

Oxidation of sorbed hexachlorobenzene in soils using catalyzed hydrogen peroxide

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Abstract

The Fenton-like oxidation of a highly hydrophobic and biorefractory compound, hexachlorobenzene, was investigated in silica sand and a natural soil using a number of process conditions including catalysis by soluble iron and naturally-occurring iron minerals coupled with a range of hydrogen peroxide concentrations from 3 mM to 300 mM (100 mg l⁻¹ to 10 000 mg l⁻¹). In addition, hexachlorobenzene desorption rates were quantified and compared to the rates of oxidation. Using soluble iron and peroxide concentrations ≥ 100 mM, sorbed hexachlorobenzene was oxidized more rapidly than the measured desorption rate, indicating that it may have been, in part, oxidized on the surface of the silica sand. The results suggest that hydroxyl radicals may cross the liquid–solid interface under aggressive reaction conditions. Alternatively, the aggressive Fenton-like reaction conditions may alter the hexachlorobenzene sorption characteristics and increase its rate of desorption resulting in an enhanced coupled desorption–oxidation mechanism.

In the second phase of study using natural iron minerals as the catalyst, hexachlorobenzene was oxidized more slowly than it was desorbed. The probable mechanism for mineral-catalyzed oxidation is desorption followed by oxidation through a Fenton-like process at the mineral surface. In the treatment of a natural sandy loam soil, hexachlorobenzene was oxidized at rates slower than it was desorbed. The most efficient process condition (mineral-catalyzed oxidation) was optimized using a central composite rotatable factorial design analysis. These experiments showed that maximum hexachlorobenzene removal occurred with H₂O₂ concentrations of 3 to 5 mM and slurry volumes of 25 to 30 times the field capacity of the soil.

1. Introduction

The use of catalyzed hydrogen peroxide has recently gained increased attention for the treatment of contaminated soils [1–4]. The process is based on Fenton's reagent,

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in which the decomposition of hydrogen peroxide is catalyzed by soluble iron or other transition elements [5]. The peroxide decomposes to hydroxyl radicals, which are strong, nonspecific oxidants that react with most organic compounds at near-diffusion controlled rates [6, 7]. The oxidation of organic contaminants in a variety of aqueous Fenton's systems has been demonstrated. Early research by Merz and Waters [8] documented the oxidation of toluene, nitrobenzene, and chlorobenzene to the products phenol, cresols, biphenyls, and benzaldehydes. Davidson and Busch [9] oxidized a waste stream of phenol and demonstrated ring opening, and Barbeni et al. [10] degraded a number of chlorophenols and documented mineralization by stoichiometric chloride recovery. Murphy et al. [11] investigated the treatability of formaldehyde using iron (III) as a catalyst, and Sedlak and Andren [12] documented ring cleavage and partial mineralization of chlorobenzene and chlorophenol.

The use of Fenton-like reactions for soil remediation was first reported by Watts et al. [1]. They documented that pH 2–3 was optimum for soil treatment, and that pentachlorophenol was mineralized in silica sand systems. Tyre et al. [2] subsequently demonstrated the oxidation of pentachlorophenol, hexadecane, trifluralin, and dieldrin in soils, and found that the most efficient stoichiometry (i.e., the minimum moles of H_2O_2 consumed per mole of contaminant oxidized) during treatment occurred without the addition of soluble iron. The oxidation of substituted aromatics by a Fenton's system was demonstrated using alumina-supported iron as a heterogeneous catalyst [13]. Because soils contain a number of iron oxyhydroxides minerals, such as goethite ($\alpha\text{-FeOOH}$), Watts et al. [14] proposed that analogous mineral-catalyzed reactions may provide a mechanism for the Fenton-like treatment of contaminated soils.

Hydrophobic organic contaminants in soils are found primarily in the sorbed phase. However, hydroxyl radicals are generated in aqueous solution by Fenton-like reactions, and react almost instantaneously, which may limit their ability to oxidize sorbed contaminants. For example, Sheldon and Kochi [15] stated that nonaqueous phase substrates have minimal potential for attack by hydroxyl radicals because of mass transfer limitations. However, Watts et al. [16] suggested that aggressive catalyzed peroxide treatment could oxidize sorbed and particulate pentachlorophenol, and emphasized that the oxidation of sorbed species may be necessary for the remediation of some contaminated soils.

Hexachlorobenzene has ideal characteristics as a model substrate for investigating the Fenton-like treatment of a highly hydrophobic, sorbed contaminant in a soil–water system. Hexachlorobenzene was formerly employed as a wheat fungicide in the US, and has been used as a surrogate for studying the degradation and chemodynamics of 2, 3, 7, 8-tetrachlorodibenzo-*p*-dioxin [17]. Like the dioxin, hexachlorobenzene is characterized by low water solubility, a high octanol–water partition coefficient, and low vapor pressure (Table 1). Because of its high degree of halogenation, hexachlorobenzene is deactivated toward electrophilic attack and is, therefore, highly biorefractory. Biodegradation studies have shown no significant degradation over a six month period [20]. Therefore, the purpose of this research was to document the oxidation of sorbed hexachlorobenzene and to determine the process conditions that promote the oxidation of this sorbed model contaminant.

