Degradation of carbon tetrachloride by modified Fenton's reagent

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Abstract

The degradation of tetrachloromethane (carbon tetrachloride—CT) by modified Fenton's reagent (catalyzed hydrogen peroxide) was investigated using a range of hydrogen peroxide concentrations and 1 mM iron(III) catalyst. The documented reactive species in modified Fenton's reactions, hydroxyl radical ($OH^•$), is not reactive with CT, yet CT degradation was observed in the Fenton's reactions and was confirmed by chloride generation. Because CT is not reactive with $OH^•$, a reductive mechanism which may involve superoxide radical anion is proposed for CT degradation in modified Fenton's systems. Scavenging of reductants by excess chloroform prevented CT degradation, confirming a reductive mechanism. Similar to CT, three other oxidized aliphatic compounds, hexachloroethane, bromotrichloromethane, and tetranitromethane, were also degraded by modified Fenton's reagent. The results show that modified Fenton's reactions act through a reductive mechanism to degrade compounds that are not reactive with $OH^•$, which broadens the scope of this process for hazardous waste treatment and remediation.
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1. Introduction

The widespread use and improper disposal of organic chemicals has led to significant contamination of soils and groundwater throughout much of the world. Carbon tetrachloride (CT) is a perchlorinated biorefractory contaminant that has been used in a wide range of commercial and military applications. Carbon tetrachloride was once used widely as a solvent, pesticide, refrigerant, and aerosol propellant [1]. It was also used extensively in nuclear weapons production, resulting in widespread contamination of soils and groundwater at nuclear reservation sites such as Hanford, WA, and Oak Ridge, TN [2]. Toxic effects

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of CT are initiated by enzymatic reactions that transform it into trichloromethyl radicals ($CCl_3^\bullet$), resulting in damage to the liver, lungs, and kidneys [3]. In addition, CT is classified by the International Agency for Research on Cancer (IARC) and the US Environmental Protection Agency as a Group B2 carcinogen [4,5].

In the past decade, advanced oxidation processes (AOPs) have seen increased use for the in situ and ex situ chemical oxidation of contaminated soils and groundwater. Fenton's reagent is the catalytic decomposition of dilute hydrogen peroxide by iron(II), which results in the generation of hydroxyl radicals ($OH^\bullet$); the classic Fenton's reaction is usually conducted by gradually adding dilute hydrogen peroxide to a degassed solution of excess iron(II). This procedure produces hydroxyl radicals in near-stoichiometric quantities:

$$H_2O_2 + Fe^{2+} \rightarrow OH^\bullet + OH^- + Fe^{3+} \tag{1}$$

Hydroxyl radical, a relatively non-specific oxidant that reacts with most organic compounds at near-diffusion-controlled rates, readily attacks even highly chlorinated alkenes and aromatics, such as trichloroethylene (TCE), perchloroethylene (PCE), and polychlorinated biphenyls (PCBs) [6], though it is essentially unreactive with perchlorinated alkanes such as CT and hexachloroethane. Fenton's reagent is usually modified for in situ chemical oxidation (ISCO) by using a one-time addition of higher concentrations of hydrogen peroxide and varying the type of catalyst (i.e. iron(III), iron chelates, or iron oxyhydroxide minerals). The stoichiometry of hydroxyl radical generation in such modified systems is not as efficient as the standard Fenton's procedure; however, it does provide the advantages of enhanced contaminant desorption and possible destrution of dense nonaqueous phase liquids (DNAPLs) in the subsurface [4].

