packard Model 5890 gas chromatograph equipped with a DB5 capillary column (J and W Scientific), an electron capture detector, and a Model 19395A headspace autosampler. Peaks were quantified by comparison with the retention times and response factors of standard compounds. The limit of detection of this procedure is approximately 1 µg/l for either CCl_4 or $CHCl_3$. Hydrogen and methane were analyzed using a Trace Analytical Model RGA3 reduction gas analyzer. pH was measured with a Beckman Model 71 pH meter, and DO was measured electrochemically with a YSI Model 5300 oxygen monitor (detection limit ca. 0.05 mg/l). The Fe^0 powder was 99.9 + % pure, and had a nominal particle diameter of 10 µm (Aldrich Chemical). Initial Fe^0 surface area (2.4 ± 0.2 m²/g) was analyzed by Porous Material Inc. (Ithaca, NY) using a BET isotherm procedure. CH_2Cl_2, CCl_4 (A.C.S. Certified, Spectranalyzed[R]), and $CHCl_3$ (A.C.S. Certified, HPLC grade) were obtained from Fisher Chemical.

3.3. Data analysis

Instantaneous K_1 values were evaluated over the length of selected dechlorination tests by linear regression of $-\ln [CCl_4]$ versus time. Whether changes in K_1 were significant was assessed using Students' t-test on slopes at the 95% confidence

level [26]. The fraction of CCl_4 transformed to $CHCl_3$ (α) was estimated as the average (molar) ratio of $CHCl_3$ plus other dechlorinated homologues over the amount of CCl_4 removed. This value was used to assess carbon mass balance and reaction pathways.

4. Results and discussion

CCl_4 (1.5–5.5 μM) was rapidly removed in anoxic, continuously stirred batch reactors amended with either 1 or 10 g Fe^0, but not in no-treatment controls (Fig. 2). This indicates that Fe^0 was responsible for CCl_4 removal. Although water-derived hydrogen gas was generated, the pH of all anoxic systems did not increase significantly from the initial value of 7.7 (data not shown). This indicates that the consumption of protons by anaerobic corrosion (Eq. (3)) and hydrogenolysis (Eq. (1)) was offset by other reactions, such as the formation of iron hydroxides.

On a molar basis, the appearance of $CHCl_3$ accounted for less than 100% of the CCl_4 removed in either initially oxic or anoxic reactors (e.g., Fig. 3(a)). Because losses due to sorption and volatilization were negligible in the control, transformation processes other than hydrogenolysis must account for the missing mass. Conversion of CCl_4 to $CHCl_3$ typically accounted for 49% of the CCl_4 removed (i.e., α (in
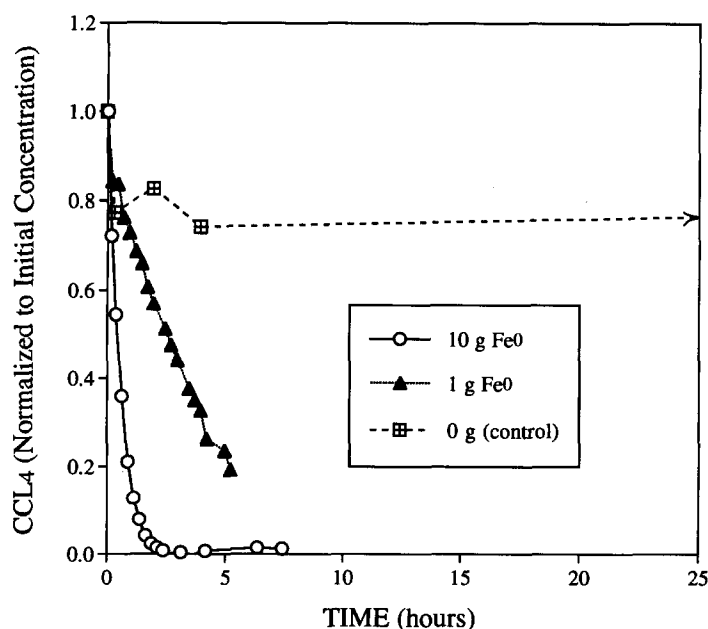