Table 1
Characteristics of hexachlorobenzene (from [18, 19])

Specific gravity	2.044
Water solubility	5 $\mu\text{g l}^{-1}$
Vapor pressure	1.1 $\times 10^{-5}$ mm Hg
Log K_{ow}	6.2

2. Materials and methods

2.1. Materials

Hexachlorobenzene was obtained from Aldrich (Milwaukee, WI), and hexane (HPLC grade), silica sand, and FeSO_4 were purchased from Fisher Scientific (San Francisco, CA). Goethite was obtained from D.J. Minerals (Butte, Montana), and hydrogen peroxide was provided by Solvay Interlox (Deer Park, TX). All aqueous solutions were prepared with water from a Continental Water Systems Corporation (San Antonio, TX) Modupure deionizing system.

The natural soil used was a grayish-brown gravelly loamy coarse sand, mixed, mesic Torriothentic Haploxeroll, sampled from the Carson Valley, Nevada. Its particle size distribution was determined by the pipette method [21]. Organic carbon was determined by combustion at 900 °C with evolved CO_2 trapped in KOH and measured by back titration of unreacted KOH [22]. Amorphous and crystalline iron and manganese oxyhydroxides were determined by citrate–bicarbonate–dithionite extractions [23]. Cation exchange capacity was established by saturation with sodium acetate at pH 8.2 [24]. The soil characteristics are listed in Table 2. These data indicate that the Carson Valley soil is primarily sand, and that it contains crystalline iron oxides sufficient to catalyze Fenton-like reactions [2].

2.2. Materials preparation

Silica sand was passed through a 0.18 mm (80 mesh) sieve to provide a consistent surface area for the sorption of hexachlorobenzene. Goethite was crushed and passed through a 0.095 mm (150 mesh) sieve. Spiked sand and soil were prepared by adding hexachlorobenzene dissolved in hexane and allowing the solvent to evaporate. For the mineral-catalyzed systems, the goethite was added after the sand was spiked with hexachlorobenzene.

2.3. Hexachlorobenzene residual on silica sand after washing

To determine the capacity of the silica sand to sorb hexachlorobenzene, 2.5 g of the sand was spiked with 250 $\mu\text{g kg}^{-1}$ hexachlorobenzene in hexane and the solvent was allowed to evaporate. The sand was then washed five times with 10 ml of deionized water; the washings were extracted with hexane and analyzed for hexachlorobenzene.

Table 2
Characteristics of the Carson Valley soil

Organic carbon content (mg kg ⁻¹)	3700
Sand (%)	86.5
Silt (%)	11.0
Clay (%)	2.5
Crystalline Fe oxides (mg kg ⁻¹)	4400
Crystalline Mn oxides (mg kg ⁻¹)	100
Amorphous Fe oxides (mg kg ⁻¹)	4400
Amorphous Mn oxides (mg kg ⁻¹)	100
Cation exchange capacity (cmol kg ⁻¹)	4.28
pH	6.4

The hexachlorobenzene concentration remaining on the sand (i.e., that associated with no removal in the washes) was the level used in subsequent experiments.

2.4. Rate of hexachlorobenzene desorption

The gas purging (GP) procedure reported by Brusseau et al. [25] was used to measure desorption rates in soils. The GP procedure is based on two steps – desorption and volatilization. Desorption is the rate limiting step because, when purged from the aqueous phase of the soil slurry, hydrophobic compounds have a rapid escaping velocity because of their low water solubility. Desorption of hexachlorobenzene was quantified using 15 ml of deionized water and 7.5 g of spiked sand or soil. The aqueous phase was purged with compressed air at a flow rate of 20 ml min⁻¹, and aliquots were analyzed over time for residual hexachlorobenzene. Aliquots were collected at a minimum of five time periods and analyzed for residual hexachlorobenzene.

2.5. Oxidation procedures

Three systems of varied complexity were used to study the Fenton-like treatment of hexachlorobenzene: (1) silica sand with soluble iron addition; (2) silica sand with Fenton-like reactions catalyzed by the iron mineral goethite, and; (3) the Carson Valley soil catalyzed by naturally-occurring iron oxides. All reactions were conducted at 20 ± 2 °C using 2.5 g of sand or soil in 40 ml borosilicate volatile organic analysis (VOA) screw-top, PTFE-sealed vials. Five initial concentrations of H₂O₂ were used: 3 mM, 30 mM, 100 mM, 200 mM, and 300 mM. In silica sand-soluble iron experiments, a molar H₂O₂:Fe ratio of 2:1 was used [12]. Mineral-catalyzed systems contained 5% goethite in silica sand (w/w), which is representative of natural soils [26].

The H₂O₂ (5 ml) was added to the spiked sand or soil, followed by soluble iron addition (if necessary) and adjustment to pH 3 using 1.0 N NaOH or 1.0 N H₂SO₄. Previous work by Watts et al. [1] showed that a pH range of 2 to 3 provides optimum

condition for the degradation of pentachlorophenol. Experiments were stopped by adding 0.3 ml of concentrated H_2SO_4 . The ability of H_2SO_4 to quench Fenton-like reactions was verified by Watts et al. [1]. They found that its addition to aggressive (7%) H_2O_2 -soluble iron systems quenched the oxidation of pentachlorophenol.

