This is to certify that the

thesis entitled

Degradation of Dimethylsilanediol and Polydimethylsiloxane in water and soil by Fenton's Reaction

presented by

Hristina Gueneva-Boucheva

has been accepted towards fulfillment
of the requirements for

MS degree in Crop and Soil Sciences

Stephen A. Boyd
Major professor

Date May 10, 1999

DEGRADATION OF POLYDIMETHYLSILOXANE AND DIMETHYLSILANEDIOL IN WATER AND SOIL BY FENTON REAGENT

By

Hristina Gueneva-Boucheva

A THESIS

Submitted to
Michigan State University
in partial fulfillment of the requirements
for the degree of

MASTER OF SCIENCES

Department of Crop and Soil Science

1999

ABSTRACT

DEGRADATION OF POLYDIMETHYLSILOXANES AND DIMETHYLSILANEDIOL IN WATER AND SOIL BY FENTON'S REACTION

By

Hristina Gueneva-Boucheva

Silicones fluids consist of polydimethylsiloxanes (PDMS) and are widely used in industrial and consumer products and enter the environment as components of municipal sludges applied to the land, or through accidental spills. PDMS derivatives are thought to be extremely resistant to degradation under ambient environmental conditions. Previous studies have shown that in soil PDMS degrades to dimethylsilanediol (DMSD) depending on the environmental conditions. Fenton's reagent, in which the decomposition of hydrogen peroxide is catalyzed by iron (II) to form hydroxyl radicals, has recently been applied to remediation of contaminated soils and wastewaters. Here for the first time the Fenton reaction was used as a simple and rapid method for PDMS and DMSD mineralization in water and soil. This reaction successfully breakdown the PDMS and DMSD at a laboratory conditions. The efficiency of the Fenton reagent to destroy DMSD was affected by initial H_2O_2, iron and DMSD concentrations as well as the oxidation state of the iron catalysts and iron counterions.

ACKNOWLEDGEMENTS

My research advisor for the past three years has been Professor Stephen Boyd. I have benefited greatly from his considerable abilities as a scientist and a teacher. I thank him for his support and guidance during the course of this work.

I also wish to thank Dr. Yucheng Feng who devoted much of her time to getting me started on my research and for her continuous help and willingness to tech me about soil sciences and perfect analytical practices.

This work was supported by Dow Corning Inc., Midland, MI

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

INTRODUCTION

CHAPTER I

CHAPTER II

INTRODUCTION

Silicone is used in a broad range of food, medical, personal care and household applications. It enters the environment mainly through land disposal of wastewater treatment plants sludges. Although uncommon, accidental spills or improper usage of silicones could contrubute to contamination of soils and waters. With this in mind it is prudent to explore the environmental fate of silicone products and possible ways to manage accidental releases of silicones.

Fenton's reagent has been applied to the remediation of contaminated soil (1) and wastewater (2). The term Fenton reagent or Fenton reaction is used to describe an iron (II)/hydrogen peroxide system. Fenton's reagent produces hydroxyl radical ($OH^{\bullet}$) by the following reaction:

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

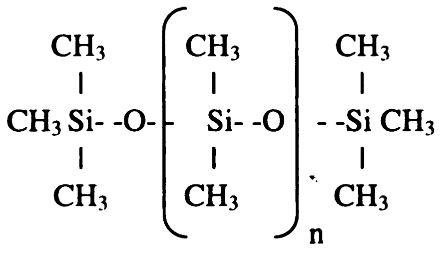
Hydroxyl radicals are powerful oxidizing agents. Fenton's reagent has been used to oxidize recalcitrant organic compounds such as PCBs (3), benzene, chlorobenzene (4), diesel fuel (5), 2,4-D (6) and pyridine (7).

Silicone polymers have high chemical and biological stability. There are no previously reported attempts to mineralize polymeric compound such as polydimethylsiloxane (PDMS; also refered to as silicone) or its monomer dimethylsilenediol (DMSD) by Fenton's reagent. If successful, the use of Fenton's reagent to decompose PDMS or DMSD could be applied to contaminated waters. There is also the potential for utilizing Fenton's reagent to remediate soil contaminated with PDMS or DMSD. Iron is not generally a limiting factor for the reaction to occur in soil, however hydrogen peroxide would need to be added. The objective of this project was to determine whether and to what extent Fe/H_2O_2 oxidation of PDMS and DMSD can occur in water and soil.

Terminology

The term "silicone" is not used consistently. It is sometimes employed generically to designate all monomeric and polymeric organosilicon compounds containing Si-C bonds, and other times as a collective term for organosilicon polymers of all types (8). It is also used strictlly to describe organosilicone polymers containing Si-O-Si bonds. This usage will be adopted herein. Silicones occupy an intermediate position between organic and inorganic compounds, and in particular between silicates and organic polymers. Few chemical compounds are capable of so many applications as the silicones. The 1991 domestic consumption of silicone fluids was estimated at 155-160 million pounds (9). They are produced as oils, greases, resins and rubbers. They are used as engineering materials in the construction of machines and other apparatus, as hydraulic fluids or heat transfer media, as water-repellent agents in the textile and leather industry. The silicones are purportedly physiologically inert so they have also been used widely as auxiliaries in medicine, pharmacy and cosmetics.

Polydimethylsiloxane (PDMS) is a part of a group of man-made organosilicone compounds that range from low molecular weight volatile materials to high molecular weight solids. The focus of this study is nonvolatile polymeric PDMS represented by the generic formula:



$$CH_3\underset{CH_3}{\overset{CH_3}{Si}}-O-\left[\underset{CH_3}{\overset{CH_3}{Si}}-O\right]_n-\underset{CH_3}{\overset{CH_3}{Si}}CH_3$$

where n may vary from 10 to > 10 000.

PDMS has very low water solubility. The water solubility of trimethylsilyl capped oliogomers, from the dimer to the pentamer, has been measured recently (10). Solubility of the linear oligomers dropped from 930 ppb for the dimer to only 0.07 ppb for the linear pentamer. Since the log of solubility was found to decrease linearly with increasing molecular weight, the authors concluded that there is "an essential absence of any ecologically significant water solubility for the conventional higher molecular weight PDMS of commerce".

Environmental occurrence of PDMS

PDMS is used in a broad range of food, medical, personal care and household applications (8). Its annual production is steadily increasing. These facts led to developing concern over its potential adverse ecological impact due mainly to the following facts: (1) PDMS fluids are essentially non reactive, except when catalyzed by strong acids and bases; (2) PDMS based elastomers are uniquely resistant to weathering (i.e. hydrolysis and oxidation); (3) no evidence has been found for biodegradation of these polymeric fluids. In many of its applications, PDMS is disposed into wastewater treatment system and has the potential to enter the environment as a component of effluents and sludges from wastewater treatment plants.

The PDMS sorption constants (Kd) reported for a series of seven surface soils were average 4,900±1,250 L/kg. The corresponding organic carbon matter normalized sorption constants (Koc) were 590,000±510,000 L/kg (12). The small siloxanes and water soluble silanols probably influence these values. Sorption constants for the large polymers, which constitutes the majority of PDMS are probably much higher. A Koc of 590,000 means that PDMS is essentially immobile in soil.

A review of the environmental fate and ecological impact of organosilicon materials suggested that they do not appear today to present any demonstrable ecological threat (11). Studies of methylsiloxanes indicated that PDMS did not bioaccumulate or exhibit significant environmental toxicity. Furthermore PDMS in sludge amended topsoil present at concentrations of between 290 - 3500 mg/kg appeared to have no effect on (1) seed germination or seedling survival, (2) cumulative loss of nitrate, (3) immature shoots, mature shoots, mature grain/seeds or total biomass, and (4) number of soil microorganisms including bacteria, fungi and actinomycetes. The quantity and timing of sludge amendment, however, may affect loss of nitrate in leachates and soybean yields (4).

Polyimethylsiloxane that enters wastewater treatment systems is expected to be removed primarily by sorption to sludge solids given to its very low water solubility (13, 14). PDMS is expected to remain unchanged during wastewater treatment because of its chemical and thermal stability (13). PDMS, not removed on sludge solids, will be present in wastewater treatment effluent as a component of the suspended solids. It could be deposited in sediments downstream of the facility. Most municipal sewage sludge today is landfilled, incinerated, or applied to soil as fertilizer (Fig.l). Incineration converts PDMS to water, CO_2 and Si. The predominant pathway of PDMS entry into the environment is expected to be as a component of sludge added to the soil.

The earliest work of Bush et al. (16) indicated that PDMS fluids in many soils undergo siloxane bond redistribution and hydrolysis, resulting in the formation of low molecular weight cyclic and linear oligomers. Clays were shown to be the catalytic soil component responsible for the above oligomerization and hydrolysis. In the absence of clay minarals, PDMS is stable under mild environmental conditions (e.g., at ambient temperature, pH 5-9, lack of strong oxidants). Once in contact with clay minerals, it does degrade via the general pathway:

$Me_3SiO(SiMe_2O)_nSiMe_3(PDMS) \rightarrow \text{polymeric residue} \rightarrow mHO(SiMe_2O)_xH + 2Me_3SiOH$

where Me is the methyl group; $n>100$; $m<n-3x$; with $x=1-3$, mainly 1.

The activity of all types of clays as catalysts for PDMS dagradation was shown to be inversely related to the level of clay hydration. Furthermore, in the presence of montrillonite attack was preferentially upon trimethylsilicone sites, leading primarily to linear oligomerization, whereas kaolinite led predominantly to cyclic oligomers. These results suggested the half-life of PDMS in soil could range from several minutes to weeks or substantially longer. Relatively moist or wet soils exhibited significantly less catalytic rearrangement activity.

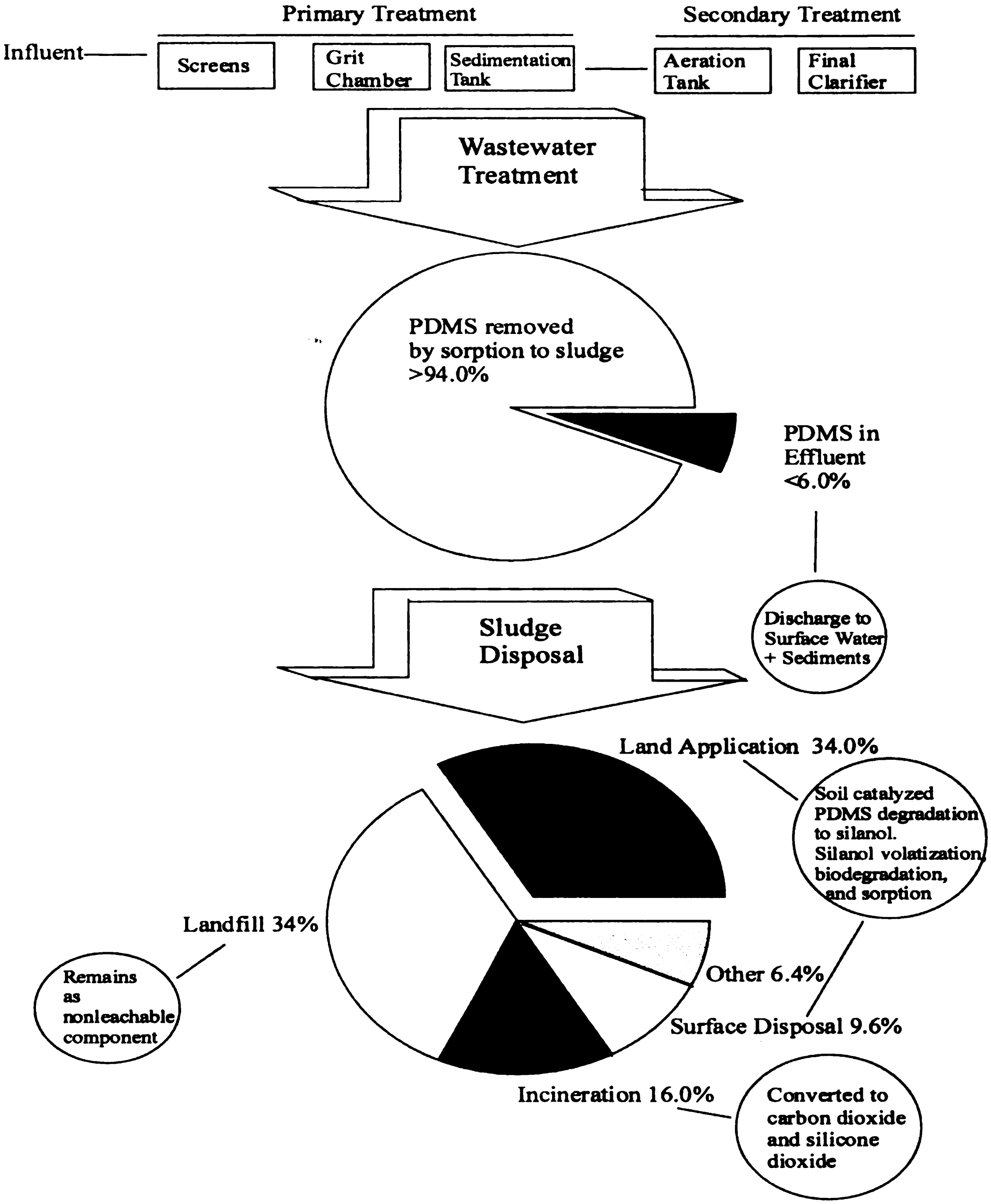


Figure 1. Overview of PDMS environmental mass flow as a result of wastewater treatment practices. Fraction of sludge disposed by various techniques. Obtained from EPA survey (15).

Similar results were shown by Xu (17) in a study aimed at investigating the ability of 12 different Ca-saturated clay minerals to catalyze the degradation of PDMS. Kaolinite, beidellite and nontronite were most effective with 70-80% of the PDMS hydrolyzed to DMSD within 24 hours. The variation in PDMS degradation rates among Ca-saturated clays was thought to be due to the differences in the clay particle surface areas, surface Bronsted and Lewis acidities and soil moisture. Higher surface area provided higher rates and extents of PDMS degradation. In a related study, Xu (18) observed a 50% to 120 fold increase in hydrolysis when the exchangeable cations were changed from Na^+ to Ca^{2+} or Al^{3+}. Increasing the relative humidity from 32-100% significantly decreased degradation of PDMS and led to the formation of volatile dimethyl cyclic compounds such as oxtamethylcyclotetrasiloxane (D4). The suggested mechanism of degradation, regardless of humidity, was via both random scission and end cutting. These studies indicated that PDMS rearrangement products partition largely to the atmosphere. Approximately 10 to 25 % of the original PDMS may partition to waterways as short chain siloxanols. However, soil composition and hydration have a marked influence on the amount and distribution of the rearrangement products.

Recent work by Lehmann et al. (12, 19) has shown that once ^{14}C-PDMS is introduced into the soil environment, it can undergo extensive chemical hydrolysis to low molecular weight water soluble products. Gas chromatography-mass spectrometry identified the main product in all soils as dimethylsilane-l,1-diol (DMSD). Other small silanols and cyclic siloxanes were either not detected or were present in only trace amounts. No volatile ^{14}C was captured by plugs of activated carbon on a polyester support, and quantitative recovery of ^{14}C showed no loss of unidentified volatiles. The breakdown of PDMS was much more rapid under dry conditions, i.e. when soil moisture content dropped below 5%. Carpenter et al. (14) demonstrated that within 4-6 weeks more than half of the initially spiked silicone was converted to a water-soluble fraction containing mostly DMSD.

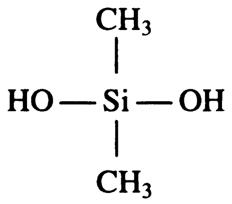
Although sludge can be incorporated to 20-30 cm depths, PDMS will only hydrolyze extensively to DMSD in the top few cm, where soil drying is most likely. PDMS hydrolysis at lower depths will occur more gradually because of higher soil moisture (21). A similar transformation that occurs at a much slower rate has also been observed in sediments (22).

An extensive monitoring program was conducted to determine the occurrence of PDMS in environments impacted by waste disposal practices (23). Eight wastewater treatment plants in North America were monitored to determine PDMS removal during wastewater treatment. Surface waters, sediments, and sludge-amended soils were also monitored for a complete assessment of the environmental fate of PDMS. PDMS sludge concentrations reported were in the range of 290-5155 mg/kg and varied as a function of influent concentration and sludge processing method. PDMS was found to be efficiently removed from water during the wastewater treatment process (Figure 1). Sediment levels of <6mg/kg were measured near the outfall of the wastewater treatment plants. Measured concentrations of sludge amended soils ranged from <0.41 to 10.4 mg/kg and were lower than expected in most cases based on calculated PDMS loading via historical sludge applications. The lower than expected PDMS concentration in sludge -amended soil suggests degradation of PDMS in the soil environment to low molecular water extractable fractions. According to all these studies, accumulation of PDMS is not likely to occur in soils. Rather, the fate of silicones may ultimately depend on the environmental fate of DMSD.

Rapid degradation of a water soluble mixture of oligomeric dimethylsiloxanes by sun light in the presence of environmentally relevant levels of nitrates was reported (24). Silicate was demonstrated to be the final photodegradation product of these water soluble siloxanes. When an aqueous emulsion of high molecular weight PDMS was irradiated in the presence of the nitrate ion a level of silicate corresponding to 1.7% of the original quantity of PDMS was found after 5 weeks. This was explained to be due to the very low solubility of PDMS and only a monomolecular surface layer of the polymer can react with the hydroxyl radicals formed in the water. Thus droplet formation can be expected in the relatively small irradiation cells resulting in a very small siloxane water interface area.