The use of Fenton-like reactions for soil and groundwater remediation was first reported by Watts et al. [7] who documented the mineralization of pentachlorophenol (PCP) in silica sand systems. A significant amount of research has since been devoted to hydrogen peroxide requirements and alternative catalysts in the application of Fenton-like processes to soils and groundwater systems. Tyre et al. [8] found that hydrogen peroxide concentrations >1% are necessary to treat hydrophobic contaminants sorbed to soils. They also proposed that naturally-occurring iron minerals in soils can catalyze the decomposition of hydrogen peroxide and promote Fenton-like reactions. Subsequent research by Ravikumar and Gurol [9], Miller and Valentine [10], Watts et al. [11], and Lin and Gurol [12] investigated mechanisms of mineral-catalyzed Fenton's reactions. Systems for injecting Fenton's reagent into contaminated soils have been developed by Ho et al. [13] and Gates and Siegrist [14]. They found that hydrogen peroxide and catalysts can be injected into the vadose zone and groundwater; however, effective remediation of the subsurface is not only a function of delivery, but also depends on using the most effective process chemistry, which may include taking maximum advantage of non-$OH^\bullet$ species generated in modified Fenton's reactions [15].

A limitation of modified Fenton's reactions and other AOPs has been the low reactivity of hydroxyl radicals with highly oxidized contaminants such as 1,3,5-trinitrobenzene, hexachloroethane, and carbon tetrachloride ($k_{OH^\bullet}$ for CT $< 2 \times 10^6$ [4]; rate constants are unavailable for 1,3,5-trinitrobenzene and hexachloroethane). These compounds are oxidized organics because electrons of the carbon atoms are drawn toward the halogen or nitro groups. Based on oxidation–reduction thermodynamics, the degradation of oxidized compounds, such as CT, proceeds through reductions rather than oxidations; as a result,

CT is essentially non-reactive with hydroxyl radicals, but is highly reactive with reductants such as solvated electrons [3], with a k_e of 1.6×10^{10} [4]. Therefore, the transformation of CT in a chemical treatment system would proceed through reductive processes rather than chemical oxidations.

Recent results have shown that a non-OH$^\bullet$ species generated in modified Fenton's reactions using high hydrogen peroxide concentrations ($\geq 0.3\,M\,H_2O_2$) can reduce the oxidized compound hexachloroethane, yielding the product pentachloroethane; the reductants proposed included superoxide radical anion ($O_2^{\bullet-}$), hydroperoxide (HO_2^-), or both [16]. Evidence of reductants in modified Fenton's systems is not without precedent, as reductions have also been demonstrated in other advanced oxidation processes, such as illuminated titanium dioxide systems and UV/ozone systems [17–19]. The purpose of this research was to further investigate the activity of reductants in modified Fenton's reactions by evaluating their ability to degrade CT, a toxic and biorefractory oxidized organic compound.

2. Materials and methods

2.1. Materials

Carbon tetrachloride (>99%), potassium hydroxide (92.3%), potassium nitrate (99%), isopropanol, and chloroform were purchased from J.T. Baker (Phillipsburg, NJ). Ferric sulfate was obtained from Sigma Chemical Co. (St. Louis, MO). Reagent grade hexane was purchased from Fisher Scientific (Fair Lawn, NJ) and hydrogen peroxide (50%) was supplied gratis by Solvay Interox (Deer Park, TX). Double deionized water was purified to greater than $18\,M\Omega\,cm$ using a Barnstead Nanopure II deionizing system.

2.2. Modified Fenton's reactions

Stock solutions of carbon tetrachloride were prepared in double deionized water and used within 2 days of preparation. Modified Fenton's reactions were conducted in closed batch reactors which consisted of 40 ml volatile organic analysis vials fitted with caps lined with Teflon septa. The initial carbon tetrachloride concentration was 0.5 mM. The probe stock solution (5 mM carbon tetrachloride), iron(III) solution, and hydrogen peroxide were added to the batch reactors to a total volume of 10 ml. The iron(III) concentrations were 1 mM and the initial hydrogen peroxide concentrations ranged from 60 to 590 mM. The pH was adjusted to 3.0 using $1\,M\,H_2SO_4$ for all reactions with the exception of reactions evaluating pH effects, which were adjusted to pH 2.0, 2.5, or 3.0. At varying time intervals over 2 h, the reactions were stopped by extracting the aqueous solutions with 10 ml of hexane. The extraction efficiency of CT was greater than 90%. All experiments were conducted in triplicate, and control reactions were evaluated in parallel using deionized water in place of hydrogen peroxide.