2.6. Process optimization

To optimize the treatment process, a central composite rotatable factorial design treatment matrix [27] was used, and the corresponding response surfaces were generated to determine the volume and concentration of hydrogen peroxide that provide the most efficient stoichiometry. Hydrogen peroxide concentrations from 0.05 to 30 mM and peroxide volumes of 5 to 30 times the soil field capacities were used as experimental matrices. The field capacity for the silica sand was 0.56 ml g^{-1} ; the field capacity for the Carson Valley soil was 0.48 ml g^{-1} . The experiments were conducted until the H_2O_2 was depleted, and the residual hexachlorobenzene was determined at that time.

2.7. Analyses

Degradation of hexachlorobenzene was monitored by shake-extracting the vial contents for 24 h with 5 ml of hexane and analyzing the extract by gas chromatography. A Hewlett–Packard 5890A gas chromatograph with electron capture detector and Supelco PTE-5 glass capillary column (0.32 mm i.d. \times 15 m length) was used with initial oven temperature 130°C , program rate 5°C min^{-1} , final temperature 180°C , and nitrogen carrier gas flow rate 8 ml min^{-1} . Integrated peak areas were calibrated using a series of standard hexachlorobenzene concentrations made from a single volumetrically-prepared stock solution which encompassed the range of hexachlorobenzene values detected.

Hydrogen peroxide concentrations below 0.1% were monitored by TiSO_4 spectrophotometry [28] after passing an aliquot through a $0.45 \mu\text{m}$ membrane filter. Hydrogen peroxide concentrations greater than 0.1% were monitored by iodometric titration [29].

3. Results and discussion

Hexachlorobenzene was originally added to the silica sand at a concentration of $250 \mu\text{g kg}^{-1}$. Inspection of the spiked sand by visible microscopy ($100\times$) showed small particles of hexachlorobenzene within the matrix and attached to the sand surfaces, indicating that the adsorptive capacity of the sand had been exceeded. The five deionized water washings were then used to remove the loosely bound particulates, while leaving sorbed hexachlorobenzene. The results of the procedure for determining hexachlorobenzene residual after five deionized water washings of the silica sand are shown in Fig. 1. Analyses of the series of deionized water washings and the silica sand showed that no hexachlorobenzene was removed below $50 \mu\text{g kg}^{-1}$.

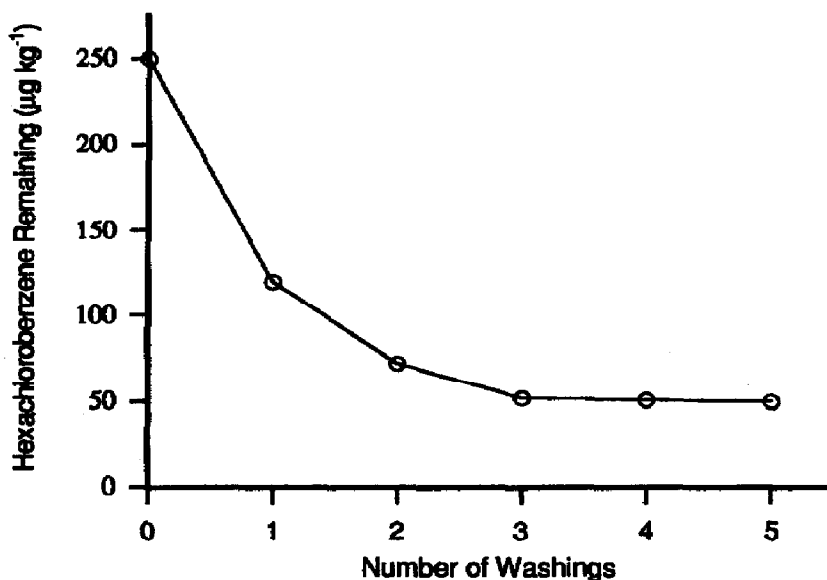


Fig. 1. Hexachlorobenzene residual on silica sand during five deionized water washings.

Separate silica sand samples spiked with $50 \mu\text{g kg}^{-1}$ hexachlorobenzene showed no loss of sorbed hexachlorobenzene by repeated washings. The ability of the Carson Valley soil to sorb $50 \mu\text{g kg}^{-1}$ hexachlorobenzene was verified when no hexachlorobenzene was detected by filtering ($0.45 \mu\text{m}$ membrane filter) and analyzing the aqueous phase by gas chromatography.