Environmental fate of DMSD

DMSD has the folloing structure:



$$\mathrm{HO-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{Si}}-OH}$$

The appearance of DMSD in soil represents hydrolysis of the PDMS to its monomeric units. When the reaction of PDMS hydrolysis was investigated in variety of soils having different pH, organic matter contents, textures and mineralogy, DMSD was the sole reaction product (12). The fact that dimer, trimer, and larger siloxanols were not seen is consistent with experiments showing that equilibrium in water favored the monomeric form over the various oligomers (25).

Lehmann et. al. showed that DMSD could biodegrade and volatilize from soil (26). Volatilization of' ^{14}C-DMSD from soil was investigated in open tubes with weekly remoistening (27). The loss of about 30% of the total ^{14}C after seven weeks was assumed to be due to volatilization. A portion of the ^{14}C was also bound to the soil in a form releasable by extraction with 0.1 M HC1. Some of the soil-bond ^{14}C was released by water after weekly remoisturing of the soil. These fractions are thus not irreversibly bound. DMSD was incubated in soils from permanent grass, crop field, deciduous woodland, and pine woodland for 30 weeks at room temperature. After 30 weeks, most of the remaining ^{14}C in the soil was no longer water extractable but was acid and base extractable. These fractions were not formed by microbial means. Incubations with 2% plant litter showed reduced volatilization of the DMSD. In the presence of litter, incubation with a microbial inhibitor resulted in less DMSD degradation. The cold storage of soils almost completely stopped degradation, meaning that little transformation of DMSD was expected during the colder months. DMSD is more likely to volatilize from sandy than from clayey soils.

DMDS was found to be biodegradable in soils from residential gardens and sludge disposal areas (28). The fungus *Fusarium oxysporum* Schlechtendahl, and a bacterium, an *Arthrobacter* species, were isolated from two different soils and both microorganisms were able to cometabolize ^{14}C-DMSD to $^{14}CO_2$. Active cultures of *F. oxysporum* Schlecht. converted 19% of ^{14}C-DMSD to $^{14}CO_2$ after 240 days and cultures of the *Arthrobacter* sp. converted more than 10% of it after 90 days.

After DMSD volatilizes into the atmosphere, it should undergo oxidation of its methyl groups by reaction with sunlight-induced hydroxyl radicals in the air (in a similar fashion to other volatile siloxanes) (29, 30). If the compound is washed out of the air in rainfall, it may be oxidized in water by photolytic demethylation (2, 31), or it could be microbially oxidized in soil (27). In either event, expected degradation products of DMSD are CO_2 and silicic acid. The latter will precipitate to form amorphous soil minerals (32).

Fenton chemistry

In April 1876, Henry John Fenton (then an undergraduate at Chist's College, Cambridge, England) wrote a letter to the editor of Chemical News (33) reporting a reaction between ferrous sulfate, hydrogen peroxide (H_2O_2) and tartaric acid. The purpose of the letter was to describe a color test for tartaric acid. Later it became evident that this mixture, called Fenton reagent, was an effective oxidation agent for various organic compounds. Fenton's first report (33) and his full paper (34) demonstrated three key features of what we now term "Fenton Chemistry": (1) an oxidant (2) a reduced form of a heavy metal (in this case iron); and (3) a higher oxidation state of iron involved as an intermediate. The reaction is believed to proceed as follows:

$$\mathrm{Fe\ (II)} + H_2O_2 \rightarrow \mathrm{Fe\ (III)} + {}^{\cdot}OH + OH^{-0} \qquad (1)$$

A few years after Fenton's death in 1929, Haber, at al. (35) proposed the involvement of hydroxyl radical in the iron-catalyzed decomposition of hydrogen peroxide: They proposed the following scheme:

$${}^{\cdot}OH + H_2O_2 \rightarrow HOO^{\cdot}{}_2 + H_2 \qquad (2)$$

$$HOO^{\cdot} + H_2O_2 \rightarrow O_2 + {}^{\cdot}OH + H_2 \qquad (3)$$

$$HOO^{\cdot} \Leftrightarrow H^+ + O^{\cdot}{}_2 \qquad (4)$$

often described as the "Haber-Weiss" reactions. Equation (3) is thus the potential source of $^{\cdot}OH$ from superoxide/peroxide in the absence of metals. The superoxide radical $HO^{\cdot}_2$ is known to have lower oxidation capability compared to the hydroxyl radical.

Barb et. al. (36) later studied the decomposition of hydrogen peroxide catalyzed by ferrous and ferric ions and modified the original Haber-Weiss mechanism in the following way:

Initiation: $Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HOO^{\cdot} + H^+$ (5)

Propagation: $Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\cdot}OH + OH^-$ (6)

$^{\cdot}OH + H_2O_2 \rightarrow H_2O + HOO^{\cdot}$ (7)

$HOO^{\cdot} + Fe^{3+} \rightarrow Fe^{2+} + H^+ + O_2$ (8)

Termination: $HOO^{\cdot} + Fe^{2+} \rightarrow HOO^- + Fe^{3+}$ (9)

$^{\cdot}OH + Fe^{2+} \rightarrow HO^- + Fe^{3+}$ (10)

An important finding was that the oxidation effects of Fenton reagent strongly depended on the concentration ratio of H_2O_2 and Fe^{2+}. If an organic compound is present in the system, the reaction includes two more steps:

$RH + {}^{\cdot}OH \rightarrow H_2O + R$ (11)

$R^{\cdot} + Fe^{3+} \rightarrow Fe^{2+} + \text{products}$ (12)

The parallel application of H_2O_2 photolysis and Fenton reaction has lead to the substantial improvement in efficiency of the pollution degradation. In the Fenton reaction, Fe^{3+} ions are accumulated in the system and, after the Fe^{2+} ions are exhausted, the reaction terminates. To avoid this problem, the photochemical regeneration of ferrous ions by photoreduction of ferric ions was proposed. It has been known for a long time that the photochemical irradiation of ferric species leads to their reduction (37). The following reaction proceeds in water solution:

$$Fe^{3+} + H_2O + hv \rightarrow Fe^{2+} + HO^{\cdot} + H^+$$

It was further ascertained that Fe (III) ions accelerate the photodecomposition of hydrogen peroxide, thus catalyzing more efficiently the photochemical oxidation of different compounds.

Application of the Fenton reaction

Recently, considerable interest has developed in utilizing of the Fenton reaction for environmental remediation. Numerous transformation reactions take place in the environment. In natural waters exposed to solar radiation, reactive intermediates are formed which than take part in photo-oxidation reactions. They are known to be primary sources of photochemical self cleaning of the atmosphere and aquatic environment (38). The extent to which the Fenton reaction occurs in natural waters depends on the concentrations of Fe^{2+}, Fe^{3+}, Cu^{2+} and H_2O_2. This chemistry has recently been applied to the destruction of environmental pollutants (39, 2).

The aim of these reactions is to attain complete mineralization of the contaminants to innocuous end-products such as CO_2 and water. The extent of mineralization via Fenton's reaction can be measured by the final value of COD (chemical oxygen demand) or TOC (total organic carbon). Systems generating hydroxyl radicals are among the most efficient ones used for destruction of pollutants due to the high reactivity of the radical species.

Utilization of the Fenton reaction in water treatment

A growing number of published papers in this field demonstrate the suitability of the application of the Fenton reaction in water treatment. The use of the Fenton reagent is advantageous over some other treatment procedures mainly because H_2O_2 decomposes to harmless substances. Also only catalytic amounts of Fe^{2+} are used in the reaction and the equipment needed for this treatment process is technically simple. Another advantage of this process is that reactive hydroxyl radicals generated in the Fenton reaction can mineralize recalcitrant pollutants. It was found (40) that the reaction yield strongly depends on pH. At low pH, $Fe(OH)^+$ intermediate contributed to additional formation of hydroxyl radicals. The reaction rate drops off sharply above and below the optimum pH of about 2.8. At higher pH the loss of reactivity is due to precipitation of Fe (III) as hydrous oxyhydroxide, $Fe_2O_3.n\ H_2O$

The Fenton reaction is most often used either in the pretreatment of waters with a high value of COD prior to biological treatment or in the mineralization of toxic or difficult to degrade pollutants. Heavily polluted and biologically harmful wastewater from pharmaceutical industry was successfully pretreated in this fashion for biological treatment. The total effect of the pretreatment was 92-95% decomposition, in contrast to the conventional processes used (36). The Fenton reagent is frequently used for the degradation of chlorinated organic pollutants. Koyoma et al. investigated the degradation of 10 chlorinated aromatic compounds (39). The Fenton reaction was applied in the first stage of degradation process followed by methanogenic fermentation using anaerobically digested sludges. The results indicated that the chlorinated aromatic compounds were degraded completely after Fenton reaction and some of them were even mineralized.

Oxalic and formic acids were isolated as the main semiproducts of the oxidation. Application of the Fenton reaction in the degradation of nitrobenzene and nitrophenols was also investigated (41). The Fenton reaction was much more efficient in the degradation of these compounds than photolysis in the presence of H_2O_2. 2,4-dinitrotoluene was completely mineralized within 5 hours at molar ratio 2,4-dinitrotoluene:H_2O_2 : Fe^{2+} of 1:20:2.5 (2).

The efficacy of the Fenton reaction is substantially improved in the photo Fenton reaction. This consists of the parallel application of classical Fenton reaction and photolysis. Presently the photo Fenton reaction is used more often in water treatment processes. Sun and Pignatello (3) compared the efficiencies of the Fenton and photo Fenton reactions in the degradation of 2,4-dichloroacetic acid (2,4-D) and 2,4,5-trichloroacetic acid (2,4,5-T). They showed that the classical Fenton reaction catalyzed by Fe^{2+} was more efficient than the reaction catalyzed by Fe^{3+} ions. Application of radiation at wavelengths above 300 nm significantly increased the rate of mineralization. The consumption of H_2O_2 was reduced in this process to 5 mol peroxide per 1 mol herbicide. Photo-Fenton reaction was also used for mineralization of 4-chlorophenol in water (42). The authors suggested that the applied radiation (320) nm substantially accelerated the degradation of 4-chlorophenol in the presence of H_2O_2 and Fe^{2+}. It was stressed that an advantage of photo-Fenton reaction was the small amount of iron used as a catalyst and the low loading of the treated water. Pignatello et al. (43) reported successful degradation of the commercial PCB mixture Arochlor 1242 in acidified water at 66°C. Up to 88% PCB removal and 85% dechlorination were obtained. Perfluorinated surfactants added to increase PCB solubility or rates of dissolution had a detrimental effect on degradation. Minimal reaction was observed at room temperature owning to the low water solubility of PCBs and lower rate of generation of hydroxyl radicals.

Fenton's reaction has been shown to be temperature dependent. Two studies performed to follow the effect of temperature on the degradation of methyl parathion (44) and 2,4-dinitrotoluene (2) showed that the loss of the compounds increased from about 20% at 10°C to about 90% at 35°C, with no further improvement up to 60°C.

Recently, Rabek et al. reported a project aimed to implement Fenton and photo-Fenton reaction for destroying water-soluble polymers like poly (acrylic acid) and poly (ethylene dioxide) (45). The results showed that the process is completed in 15 to 30 min. In the presence of dissolved oxygen a chain scission reaction occurred with a concurrent decrease in solution viscosity.

Utilization of the Fenton reaction in soil treatment

Contaminants in soils are often sorbed or present as nonaqueous phase liquids. This can have significant impact on the effectiveness of Fenton's process chemistry. Watts et al. (46) first reported the use of a Fenton-like reaction for soil remediation and showed that pentachlorophenol in silica sand slurry was destroyed at pH 2-3. They confirmed that when high concentrations of H_2O_2 were used for soil remediation, soluble iron concentrations decline rapidly over first 30 minutes of the reaction with subsequent formation of an amorphous floc over the following three hours. In a separate study Fenton's reagent was used to oxidize pentachlorophenol, trifluralin, hexadecane, and dieldrin in soils, and it was found that iron oxyhydroxides effectively catalyzed

Fenton-like reactions (47). The most effective oxidation of soluble pentachlorophenol in silica sand was catalyzed by naturally occurring iron oxyhydroxides, however sorbed pentachlorophenol was not oxidized with goethite as the only Fenton's catalyst (5). These results suggest that naturally occurring iron oxyhydroxides can serve as effective Fenton catalysts. A possible mechanism for mineral catalyzed Fenton's reaction has been proposed by Kitajima et al. (48):

$$H_2O_2 + S \rightarrow S^+ + {}^{\cdot}OH + OH^-,$$

where S is the mineral surface and S^+ is an oxidized region on the mineral. These heterogeneous mineral catalysts are effective because they provide consistent rates of hydroxyl radical generation when high concentration of H_2O_2 are used.

In most of the soil remediation studies using Fenton's reaction, the soil pH was adjusted to about 3.0 with 0.1 N H_2SO_4 to reach the effective pH range (1). Acidification of the soil to the proper pH however is cumbersome and may preclude or severely restrict implementation of the Fenton's reaction for in situ treatment. Moreover acidification and subsequent neutralization will add two additional steps to any scheme. In order to avoid this Sun and Pignatello (40) tested a number of structurally diverse organic and inorganic polydentate chelators for their ability to solubilize Fe (III) at pH 6.0 and catalyze oxidation of 2,4-D in aerated aqueous solutions. Most of the compounds tested that contained organic ligands, formed soluble Fe (III) and were capable of oxidizing 2,4-D in periods from minutes to less than 5 hours. All active organic ligands were themselves oxidized, but in many cases the resulting iron complexes remained soluble and reactive. From a practical perspective, degradation of the ligands may be viewed as advantageous because provided iron remains soluble and catalytically active long enough to carry out degradation.

Iron complexes have also been shown to catalyze the Fenton-like oxidation of pesticides. The primary advantage of the iron complexes is the potential for effective generation of hydroxyl radical at near-neutral pH. Pignatello and Day (44) screened several iron (III) complexes for their potential to promote the oxidation of pesticides by Fenton-like reactions. Nitrilotriacetic acid, tetraxydroxy-1,4-quinone and hexaketocyclohexane were among the most effective ligands evaluated. Watts et al. (47) treated diesel-contaminated soils with H_2O_2 and six iron compounds and naturally occurring minerals. Iron (II) compounds were less effective catalysts than iron (III) species owing to the initial loss of H_2O_2 in oxidizing iron (II) to iron (III). The most effective iron salt catalysts were:

$$C1O_4^- = NO_3^- > SO_4^{2-} > PO_4^-.$$

Watts et al. (49) applied Fenton chemistry to decompose pentachlorophenol in soils. They used H_2O_2 concentrations ranging from 3 to 300 mM and iron (II) sulfate as a catalyst rather than natural occurring iron oxyhydroxides. Oxidation of sorbed to soil pentachlorophenol was effective at H_2O_2 concentrations as low as 30 mM if catalysts were presented as soluble iron rather than natural iron oxyhydroxides. Because of the high relative concentration of the iron mineral catalysts in a slurry with a low volume ratio of liquid to soil, H_2O_2 decomposition was rapid (i.e., < 8 h.). Therefore, the use of soluble iron to catalyze the Fenton-like oxidation of sorbed contaminants may provide more economical and effective process conditions.