2.3. Verification of probe degradation

Chloride ions released from carbon tetrachloride were monitored in parallel Fenton-like reactions to confirm carbon tetrachloride degradation. At selected time points, the reactions

were quenched by adding 0.5 ml of concentrated H_2SO_4 [8]. An aliquot from each batch reactor sample was then analyzed using a Fisher Accumet pH/Ion Meter with double junction reference electrode.

2.4. Modified Fenton's reactions with scavengers

Several scavengers were used based on their potential to react with hydroxyl radicals, solvated electrons, and reduced intermediates. Isopropanol was used as a hydroxyl radical scavenger because of its high reactivity with oxidants ($k_{OH^\bullet} = 3 \times 10^9\,M^{-1}\,s^{-1}$) and low reactivity with reductants ($k_e = 1 \times 10^6\,M^{-1}\,s^{-1}$) [20]. In contrast, chloroform was chosen as a reductant scavenger because of its minimal reactivity with hydroxyl radicals ($k_{OH^\bullet} = 7 \times 10^6\,M^{-1}\,s^{-1}$) and high reactivity with reductants ($k_e = 3 \times 10^{10}\,M^{-1}\,s^{-1}$) [20]. Another scavenger used was nitrate, an oxidized species that reacts rapidly with solvated electrons but not with other reductants ($k_e = 9.7 \times 10^9\,M^{-1}\,s^{-1}$) [20].

Stock solutions of scavengers were prepared similarly to that of the probe compounds and added to the reaction vials. The scavenger concentration was based on the species with which it competes (e.g. the probe compound, hydrogen peroxide). Chloroform and nitrate concentrations were 2000 times the molar concentration of carbon tetrachloride. Because H_2O_2 reacts with $OH^\bullet$ to form superoxide through propagation reactions, isopropanol concentrations of 3, 15, and 30 times the molar concentration of H_2O_2 were used to stop the propagation reactions.

2.5. Analysis

Carbon tetrachloride extracts were analyzed on a Hewlett-Packard 5890A gas chromatograph with electron capture detector and a 0.53 mm (i.d.) ×10 m DB-1 capillary column. The injector and detector temperatures were 240 and 400 °C, respectively; the initial oven temperature was 40 °C, the program rate was 5 °C min^{-1}, and the final temperature was 120 °C. The standard error between replicate analyses was consistently less than 10%.

3. Results and discussion

The degradation of CT using H_2O_2 concentrations from 90 to 590 mM catalyzed by 1 mM iron(III) is shown in Fig. 1. Hydroxyl radicals are unreactive with CT, so another transient oxygen species is probably responsible for its degradation. Carbon tetrachloride degradation increased as a function of H_2O_2 concentration, which is consistent with the increased generation of superoxide driven by the succeedingly high H_2O_2 concentrations:

$$H_2O_2 + OH^\bullet \rightarrow HO_2^\bullet + H_2O \tag{2}$$

$$HO_2^\bullet \leftrightarrow O_2^{\bullet -} + H^+ \quad pK_a = 4.8 \tag{3}$$

Superoxide is likely the transforming species in this modified Fenton's process. Superoxide is a weak reductant that reacts with CT with a rate constant of 3800 M^{-1} s^{-1} in dimethyl sulfoxide. Although this rate constant for superoxide is relatively low compared to those
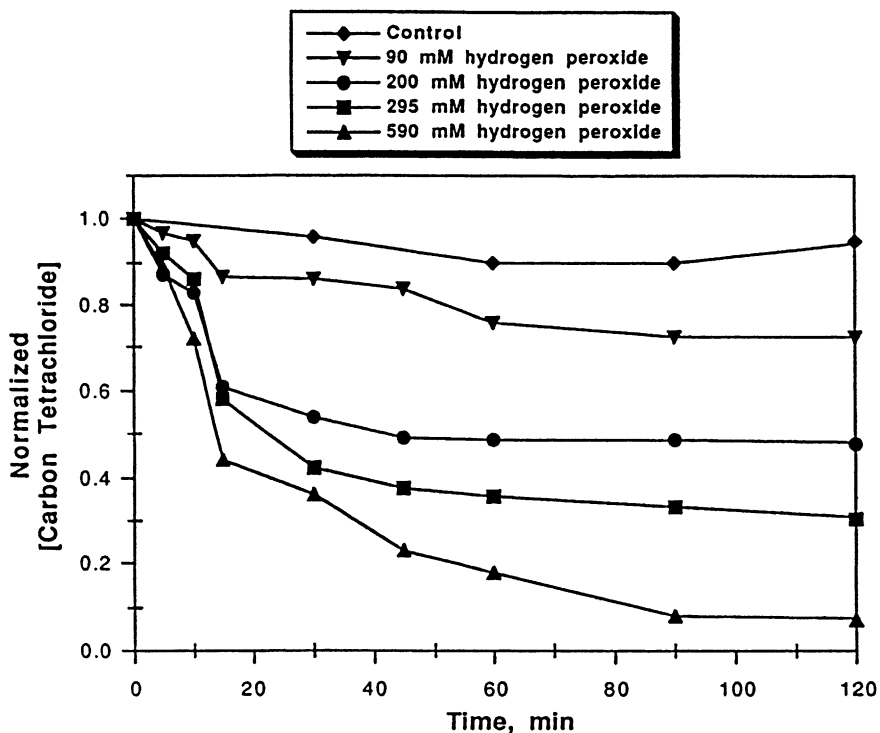
Fig. 1. Carbon tetrachloride degradation by modified Fenton's reagent with varying hydrogen peroxide concentrations and 1 mM iron(III).

for OH$^\bullet$, the observed rate of CT degradation can still be significant because of the high concentrations of superoxide generated in modified Fenton's systems.

Carbon tetrachloride is volatile (Henry's Law constant $= 0.0302$ atm m^3/mole) [21,22] so chloride generation was monitored to verify the transformation of CT (Fig. 2). Chloride formation was directly proportional to the loss of CT, confirming its degradation. These data are consistent with previous results showing that hexachloroethane, a compound unreactive with hydroxyl radicals, is also degraded in a modified Fenton's system [16].

To determine the role of hydroxyl radicals in the degradation of CT, the Fenton's reactions were repeated with the addition of excess isopropanol to scavenge hydroxyl radicals. The results, shown in Fig. 3, document that CT was degraded even with hydroxyl radicals scavenged from the system. These data confirm that hydroxyl radicals are not involved in CT degradation and that a non-hydroxyl radical species that degrades CT is generated in modified Fenton's reactions.