Based on the GP procedure, desorption of hexachlorobenzene from the washed silica sand followed first-order kinetics (Fig. 2), and approximately 50% of the hexachlorobenzene was desorbed from the sand in the 4 h period. The basis for investigating the oxidation of sorbed hexachlorobenzene is the rate of oxidation relative to the rate of desorption. If oxidation occurs more rapidly than desorption, then at least part of the hexachlorobenzene oxidation may have occurred in the sorbed state. Fig. 2 shows that hexachlorobenzene was oxidized at a rate slower than desorption for the 3 mM H_2O_2 slurries. With a 30 mM H_2O_2 concentration, the rate of oxidation was nearly equal to the rate of desorption. With both the moderately low 3 mM and 30 mM concentrations, the rate of desorption controlled the rate of hexachlorobenzene oxidation. For the 100, 200, and 300 mM H_2O_2 concentrations, the rate of hexachlorobenzene oxidation was significantly greater than the rate of desorption. The rate of hexachlorobenzene oxidation was highest in the first 0.5 h, and the reaction was completed within 1 h due to H_2O_2 depletion. For the three highest H_2O_2 concentrations, 80% of the sorbed hexachlorobenzene was oxidized in the first 0.5 h, while only 34% of the hexachlorobenzene was desorbed. By difference, approximately 46% of the sorbed hexachlorobenzene was degraded during the 0.5 h time period. These data show that the aggressive oxidation conditions characteristic of higher H_2O_2 concentrations combined with catalysis by soluble iron significantly increased the rate of hexachlorobenzene oxidation relative to the measured rate of desorption.

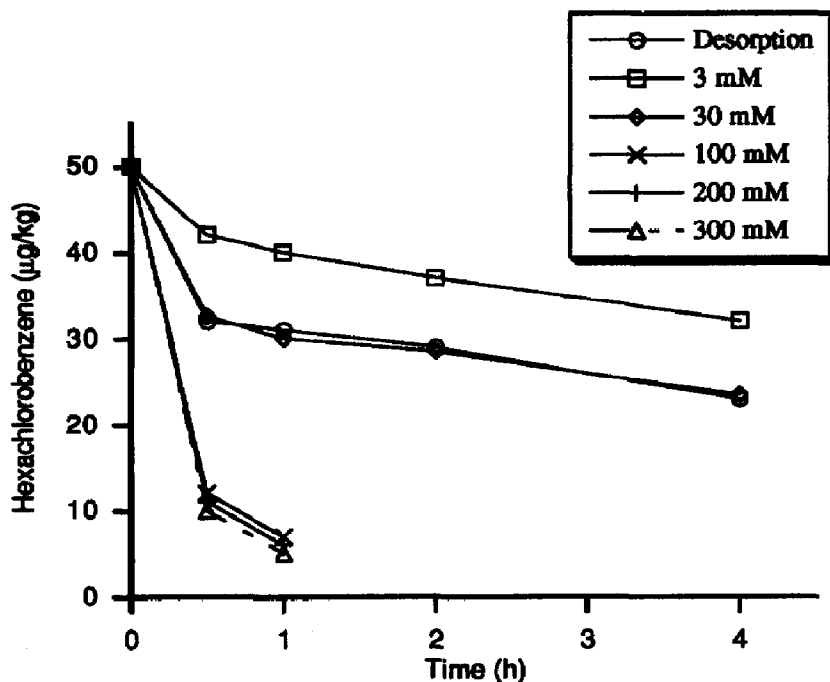


Fig. 2. Hexachlorobenzene desorption and oxidation in the silica sand-soluble iron system.

Mass flux rates, such as the rate of desorption of hexachlorobenzene from silica sand, may be described by:

$$dC/dt = K(C_s - C), \quad (1)$$

where C_s is the aqueous phase hexachlorobenzene saturation concentration; C is the steady-state aqueous phase hexachlorobenzene concentration; K is a mass transfer coefficient describing hexachlorobenzene flux from the sorbed phase to the aqueous phase.

If the steady state hexachlorobenzene concentration (C) is negligible or nearly equal during both the oxidation and GP desorption procedures, then two possible conceptual mechanisms may describe the phenomenon of oxidation rates that proceed more rapidly than the measured desorption rate. First, the aggressive conditions associated with H_2O_2 concentrations ≥ 100 mM may be capable of promoting the transfer of hydroxyl radicals across the liquid-solid interface to oxidize sorbed hexachlorobenzene. Alternatively, the Fenton-like reactions may alter the hexachlorobenzene-silica sand adsorption characteristics resulting in a more rapid rate of desorption and an higher value for the mass transfer coefficient (K). In this second mechanism of enhanced desorption-oxidation, hexachlorobenzene oxidation would occur in the aqueous phase, but the rate at which the hexachlorobenzene becomes available for oxidation (i.e., the rate of desorption) would have increased significantly.

Fundamental studies of Fenton's chemistry have used dilute H_2O_2 , which provides minimal quenching for the elucidation of kinetics and mechanisms [30]. The inability of dilute Fenton's reactions to oxidize nonaqueous phase substrates has been well

documented [15]. However, aggressive Fenton-like reactions have been used to oxidize organics in complicated matrices. For example, the addition of 35% H_2O_2 to soils is used as a standard procedure for the removal of organic carbon prior to mineralogical analysis [31], and Torrijos and Perez-Bustamante [32] used 30% catalyzed H_2O_2 to degrade the polymer methyl carboxycellulose. Based on these procedures, Watts et al. [1] and Tyre et al. [2] used catalyzed H_2O_2 in the percent range to treat hydrophobic contaminants in soils of varying complexity. In contrast to previous studies, the results of this research show that aggressive conditions may be capable of oxidizing nonaqueous phase substrates, even at hydrogen peroxide concentrations lower than the percent range.