REFERENCES

1. Spencer, C.J., P.C. Staton, R.J. Watts, *A central composite rotatable analysis for the catalized hydrogen peroxide remediation of diesel contaminated soils*, J.Air Waste Manage.Assoc., 46:1067, 1996

2. Mohanty, N.R., I.W.Weil, *Oxidation of 2,4-Dinitrotoluene using Fenton's reagent. Reaction mechnisms and their practical applications.*, Haz.Waste Haz. Mater., 10:171, 1993

3. Sun, Y., J.J. Pignatello, *Photochemical reactions involved in the total mineralization of 2,4-D by* $Fe^{3+}/H_2O_2/UV$, Environ.Sci.Technol., 27:304, 1993

4. Tolle, D.A., C.L. Frye, R.G. Lehmann, T.C. Zwick, *Ecological Effects of PDMS augmented sludge amended to agricultural microcosms*, Sci. Total Environ., 162:193-207, 1995

5. Watts, R.J.,M.D.Udel, R.M.Monsen, *Oxidation of pentachlorophenol catalyzed by* H_2O_2 *and naturally occurring iron oxyhydroxides*, Water Environ.Res., 65:893, 1993

6. Barberini, M., C. Minero, E. Pelizzetti, E. Borgarello, N. Serpone, *Chemical degradation of chlorophenols by Fenton's reagent.*, Chmosphere, 16:2225, 1987

7. Watts, R.J., S.E.Dilly, *Evaluation of iron catalysts for the Fenton-like remediation of diesel contaminated soil,* J.Haz.Mater., 51:209, 1996

8. Noll, W., *Chemistry and Technology of Silicones*, Academic Press Inc., New York, NY 10003, 1968

9. Chemical Economics Handbook, SRI International, 1990

10. Varaprath, S.,C.L.Frye, J.Hamelink, *Aqueous solubility of permethylsoloxanes (silicones)*, Environ.Toxicol.Chem., 8:1263, 1996

11. Frye, C.L., *Environmental fate and ecological impact of organosilicon materials: a review*, Sci. Total Environ., 73:17-22, 1988

12. Lehmann, R.G., S.Varaprath, .J.L.Arndt, *Degradation of silicone polymers in a variety of soils,* Environ.Toxicol.Chem., 8:1299, 1995

13. Watts, R.S., S.King, C.S.Haling, L.Gearhart, B.Vigon, Water Res., 29:2405, 1995

14. Lentz, C., *Silicones in the environment*, Ind.Res.Dev., 22:139, 1980

15. Standard for use and disposal of sludge, Fed.Regist., 58:9257, 1993

16. Buch, R.R., D.N.Ingerbrigsten, *Rearragement of Poly(dimethylsiloxane) fluids on soil*, Environ.Sci.Technol., 6:676, 1979

17. Xu, Shihe, R.G. Lehmann, J.R. Miller, G. Chandra, *Degradation of PDMS (Silicones) as influenced by clay minerals,* Environ. Sci. Technol., 32:1199-1206, 1998

18. Xu, Shihe, *Hydrolysis of PDMS (silicone) as catalyzed by clay minerals at two different moistures,* Environ. Sci. Technol., Submitted for publication

19. Lehmann, R.G., S.Varaprath, C.L. Frye, *Degradation of silicone polymers in soil,* Environ.Toxicol.Chem., 7:1061, 1994

20. Carpenter, J.C., J.A.Cella, S.B.Dorn, *Study of degradation of PDMS on soil,* Environ.Sci. Technol., 29:864, 1995

21. Lehmann, R.G., C.L.Frye, D.A. Tolle, T.C.Zwick, *Fate of sludge-applied silicones in agricultural soil microcosms*, Water,Air Soil Poll., 83:1, 1995

22. Dorn, S.B., S.Frame, *Development of high-performance liquid chromatographic-inductively coupled plasma method for speciation and quantification of silicones: from silanols to polysiloxanes*, Analyst, 119:1687, 1994

23. Fendinger, N.J., D.C.McAvoy, W.S.Eckhoff, B.B.Price, *Environmental occurance of PDMS*, Environ.Sci.Technol., 31:1555,1997

24. Buch, R.R., T.H.Lane, R.B.Annelin, C.L.Frye, *Photolytic oxidative demethylation of aqueous dimethylsiloxanols,* Environ.Toxicol.Chem., 6:676, 1984

25.Spivac, J., S.B. Dorn, *Hydrolysis of oligodimethylsiloxane-*α,ω*-diols and the position of hydrolytic equlibrium,* Environ. Sci. Technol., 28:2345, 1994

26. Lehmann, R.G., C.L. Frye, *Fate of silicone dagradation products in soil,* Environ. Toxicol. Chem., 13:1753, 1994

27. Lehmann, R.G., J.R.Miller, *Volatilization and sorption of DMSD in soil,* Environ. Toxicol. Chem., 9:1455, 1996

28. Sabourin, C.L.,J.C. Carpenter, T.K. Leib, J.L. Spivack, *Biodegradation of dimethylsilanediol in soils,* Appl. Environ. Microbiol., 62:4352-4360, 1996

29. Atkinson, R., *Kinetics of the gas-phase reactions of a series of organosilicon compounds with* $^{\bullet}OH$ *and* $NO^{\bullet}{}_3$ *radicals and* O_3 *at 295K,* Environ.Sci.Technol., 25:863, 1991

30. Sommerlade, R., H.Parlar, D.Wrobel, P.Kochs, *Product analysis and kinetics of the gas-phase reactions of selected organosilicon compounds with OH radicals using a smog hamber-mass spectrometer system,* Environ.Sci.Technol., 27:2435, 1993

31. Anderson, C.R., *Studies of the oxidative photoinduced degradation of silicones in aquatic environment*, Chemosphere, 16:2567, 1987

32. Lindsay, W.L., *Chemical Equilibrium in Soils*, John Wiley, New York, NY, USA, 1979

33. Fenton, H.J.H., *On a new reaction of tartaric acid*, Chem.News, 28:39, 1876

34. Fenton, H.J.H., *Oxidation of tartaric acid in presence of iron*, Chem.Soc., 65:899, 1894

35. Haber, F., J. Weiss, *Uber die katalyse deshydroperoxide*, Naturwissenschaften, 20:948, 1932

36. Barb, W.G., J.H. Baxendale, P.George, K.R. Hargrave, *Reactions of ferrous and ferric ions with hydrogen peroxide*, Trans.Faraday Soc., 47:462, 1951

37. Prousek, J., *Fenton reaction after a century*, Chem.Lisy, 89:11, 1995

38. Prousek, J., *Advanced oxidation processes for water treatment. Photochemical processes.*, Chem. Lisy, 87:165, 1993

39. Koyama, O., Y.Kamagata, K.Nakamura, *Degradation of chlorinated aromatics by Fenton oxidation and methanogenic digester sludge*, Water Res., 28:895, 1994

40. Sun, Y., J.J.Pignatello, *Chemical treatment of pesticide waste. Evaluation of Fe(III) chelate complexes catalytic H_2O_2 oxidation of 2,4-D at curcumneutral pH*, J.Agric.Food Chem., 40:322, 1992

41. Lipczinska-Kochany, E., G.Sprah, S.Harms, *Influence of some groundwater and surface waters constituents on the degradation of 4-chlorophenol by the Fenton reaction*, Chemosphere, 30:9, 1995

42. Ruppert, G., R.Bauer, G.Heisler, *The photo-Fenton reaction - an effective photochemical wastewater treatment process*, J.Photochem.Photobiol.A. Chem., 73:75, 1993

43. Pignatello, J.J., G.Chapa, *Degradation of PCBs by ferric ion,* H_2O_2 *and UV light,* Environ.Toxicol.Chem., 13:423, 1994

44. Pignatello, J.J., Day, *Mineralization of methyl parathion insecticide in soil by hydrogen peroxide activated with iron(III)-NTA or HRIDA complexes,* Haz. Waste Haz. Mater., 13:237-244, 1996

45. Linden, L.A., J.F.Rabek, H.Kaszmarek, A.Kaminska, M.Scoponi, *Photooxidative degradation of polymers by* $HO^\bullet$ *and* $HO_2^\bullet$ *radicals generated during the photolysis of* H_2O_2*,* $FeCl_3$ *and Fenton reaction,* Coord.Chem.Rev., 125:195, 1993

46. Watts, R.J., M.D.Udel, P.A.Rauch, S.W.Leung, *Treatment of Pentachlorophenol-contaminated soils using Fenton's reagent,* Haz.Waste Haz.Mater., 7:335, 1990

47. Tyre, B.W., R.J.Watts, G.C.Miller, *Treatment of four biorefractory contaminants in soils using catalyzed hydrogen peroxide,* J.Environ.Qual., 20:832, 1991

48. Kitajima, N., S. Fukuzumi, Y.Ono, *Formation of superoxide ion during the decomposition of hydrogen peroxide on supporetd metal oxides,* J.Phys.Chem., 82:1505, 1978

49. Watts, R.J., S.Kong, M.Pippre, *Treatment of contaminated soils using catalyzed* H_2O_2, Chemical Oxidation, 39:33, 1994

CHAPTER I

INTRODUCTION

Dimethylsilanediol (DMSD) is the major product of the polydimethylsiloxane (PDMS) hydrolysis in soil (1,2). PDMS is introduced in the environment as component of municipal sewage sludge applied to soil. Previous research has demonstrated that PDMS may undergo extensive degradation in dry soil (3). The clay constituents of the soil were found to promote this process but degradation was found to be markedly inhibited by moisture. In soil, PDMS is converted to a water soluble fraction containing mostly dimethylsilanediol (DMSD). DMSD has the structure $OH\text{-}Si\text{-}(CH_3)_2\text{-}OH$. Once formed, DMSD may remain bound to soil particles, undergo complete biodegradation to CO_2 or volatilize in the atmosphere and be oxidized photochemically.

Fenton reagent has proved to be an expensive and powerful oxidant that has been shown to oxidize a wide variety of organic compounds (4, 5). In the Fenton's reaction both Fe(II) and Fe(III) react with hydrogen peroxide (H_2O_2) to produce hydroxyl radicals ($^{\cdot}OH$). The $^{\cdot}OH$ radicals are capable of oxidizing a range of contaminants because they react with most organic compounds in solution at near diffusion controlled rates (6). The use of Fenton's reagent for oxidizing biorefractory organic compounds in aqueous solution and contaminated soil has been studied extensively (7, 8).

The purpose of this research was to evaluate the potential for DMSD degradation by Fenton reagent in water and soils and to optimize the reaction conditions based on (1) the concentration and oxidation state of the iron catalyst, (2) the chemical form of the iron catalysts, (3) H_2O_2 concentration and (4) the slurry volume.

MATERIALS AND METHODS

Materials:

Dimethylsilanediol (DMSD), ^{14}C-DMSD, polydimethylsiloxane (PDMS) and ^{14}C-PDMS with 99% radiochemical purity were provided by the Dow Corning Co. (Midland, MI). Hydrogen peroxide and ferric nitrate were purchased from J.T.Baker (Phillipsburg, NJ). Ferrous chloride, ferric chloride, ferrous peroxide and ferric peroxide were obtained from Fisher Scientific (Fail Lawn, NJ). All other chemicals used (NaOH, HCl, methanol) were analytical grade.

Samples of the Capac sandy loam A-horizon soil were collected in East Lansing, MI. Particle size distribution was determined by the pipette method (9). Organic carbon content was measured by combustion at 900°C with CO_2 trapped in KOH (10). Cation exchange capacity (CEC) was determined by sodium acetate saturation at pH 8.2 (11). Crystalline and amorphous iron and manganese concentrations were quantified by citrate-dithionate-extractions (12). The soil characteristics are given in Table 1.

Table I-1. Characteristics of the Capac A soil

Characteristic	Value	Characteristic	Value
Organic carbon (%)	3.28	Crystalline Iron (mg/kg)	12404
Sand (%)	54.6	Crystalline Manganese (mg/kg)	239
Silt (%)	24	Amorphous Iron (mg/kg)	8481
Clay (%)	21.4	Amorphous Manganese (mg/kg)	136
pH	6.85		
CEC (meq/lOOg)	43.0		

Methods:

DMSD - Water experiments:

A slightly modified version of the method described by Ronen et al. (13) was used to evaluate the decomposition of DMSD in water by Fenton reaction. Reactions were run in 60 ml serum bottles containing a reactant volume of 10 ml. All reactant were prepared in deionized (DI) water. A stock solution of 5 mM DMSD/ ^{14} C- DMSD were prepared in advance, and introduced into the reaction vessel. The amount of ^{14} C- DMSD for each bottle was about 5 nCi. Stock solutions of ferrous and ferric salts (20 mM) were made in fresh in DI water acidified with HCl, and introduced into the reaction vessel. The iron (II) chloride and iron (III) chloride concentrations were varied from 0.1 to 10 mM and the H_2O_2 concentrations ranged from 5.5 to 880.0 mM. The pH of the reaction solution dropped below 3.0 after addition of H_2O_2. The influence of the initial DMSD concentrations on reaction kinetics and efficiency were evaluated between 0.1 and 3.0 mM DMSD. Other iron catalysts such as iron (II) sulfate, iron (III) sulfate, iron (II) perchlorate, iron (III) perchlorate and iron (III) nitrate were used to catalyze the reaction with final concentration in the reaction media of 2 mM. Bottles were closed with rubber stoppers fitted with center well (Kontes, Morton Grove, IL) containing a strip of 5-x-1 cm filter paper and 0.2 ml 1N NaOH used to trap $^{14}CO_2$. Reactions were performed in the dark at room temperature with shaking at 100 rpm. At specific intervals the filter paper was removed and placed in a vial with 10 ml scintillation cocktail. Vials were left overnight in the dark and then radioactivity was measured by liquid scintillation counting (LSC). An aliquot (1 ml) of the reaction solution was added to a separate scintillation vials with 10 ml cocktail and the radioactivity was counted using LSC. Each treatment was performed in duplicate, and all results are expressed as a mean value ± standard error. The range of the standard errors was 3.0-5.5%.

DMSD-Soil experiments:

Air dry (2.5 g) soil was weighed in 60 ml serum bottles and amended with 5mM DMSD/^{14}C-DMSD stock solution to yield initial concentrations of DMSD between 1-200 mg/kg. Iron concentrations ranged between 50 and 150 mM and hydrogen peroxide concentrations varied from 0.1 to 3.0 M; H_2O_2 concentrations greater than 3.0 mM were not used because the slurries produced a violent reaction. The total volume of the liquid was 2.5 ml. The contents of the serum bottles were mixed with a vortex mixer and then shaken at 200 rpm at dark for various reaction times at room temperature. The same procedure as that used in the water experiment was followed for sampling the traps. After completion of the reactions the soil was transferred to centrifuge tubes. Tubes were shaken for 6 h with 5 ml DI water and then centrifuged at 8500 rpm for 20 minutes. The water was removed and duplicate 1-ml aliquots were sampled for ^{14}C analysis. Tubes were than shaken overnight with 5 ml 0.1 M HCl, centrifuged, and 1ml of the liquid was sampled for ^{14}C as above. To investigate the most efficient form of the iron catalyst different iron species were added to the soil at a concentration of 100 mM/kg. The forms of iron used were Fe(II) chloride, Fe(III) chloride, Fe(II) perchlorate, Fe(III) perchlorate, Fe(II) sulfate, Fe(III) sulfate, Fe(III) nitrate. The reactions were allowed to proceed for 24h. It was found that after 5 hours, reactions were completed because H_2O_2 was consumed. In order to drive the reactions further additional H_2O_2 was added to the slurries after the 5th hour at the same initial concentration.

The effect of the slurry volume was investigated using the most effective catalysts and its optimum concentration. The catalyst $Fe(NO_3)_3$ at a fixed concentration of 100 mM was used with H_2O_2 concentrations of 0.625 M and liquid volume from 1.5 to 5 ml per 2.5 g of soil.

All experiments were initiated by addition of H_2O_2 to the vials. Control experiments using DMSD alone, combinations of DMSD and H_2O_2, and combinations of DMSD and iron species were performed in parallel. Each treatment was performed in duplicate, and all results are expressed as a mean value ± standard error. The range of the standard errors was 2.8-5.0%.

RESULTS AND DISSCUSION

Exposure of DMSD to Fenton reagent in water resulted in the mineralization of the chemical. During incubation for 24 hours 75% of DMSD was mineralized in water and 48% in soil as determined by the formation of $^{14}CO_2$. Control systems with D.I. water, H_2O_2 and iron (II) or iron (III) chloride alone conducted in parallel were not capable of mineralizing the DMSD. After completeion of the reactions the radioactivity remaining in the water was less than 0.5% for the Fenton treated samples; volatilization loss of DMSD was about 25%. For the control experiments the recovery ranged between 90.7 and 100.6%. The initial concentration of DMSD, H_2O_2 and Fe (II)/Fe (III) ions as well as the iron catalyst source influenced the mineralization of DMSD.

Mineralization of DMSD by Fenton's reagent in water

The transformation of DMSD by Fenton's reagent was practically independent of initial pH of the reaction solution. The pH dropped to 2.8-3.0 within seconds on addition of H_2O_2, presumably due to release of protons from hydrolysis of the Fe (III) products. These observations are consistent with previous reports regarding the effect of pH on Fenton oxidation of organic pollutants (14) in unbuffered water solutions. They immediately became acidic upon addition of the reagents and thus post treatment neutralization may be needed. Our system was also unbuffered because the presence of 0.1-0.02 M borate, phosphate and universal buffer drastically reduced the mineralization of the DMSD (up to 20%) or completely stopped it. Similar results were demonstrated by Lipczinska-Kochany et al. (15) in a study of the effect of several anions in concentrations close to those found in groundwater on Fenton degradation of 4-chlorophenol. The following order of anions was shown to inhibit the reaction:

$$ClO_4^- \sim NO_3^- < SO_4^{2-} < Cl^- << HPO_4^- < HCO_3^-$$

The observed retardation was explained as the combined effect of the anions on the rate of oxidation of Fe (II) anions as well as their role in the scavenging of hydroxyl radicals. It is well known that phosphate and bicarbonate are efficient scavengers of the hydroxyl radical (16).

A major aim of this study was to optimize the Fenton reaction conditions for DMSD mineralization in water as well as to compare the efficacy of Fe (II) and Fe (III) ions as catalysts. The chemical mineralization of DMSD was affected by the initial concentrations of the iron catalyst and its oxidation state. Figure I-1 shows the effect of Fe (II) and Fe (III) concentrations on decomposition of DMSD. In water the optimal concentration of Fe (II) chloride needed to reach maximum conversion of DMSD to CO_2 was reached at 2 mM (Figure I-1), was constant up to 4 mM, and slightly diminished at 8 and 10 mM. The optimal concentration of Fe (III) chloride was between 1-4 mM (Figure I-2). At the optimum Fe (II) concentrations, about 70 % DMSD removal was obtained after 1 to 10 hours treatment. For Fe (III) the time needed for the reaction to be completed was 1 to 5 hours. Within the optimal concentration ranges the DMSD decomposition rate during the first 5 hours increased with increasing Fe (II)/Fe (III) concentrations, perhaps due to the increased hydroxyl radical formation rate. Perhaps at higher than optimal iron concentrations the initial formation rate of $^\bullet OH$ radicals originating from the decomposition of H_2O_2 was so high that they were consumed by competing side reactions before being utilized effectively for DMDS mineralization.