Carbon tetrachloride is characterized by an oxidized carbon atom in which valence electrons are drawn away by the four chlorine atoms. Such oxidized organic compounds (e.g. CT, chloroform, chlorofluorocarbons) tend to react through reductive pathways rather than oxidative pathways [4]. To evaluate the presence of a reductive pathway, the Fenton's reactions were repeated with the addition of nitrate as a solvated electron scavenger
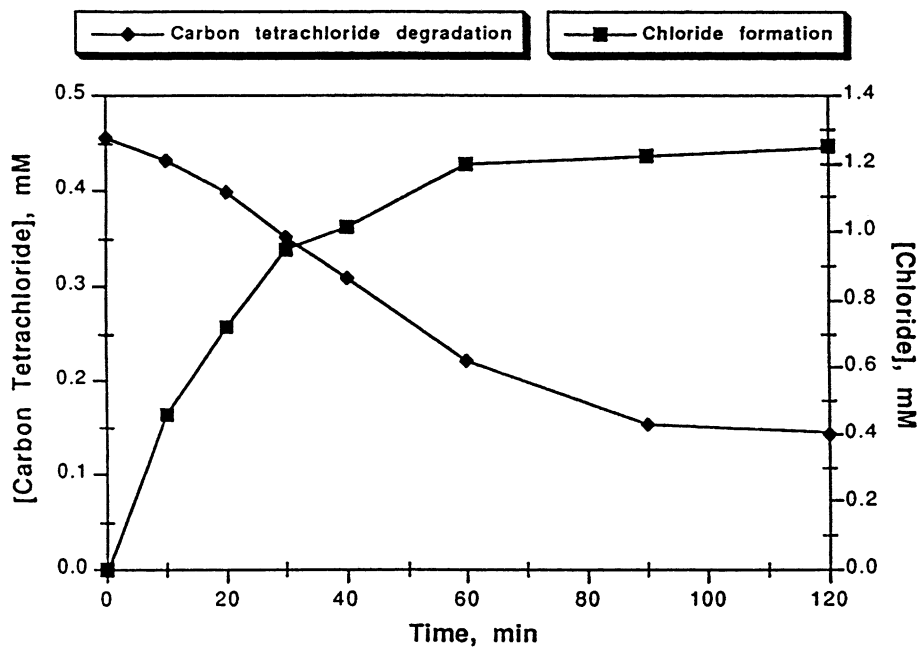
Fig. 2. Verification of carbon tetrachloride degradation in a modified Fenton's system using 295 mM H_2O_2 and 1 mM iron(III).
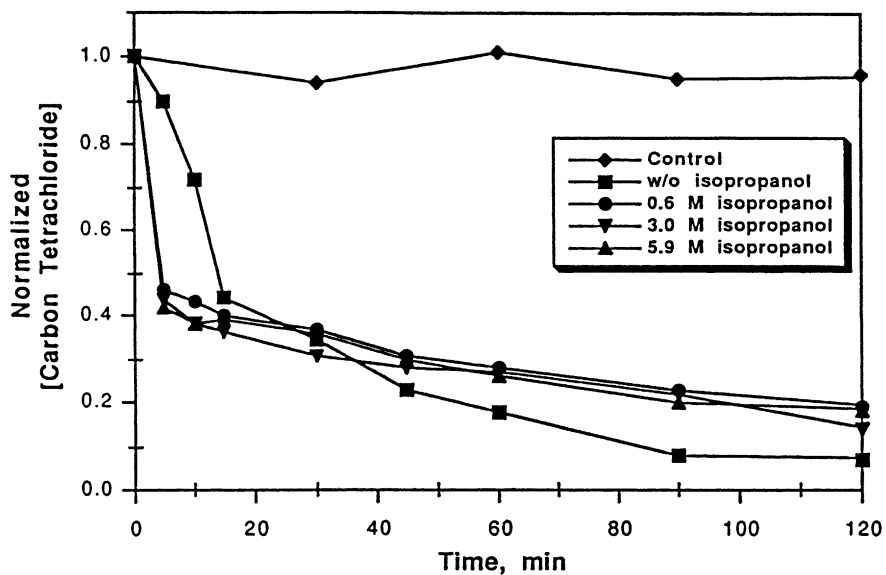

