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Mineralization of a sorbed polycyclic aromatic hydrocarbon in two soils using catalyzed hydrogen peroxide

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Abstract

Hydrogen peroxide (H_2O_2) catalyzed by soluble iron or naturally occurring soil minerals, (i.e., modified Fenton's reagent) was investigated as a basis for mineralizing sorbed and NAPL-phase benzo[a]pyrene (BaP), a hydrophobic and toxic polycyclic aromatic hydrocarbon, in two soils of different complexity. ^{14}C -Benzo[a]pyrene was added to silica sand and a silt loam soil, and mineralization was investigated using three-level central composite rotatable experimental designs. The effects of H_2O_2 concentration, slurry volume, and iron(II) amendment were investigated in the silica sand systems. In a Palouse loess silt loam soil, the variables included H_2O_2 concentration, slurry volume, and pH, with H_2O_2 catalyzed by naturally occurring iron oxyhydroxides. Regression equations generated from the data were used to develop three-dimensional response surfaces describing BaP mineralization. Based on the recovery of ^{14}C - CO_2 , 70% BaP mineralization was achieved in the sand within 24 h using 15 M H_2O_2 and an iron(II) concentration of 6.6 mM with a slurry volume of $0.3 \times$ the field capacity of the sand. For the silt loam soil, 85% mineralization of BaP was observed using 15 M H_2O_2 , no iron amendment, and a slurry volume of $20 \times$ the soil field capacity. The balance of the radiolabeled carbon remained as unreacted BaP in the soil fraction. Gas-purge measurements over 5 d confirmed negligible desorption under nontreatment conditions. However, oxidation reactions were complete within 24 h and promoted up to 85% BaP mineralization, documenting that the natural rate of desorption/dissolution did not control the rate of oxidation and mineralization of the BaP. The results show that catalyzed H_2O_2 has the ability to rapidly mineralize sorbed/NAPL-phase BaP and that partitioning, which is often the rate-limiting factor in soil remediation, does not appear to limit the rate of vigorous Fenton-like treatment. © 2002 Published by Elsevier Science Ltd.

Keywords: Benzo[a]pyrene; Catalyzed hydrogen peroxide; Hydroxyl radicals; Fenton's reagent; Hydrocarbons; Oxidations; Soil remediation

1. Introduction

The contamination of surface and subsurface soils with biorefractory organic chemicals, such as polycyclic aromatic hydrocarbons (PAHs), is a widespread problem. Polycyclic aromatic hydrocarbons are relatively stable, fused-ring compounds that are found in the heavier fractions of petroleum and as products of combustion. These stable, biorefractory compounds,

such as benzo[a]pyrene (BaP), are Group A (confirmed) carcinogens. Polycyclic aromatic hydrocarbons greater than four rings are also highly hydrophobic and, therefore, strongly sorbed to soils and sludges [1]. A major source of PAH contamination has been from the gas plants. Soils and sludges around these plants are often difficult to treat because of the high concentrations of PAHs, long-chain aliphatics, and phenolics [2].

In situ and ex situ chemical oxidations have the potential for rapidly treating or pretreating soils contaminated with toxic and biorefractory organic wastes. One mechanism for introducing oxidants into contaminated soils is the catalyzed decomposition of

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hydrogen peroxide to form hydroxyl radicals ($\text{OH}\cdot$), commonly known as Fenton's reagent:

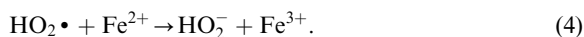
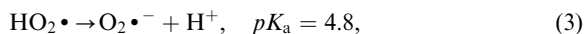
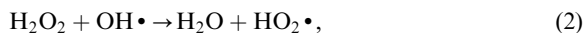


Hydroxyl radicals are strong, relatively nonspecific oxidants that react with alkenes and aromatic compounds, even those with a high degree of halogenation, at near diffusion-controlled rates (i.e., $k_{\text{OH}\cdot} > 10^9 \text{ M}^{-1}\text{s}^{-1}$) [3]. Numerous competing reactions occur in Fenton's systems including the production of perhydroxyl radicals through the reaction of H_2O_2 and iron (III), cycling of iron(III) to iron(II) by short-lived reactants, and quenching of $\text{OH}\cdot$ by iron(II) and H_2O_2 [4].