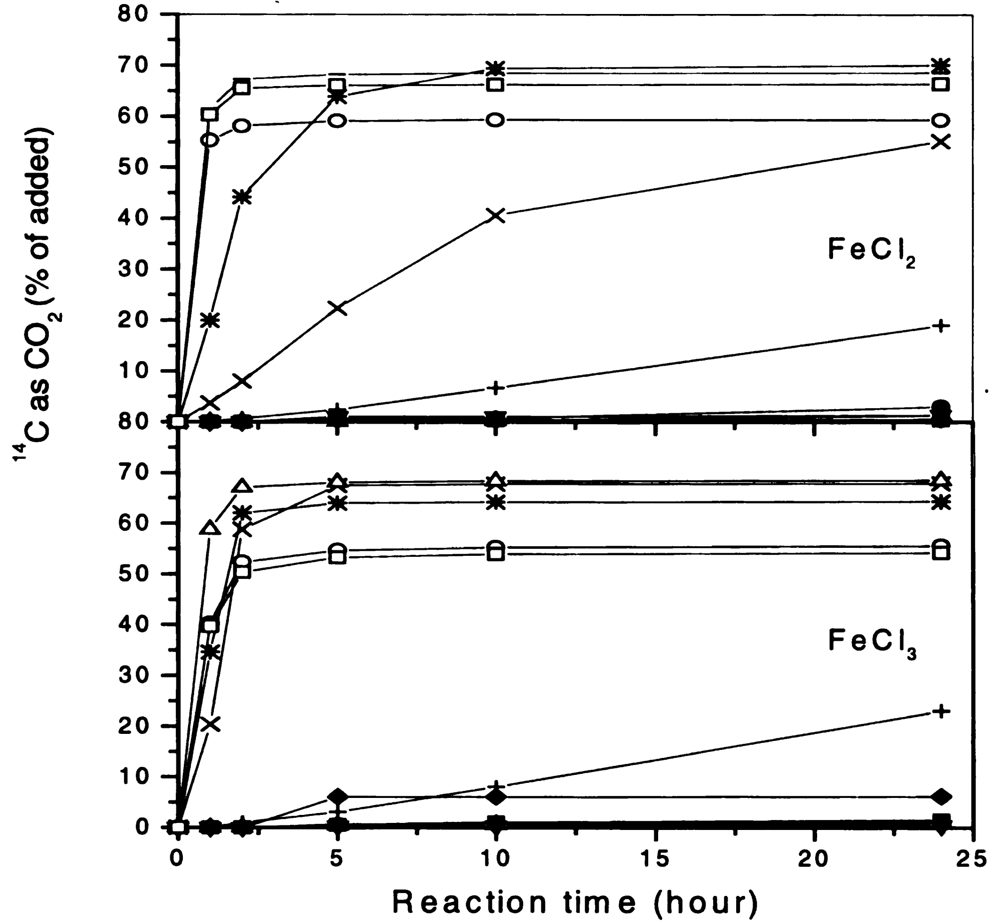


Figure I-1. Mineralization of DMSD in water by Fenton's reagent with different iron catalysts concentrations (1mM DMSD, 440 mM H_2O_2). Treatments consisted of (■) DMSD only, (●) H_2O_2 only, (▲) 0.1 mM iron only,(▼) 2 mM iron only, (◆) 10 mM iron only, (+) 0.1 mM iron, (×) 1 mM iron, (✶) 2 mM iron, (Δ) 4 mM iron, (O) 8 mM iron, (□) 10 mM iron.

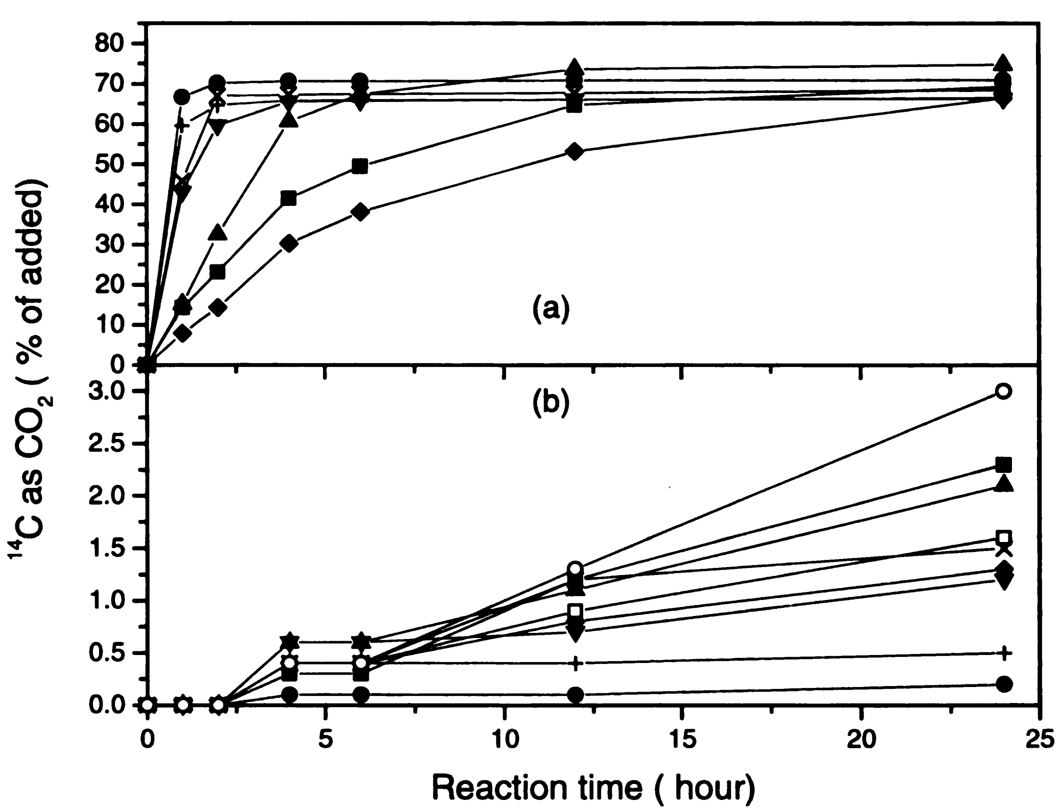


Figure I-2. Mineralization of DMSD in water by Fenton's reagent with different iron catalysts (1mM DMSD, 2mM Fe(II)/Fe(III), 440 mM H_2O_2). Treatments consisted of (a) Fenton's reagent samples, (b) controls. (■) $FeCl_2$, (●) $FeCl_3$, (▲) $FeSO_4$, (▼) $Fe_2(SO_4)_3$, (◆) $Fe(ClO_4)_2$, (+) $Fe(ClO_4)_3$, (×) $Fe(NO_3)_3$, (□) DMSD only, (O) H_2O_2 only.

Therefore, one possible reason for the existence of an optimum Fe (II)/Fe (III) dosage was the need to attain a proper $^{\bullet}$OH radical formation rate.

Another potential factor was the formation of iron hydroxide precipitate. The ferric ions exist mainly in the form of soluble $Fe(OH)_2^+$ at pH 3.0. Iron hydroxide precipitates would form at concentrations slightly higher than 1 mM, and iron in this form could not be effectively utilized as a catalyst (17). At the higher than optimal iron concentrations the reaction solution had persistent deep red color formed after several hours, which is characteristic of soluble polynuclear ferric oxyhydroxides (18). The faster reaction kinetics observed for the Fe (III) catalyzed reaction may be due to the additional time needed for Fe (II) to be oxidized to Fe (III). The Fenton reaction nominally between Fe (II) and H_2O_2 under conditions of excess peroxide (as in our case) may be actually predominantly the reaction between Fe (III) and H_2O_2 since Fe (II) is rapidly oxidized.

The degradation reactions were sensitive to the anion in solution originating from background electrolyte and Fe (II)/Fe (III) or H^+ counterions. Seven iron species were evaluated for their ability to catalyze DMSD degradation. The data for mineralization show that Fenton reaction catalyzed by iron (III) was completed in shorter times compared to the reaction catalyzed by Fe (II) species. All of the iron salts tested resulted in about 70% mineralization of DMSD. However, differences were found in the initial rates (Table I-2). The initial reaction rates for Fe(II) catalysts were detrmined by using the initial experimental portion of the experimental kinetic curves and compared to the initial rates calculated using the first order kinetic model.:

$$\ln\{Cmax/[Cmax-C(t)]\} = kt,$$

where Cmax is the final CO_2 percentage, C(t) is the CO_2 persentage at time t, and k is the rate constant.

The fitting procedure was carried out by the computer program "SigmaPlot" (version 4.0 for Windows, by SPSS Inc., 1997). The regression parameter R^2 was in the range 99.86 to 99.99%. First order kinetic model did not describe properly the data for Fe(III) catalyzed reactions.

Table I-2. Kinetic parameters for DMSD degradation in water with different iron catalysts.

Iron Catalyst	Initial rates $mmol.L^{-1}.sec^{-1}$ (experimental)	$T_{1/2}$, hour (experimental)	Initial rates $mmol.L^{-1}.sec^{-1}$ (calculated)	$T_{1/2}$, hour (calculated)
$FeCl_2$	14.3	3.0	15.8	3.0
$FeCl_3$	66.6	0.5	-	
$FeSO_4$	32.0	2.4	26.9	2.0
$Fe_2(SO_4)_3$	43.1	0.7	-	
$Fe(ClO_4)_2$	7.9	4.9	9.3	5.0
$Fe(ClO_4)_3$	59.6	0.5	-	
$Fe(NO_3)_3$	45.7	0.4	-	

The most effective iron catalysts were $Fe(ClO_4)_3$ and $FeCl_3$ followed by the chloride and sulfate salts (Figure I-2 (a) and Figure I-2 (b). The classical Fenton reagent $FeCl_2$ /H_2O_2 produced the slowest initial rate of mineralization of DMSD, followed by $FeSO_4$. These results indicate that to achieve mineralization there is little or no advantage starting with Fe (II) under conditions with excess peroxide, as used here.

The concentration ratio of H_2O_2 to DMSD also influenced the effectiveness of DMSD mineralization. The effect of H_2O_2 on the mineralization of DMSD in water is evident at lower concentrations. The degree of DMSD mineralization in the presence of $FeCl_3$ increased steadily when the H_2O_2 concentration increased between 5.5 and 110 mM (Figure I-3). However the mineralization rate did not increase when H_2O_2 concentration was further between 110 and 880 mM. In the presence of $FeCl_2$, concentrations above 5.5 mM supported maximal rates except at an 880 mM when the rate declined (Figure I-3). The ranges of molar ratios of 880 DMSD to H_2O_2 tested in this the rate declined (Figure I-3). The ranges of molar ratios of DMSD to H_2O_2 tested in this study were between 1:5 to 1:880. Only the higher molar ratios had an effect on mineralization. The maximal initial rates were achieved at the ratios 1: 110 to 1:660. Pignatello (21) studied the effect of H_2O_2 levels on 2,4-D mineralization by Fenton reagent and demonstrated that at ratios of above 20:1 H_2O_2:2,4-D, 2,4-D was mineralized to CO_2 almost independently of H_2O_2 concentrations. The largest amount of H_2O_2 needed to mineralize DMSD as compared to 2,4-D is most likely the result of a higher degree of resistance of DMSD to oxidation.

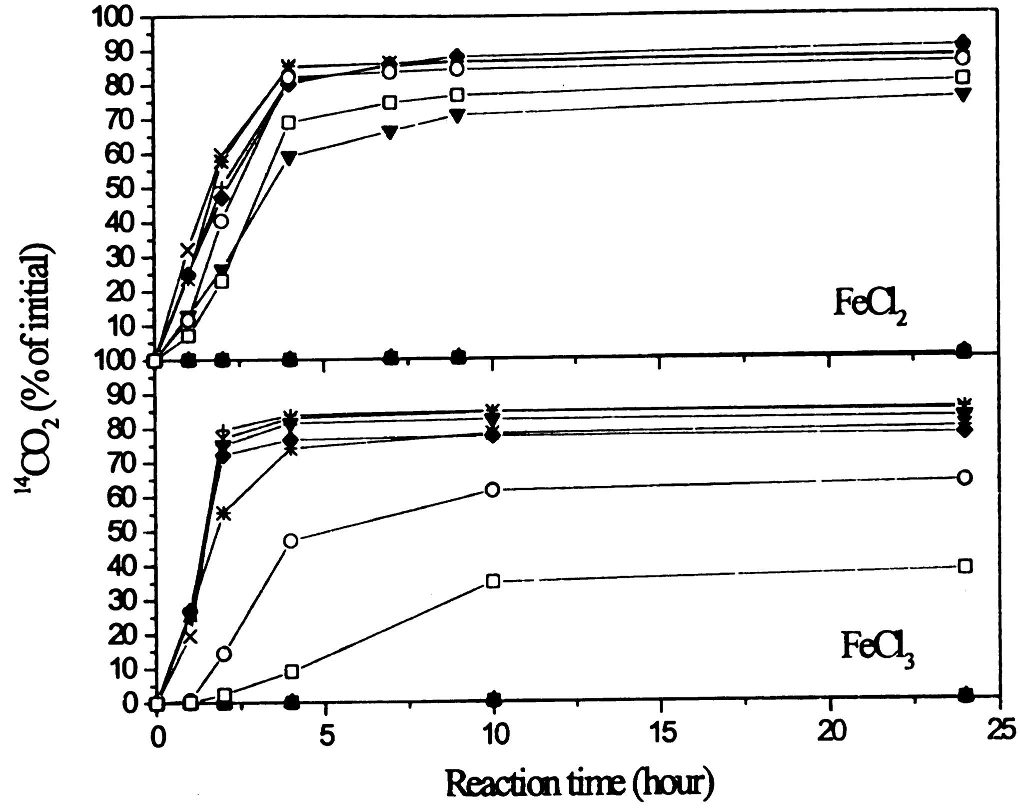


Figure I-3. Mineralization of DMSD in water by Fenton's reagent with different H_2O_2 concentrations (1mM DMSD, 2 mM iron catalyst). Treatments consisted of (■) DMSD only, (●) iron only, (▲) 440 mM H_2O_2 only, (▼) 880 mM H_2O_2, (◆) 660 mM H_2O_2, (+) 440 mM H_2O_2, (×) 220 mM H_2O_2, (✱) 110 mM H_2O_2, (O) 55 mM H_2O_2, (□) 5.5 mM H_2O_2.

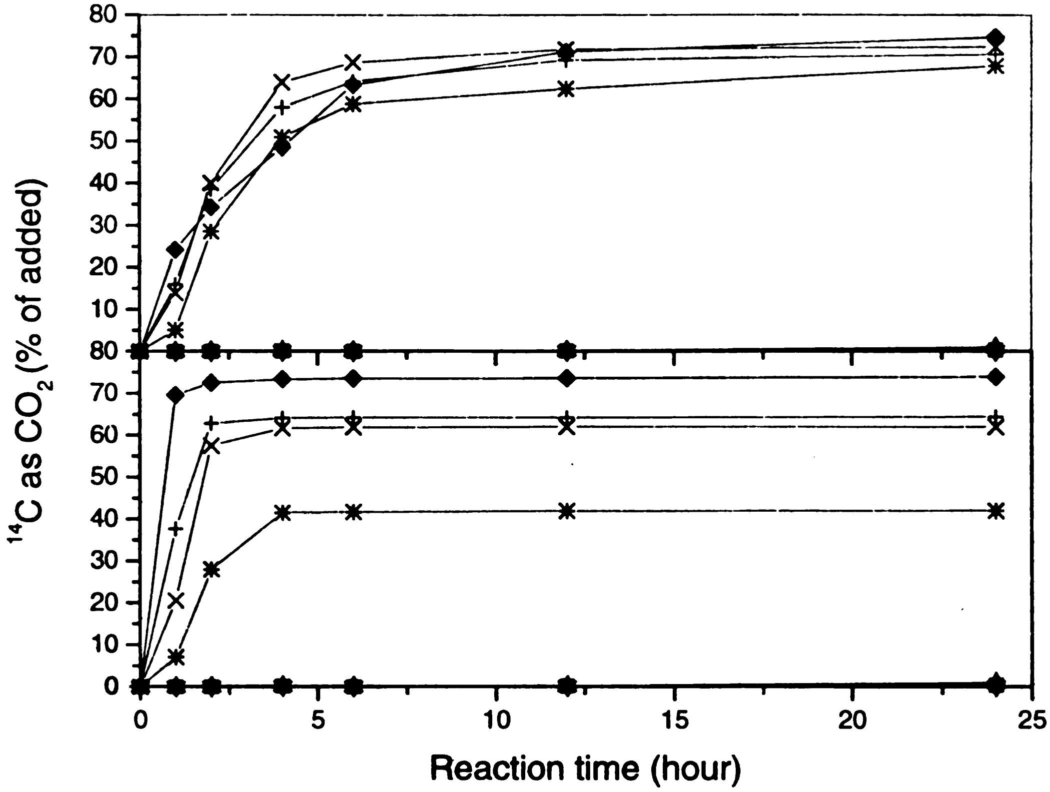


Figure I-4. Mineralization of DMSD in water by Fenton's reagent with different DMSD concentrations (2 mM iron catalyst, 440 mM H_2O_2). Treatments consisted of (■) 0.1 mM DMSD only, (●) 3 mM DMSD only, (▲) iron catalyst only,(▼) H_2O_2 only, (◆) 0.1 mM DMSD, (+) 1 mM DMSD, (×) 2 mM DMSD, (✶) 3 mM DMSD.

DMSD mineralization in Soil Slurries

A major advantage in working with Fenton reaction in soil is that soils naturally contain sources of iron (e.g. iron oxyhydroxides) that can catalyze oxidation and mineralization of the target contaminants. Unfortunately, soil colloidal material may reduce the effectiveness of the Fenton oxidation by competing with target contaminants for $^{\bullet}OH$ radicals or catalyzing peroxide decomposition to H_2O and O_2 (19). Dissolved natural organic matter can scavenge $^{\bullet}OH$ radicals (59). Also, in contrast to water soluble compounds, contaminants in the soils are usually sorbed to a certain extent or present as nonaqueous phase liquids, and this can have significant effect on Fenton process chemistry. Due to its high water solubility DMSD is expected to stay mostly in solution under ambient conditions in soil. Overall, the rates of DMSD mineralization were lower for Fenton-reagent treated soil slurries than in water. This despite the fact that much higher concentrations of iron (II) and H_2O_2 were used.