Hydrogen peroxide residuals during the silica sand-soluble iron experiments are shown in Fig. 3. These data show that nearly all of the H_2O_2 was depleted within 4 h for the 3 mM and 30 mM H_2O_2 concentrations and within 1 h for the higher H_2O_2 concentrations with no corresponding hexachlorobenzene oxidation after the H_2O_2 was consumed. These results show that the batch treatment of soils to promote the degradation of sorbed hexachlorobenzene may be possible using ≥ 100 mM H_2O_2 with added soluble iron. The data also suggest that the oxidation of sorbed contaminants may provide a process design for rapidly treating other highly hydrophobic compounds such as polychlorodibenzo-*p*-dioxins (PCDDs) and polychlorinated biphenyls (PCBs).

For the silica sand-goethite system, hexachlorobenzene degradation proceeded more slowly than desorption for all of the H_2O_2 concentrations investigated (Fig. 4). These results show that no oxidation of sorbed hexachlorobenzene occurred. The slow oxidation rate with goethite as the catalyst is typical of the results described by Tyre et al. [2]. Mineral-catalyzed oxidations may be a combination of surface

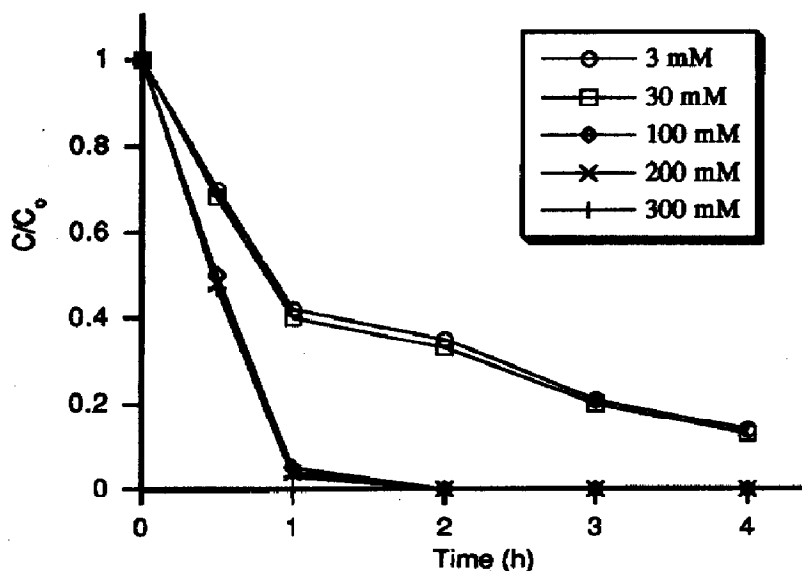


Fig. 3. Hydrogen peroxide concentration as a function of time during the oxidative treatment of the silica sand-soluble iron system.

Fenton-like reactions and homogeneous oxidations resulting from iron dissolution of the minerals. The conceptual model for this system is desorption of the hexachlorobenzene into the aqueous H_2O_2 phase of the slurry where it is oxidized on the surfaces of the minerals or by homogeneous reactions promoted by the dissolution of the goethite. These mechanisms provide a slow rate of oxidation as well as a slow rate of H_2O_2 consumption (Fig. 5). The use of iron minerals to promote Fenton-like

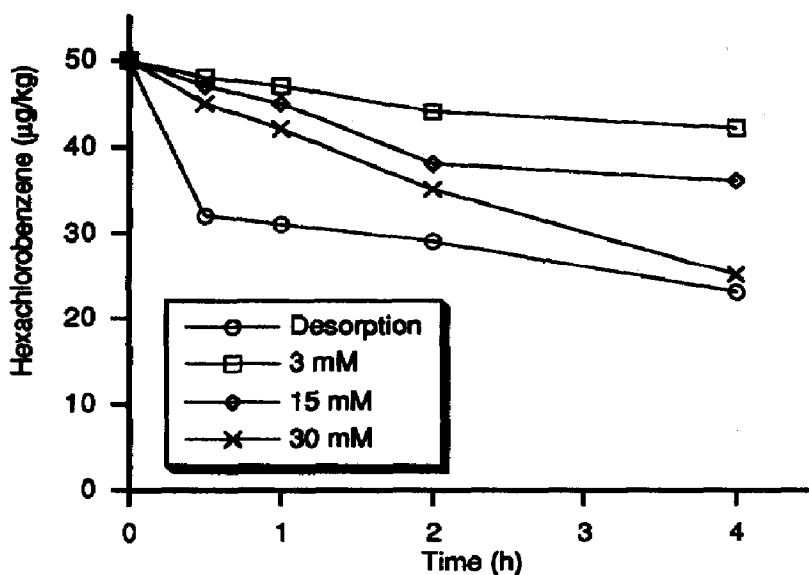


Fig. 4. Hexachlorobenzene desorption and oxidation in the silica sand-goethite system.