The application of Fenton's reagent in treating industrial waste streams has been studied extensively with emphasis on water-soluble compounds such as chlorophenols and substituted benzenes [5,6]. Based on the successful results obtained in the treatment of aqueous wastes, catalyzed H_2O_2 has been applied to the remediation of contaminated soils. Watts et al. [7] documented the oxidation of pentachlorophenol (PCP) and showed that effective treatment in both silica sand and natural soils occurred at pH 2–3. Tyre et al. [8] found that four biorefractory compounds were oxidized by H_2O_2 in soils with no soluble iron addition, and proposed that naturally occurring iron minerals may catalyze the decomposition of H_2O_2 and promote Fenton-like reactions. The iron mineral goethite and H_2O_2 were used to treat PCP-contaminated silica sand by Watts et al. [9], who found that the mineral-catalyzed Fenton's system was slower but more stoichiometrically efficient compared to a soluble iron(II) system. Ravikumar and Gurol [10] subsequently used a Fenton-like process, with and without soluble iron addition, to oxidize PCP and trichloroethylene (TCE) in sand columns. Quinoline oxidation was documented by Miller and Valentine [11,12] in Fenton-like reactions catalyzed by aquifer solids. Lin and Gurol [13] developed a kinetic model for hydrogen peroxide decomposition catalyzed by goethite based on Langmuir–Hinshelwood kinetics. Fenton-like reactions can also be catalyzed by hematite and magnetite [14], but not by ferrihydrite [15].

A common problem in the treatment of contaminated soils is the high degree of sorption of hydrophobic contaminants and the presence of nonaqueous-phase liquids (NAPLs), because hydroxyl radicals generated by dilute Fenton's reactions are incapable of oxidizing organic compounds that do not exist in the aqueous phase [16]. However, the addition of excess H_2O_2 ($>0.3 \text{ M}$) has been shown to enhance the oxidative treatment of sorbed and NAPL contaminants [17–19]. Vigorous Fenton-like reactions using high concentrations of H_2O_2 generate nonhydroxyl radical species, such as superoxide radical ($\text{O}_2\cdot^-$) and hydroperoxide anion (HO_2^-), which are reductants and nucleophiles

that appear to be responsible for the rapid treatment of sorbed and NAPL contaminants relative to natural rates of desorption and dissolution [20]:



Numerous studies have shown that Fenton's reactions using dilute H_2O_2 result in incomplete mineralization of organic compounds [21,22], a conclusion that is expected because many degradation products, such as β -keto acids, are not reactive with hydroxyl radicals [23]. However, the mix of oxidants, reductants, and nucleophiles generated using H_2O_2 concentrations $>0.3 \text{ M}$ may not only provide the reactants necessary to promote the enhanced treatment of sorbed contaminants, but these same conditions may also provide the added benefit (via the same matrix of reactants) of mineralizing the BaP degradation products. Therefore, the purpose of this research was to investigate the process conditions that not only provide enhanced treatment of sorbed benzo[a]pyrene (BaP), but also mineralize BaP degradation products in the Fenton-like treatment of two contaminated soils.

2. Methodology

2.1. Chemicals

[2,4- ^{14}C]-Benzo[a]pyrene (^{14}C -BaP; 99% purity) with a specific activity of 10.7 mCi/mmol was purchased from Aldrich. Scintilene, sulfuric acid, sodium hydroxide, and ethyl acetate were obtained from Fisher Scientific. Carbosorb and Scint-A-XF, used for CO_2 recovery, were purchased from Packard. Hydrogen peroxide (50%) was provided gratis by Solvay Interlox. The double-deionized water ($>18 \text{ M}\Omega\text{cm}$) used in all aqueous solutions and dilutions was purified using a Barnstead Nanopure II deionizing system. Washed silica sand (80–100 mesh; $0.15\text{--}0.18 \text{ mm}$) was obtained from JT Baker. Sand characteristics were reported previously by Watts et al. [24]: Fe content was 40 mg kg^{-1} ; organic carbon content was undetectable; and sand pH was 7.2.