In the case of DMSD mineralization in soil only $FeCl_2$ concentrations were optimized, as this is the classical Fenton reagent. The most effective level was found to be 100 mM/kg (Figure I-5). Increasing the concentration above this level did not cause increase in mineralization (data not shown). Control experiments in soil with H_2O_2 and no iron addition resulted in degradation of 10 % of the DMSD. Therefore, naturally occurring iron in the form of amorphous and crystalline iron oxides (Table 1) may not supply sufficient iron for Fenton-like reaction. These results are consistent with the results of Watts et al. (20) who found that oxidation of sorbed pentachlorophenol was effective using low H_2O_2 concentration if catalysis was promoted by soluble iron rather than natural iron hydroxides.

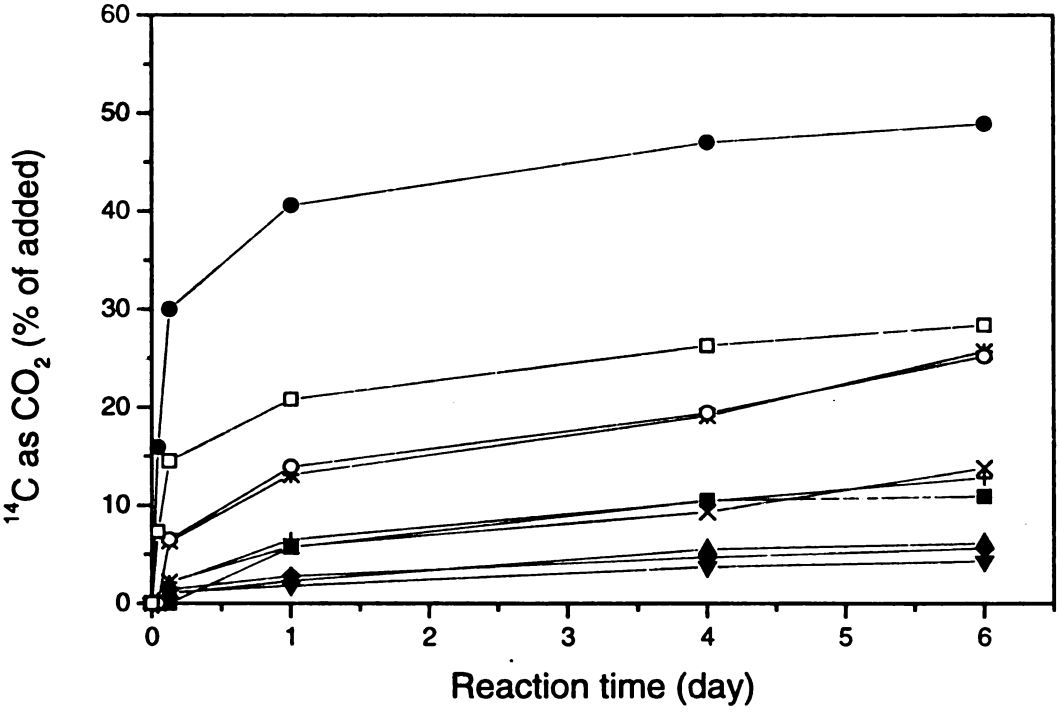


Figure I-5. Mineralization of DMSD in soil by Fenton's reagent with different iron catalysts concentrations (10 mM DMSD, 1.5 M H_2O_2). Treatments consisted of (■) DMSD only, (+) H_2O_2 only, (▲) 100 mM iron only,(▼) 50 mM iron only, (◆) 100 mM iron only, (×) 10 mM iron, (✶) 25 mM iron, (Δ) 4 mM iron, (O) 50 mM iron, (□) 75 mM iron, (●)100 mM iron.

Seven iron catalysts were compared for their ability to catalyze DMSD mineralization in soil (Figure I-6). Iron (III) nitrate was most effective among those tested. It promoted 42% oxidation of 10 mM DMSD in soil slurry. Other iron catalysts, i.e. (iron (II) chloride, iron (II) perchlorate, iron (II) sulfate, iron (III) chloride, iron (III) perchlorate and iron (III) sulfate) provided 16-32% DMSD mineralization under the same reaction conditions. Iron (II) compounds were less effective catalysts than iron (III) species, presumably owing to the initial loss of H_2O_2 in oxidizing Fe (II) to Fe (III). The most effective iron catalysts were in the order:

$$NO_3^- > SO_4^{2-} > Cl^- > ClO_4^-$$

The effectiveness $Fe(NO_3)_3$ is probably because of nitrate salts quenched $^\bullet OH$ radicals at the lowest rates and, therefore, provided the highest degree of mineralization of DMSD. Iron sulfates provided intermediate mineralization while perchlorates were least efficient in promoting the mineralization. Control experiments (Figure I-6) with Fe (II)/Fe (III) alone showed no DMSD mineralization. The initial H_2O_2 concentration in soil affected the initial rate and extent of DMSD mineralization (Figure I-7). Concentrations of H_2O_2 between 0.1 and 1.0 M were tested. The least effective level was 0.1 M. The most effective level was 0.25 M. Increasing H_2O_2 level above 0.25 M did not increase the initial rate or extent of DMSD mineralization. Concentrations of H_2O_2 over 2.0-2.5 M led to violent reactions and hence were not evaluated further. This effective concentration is moderate considering that several organic components of the system competed with DMSD for oxidant, e.g. dissolved soil organic matter, and that soil particles can catalyze H_2O_2 decomposition. Hydrogen peroxide is relatively unstable in soils and is affected by the concentration of catalase, iron and manganese (21). In addition the pH of the soil-peroxide slurry significantly affects H_2O_2 decomposition rates.

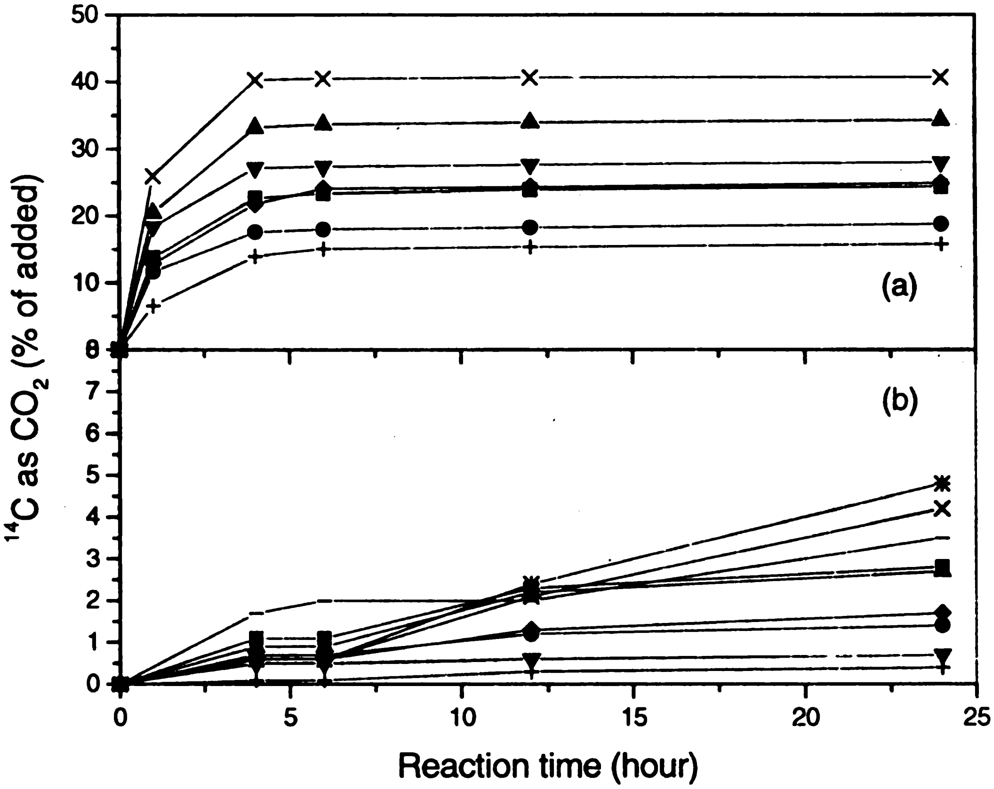


Figure I-6. Mineralization of DMSD in soil by Fenton's reagent with different iron catalysts (10 mg/kg DMSD, 100 mM Fe(II)/Fe(III), 0.625 mM H_2O_2). Treatments consisted of (a) Fenton's reagent samples, (b) controls. (■) $FeCl_2$, (●) $FeCl_3$, (▲) $Fe(SO_4)_2$, (▼) $Fe_2(SO_4)_3$, (◆) $Fe(ClO_4)_2$, (+) $Fe(ClO_4)_3$, (×) $Fe(NO_3)_3$, (✱) DMSD only, (-) H_2O_2 only.

Watts et al. (46) found that H_2O_2 decomposed rapidly at pH>5, however at pH 3 the H_2O_2 consumption rates were low while the rate of contaminant degradation was high. The higher H_2O_2 concentrations required to mineralize DMSD in soil versus water were comparable to the results of previous Fenton-like soil remediation studies (14). Watts et al. (20) found that ≥ 0.1 M H_2O_2 with soluble iron oxidized sorbed pentachlorophenol, and Spencer et al. (1) determined that 3 to 9 M H_2O_2 was required to oxidize sorbed diesel using oxyhydroxides as the only source of iron catalysts. The use of moderate concentrations of H_2O_2 (0.75 M) catalyzed by soluble iron appears to be the most effective process conditions for the oxidation of DMSD. An attempt to increase the mineralization of DMSD in soil was done by adding a second increment H_2O_2 (0.65 M) to the soil five hours after the initial Fenton reaction commenced (Figure I-8). The result shows that the reaction can be driven further by additional H_2O_2 and a total increase of about 10% was achieved.

The extent of DMSD mineralization was also influenced by its initial concentration in the soil. Figure I-9 shows that 1mg/kg was mineralized to the great extent (about 35%). Increasing the concentration over 10 mg/kg resulted in a somewhat lower extent of mineralization (29%).

The ability of Fenton-like reactions to remediate DMSD contaminated soil increased as a function of the liquid volumes. The slurry volumes from 2.5 to 5 mL per 2.5 g soil were evaluated. The highest degree of mineralization was achieved in solution:soil ratio 2:1 (Figure I-10).

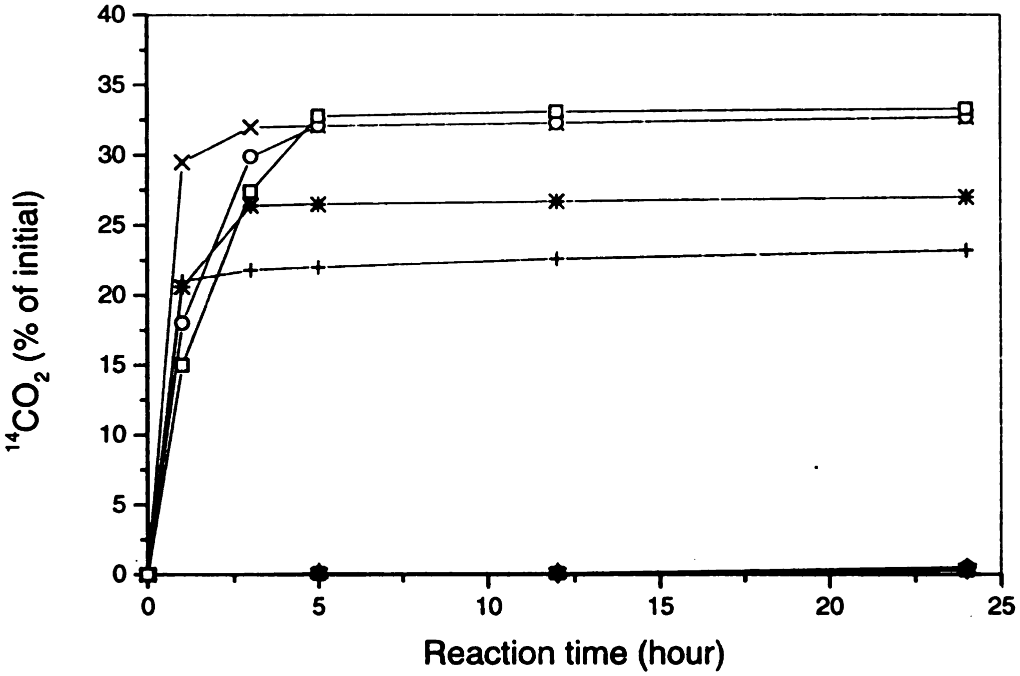


Figure I-7. Mineralization of DMSD in soil by Fenton's reagent with different H_2O_2 concentrations (10mg/kg DMSD, 100 mM iron catalyst). Treatments consisted of (■) DMSD only, (●) iron only, (▲) 0.1 M H_2O_2 only,(▼) 0.5 M H_2O_2 only, (◆) 1.0 M H_2O_2 only, (+) 0.1 M H_2O_2, (×) 0.25 M H_2O_2, (✱) 0.5 M H_2O_2, (O) 0.75 M H_2O_2, (□) 1 M H_2O_2.

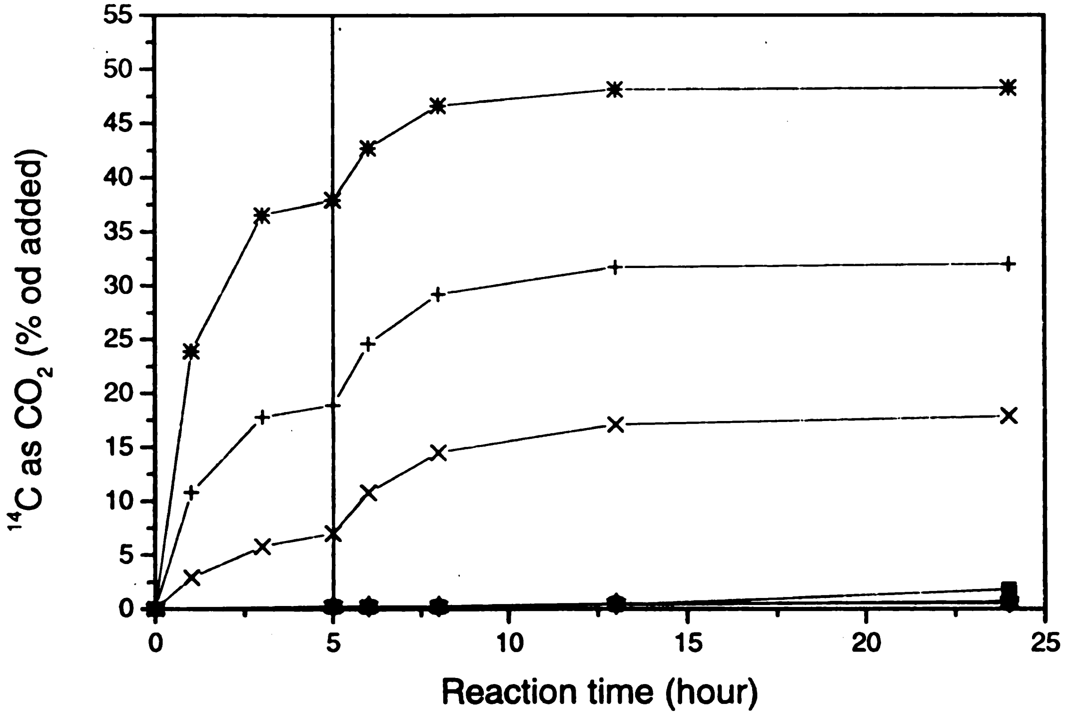


Figure I-8. Mineralization of DMSD in soil by Fenton's reagent with addition of H_2O_2 at thr fifth hour (10 mg/kg DMSD, 100 mM iron (III) catalyst, 0.625 M H2O2). The vertical line indicate H_2O_2 addition. Treatments consisted of (■) DMSD only, (●) $FeCl_3$ only, (▲) $Fe(ClO_4)_3$ only, (▼)$Fe(NO_3)_3$ only, (+) $FeCl_3$, (×) $Fe(ClO_4)_3$, (✱) $Fe(NO_3)_3$.