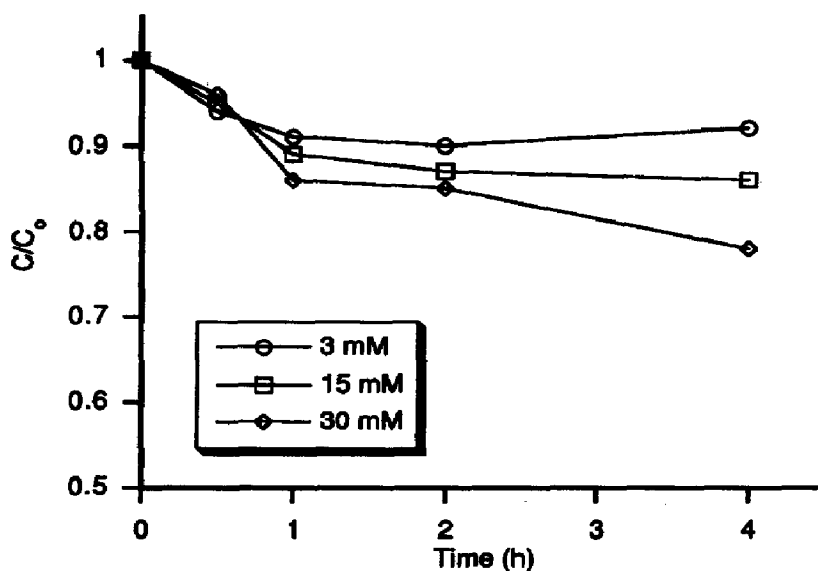


Fig. 5. Hydrogen peroxide concentration as a function of time during the oxidative treatment of the silica sand-goethite system.

reactions appears to provide an efficient, but slow, means of oxidizing soil contaminants.

Treatment of the Carson Valley soil showed that extractable hexachlorobenzene concentrations first increased followed by a decrease after 12 h in the 30 mM H_2O_2 system (Fig. 6). The oxidation may have released the hexachlorobenzene that was not extractable in the controls (i.e., increased its extraction efficiency). This concept is consistent with the work of Griffith and Schnitzer [33], who found that H_2O_2 was capable of releasing minor portions of strongly bound water-insoluble organic compounds associated with soil organic matter which were not initially solvent extractable. Also, the data of Fig. 6 are consistent with the premise that the bulk of organic compounds resistant to H_2O_2 oxidation are humic substances (which may contain the hexachlorobenzene) strongly sorbed to inorganic soil fractions. Another reason for the lower rate of hexachlorobenzene oxidation in the Carson Valley soil may be the ratio of organic carbon to hexachlorobenzene, which is 74 000:1 by weight. Because hydroxyl radical is a nonspecific oxidant, the second-order rate model favors oxidation of soil organic carbon.

Hydrogen peroxide was consumed slowly in the Carson Valley soil (Fig. 7) which was probably due to the limited availability of iron oxide surfaces, as was the case in the silica sand-goethite system. The optimum process design for catalyzed peroxide treatment of soils may be to match the hydroxyl radical generation rate (through the use of naturally occurring iron minerals combined with soluble iron addition) with the rate of desorption. These results also suggest that in natural soils, H_2O_2 may partially

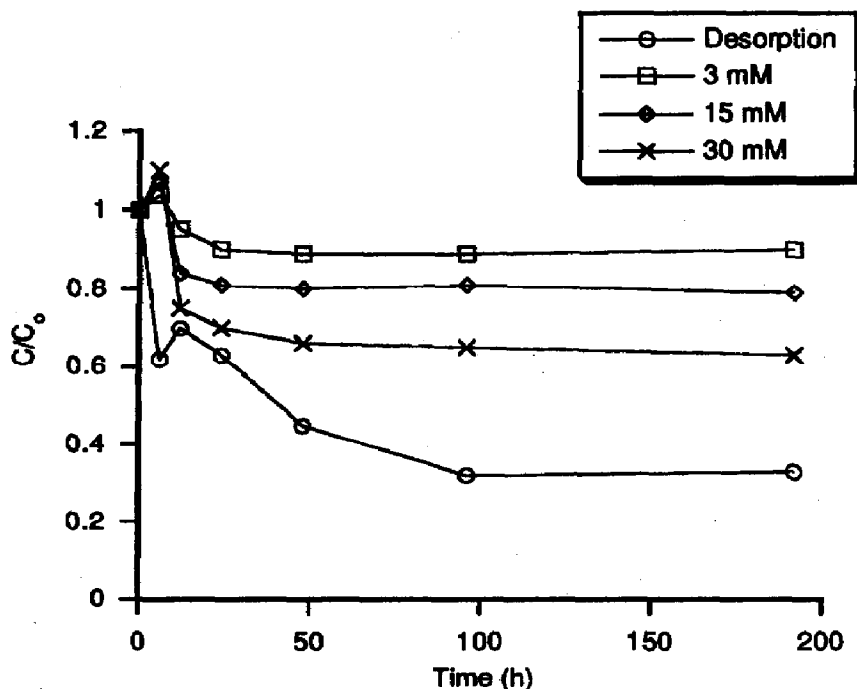


Fig. 6. Hexachlorobenzene desorption and oxidation in the Carson Valley soil.

decompose some of the soil organic carbon, which in turn may release hexachlorobenzene, followed by oxidation of the released contaminant.