2.2. Soil characterization

A Palouse loess soil was sampled from a wheat field near Pullman, WA. Particle size distribution was determined by the pipette method [25]. Organic carbon content was determined by combustion at 900°C with evolved CO_2 trapped in KOH and measured by back titration of unreacted OH^- [26]. Amorphous and crystalline iron and manganese oxyhydroxides were

assayed by citrate-bicarbonate-dithionite extractions [27]. Cation exchange capacity was established by saturation with sodium acetate at pH 8.2 [28]. The soil pH was 7.8. The soil characteristics are listed in Table 1. Based on the particle size distribution, the soil is classified as a silt loam.

2.3. Experimental design

The experimental matrix for investigating BaP degradation conditions was a central composite rotatable experimental design using the concept of response surfaces [29]. Central composite rotatable designs are multivariable, multilevel experimental procedures that analyze the interactions between variables and produce response equations. These procedures have the potential to show statistically significant interactions between variables, unlike a one-variable-at-a-time strategy, and can also lower the ultimate number of experiments conducted while maintaining a high degree of statistical significance in the results. In central composite designs,

Table 1
Characteristics of the Palouse loess soil

Characteristic	Concentration
Organic content (%)	0.11
Sand (%)	20.4
Clay (%)	18.8
Silt (%)	60.8
Crystalline Fe oxides (mg/kg)	33,500
Amorphous Fe oxides (mg/kg)	22.5
Crystalline Mn oxides (mg/kg)	7130
Amorphous Mn oxides (mg/kg)	35.5
Cation exchange capacity (cmol/kg)	22.5

Table 2
Experimental conditions used in central composite rotatable designs

[H ₂ O ₂] (mM)	Slurry volume (× field capacity)	Iron(II) (mM)	Experimental design code	No. of trials
<i>Silica sand</i>				
2400	0.3	6.5	− Ψ	1
3850	0.8	9.0	−1	2
7350	2.0	15	0	5
10,850	3.2	21	+1	2
12,300	3.7	23.4	+ Ψ	1
<i>Palouse loess</i>				
1500	1.0	2.0	− Ψ	1
3350	1.8	3.9	−1	2
7750	9.5	5.0	0	5
12,150	17.2	7.1	+1	2
14,000	20.0	8.0	+ Ψ	1

experimental parameters are chosen to achieve complete rotatability around the central point of a two-level matrix. Using such matrix designs, all of the vertices within the experimental boundaries are tested, and interpolation anywhere within the three-dimensional space is valid [30].

The three variables investigated for oxidation of BaP in silica sand were H₂O₂ concentration (2400–12,300 mM), slurry volume (0.3–3.7 × 0.31 ml/g, the field capacity of the silica sand), and iron(II) amendment (6.6–23.4 mM). The levels for each variable were chosen to produce a completely rotatable design. The three variables investigated for oxidation of BaP in the Palouse loess soil were H₂O₂ concentration (1500–14,000 mM), slurry volume (1.0–20.0 × 0.42 ml/g, field capacity of the Palouse loess), and pH (2.0–8.0) with Fenton-like reactions catalyzed by naturally occurring iron oxyhydroxides [9,10]. The specific conditions and concentrations used for each variable based on the algorithm used for central composite rotatable experimental designs [30] are listed in Table 2. The experimental data were analyzed by linear regression through least-squares analysis to develop regression equations to describe the systems and to provide graphical representations of the data in the form of response surfaces [31]. Each term of the regression equation was validated by quantifying its standard error to ensure that it was within the 90% interval of a single sided *t*-distribution. In addition, the entire regression equation was evaluated based on the *R*² fit. The corresponding response surfaces were created using a SYSTAT[®] software package.

2.4. Oxidation procedures

Soil and sand were dried at 105°C for 24 h followed by cooling in a dessicator for 2 h. Fenton-like reactions

were conducted in 40-ml borosilicate glass vials containing 5 g of silica sand or Palouse loess spiked with 0.1 mmol/kg ^{14}C -BaP. The soils were prepared by adding 100 μl of a 1000 mM solution of BaP in ethyl acetate to produce a final concentration of 0.1 mmol/kg BaP with an activity of 548 μCi . The ethyl acetate was allowed to evaporate with the BaP remaining on the soil. It is likely that a portion of the BaP was not sorbed but remained as NAPL. In a similar study using hexadecane, 43% of the hexadecane remained in NAPL form in the soil and was destroyed along with sorbed hexadecane by Fenton-like reactions [19].