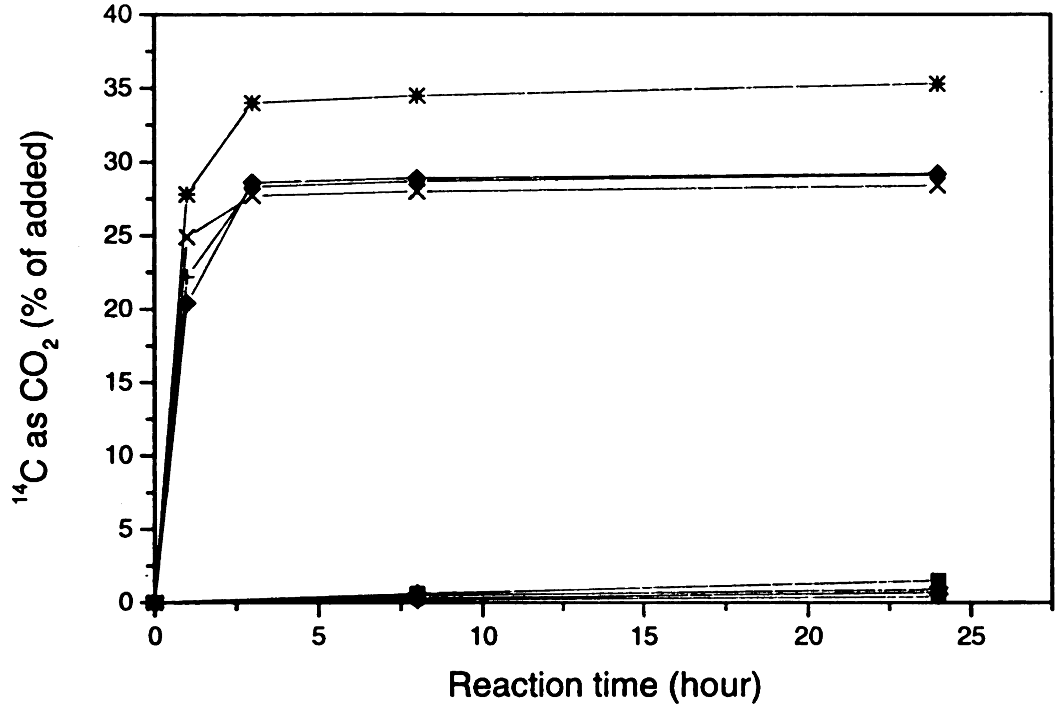


Figure I-9. Mineralization of DMSD in soil by Fenton's reagent with different DMSD concentrations (100 mM iron catalyst, 0.625 M H_2O_2). Treatments consisted of (■) 1 mg/kg DMSD only, (●) 100 mg/kg DMSD only, (▲) $FeCl_2$ only,(▼) H_2O_2 only, (◆) 200 mg/kg DMSD, (+) 100 mg/kg DMSD, (×) 10 mg/kg DMSD, (✶) 1 mg/kg. DMSD.

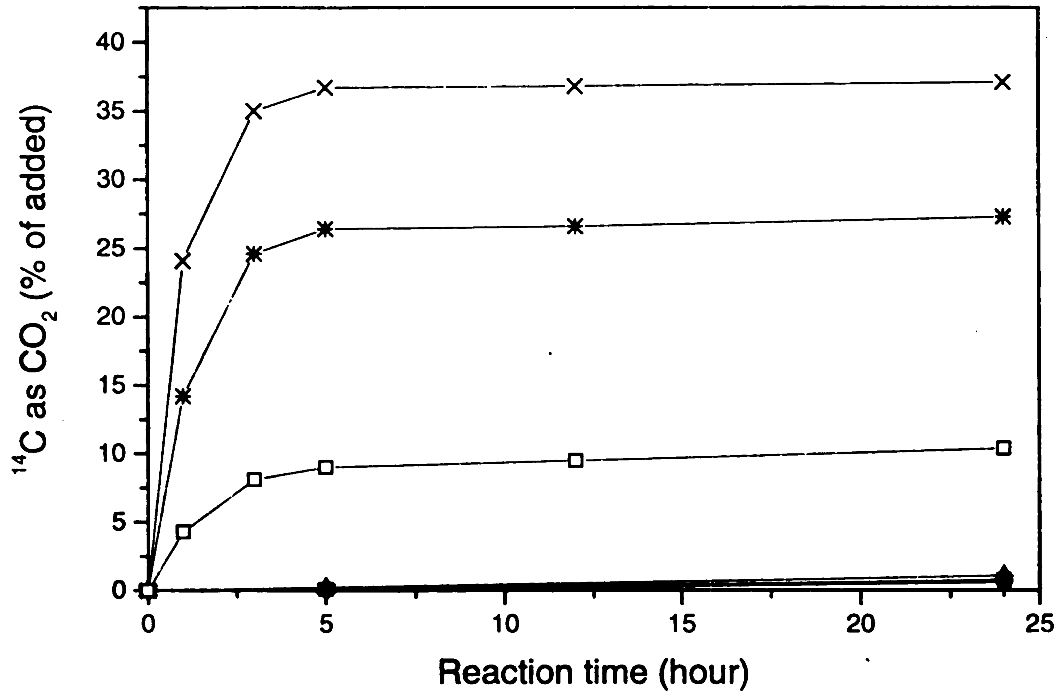


Figure I-10. Mineralization of DMSD in soil by Fenton's reagent at different solution:soil rates (10 mg/kg DMSD, 100 mM FeCl2, 2 M H2O2). Treatments consisted of (■) 0.5/1 DMSD only, (●) 2/1 DMSD only, (▲) 0.5/1 $FeCl_2$ only,(▼) 2/1 $FeCl_2$ only, (◆) 0.5/1 H_2O_2 only, (+) 2/1 H_2O_2 only, (×) 2/1 Fenton's reagent, (✱) 1 /1 Fenton's reagent, (□) 0.5/1 Fenton's reagent.

SUMMARY

The characteristics of the Fe(II)/ H_2O_2 and Fe(III)/H_2O_2 systems were evaluated for the mineralization of DMSD in water and soil. It was found that the Fenton reagent could effectively mineralize DMSD in solution and soil slurries. The efficiency of the Fenton reagent to destroy DMSD was affected by initial H_2O_2, iron and DMSD concentrations as well as the oxidation state of the iron catalysts and iron counterions. The rate of Fenton reaction was slowed in soil-water mixtures as compared to pure water and higher concentrations of the reagents had to be used. Mineralization of DMSD in water increased when peroxide concentration increased from 5.5 to 110 mM, but decreased slightly at a peroxide level to 880 mM. For the soil slurries a peroxide concentration between 0.25 and 0.75 M was needed for maximal mineralization of DMSD, generally between 32 and 42%. Also addition of a second increment of H_2O2 improved mineralization by 10%. The time required for completion of aqueous phase DMSD mineralization was 1 to 5 hours when FeCl3 was used while the Fe (II) system needed 1 to 10 hours to reached the same extent of mineralization, ~ 72%. In the soil slurry experiment the process of mineralization was completed somewhat faster, generally<5 hours. This may be due to the faster decomposition of H2O2 catalyzed by the soil particles. Seven iron species were investigated for their effectiveness in catalyzing DMSD mineralization in aqueous and soil media. Generally iron (II) compounds were less effective than iron (III) due to the initial loss of H2O2 in oxidizing Fe(II) to Fe(III). There were differences in the initial rates of the mineralization process due to the presence of different counterions in the solution. The most effective iron catalysts were

Fe(NO3)3 and FeCl3 in the aqueous phase and Fe(NO3)3 in the soil slurries. A higher percent of mineralization was achieved with lower initial DMSD concentration and higher liquid to soil ratios.

The Fenton reagent effectively destroyed DMSD in aqueous solutions and soil slurries, and indicated that Fenton oxidation may be a useful remediation treatment for DMSD contaminated water and soils.

REFERENCES:

1. Buch, R.R., D.N.Ingerbrigsten, Rearragement of Poly(dimethylsiloxane) fluids on soil, Environ.Sci.Technol., 6:676, 1979

2. Lehmann, R.G., S.Varaprath, C.L. Frye, Degradation of silicone polymers in soil, Environ.Toxicol.Chem., 7:1061, 1994

3. Carpenter, J.C., J.A.Cella, S.B.Dorn, Study of degradation of PDMS on soil, Environ.Sci. Technol., 29:864, 1995

4. Barberini, M., C. Minero, E. Pelizzetti, E. Borgarello, N. Serpone, Chmosphere, *Chemical degradation of chlorophenols by Fenton's reagent,*16:2225, 1987

5. Mohanty, N.R., I.W.Weil, Oxidation of 2,4-Dinitrotoluene using Fenton's reagent. Reaction mechnisms and their practical applications., Haz.Waste Haz. Mater., 10:171, 1993

6. Seldak, D.L., A.W. Andren , Aqueous-phase oxidation of polychlorinated biphenyls by hydroxyl radicals, Environ.Sci. Technol., 25:1419, 1991

7. Watts, R.J., S.E.Dilly, Evaluation of iron catalysts for the Fenton-like remediation of diesel contaminated soil, J.Haz.Mater., 51:209, 1996

8. Ruppert, G., R.Bauer, G.Heisler, The photo-Fenton reaction - an effective photochemical wastewater treatment process, J.Photochem.Photobiol.A. Chem., 73:75, 1993

9. Gee, B.W., J.W.Bawder,. Particle-size analysis. in: Methods of soil analysis. Part 1 Physical and mineralogical methods, p.399-404, Madison, WI, 1986

10. Nelson, D.W., L.E. Sommers, Total Carbon, Organic Carbon, and Organic matter. in: Methods of soil analysis. Part 2 Chemical and microbiological Properties, p.539-579, Madison, WI, 1986

11. Soil Conservation Service. Soil survey laboratory methods and procedures for collecting soil samples, Soil survey investigation:Report 1 U.S. Government Printing Office. Washington D.C., 1972

12. Jackson, M.L., C.H.Lin, L.W.Zelazny, in: Methods of soil analysis. Part 1 Physical and mineralogical methods, p.113-124, Madison, WI, 1986

13. Ronen, Z., M.H. Gordon, J.M. Bollag, Biological and chemical minaralization of pyridine, Environ.Sci.Technol., 13:21, 1994

14. Pignatello, J.J., Dark and photoassisted Fe(III)-catalyzed degradation of chlorophenoxy herbicides by hydrogen peroxide, Environ.Sci.Technol., 26:5, 1992

15. Kochany, J., E. Lipczinska-Kochany, Chemosphere, 25:1769, 1992

16. Yang, M., J.Hu, K. Ito, Characterization of Fe(II)/H2O2/UV oxidation process, Environ.Sci.Technol., 19:183, 1998

17. Silva, R.N., Rev.Pure Appl. Chem., 22:115, IES Lighting handbook, 4th ed.,N.Y., 1966

18. Anderson, L.I., J.O.johnson, R.F. Christman, Extent of ozone's reaction with isolated aquatic fulvic acid, Environ.Sci.Technol., 2:793, 1986

19. Schumb, W.C., C.N. Sherfield, R.L. Wentworth, Hydrogen peroxide, ACS Monography, 128 Am.Chem.Soc., Washington D.C., 1955

20. Watts, R.J.,M.D.Udel, R.M.Monsen, Oxidation of pentachlorophenol catalyzed by H2O2 and naturally occurring iron oxyhydroxides, Water Environ.Res., 65:893, 1993

21. Pignatello, J.J., K.Baehr, Ferric complexes as catalysts for degradation of 2,4-D and metolachlor in soil, J.Environ.Qual., 23:355, 1994

CHAPTER II

INTRODUCTION

Polydimethylsiloxane (PDMS) is synthetically produced organosilicone polymeric material widely used in industry and consumer products. PDMS is characterized by low surface tension, resistance to chemical and thermal attack, water repellency, and resistance to oxidation and UV reactions (1). Because of its recalcitrance, many of the PDMS uses result in the presence of PDMS in waste waters. It can than enter the environment as a component of effluents and sludges from wastewater treatment plants. PDMS is expected to partition onto sediment solids and be applied to soil via land application of sewage sludges (2).

Recent work by Lehman et al.(3) and Carpenter et al. (4) have shown that once PDMS is introduced into soil, it can undergo chemical hydrolysis to low molecular water-soluble dimethylsilanediol (DMSD). The hydrolysis reaction is moisture dependent and much faster in dry soil. Buch et al. (5) demonstrated the clay catalyzed conversion of PDMS to water-soluble dimethylsiloxanoles and volatile oligomeric methylsiloxane species. Recently Xu et al. (6) found that soil factors such as clay content and clay type are very important in determining the degradation rates of PDMS in soil. The differences arrived from the different interaction strength between clay minerals and PDMS degradation products. Surface area of the clay particles played an important role in PDMS degradation. Higher surface area provided more PDMS degraded and speeded up the process.

Silicones may also be subject to photochemical degradation. Rapid degradation of water soluble mixture of oligomeric dimethylsiloxanes by sun light in the presence of environmentally relevant levels of nitrates has been reported (10). Silicate was demonstrated to be the final photodegradation product of these water soluble siloxanes. When an aqueous emulsion of high molecular weight PDMS was irradiated in the presence of nitrate ion, a level of silicate corresponding to 1.7% of the original quantity was found after 5 weeks. The low conversion was though to be due to the very low solubility of PDMS such that only a monomolecular surface layer of the polymer could react with the hydroxyl radicals formed in the water.

Fenton reaction (7) is recognized as one of the oldest powerful oxidizing reactions available. This reaction has been used to decompose a wide range of refractory organic pollutants (8, 9). The Fenton reagent is a mixture of H_2O_2 and ferrous salt which produces hydroxyl radical ($^{\cdot}OH$). The $^{\cdot}OH$ radical is capable of nonspecific oxidation of many organic compounds.

The objective of the present research was to investigate the potential of the Fenton reagent to mineralize PDMS in water and soil and to optimize the process conditions.

MATERIALS AND METHODS

PDMS-Water experiment

A stock solution of 0.97 mg/ml polydimethylsiloxane (PDMS) and ^{14}C-PDMS dissolved in tetrahydrofurane (THF) was prepared in advance and placed into 60 ml serum bottles. The total final PDMS concentration in water ranged between 0.05 to 200 mg/mL. The amount of ^{14} C-PDMS in each bottle was about 5 nCi. A stock solution of 20 mM iron (II) chloride was prepared fresh every time, and the concentrations evaluated varied between of 2.0 to 3.0 mM. Hydrogen peroxide concentrations of 880 and 440 mM were used to initiate the Fenton reaction. In several experiments the reaction reached plateau due to the consumption of the hydroxyl radicals available. At this point H_2O_2 were added to the bottles, at the same initial concentrations, in order to stimulate the mineralization process. Bottles were closed with rubber stoppers fitted with center well (Kontes, Morton Grove, IL) containing a strip of 5-x-1 cm filter paper and 0.2 ml 1N NaOH used to trap $^{14}CO_2$. Reactions were performed in dark with shaking at 100 rpm. At specific intervals the filter paper was removed and placed in a vial with 10 ml scintillation cocktail. Vials were left overnight in the dark and then radioactivity was measured by liquid scintillation counting (LSC). Each treatment was performed in duplicate, and all results are expressed as a mean value ± standard error. Temperature controlled experiments were performed in Control Environment Incubator Shaker (New Brunswick Scientific, Edison, NJ). After the completion of the reaction 10 mL THF were added to the reaction mixture to help dissolve the PDMS. The bottles were than shaken overnight at 200 rpm. Aliquots (1 mL) were placed in 10 mL scintillation cocktail and radioactivity remaining in the medium was measured; 80% of the radioactivity in the aqueous phase was recovered by this method. Analysis of the degradation products are subject of a future research.

The photo-Fenton reactions were carried out in Rayonet Photochemical Reactor (The Southern New England Ultraviolet Co.) fitted with RUL 3000 lamps having a peak energy output at 300 nm. During irradiation the samples were shaken at 200 rpm. The irradiation chamber temperature was 30-40°C. The glass UV cut off was at 290 nm.

Cationic (cethyltrimethylammonium bromide), anionic (sodium dodecyl sulfate) and neutral (Triton-X 450) surfactants were tested for their ability to increase PDMS solubility in the water phase. They were dissolved in DI water and added to the bottles at concentrations at, below and above their critical micelles concentration (CMC).

PDMS - soil experiments

PDMS dissolved in THF was applied to 2.5 g dry soil in 60 ml serum bottles in the concentration range of 10-1000 mg/kg. The maximum contaminant concentration was based on typical PDMS levels found in wastewater treatment sludges (3). The THF was allowed to evaporate completely. Aqueous solutions of iron (II) chloride and H_2O_2 were added to soil. The concentrations of $FeCl_2$ and H_2O_2 on a dry soil weight base were 100 mmol/kg and 1 to 2 mol/kg, respectively. Total liquid volume in the bottles was 2.5 mL. The reactions were performed in the dark and bottles were shaken at 200 rpm.

All experiments were initiated by addition of H_2O_2 to the vials. Control experiments using PDMS alone, combinations of PDMS and H_2O_2, and combinations of PDMS and iron species were performed in parallel.

RESULTS AND DISSCUSION

Degradation of PDMS by Fenton reagent in water

PDMS is characterized by low surface tension, resistance to chemical and thermal attack, water repellency, and resistance to UV radiation and oxidation. No data for its biodegradation exist. The room temperature solubility of PDMS is very low. Therefore, in mixtures with water ,essentially all PDMS existed as a separate liquid phase. PDMS was presented as a 0.05 mg/L suspension in the reaction vessel. No evaporative loss of PDMS from the vessel occurred.

Mineralization of PDMS under various reaction conditions was investigated quantitating the $^{14}CO_2$ released. The maximum observed conversion of PDMS to CO_2 was 80% at 66°C in presence of 2mM $FeCl_2$ and 880 mM H_2O_2 with stepwise addition of H_2O_2 over 3 days (Figure II-1). Under similar conditions but at room temperature only 8.5% transformation was observed after 5 days (Figure II-2). Thus temperature plays an important role in the Fenton degradation of PDMS. The effect of an incremental increase in temperature from 42°C to 65°C to the extend of PDMS transformation is shown in Figure II-3. At 42°C no ^{14} CO_2 was trapped over a 2 day reaction time, indicating no reaction. At 54°C the reaction commenced and was further accelerated at 66°C. A similar temperature effect was observed in a study by Pignatallo and Chapa (11), where a two phase mixture of comersial PCB oil Aroclor 1242 in water at 66°C was degraded by a photoassisted Fenton-type reaction consisting of Fe(III), H2O2, and UV light (300-400 nm).Up to 88% PCB removal and 85% dechlorination were obtained. Degradation at room temperature was minimal. The reason for the improved degradation at 66 °C was not clear according to the autors. They suggested that the temperature effect was due to either enhanced rate of PCB dissolution into water, or inorganic phototchemical kinetic factors affecting the oxidation reactions. An increase in the temperature leads to higher rate of $^{\bullet}$OH formation and this may in part account for the higher reactivities observed by Pignatell0 and Chapa, and in our studies with PDMS. In adition the improved degradation at 66^{o}C compared with room temperature may be due to the increased water solubility of the PDMS at the higher temperature. It is reasonable to assume that little oxidation occurs in the neat PDMS phase or for the PDMS absorbed or coated on surfaces.