Fig. 3. Effect of the hydroxyl radical scavenger isopropanol on carbon tetrachloride degradation in a modified Fenton's reaction using 590 mM H_2O_2 and 1 mM iron(III).
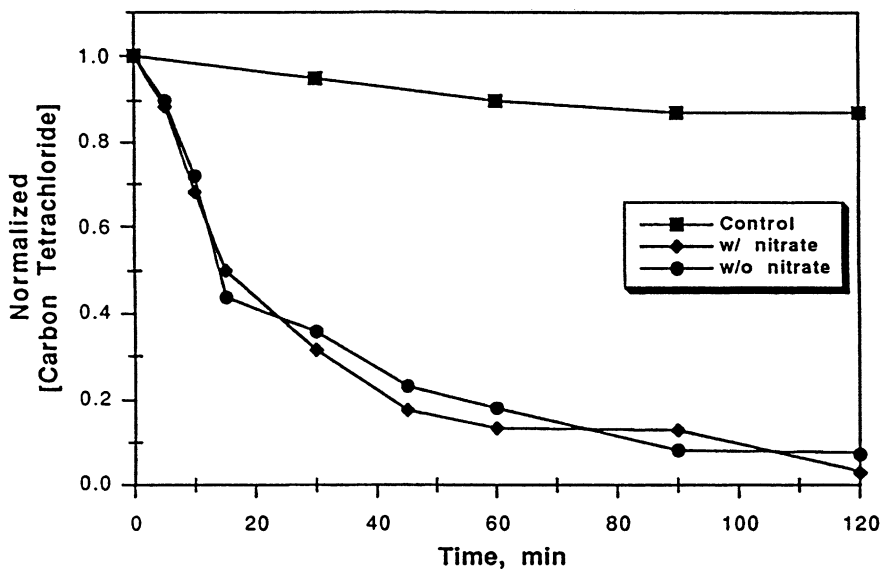
Fig. 4. Effect of the solvated electron scavenger nitrate on carbon tetrachloride degradation in a modified Fenton's reaction using 590 mM H_2O_2 and 1 mM iron(III).

($k_e = 9.7 \times 10^9 \, M^{-1} \, s^{-1}$) [20] and chloroform as a scavenger of other reductive species [16]. The results of nitrate scavenging are shown in Fig. 4. Nitrate addition did not scavenge reductants in the Fenton's system, indicating that solvated electrons are not a likely source of reductants in modified Fenton's systems. Hasan et al. [23] proposed a reductive pathway in the manganese dioxide-catalyzed decomposition of hydrogen peroxide in which hydrogen peroxide decomposed to oxygen, water, and a solvated electron. However, the results of Fig. 4 suggest that such a reaction is not occurring in the iron-catalyzed Fenton's system used in this study.

The results of Fenton's reactions scavenged by excess chloroform are shown in Fig. 5. Excess chloroform stopped CT degradation by scavenging the reductive species. These results suggest that the reductant is a transient oxygen species that can be scavenged by high concentrations of chloroform, which is likely superoxide anion. Although chloroform reacts somewhat slowly with superoxide ($k = 2 \, M^{-1} \, s^{-1}$) [24], in these reactions chloroform was present in such excess (2000-fold) that superoxide reaction with chloroform was likely favored over the reaction with CT.