Fig. 2. Effect of added Fe^0 on CCl_4 removal in anoxic batch reactors. Initial CCl_4 concentrations were 4.1 μM for 10 g Fe^0, 1.5 μM for 1 g Fe^0, and 4.4 μM for controls.
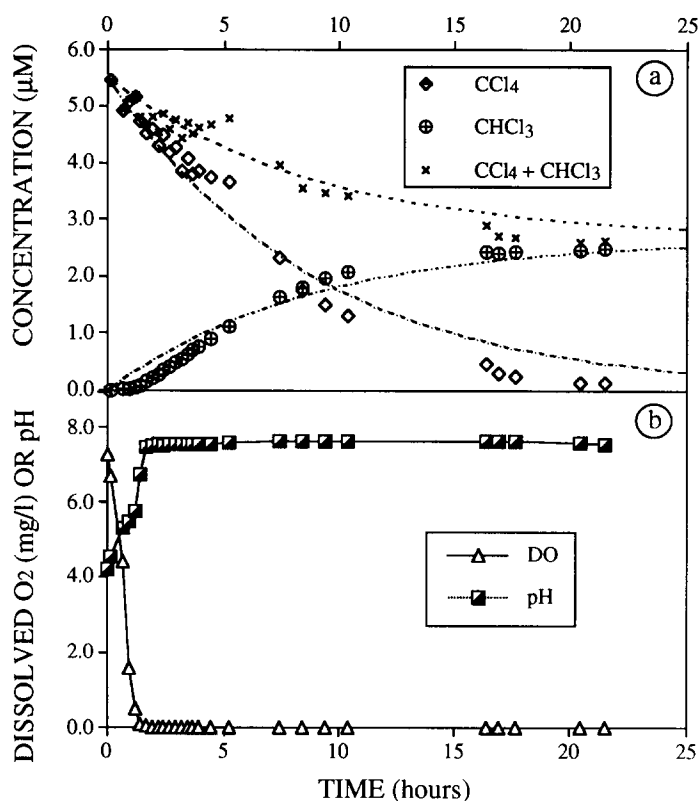
Fig. 3. Reductive dechlorination of carbon tetrachloride to chloroform (a) and concomitant increase in pH (b) in (initially) oxic batch reactor. Dotted lines depict simulations with Eqs. (6) and (7). Model coefficients (i.e., $K_1 = 0.11 \, h^{-1}$, $K_2 = 0$, and $\alpha = 0.49$) were estimated by nonlinear regression of empirical data against Eqs. (6) and (7).

Eq. (5)) $= 0.49$). An α value of less than 1 indicates the occurrence of competing reactions such as reductive hydrolysis through a dichlorocarbene intermediate, or dimerization of trichloromethyl radicals. This behavior is characteristic of CCl_4 reductive dechlorination [14] [18], which often results in measurable levels of reductive hydrolysis byproducts such as formate and carbon monoxide [24]. Apparently, competing reactions to the sequential hydrogenolysis of CCl_4 were significant in this experiment. An additional anoxic batch reactor containing a much greater concentration of CCl_4 (2.1 mM) and 10 g Fe^0 removed all CCl_4 and $CHCl_3$ within 90 days (data not shown). However, no further dechlorinated products other than CH_2Cl_2 (such as CH_3Cl or CH_4) were positively identified.

In all experiments, CCl_4 dechlorination approximated first-order kinetics, as described in Eq. (6). Rate coefficients (K_1) increased with iron dose (Table 2), which is consistent with other work investigating Fe^0 surface-controlled reactions (e.g., Ref. [27]). Surprisingly, dechlorination of CCl_4 occurred in the presence of DO (Fig. 3),

Table 2
Pseudo-first-order decay coefficients (K_1) for removal of CCl_4 in the presence of Fe^0

Reaction conditions	n^a	K_1 $(h^{-1})^b$	Half-life $(h)^c$
Intially anoxic reactors			
1 g Fe^0, early	18	0.290 ± 0.009	2.39
1 g Fe^0, late	11	0.448 ± 0.047	1.55
10 g Fe^0, early	4	1.723 ± 0.078	0.40
10 g Fe^0, late	7	2.212 ± 0.037	0.31
Initially oxic reactor^d			
1 g Fe^0, oxic	5	0.085 ± 0.041	8.15
1 g Fe^0, early anoxic	16	0.147 ± 0.008	4.57
1 g Fe^0, late anoxic	5	0.227 ± 0.035	3.06

^{a} Number of data points used to determine K_1.

^{b} Values reported are teh slope of $-\ln[CCl_4]$ versus time $\pm$ one standard deviation.

^{c} Calculaed as $t_{1/2} = \ln(2)/K_1$.