Neither peroxide nor $FeCl_2$ is expected to be appreciably soluble in the neat phase. Increasing the solubility in water is likely to lead to partial degradation and formation of lower molecular weight compounds. Such oxidized intermediates would be more soluble than PDMS, thus increasing their effective reactivity in solution. Addition of H_2O_2 at this point causes formation of reactive $^{\bullet}$OH radicals capable of fast degradation of these products.

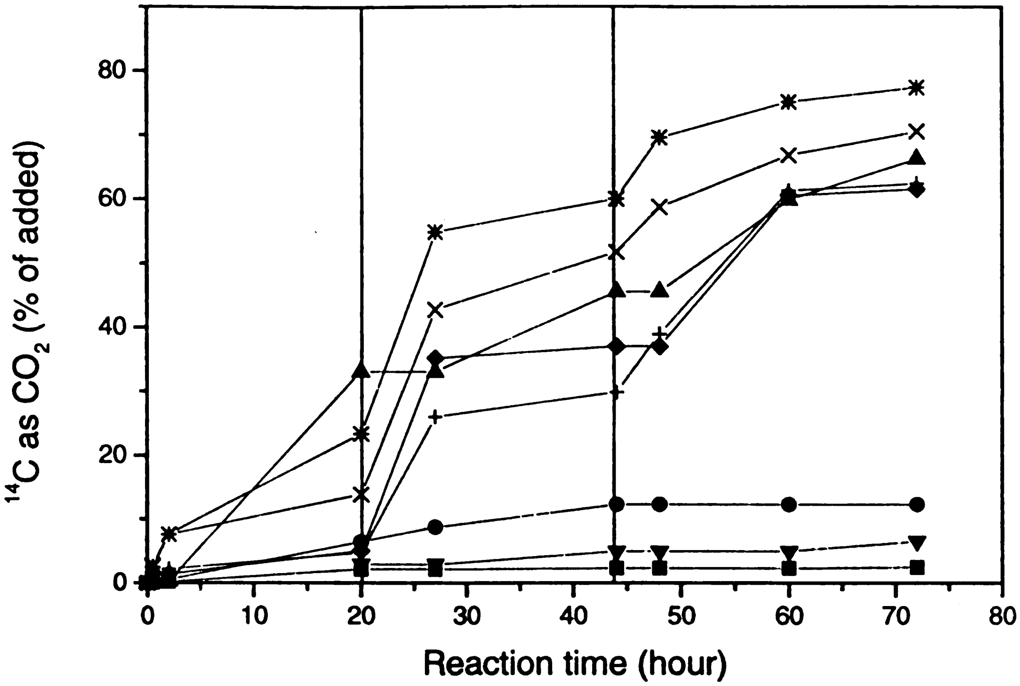


Figure II-1. Degradation of PDMS in water by Fenton's reagent at 66°C and addition of H_2O_2 indicated by the vertical lines (0.05 mg/L PDMS, 2 mM $FeCl_2$). Treatments consisted of (■) PDMS only, (●) 220 mM H_2O_2 only, (▲) 880 mM H_2O_2 only,(▼) $FeCl_2$ only, (◆) 100 mM H_2O_2, (+) 220 mM H_2O_2, (×) 1 mM iron, (-) 440 mM H_2O_2, (✶) 880 mM H_2O_2.

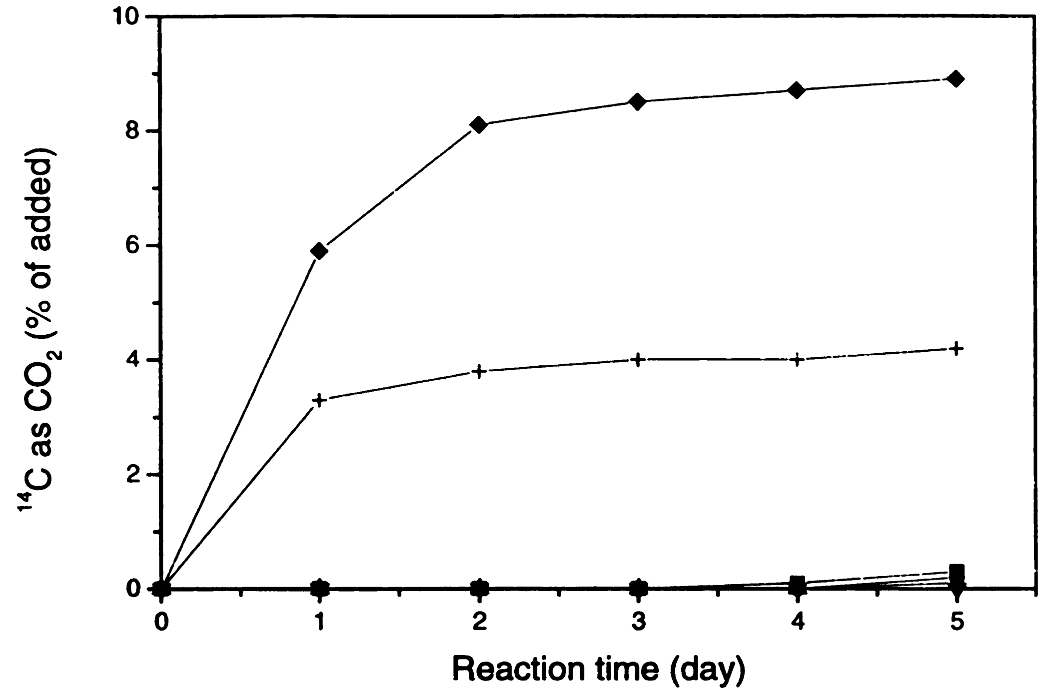


Figure II-2. Degradation of PDMS in water by Fenton's reagent and $FeCl_3/H_2O_2$ at room temperature (0.05 mg/L PDMS, 2 mM iron catalysts, 440 mM H_2O_2). Treatments consisted of (■) PDMS only, (●) H_2O_2 only, (▲) $FeCl_2$ only,(▼) $FeCl_3$ only, (◆) Fenton's reagent, (✶) $FeCl_3/H_2O_2$.

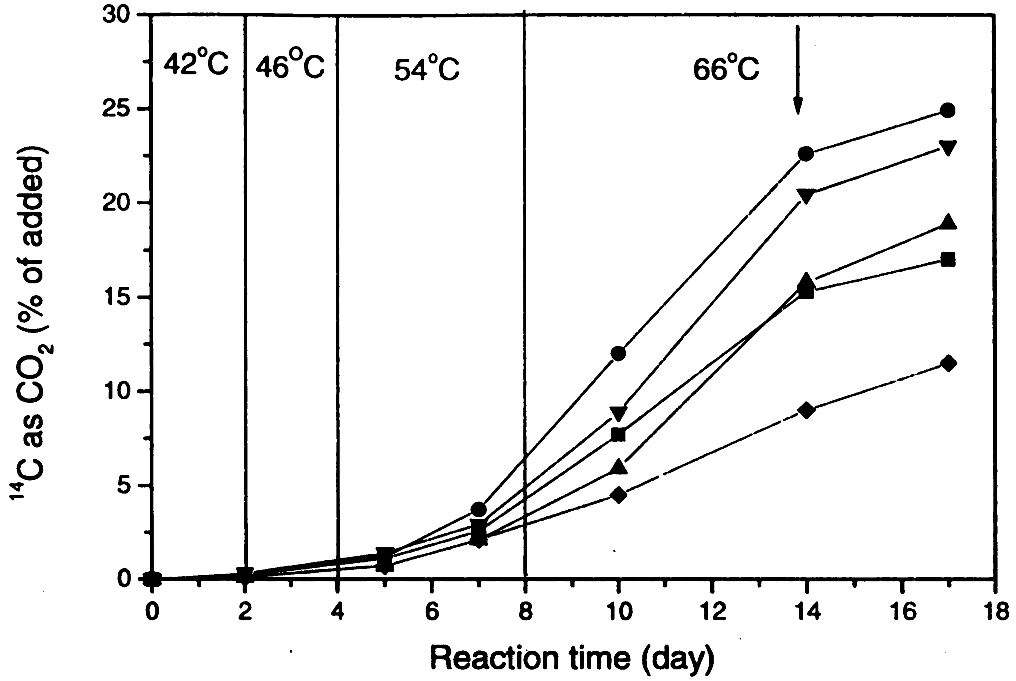


Figure II-3. Degradation of PDMS in water by Fenton's reagent and at different temperatures and adddition of H_2O_2 indicated by the arrow. Treatments consisted of (■) 0.05 mg/L PDMS, 2 mM $FeCl_2$, 440 mM H_2O_2 , (●) 0.05 mg/L PDMS, 2 mM $FeCl_2$, 880 mM H_2O_2, (▲) 0.05 mg/L PDMS, 3 mM $FeCl_2$, 440 mM H_2O_2,(▼) 0.05 mg/L PDMS, 3 mM $FeCl_2$, 880 mM H_2O_2, (◆) $FeCl_2$ only.

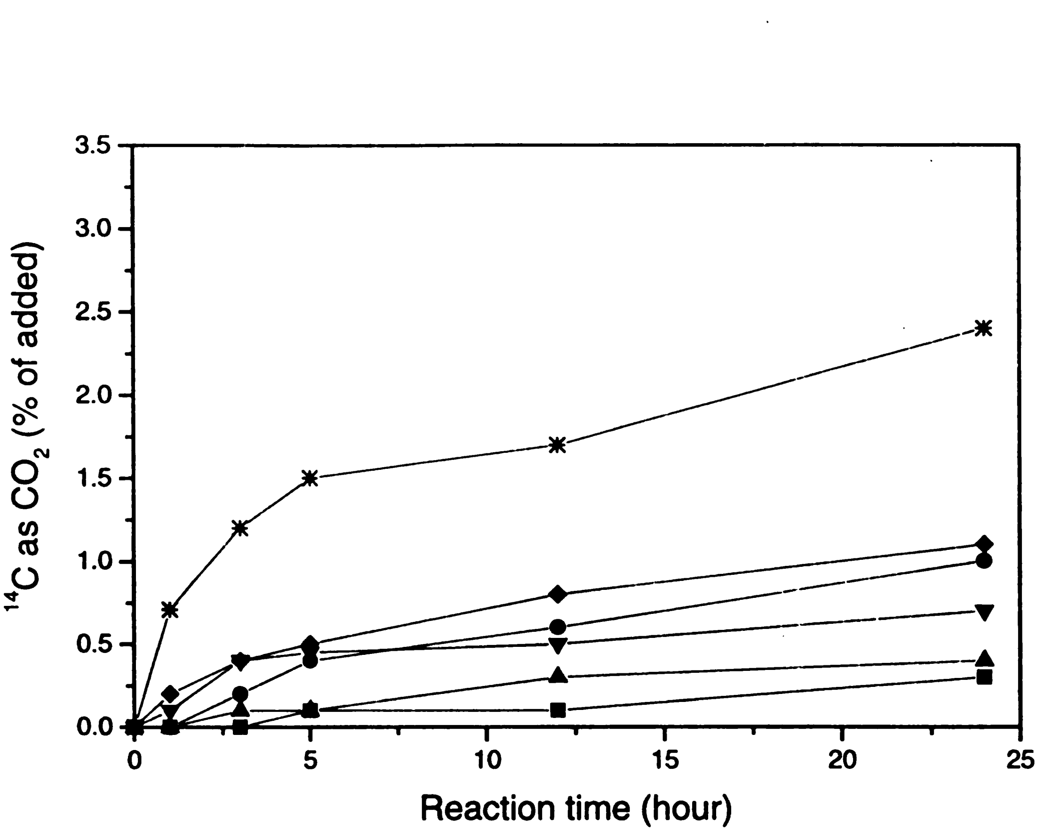


Figure II-4. Degradation of PDMS in water by Fenton's reagent at room temperature and different PDMS concentrations (2 mM $FeCl_2$, 440 mM H_2O_2). Treatments consisted of (■) PDMS only, (●) H_2O_2 only, (▲) $FeCl_2$ only,(▼) 0.01 mg/ml PDMS, (◆) 0.1 mg/ml PDMS, (✳) 0.2 mg/ml PDMS.

The extent of PDMS degradation depends on its initial concentrations in the aqueous phase. The higher concentrations were oxidized faster and to a higher extent at room temperature (Figure II-4). However, at 66°C 0,05 mg/L PDMS was oxidized to a greater extent than 0.1 mg/L PDMS (Figure II-5).

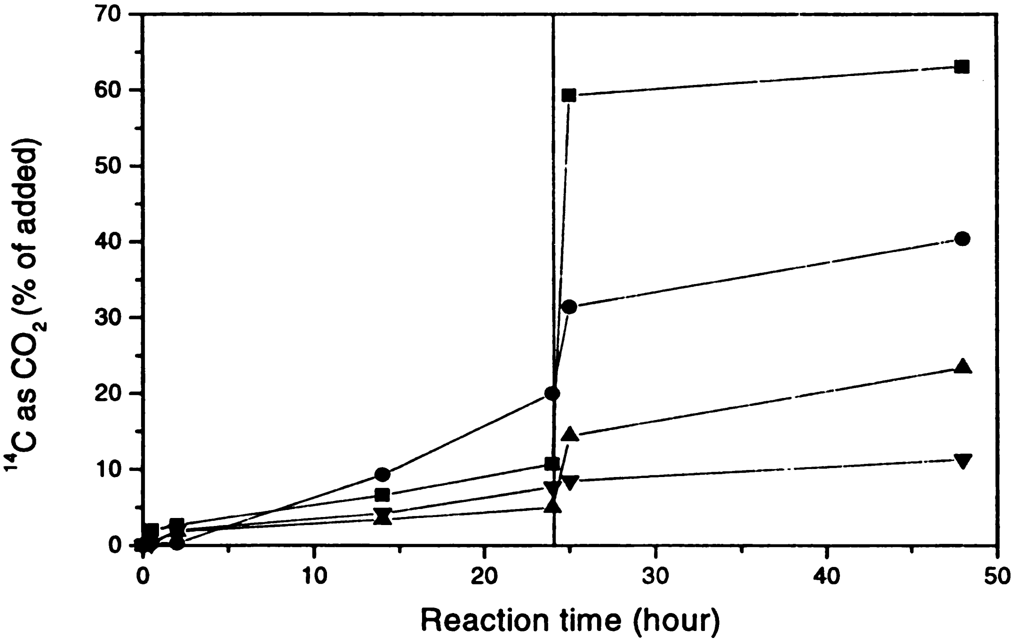


Figure II-5. Degradation of PDMS in water by Fenton's reagent at different PDMS concentrations and addition of H_2O_2 indicated by the vertical line (2 mM $FeCl_2$, 880 mM H_2O_2 ,66°C). Treatments consisted of (■) 0.1 mg/L PDMS and H_2O_2 only, (●) 0.05 mg/L PDMS and H_2O_2 only, (▲) 0.1 mg/L PDMS (▼) 0.05 mg/L PDMS.

Tetrahydrofurane (THF) had a detrimental effect on the Fenton reaction. Addition of 0.1 ml PDMS dissolved in THF (without evaporation of the THF) lead to 20 % less transformation of the PDMS as compared to the case where THF was evaporated (Figure II-6). Apparently, THF is quenching $^{\bullet}$OH radical formation and should be completely evaporated prior to addition of the other Fenton system components.

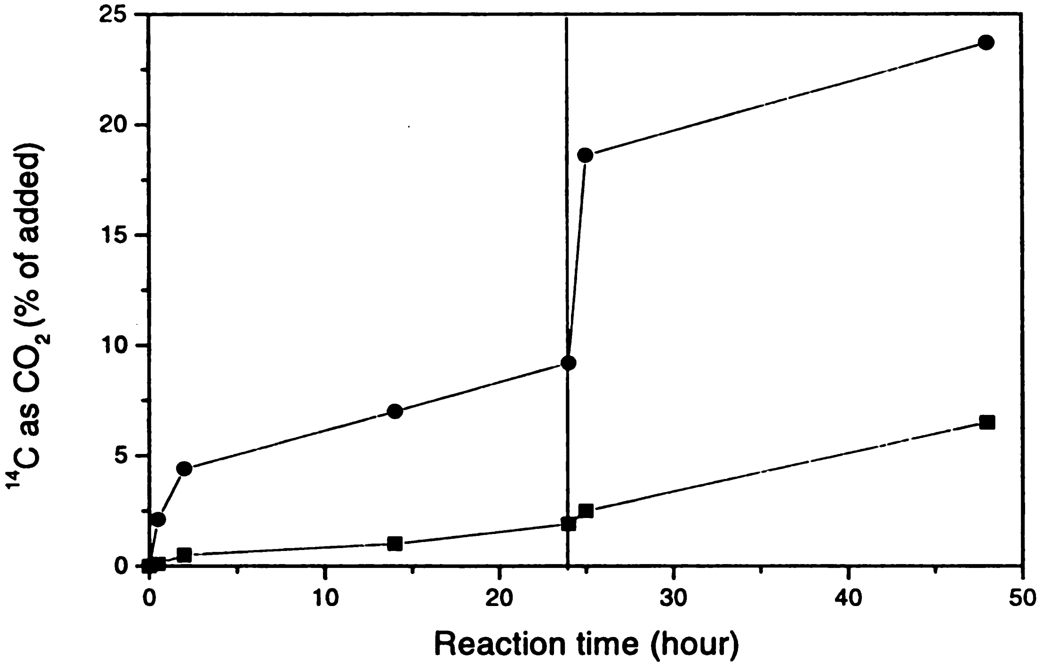


Figure II-6. Degradation of PDMS in water by Fenton's reagent at 66°C and adddition of H_2O_2 indicated by the vertical line with and without THF (0.05 mg/L PDMS, 2 mM $FeCl_2$, 440 mM H_2O_2). Treatments consisted of (■) PDMS, (●) PDMS + THF.