Fenton-like reactions were conducted in the silica sand systems by adding freshly prepared iron(II) sulfate and H_2O_2 followed by adjustment to pH 3 with 4.5 M H_2SO_4 . The H_2O_2 was diluted to the concentrations listed in Table 2 before addition to the soils. Because the Fenton-like reactions in the Palouse loess were catalyzed by naturally occurring iron minerals, only H_2O_2 was added to the soil followed by pH adjustment of 4.5 M H_2SO_4 or 4.5 M NaOH. The systems were purged with a stream of nitrogen and the off gas was trapped for scintillation counting. Gas transfer was accomplished using 0.18 mm (i.d.) fused silica tubing and the evolved ^{14}C - CO_2 was trapped in 10 ml of a 20% (v/v) solution of Carbosorb in Scint-A XF scintillation cocktail [19]. A mass balance was established by extracting the remaining ^{14}C -BaP from the vials through shake extractions with 10 ml of ethyl acetate for 24 h; 5 ml of the extract were then added to a scintillation vial containing 5 ml of Scintilene counting cocktail. Aqueous samples were filtered through a 0.45 mm membrane filter prior to scintillation counting and gas chromatography/mass spectrometry (GC/MS) analysis. All experiments were conducted in triplicate, and control experiments were carried out in parallel using deionized water in place of H_2O_2 . No significant loss of BaP was found in any of the control reactions. All experiments were conducted in a water bath at $20 \pm 2^\circ\text{C}$.

2.5. Desorption

Benzo[a]pyrene desorption from the soils was determined by gas-purge (GP) methodology [32]. Because the system is purged vigorously, contaminants volatilize rapidly after they are desorbed, and their rate of removal from the aqueous phase is equal to the rate of desorption. Vials containing 5 g of sand spiked with 0.1 mmol/kg ^{14}C -BaP were filled with 10 ml of deionized water and purged with nitrogen gas at a flow rate of 120 ml/min. The purge vial was connected to a trap vial containing Carbosorb in Scint-A XF scintillation cocktail by 0.18 mm diameter fused silica tubing. Originally, BaP concentrations were measured on the soil, in the aqueous phase, and in the off gas (trapped in gas adsorbent tubes packed with Tenax). No BaP was

detected in the aqueous phase, and the residual on the soil correlated with the mass collected on the gas adsorbent tubes; therefore, subsequent GP analyses relied on quantifying the residual sorbed on the soil. ^{14}C -Benzo[a]pyrene was determined at time intervals over 5 d. All experiments were conducted in triplicate, and control samples without purging were evaluated in parallel to account for volatilization. Experiments were conducted in a water bath at $20 \pm 2^\circ\text{C}$.

2.6. Analysis

Concentrations of H_2O_2 were determined by iodometric titration with sodium thiosulfate [33]. Radioisotope analysis was performed on a Packard 2200LL scintillation counter that was calibrated to Packard-supplied standards. Benzo[a]pyrene concentrations were determined by shake extraction for 24 h with ethyl acetate [8] followed by analysis on a Hewlett Packard 5890A gas chromatograph equipped with a flame ionization detector (FID) and a J & W DB-5 capillary column. Chromatographic conditions included an initial temperature of 200°C , program rate of $10^\circ\text{C}/\text{min}$, final temperature of 310°C , injector temperature of 250°C , and detector temperature of 350°C . Gas chromatography/mass spectrometry was performed on a Finnegan SSQ quadrupole mass spectrometer equipped with a DB-5 capillary column. The GC/MS was operated under the same chromatographic conditions used for the GC/FID analysis.

3. Results and discussion

Analysis of the data obtained through the central composite experimental design procedures first involved development of regression equations from the empirical data; secondly, response surfaces, which physically illustrate the regression equation as isoresponse lines, were generated from the regression equations.