^{d} Oxygen was rapidly consumed during this experiment (Fig. 3(b)). The rapid depletion of oxygen in a 10 g Fe^0 experiment precluded collection of data under oxic conditions.

although the dechlorination rate was significantly slower than that under anoxic conditions (Table 2). Observed CCl_4 and $CHCl_3$ concentrations departed from the values predicted by the theoretical rate model (Fig. 3(a)). Initial CCl_4 concentrations were higher while initial $CHCl_3$ concentrations were lower than model simulations with Eqs. (6) and (7). This was attributed to slower dechlorination kinetics during competition between CCl_4 and DO for electrons from Fe^0. In theory, oxygen could also inhibit the rate by binding to the iron surface and reducing the availability of reactive surface sites [28]. Whether such inhibition is significant requires further investigation.

A synchronous increase in pH and decrease in DO was observed, and no significant change in pH occurred after the DO was depleted (Fig. 3(b)). The slower dechlorination kinetics in the presence of DO, the depletion of DO, and the synchronous increase in pH indicate that aerobic Fe^0 corrosion occurred simultaneously with reductive dechlorination of CCl_4. The stabilization of pH after DO was depleted can be explained by the thermodynamically favorable precipitation of iron hydroxides (although in small quantities), which probably balanced proton consumption by anaerobic corrosion. Deposition of such oxides decreases the reactive surface area and, thus, K_1. This would explain why K_1 was smaller for the early anoxic stage of the initially oxic experiment, compared to the corresponding K_1 value for the initially anoxic experiment (Table 2).

CCl_4 concentrations were lower and $CHCl_3$ concentrations were higher than those predicted by the model at the end of the initially oxic experiment (e.g., Fig. 3(a)). This discrepancy can be explained by analysis of instantaneous CCl_4 removal rates (e.g., Fig. 4). K_1 increased over the course of each experiment. This increase suggests either an enhancement of surface chemical reactions, perhaps due to an increase in reactive
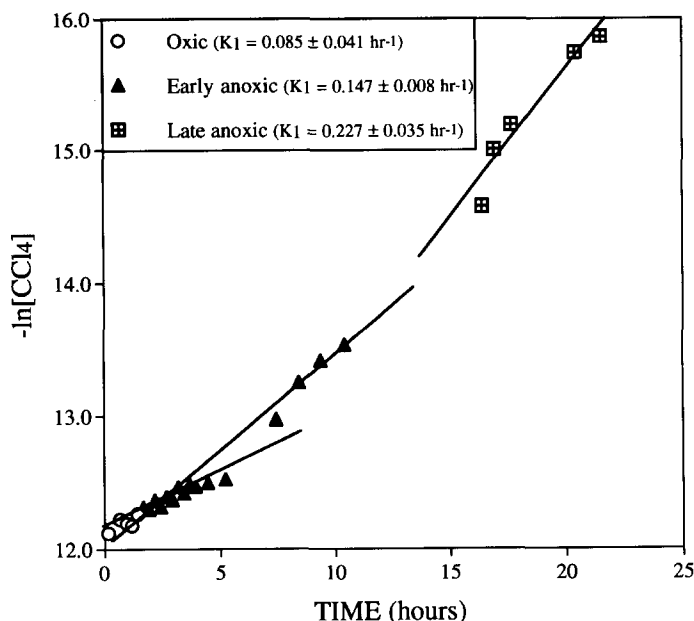
Fig. 4. Increase in pseudo-first-order rate coefficient for removal of CCl_4 in (initially) oxic batch reactor.

surface area, or the participation of additional reductants, such as Fe^{2+} or H_2 formed by cathodic depolarization of the iron surface (Fig. 1). Reduction of CCl_4 with either Fe^{2+} or H_2 is thermodynamically favorable [20]. However, iron-free batch reactors containing 2.1 mM CCl_4 under an H_2 atmosphere (200 ml headspace in a 250 ml reactor) showed no significant removal of CCl_4, and no dechlorinated products were detected within 3 days. Furthermore, the rate of CCl_4 dechlorination in anoxic water by Fe^{2+} is probably at least an order of magnitude slower (e.g., $K_1 = 4.8 \times 10^{-3}$ h^{-1} for 1.85 mM $FeCl_2$, calculated with data from Ref. [15]) than the rates observed in our batch reactors (Table 2). Although thermodynamically favorable, reduction of CCl_4 by Fe^{2+} or H_2 is apparently kinetically hindered, which corroborates the conclusion of other researchers that the dechlorination reaction proceeds primarily by a surface-controlled chemical reaction [18]. Therefore, the observed increase in K_1 over time was attributed to an increase in iron surface area due to pitting during cathodic depolarization.