Because mineral-catalyzed treatment using low H_2O_2 concentrations provided the most efficient reaction stoichiometry, the treatment of sorbed hexachlorobenzene was optimized using the central composite rotatable design and the conditions that promote mineral-catalyzed oxidation after desorption in silica sand and the Carson Valley soil. The response surfaces for the silica sand–mineral systems and the Carson Valley soil are shown in Figs. 8 and 9, respectively. These data show that up to 90% degradation was achieved, and that increased loss of hexachlorobenzene was found at both higher slurry volumes and higher H_2O_2 concentrations. This higher hexachlorobenzene loss is probably due to an increased pool of reactants, i.e., the higher volumes provide a larger pool of H_2O_2 and the reaction may proceed for a longer period. Higher H_2O_2 concentrations, which may be effective in oxidizing sorbed contaminants, provide inefficient conditions for the treatment of desorbed contaminants because of quenching reactions, particularly the reaction of hydroxyl radical with H_2O_2 , which is favored by higher H_2O_2 concentrations:



Hexachlorobenzene loss of 90% was found at H_2O_2 concentrations from 3 mM to 5 mM and volumes of 25 to 30 times field capacity in the silica sand–goethite system. Such systems of high volume and low H_2O_2 concentrations appear to be the most efficient for the treatment of contaminated soils. For example, Spencer [34] found that the most efficient treatment of diesel-contaminated soils was at low H_2O_2 concentrations and high volumes (30 × the soil field capacity). The data of Figs. 8 and 9 also show that the stoichiometric H_2O_2 requirements were approximately 7 times greater

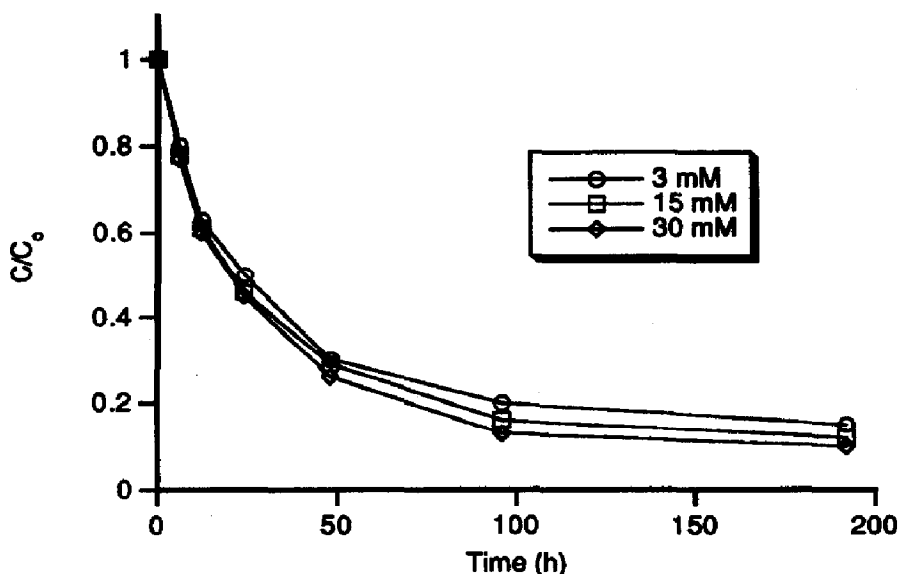


Fig. 7. Hydrogen peroxide concentration as a function of time during the oxidative treatment of the Carson Valley soil.

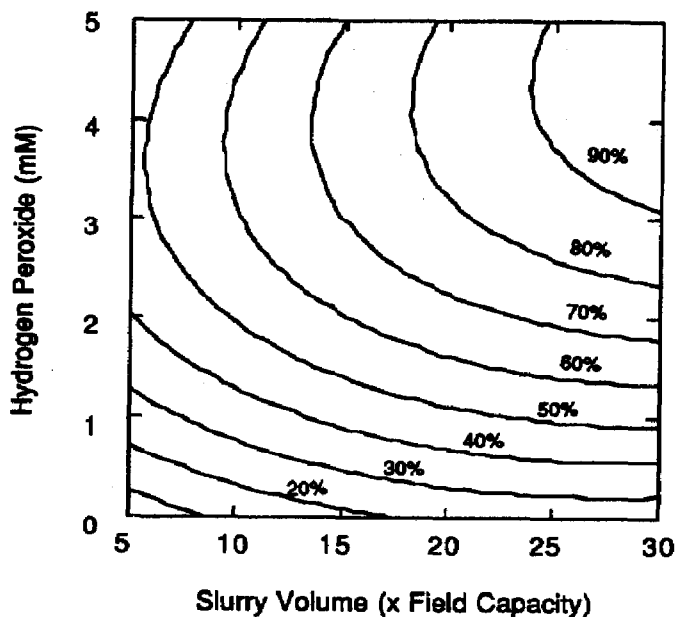


Fig. 8. Response surface for hexachlorobenzene oxidation as a function of hydrogen peroxide concentration and slurry volume in the silica sand-goethite system. Contours represent the percent hexachlorobenzene oxidized.