The effect of Fe(II) compared with Fe (III) at 66°C is negligible. Both iron catalysts resulted in about 70% mineralization after 70h (Figure II-7) and can be used interchangeable.

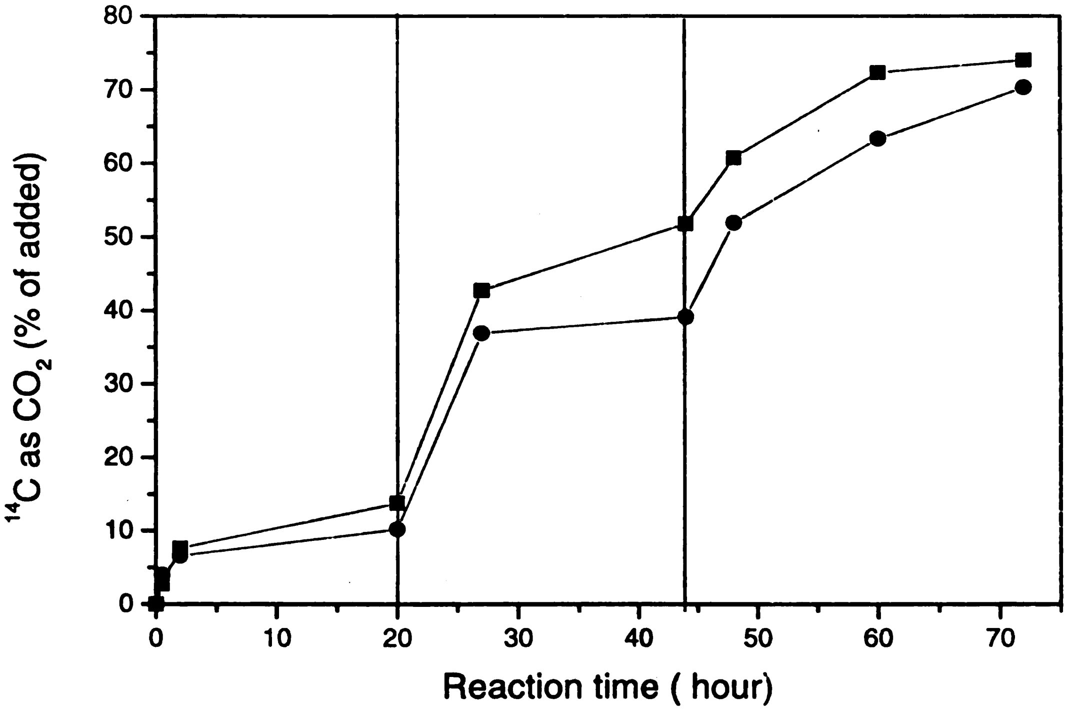


Figure II-7. Degradation of PDMS in water by Fenton's reagent and by $FeCl_3$ / H_2O_2 at 66°C and adddition of H_2O_2 indicated by the vertical line (0.05 mg/L PDMS, 2 mM iron catalyst, 440 mM H_2O_2). Treatments consisted of (■) Fe (II), (●) Fe(III).

Three types of surfactants were added in an attempt to increase PDMS solubility and hence increase the rate of reaction at room temperature. Cationic (cethyltrimethylammonium bromide), anionic (sodium dodecyl sulfate) and neutral (Triton-X 450) surfactants at concentrations below and above their critical micelle concentration (CMC), as well as very low concentrations (0.01 mg/ml) were evaluated. All the surfactants tested had a strong detrimental effect on the PDMS degradation. They probably served as competing substrates and undergo oxidation by $^{\bullet}OH$ radicals instead of PDMS, and/or they may have complexed Fe(II) leading to its inactivation.

An attempt to improve the degradation of PDMS was done by using a photo-Fenton oxidation system at room temperature. Irradiation of an aqueous solutions (0.05 and 0.1 mg/L) of PDMS with UV resulted in no greater formation of $^{14}CO_2$ as compared to non-irradiated controls. This result is consistent with a study (10) that has shown only 1.7 % degradation of PDMS after 37 days of irradiation with UV light in presence of nitrate ions. Hydroxyl radicals are formed during irradiation of nitrate or nitrite ions (10). The slow degradation was thought to be due to the very low water solubility of PDMS and the limited surface area of the polymer available to react with the $^{\bullet}OH$ radicals.

Degradation of PDMS by Fenton reagent in soil

PDMS is expected to partition onto solids and be sorbed by the soil due to its low water solubility. This fact, combined with the potential of competition of soil colloidal materials for Fenton reactive intermaediates, was expected a priori to reduce the conversion of PDMS to CO_2. When the reaction was conducted at room temperature for

24 hours a maximum conversion of only about 3% PDMS to CO_2 was obtained. This is less than half the maximum conversion obtained in aqueous (soil-free) systems at room temperature. The process was influenced by the initial PDMS concentrations (Figure II-8); lower concentrations were degraded to a higher extent.

As in pure water, temperature also was a major factor that influenced the Fenton oxidation of PDMS in soil. Figure II-9 shows the effect of a step wise increase in the temperature from 46°C to 68°C at different H_2O_2 concentrations. The highest degradation of 12% was achieved at 68 °C and 2 mol/kg H_2O_2. In attempt to increase the minaralization of PDMS, H_2O_2 was added incrementaly. The highest percent degradation achieved was 20% for 7 days at 66°C, during which, portions of H_2O_2 were added 3 times (Figure II-10). The control which contained PDMS and $FeCl_2$ had 14 % $^{14}CO_2$ trapped indicating that volatilization is probably a major route of the polymer transformation. This phenomena may be explained with the catalytic role of the soil clay minarals, which can promote PDMS degradation.

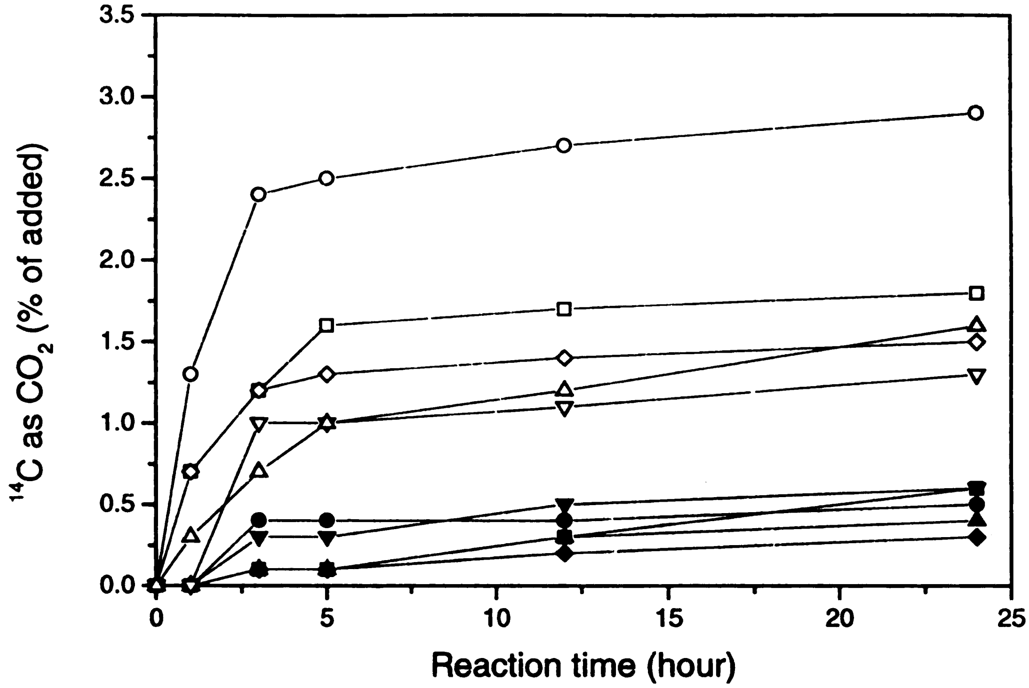


Figure II-8. Degradation of PDMS in soil by Fenton's reagent at room temperature and different PDMS concentrations (100 mg/kg $FeCl_2$, 0.7 M H_2O_2). Treatments consisted of (■) 10 mg/kg PDMS only, (●) 100 mg/kg PDMS only, (▲) 500 mg/kg PDMS only, (▼) 1000 mg/kg PDMS only, (Δ) H_2O_2 only, (✱) $FeCl_2$ only, (O) 10 mg/kg PDMS Fenton, (□) 100 mg/kg PDMS Fenton, (◇)500 mg/kg PDMS Fenton, (∇)1000 mg/kg PDMS Fenton.

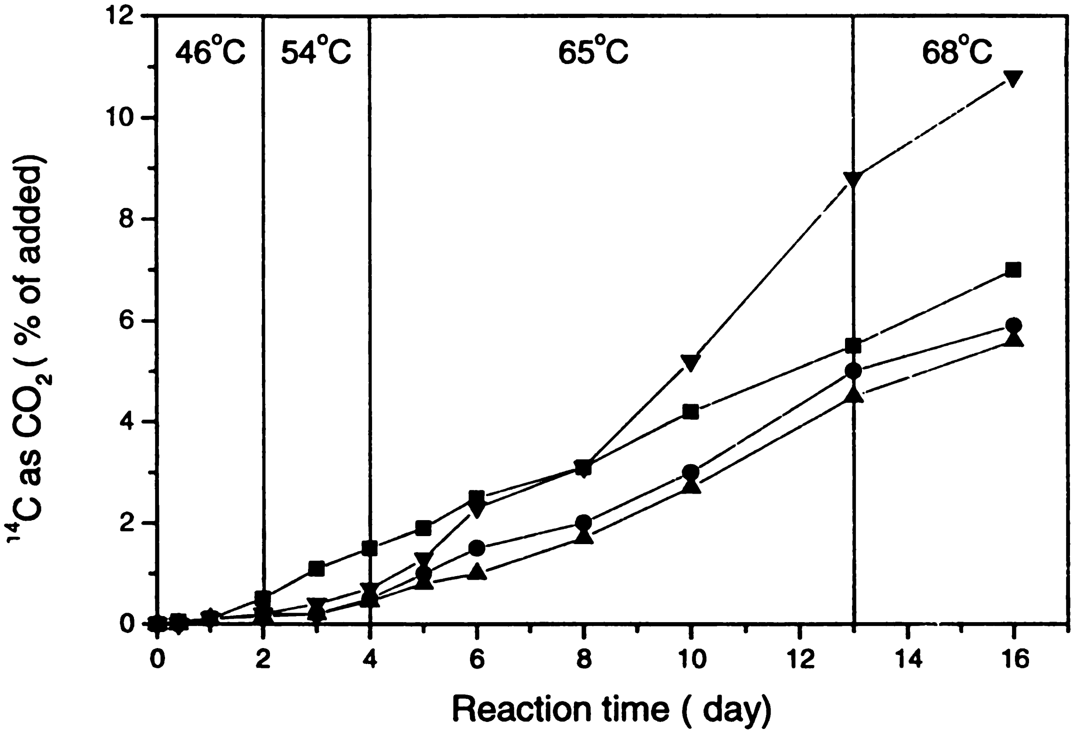


Figure II-9. Degradation of PDMS in soil by Fenton's reagent at diferent temperatures and different H_2O_2 concentrations (10 mg/kg PDMS, 100 mM $FeCl_2$). Treatments consisted of (■) 0.5 mM H_2O_2, (●) 0.75 mM H_2O_2, (▲) 0.5 mM H_2O_2, (▼) 2 mM H_2O_2.

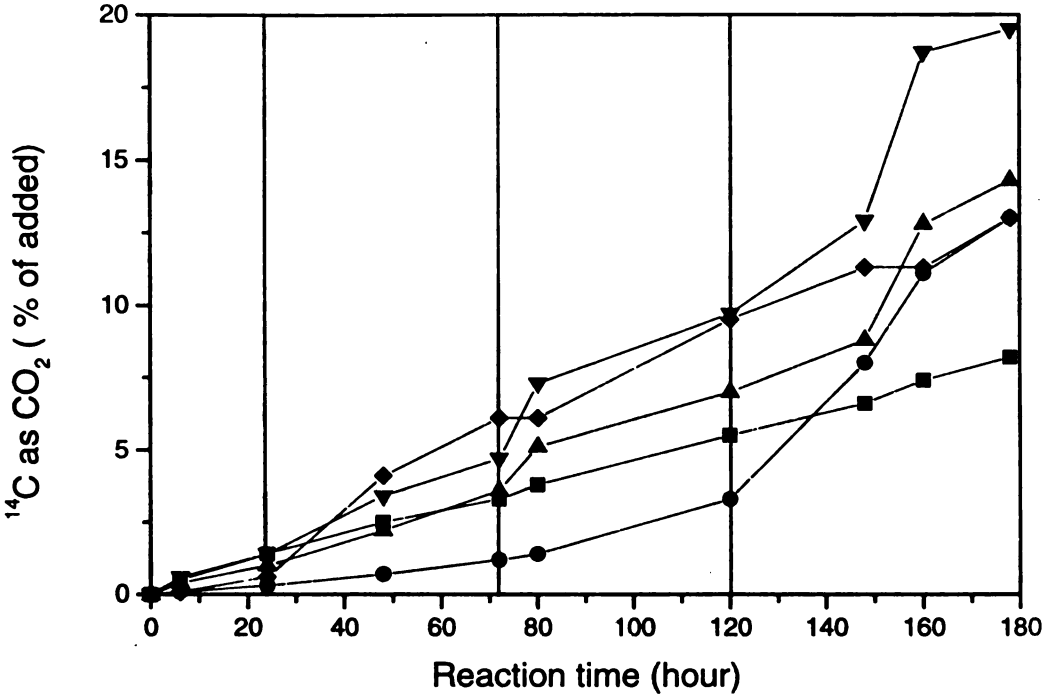


Figure II-10. Degradation of PDMS in soil by Fenton's reagent at 66°C and addition of H_2O_2 at different concentrations (10 mg/kg PDMS, 100 mM $FeCl_2$). Treatments consisted of (■) 1.0 mM H_2O_2 only, (●) 2.0 mM H_2O_2 only, (▲) 1.0 mM H_2O_2, (▼) 2 mM H_2O_2 , (◆) PDMS + $FeCl_2$ only.

CONCLUSIONS

In summary, PDMS are oxidized in aqueous systems containing ferrous ion and hydrogen peroxide above room temperature. PDMS degradation of 80% in aqueous system and 20 % in soil was achieved by repeated addition of H_2O_2 and 66°C. Temperature is obviously a critical variable. After further development these systems might be useful for treatment of wastewaters and soils contaminated with PDMS.

REFERENCES

1. Noll, W., *Chemistry and Technology of Silicones*, Academic Press Inc., New York, NY 10003, 1968

2. Lentz, C., *Silicones in the environment*, Ind.Res.Dev., 22:139, 1980

3. Lehmann, R.G., S.Varaprath, C.L. Frye, *Degradation of silicone polymers in soil,* Environ.Toxicol.Chem., 7:1061, 1994

4. Carpenter, J.C., J.A.Cella, S.B.Dorn, *Study of degradation of PDMS on soil,* Environ.Sci. Technol., 29:864, 1995

5. Buch, R.R., D.N.Ingerbrigsten, *Rearragement of Poly(dimethylsiloxane) fluids on soil,* Environ.Sci.Technol., 6:676, 1979

6. Xu, Shihe, R.G. Lehmann, J.R. Miller, G. Chandra, *Degradation of PDMS (Silicones) as influenced by clay minerals,* Environ. Sci. Technol., 32:1199-1206, 1998

7. Fenton, H.J.H., *On a new reaction of tartaric acid*, Chem.News, 28:39, 1876

8. Mohanty, N.R., I.W.Weil, *Oxidation of 2,4-Dinitrotoluene using Fenton's reagent. Reaction mechnisms and their practical applications.*, Haz.Waste Haz. Mater., 10:171, 1993

9. Sun, Y., J.J. Pignatello, *Photochemical reactions involved in the total mineralization of 2,4-D by* $Fe^{3+}/H_2O_2/UV$, Environ.Sci.Technol., 27:304, 1993

10. Buch, R.R., T.H.Lane, R.B.Annelin, C.L.Frye, *Photolytic oxidative demethylation of aqueous dimethylsiloxanols,* Environ.Toxicol.Chem., 6:676, 1984

11. Pignatello, J.J., G.Chapa, *Degradation of PCBs by ferric ion,* H_2O_2 *and UV light,* Environ.Toxicol.Chem., 13:423, 1994