3.1. Mineralization of BaP in silica sand

Based on statistical analysis of the experimental data, BaP oxidation in the silica sand was described by:

$$\begin{aligned}
 {}^{14}\text{C}\text{-CO}_2 \text{ Recovery } (\%) &= 40.7 + 1.47 \times 10^{-3}(\text{H}_2\text{O}_2) \\
 &\quad - 3.40(\text{Volume}) - 2.33(\text{Iron}) \\
 &\quad + 1.07 \times 10^{-7}(\text{H}_2\text{O}_2)^2 + 3.0 \times 10^{-2}(\text{Volume})^2 \\
 &\quad + 4.58 \times 10^{-1}(\text{Volume})(\text{Iron}), \quad (5)
 \end{aligned}$$

where (H_2O_2) is the hydrogen peroxide concentration (mM), (Volume) the slurry volume ($\times 0.31 \text{ ml/g}$, the silica sand field capacity), and (Iron) is the iron (II)

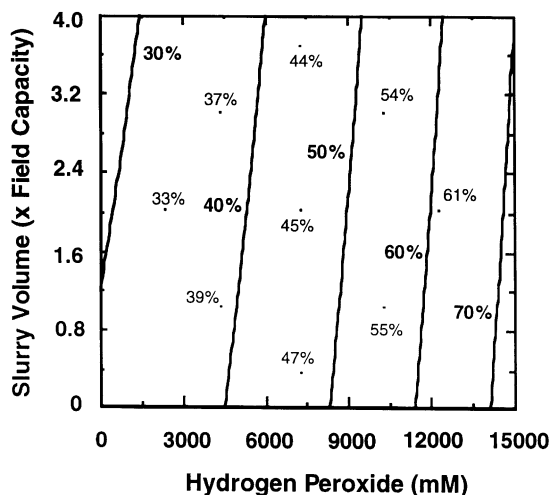


Fig. 1. Response surface for the mineralization of ^{14}C -BaP as a function of H_2O_2 concentration and slurry volume in silica sand catalyzed by 6.6 mM iron(II). Isoconcentration lines represent the percent BaP recovered as ^{14}C - CO_2 described by Eq. (5). The field capacity of the silica sand = 0.31 ml/g.

amendment concentration (mM). Treatment stoichiometry was quantified by

Stoichiometry (mol H_2O_2 /mol ^{14}C - CO_2)

$$= [1.20 - 3.71 \times 10^{-5}(\text{H}_2\text{O}_2) - 6.41 \times 10^{-1}(\text{Volume}) + 1.01 \times 10^{-1}(\text{Volume})^2 + 9.62 \times 10^{-6}(\text{H}_2\text{O}_2)(\text{Volume})]^{-1} \times 1000. \quad (6)$$

Eqs. (5) and (6) were characterized by R^2 of 0.88 and 0.91, respectively, when the experimental data were plotted against values generated by the equations. All terms were within the 90% confidence interval of a single sided t -distribution with 13 and 15 degrees of freedom. The materials balance accounted for 89% of the ^{14}C in the silica sand systems.

Inspection of Eq. (5) reveals that the relationships between H_2O_2 concentration, iron(II) amendment, and slurry volume are interactive. Graphing the $n = 3$ variables with the $n + 1 = 4$ response of ^{14}C - CO_2 recovery is not possible because of the four dimensions involved. Therefore, the iron(II) amendment was held constant at 6.6 mM and a response surface was generated for BaP oxidation in silica sand as a function of H_2O_2 concentration and slurry volume (\times the sand field capacity = 0.31 ml/g) (Fig. 1). These data show that approximately 70% of the BaP was mineralized in silica sand using 15,000 mM H_2O_2 at nearly all slurry volumes. Although slurry volume was not a significant factor, BaP mineralization increased from approximately 30% to 70% as a function of H_2O_2 concentration. Although high concentrations of H_2O_2 (30%; 8850 mM) are used

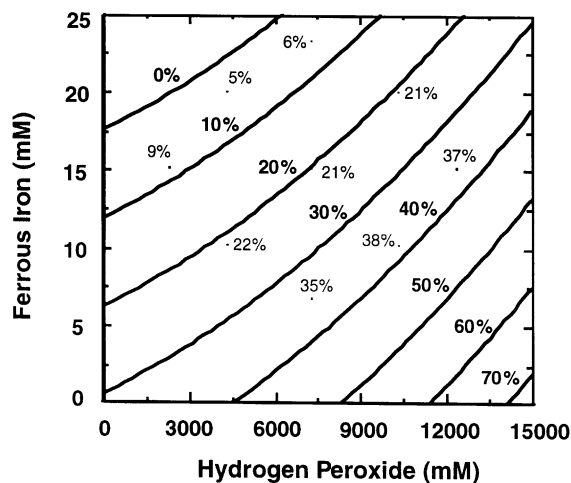


Fig. 2. Benzo[a]pyrene oxidation in silica sand as a function of H_2O_2 concentration and iron(II) concentration at an optimal slurry volume of $0.25 \times$ soil field capacity. Isoconcentration lines represent the percent BaP recovered as ^{14}C - CO_2 described by Eq. (5).

as a standard procedure for removing organic carbon from soils, this procedure does not result in the removal of all carbon, nor is the majority of the carbon mineralized [34]. Therefore, the removal and mineralization of BaP in this study is likely primarily due to reactive species produced in vigorous Fenton-like reactions, rather than direct oxidation by H_2O_2 .