To lend support to the proposed mechanism of superoxide as the reductant, modified Fenton's reactions were repeated at pH 2, 2.5, and 3 (Fig. 6). Over the 2 h reaction time CT was degraded by 50% at pH 3.0, 40% at pH 2.5, and 10% at pH 2.0. Superoxide is a weak acid with a pK_a of 4.8 and, therefore, concentrations of superoxide are greater at pH 3 compared to pH 2.5 and 2.0. The acidic form of superoxide, perhydroxyl radical ($HO_2^\bullet$), is not a reductant and is only a weak oxidant [25], so its role in CT transformations is negligible. The data of Fig. 6 are consistent with a superoxide mechanism in that a higher rate of CT transformation occurs at higher pH. A similar trend was noted by Hoigne' et al.
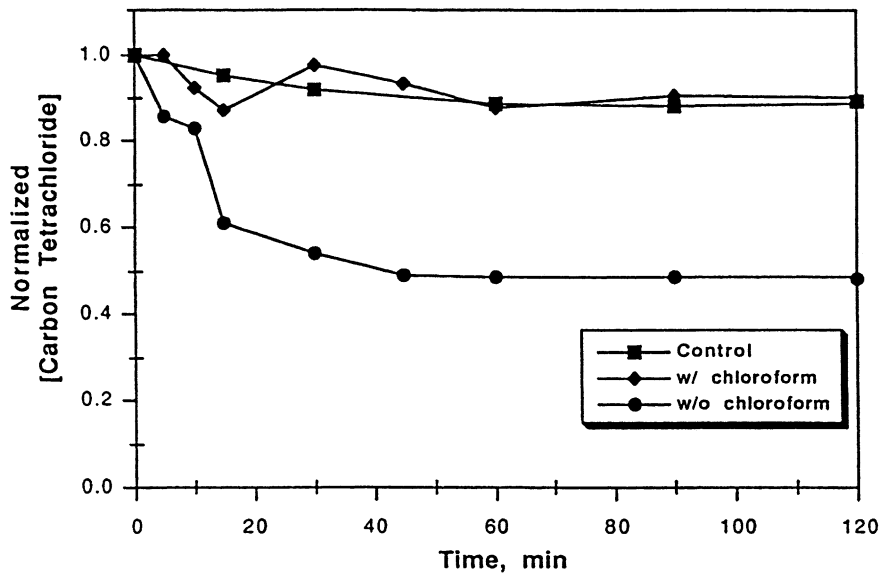
Fig. 5. Effect of the reductant scavenger chloroform on carbon tetrachloride degradation in a modified Fenton's reaction using 200 mM H_2O_2 and 1 mM iron(III).
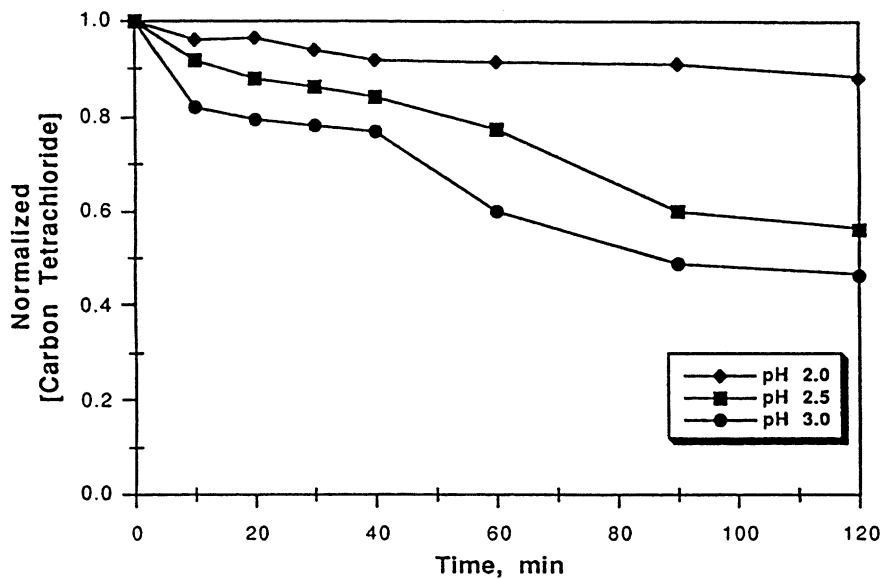

Fig. 6. Effect of pH on carbon tetrachloride degradation in a modified Fenton's reaction using 200 mM H_2O_2 and 1 mM iron(III).
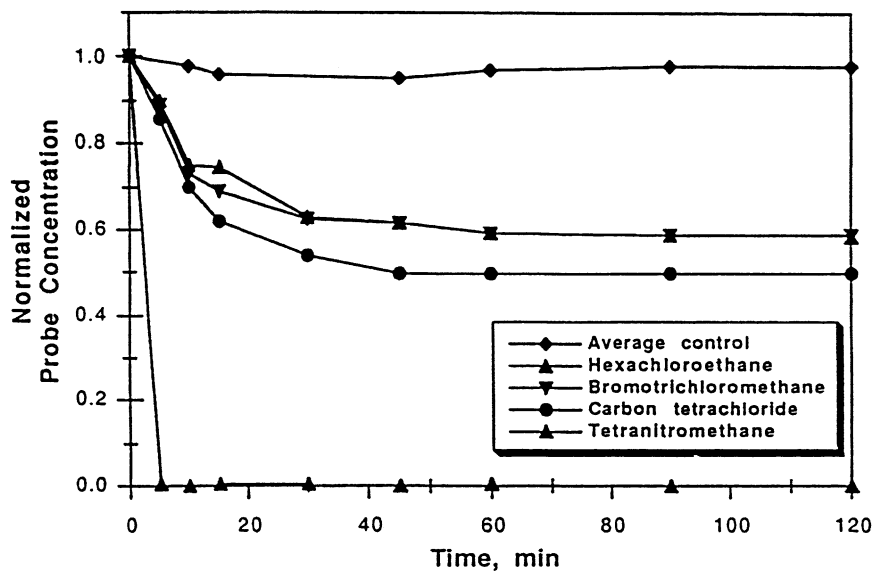
Fig. 7. Degradation of four oxidized organic compounds in a modified Fenton's reaction using 200 mM H_2O_2 and 1 mM iron(III).