Observed dechlorination rates may reflect a number of processes other than chemical reaction at the Fe^0 surface, including mass transport to the surface, adsorption of reactants, and desorption and mass transport of products from the surface [29]. Further work is required to determine which of these processes are responsible for the lack of direct proportionality between K_1 and initial surface area (which was controlled by the amount of Fe^0 added) (Table 2). The conditions under which either chemical reaction or mass transport processes are rate-limiting also need further study. For example, a positive correlation has been suggested between the mixing rate

in batch reactors and reductive dechlorination rate [18], presumably due to faster mass transport resulting from the decreased thickness of the diffusion layer [29]. This suggests that dechlorination rates might be mass transfer rather than reaction limited, and efforts to enhance contact between Fe^0 and the target contaminant would probably be well justified.

The reduction of CCl_4 with Fe^0 may offer some significant advantages in the treatment of contaminated effluents. Empirical rates obtained in our laboratory compare very favorably with hydrolysis rates for CCl_4, which are extremely slow (e.g., half-life = 7000 yr) [1], and with biological systems, which have relatively modest removal rates (e.g., half-life $\geqslant$ 10 d for a denitrifying batch incubation seeded with primary sewage effluent) [10]. Furthermore, Fe^0 could be used to treat higher contaminant loads than biological treatment processes, which are inhibited by the toxicity of chlorinated compounds to microorganisms [10, 11]. In this work, the iron surface was not visibly rusted and continued to be reactive after DO was depleted. Visible formation of iron oxides was observed only after 60 days, presumably due to anaerobic corrosion (Eq. (3)). Thus, rate inhibition due to precipitation of ferric hydroxides onto iron surfaces apparently was a minor factor in these experiments. Nevertheless, the formation of iron oxides at neutral or higher pH could significantly reduce the reactive surface area and inhibit dechlorination in other systems operated for longer periods of time. The practical implication of this observation is that buffering such systems at an acidic pH should increase the dechlorination rate by inhibiting deposition of ferric oxides [22] while enhancing cathodic depolarization and hydrogenolysis.

Although the reactivity of Fe^0 with CCl_4 was recognized as early as 1925 [30], only recently has this process received consideration for environmental applications. Several potential applications exist for the abiotic reductive dechlorination of chlorinated aliphatics with zero-valent metals. Permeable barriers composed of iron filings and buried in the path of a contaminant plume are being tested [31], and column reactors have also been tested for treating industrial wastewaters [16]. Encouraging preliminary results in both laboratory and pilot experiments have awakened considerable national and international interest in the use of metallic iron for chlorinated xenobiotic remediation. Nevertheless, a better understanding of the kinetics and mechanisms of the rate-limiting process is required to take full advantage of this new treatment technology.

5. Summary and conclusions

CCl_4 was rapidly dechlorinated in anoxic incubations amended with Fe^0 powder. Higher rates corresponded to higher initial surface area, which was controlled by the amount of Fe^0 added. Rates increased with time, presumably because of increased reactive surface area resulting from cathodic depolarization. Dechlorination also occurred under oxic conditions, although the rate was significantly slower. Aerobic corrosion of the iron surface quickly depleted the dissolved oxygen. This resulted in increased dechlorination rates probably because of reduced competition between

CCl_4 and O_2 for electrons from Fe^0. Rate inhibition due to precipitation of ferric hydroxides onto iron surfaces apparently was a minor factor in these experiments. Nevertheless, buffering the system in the acidic pH range might improve dechlorination rates by inhibiting precipitation of ferric hydroxides onto iron surfaces while enhancing cathodic depolarization and hydrogenolysis.

These results imply that deoxygenation is not a prerequisite for treatment of CCl_4 contaminated water with Fe^0. Dissolved oxygen could be beneficial in controlling product formation. Research investigating the role of oxygen in Fe^0/CCl_4 systems continues in our laboratory. We hypothesize that the dechlorination pathway for CCl_4 can be controlled by molecular oxygen (dissolved in water), resulting in the formation of a higher proportion of innocuous products (chloride ion and carbon dioxide) compared to the reductive dechlorination products (methylene chloride and chloromethane) which are increasingly recalcitrant under anoxic conditions.

Acknowledgements

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