The interactive effects of H_2O_2 concentration and iron(II) amendment were significantly higher than the effect of slurry volume. The oxidation of BaP as a function of H_2O_2 concentration and iron(II) concentration with a slurry volume held constant at $0.30 \times$ the sand field capacity is shown in Fig. 2. Benzo[a]pyrene mineralization increased as a function of H_2O_2 concentration and decreased as a function of the iron(II) amendment. A potential reason for the more effective oxidation with lower iron(II) amendments may be less quenching of reactive species by iron [35].

A response surface illustrating stoichiometries for the mineralization of BaP as a function of H_2O_2 concentration and slurry volume, with the iron(II) amendment held constant at 6.6 mM, is shown in Fig. 3. The data suggest that excess slurry volume (containing H_2O_2 that is not in contact with the sorbed or NAPL-phase BaP) consumes H_2O_2 while not degrading the sorbed or NAPL contaminant. The results also document that the reactions became increasingly inefficient with increased H_2O_2 concentrations, which was likely due to an increase in quenching reactions. The molar H_2O_2 requirements for BaP mineralization are several orders of magnitude greater than those characteristic of

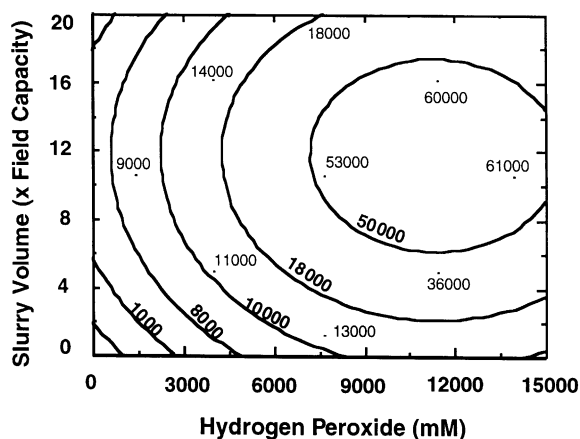


Fig. 5. Benzo[a]pyrene oxidation stoichiometry in the Palouse loess as a function of H_2O_2 concentration and slurry volume at pH 8.0. Isoconcentration lines represent the moles H_2O_2 consumed per $^{14}\text{C-CO}_2$ described by Eq. (8).

is different from the results obtained in previous studies because hydroxyl radical generation through Fenton's reactions is usually more effective under acidic pH regimes [5,7]. A possible explanation of this trend may be that the reductive pathway recently found in vigorous Fenton-like reactions [20], which may aid in the degradation of species not reactive with hydroxyl radicals, is favored at high pH.

The oxidation stoichiometries (moles of H_2O_2 consumed/moles of $^{14}\text{C-CO}_2$ recovered) for BaP mineralization in the Palouse loess are shown in Fig. 5. Similar to the results obtained in silica sand, these data indicate that the most efficient systems are those in which the slurry volume was low, i.e., the results suggest that the close proximity of the reactive species to the sorbed or NAPL-phase BaP is an important factor in promoting a stoichiometrically efficient reaction that enhances its desorption/dissolution and mineralization. Excess H_2O_2 that decomposed to reactive species away from the soil was probably not effective in degrading and mineralizing sorbed or NAPL-phase BaP. Watts and Stanton [19] obtained similar results in documenting the oxidation of ^{14}C -hexadecane; they found that the degradation of hexadecane required relatively high concentrations of H_2O_2 and that the most efficient stoichiometry was at low slurry volumes. In addition, scavenging of oxidants by mineral surfaces may be mechanism for the ineffective stoichiometries observed in these reactions [40].