[26] in describing the proposed mechanism of ozone decomposition by hydroperoxide anion in in H_2O_2/ozone systems.

The results of Fenton-like degradation of other oxidized organic compounds are shown in Fig. 7. Hexachloroethane, bromotrichloromethane, and tetranitromethane were also degraded by modified Fenton's reactions, although they exhibit low reactivities with OH$^\bullet$, as evidenced by no loss in a standard Fenton's reaction that only generates OH$^\bullet$ [20]. The results of Fig. 7 suggest that Fenton-like reductions could have widespread applications for many oxidized compounds, and provide more uses than previously thought for hazardous waste treatment and remediation.

The results of this research have shown that CT, a toxic and biorefractory contaminant commonly found in contaminated groundwater, is transformed by modified Fenton's reactions. Similar results were found for other highly oxidized organic compounds. Carbon tetrachloride is nonreactive with hydroxyl radicals; therefore, its transformation is mediated by a non-hydroxyl radical reductive species, which is likely superoxide anion. These results are in agreement with the findings of Watts et al. [16] who found a reductive mechanism in Fenton-like reactions. The generation of reductants makes modified Fenton's reactions an even more valuable process than previously thought. To date, hydroxyl radicals were considered to be solely responsible for transformations in Fenton-like reactions. However, the use of modified Fenton's reactions for the treatment of sorbed contaminants in soils and groundwater has provided results not consistent with oxidation by hydroxyl radicals. Sedlak and Andren [27] demonstrated that hydroxyl radicals are incapable of oxidizing sorbed contaminants. Therefore, the enhanced treatment of sorbed contaminants may be due the presence of other transient oxygen species, such as superoxide or hydroperoxide [16]. In

addition, these other transient oxygen species have the potential to promote the mineralization of degradation products that are resistant to oxidation by hydroxyl radicals [28]. In summary, modified Fenton's reagent, because it contains a mixture of oxidants, reductants, and desorbing agents, may provide a universal treatment matrix for soils, groundwater, and other contaminated environmental media.

4. Conclusions

The degradation of CT by modified Fenton's reagent was investigated combined with the use of a series of scavengers to evaluate the degradation pathway. Carbon tetrachloride degradation was a function of initial H_2O_2 concentration in the Fenton's system, suggesting that a species formed in Fenton's propagation reactions is responsible for CT degradation. No scavenging was found when excess nitrate was added to the reaction, indicating that solvated electrons are not responsible for the transformation of CT. However, the reactive species was scavenged by chloroform, which suggests that a reductant, such as superoxide is the species that reduces CT in Fenton's systems. The results were applied to three other oxidized organic compounds: hexachloroethane, bromotrichloromethane, and tetranitromethane. These species were also transformed by modified Fenton's reagent, with the most oxidized contaminants proceeding at the fastest rates. The results of this research show that modified Fenton's reagent not only oxidizes many contaminants, but also reduces halo- and nitro-substituted alkanes, making modified Fenton's reagent a versatile remediation process.

Acknowledgements

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