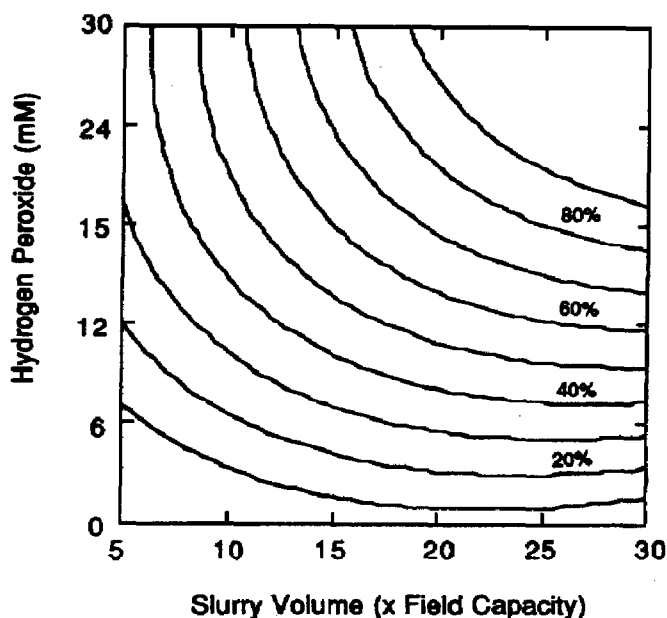


Fig. 9. Response surface for hexachlorobenzene oxidation as a function of hydrogen peroxide concentration and slurry volume in the Carson Valley soil. Contours represent the percent hexachlorobenzene oxidized.

for the natural soil compared to the sand-goethite system. These higher H_2O_2 requirements for the natural soil may have been due to quenching by soil organic matter, chloride, and amorphous iron and manganese oxyhydroxides. In addition, if the primary mechanism for catalysis of Fenton-like oxidations in soils without soluble

iron addition is mineral dissolution with release of soluble iron, the kinetics of dissolution may be slower in naturally-occurring soils than in pure goethite systems. This difference in mineral dissolution kinetics may negatively affect the treatment stoichiometry for natural soils.

The results of this research have shown that part of the hexachlorobenzene sorbed to silica sand may be oxidized in the sorbed state using soluble iron and H_2O_2 concentrations $\geq 100 \text{ mM}$, and mineral-catalyzed treatment follows desorption. The results also show that the mineral-catalyzed system is characterized by more efficient stoichiometry than the soluble iron system. Although the chemical costs would be greater, there may be some remediation situations in which oxidation of the contaminant while it is in the sorbed state may be the most favorable process design. For example, some contaminants are desorbed over months rather than hours, and in such a case, treatment of the sorbed contaminant may be the only practical method of remediation. Oxidation of sorbed contaminants would also be the process model promoted if catalyzed hydrogen peroxide is used for soil remediation under emergency response conditions. Nonetheless, coupling desorption with mineral-catalyzed Fenton-like oxidation of the desorbed contaminant appears to be the most efficient process dynamic for the catalyzed peroxide treatment of contaminated soils.

4. Summary and conclusions

Silica sand spiked with $50 \mu\text{g kg}^{-1}$ hexachlorobenzene was treated with H_2O_2 in concentrations ranging from 3 to 300 mM catalyzed by soluble iron (II) and the iron mineral goethite. In reactions with H_2O_2 concentrations $\geq 100 \text{ mM}$ catalyzed by soluble iron, sorbed hexachlorobenzene was oxidized more rapidly than the rate at which it was desorbed. However, sorbed hexachlorobenzene was also effectively degraded with lower H_2O_2 concentrations in which oxidation rates proceeded more slowly than the rate of desorption.

When goethite was used as the only source of the iron catalyst, oxidation of hexachlorobenzene was slower than desorption for all H_2O_2 concentrations investigated. Even at highly aggressive reaction conditions, hexachlorobenzene was oxidized more slowly than it was desorbed indicating that no hexachlorobenzene oxidation occurred in the sorbed state. The data suggest that, in minerals-catalyzed systems, the contaminant must be desorbed before it is oxidized in solution or at the mineral surface.

In the treatment of hexachlorobenzene-contaminated natural soils, less efficient treatment stoichiometries were found compared to the silica sand–goethite systems under the same conditions, which was probably due to the presence of soil organic carbon and other hydroxyl radical scavengers. The results suggest that sorbed hexachlorobenzene was slowly released from organic carbon, and that partial destruction of the organic carbon may have increased the rate of contaminant desorption and subsequent rate of Fenton-like oxidations. Because the most efficient Fenton-like reactions in silica sand were catalyzed by goethite, mineral-catalyzed reactions in silica sand and the Carson Valley soil were investigated further using a central composite rotatable analysis. Response surfaces from the central composite experiments

showed >90% hexachlorobenzene oxidation with H₂O₂ concentrations of 3 to 5 mM and slurry volumes of 25 to 30 times the soil field capacity.

Acknowledgments

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