Gas chromatographic and GC/MS analyses coupled with ^{14}C measurements documented that the remaining contaminant carbon in each system (41% for the silica sand system and 15% for the Palouse loess) was

undegraded BaP. Analysis of the aqueous phase by GC/MS and ^{14}C scintillation counting showed no presence of contaminant carbon in the soil water. These results indicate that all of the ^{14}C -BaP that was degraded was rapidly converted to $^{14}\text{C-CO}_2$. Polycyclic aromatic hydrocarbons, such as BaP, are oxidized by hydroxyl radicals to keto acids, such as muconic acid, pyruvate, and oxalate [41]. Most keto acids are characterized by low reactivity with hydroxyl radicals ($k_{\text{OH}\cdot} = 7.7 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ for oxalate; $k_{\text{OH}\cdot} = 3.1 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ for pyruvate); therefore, a standard Fenton's reaction producing only hydroxyl radicals would not be expected to mineralize BaP [22]. However, rapid mineralization of these species may be promoted by the generation of reductants formed in vigorous Fenton-like reactions [20], because these intermediates react rapidly with reductants ($k_{\text{e-}} = 3.2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ for oxalate; $k_{\text{e-}} = 6.8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ for pyruvate) [23]. As a result, PAHs, such as BaP, may be rapidly converted to carbon dioxide and water through the presence of both reductants and hydroxyl radicals in modified Fenton's systems.

Biological processes are often the most economical means of treating soils contaminated with refractory compounds. A number of investigations have documented the mineralization of organic contaminants in soils through biological metabolism [42–44]. These studies have shown that mineralization of xenobiotics ranges from 30% to 80% depending on the structure of the parent compound and the biorecalcitrance and toxicity of the degradation products. However, biological treatment is limited by the natural desorption rates of contaminants and, therefore, may take months to years. The data provided in Figs. 1–5 show that soil remediation using modified Fenton's reactions can promote the same degree of mineralization as bioremediation in significantly shorter time periods. While the cost of the H_2O_2 is a disadvantage of Fenton-like reactions, it may be outweighed by the advantages of rapid treatment and site closure.

Desorption of BaP from the silica sand and the Palouse loess (i.e., the mass of sorbed BaP remaining in the GP systems over time) is shown in Fig. 6; these data demonstrate undetectable desorption over 5 d. However, treatment of BaP using Fenton-like reactions was complete in 2–24 h resulting in 59–85% mineralization of the parent compound under optimum conditions. Because no GP desorption occurred over the time in which a significant amount of treatment occurred, the Fenton-like reactions were not limited by desorption. Similar results were reported by Watts et al. [37]. Gates and Siegrist [17], and Kakarla and Watts [39]. Furthermore, these data are consistent with the results of Watts et al. [20], who found that desorption of toluene was enhanced in vigorous Fenton-like reactions, even when its degradation was prevented by addition of the

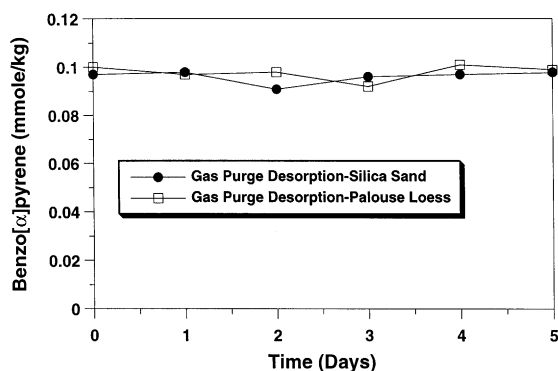


Fig. 6. Desorption of BaP from the silica sand and the Palouse loess.

hydroxyl radical scavenger isopropanol. They suggested that enhanced treatment of sorbed compounds is a two-step process: the reducing species generated in modified Fenton's reactions first desorbs contaminants, with subsequent oxidation or reduction of the contaminants in the aqueous phase.

Contaminant sorption and the presence of NAPL lenses often control the treatment of contaminated soils by chemical or biological methods. Soil washing and soil flushing are often used to overcome sorption in soil remediation [45]; however, a disadvantage of soil washing is the subsequent need to treat surfactant-laden wash water [46]. The use of surfactants to disrupt NAPLs has similar disadvantages. The Fenton-like treatment of soils contaminated with hydrophobic compounds, such as BaP, provides a mechanism in which the contaminants are desorbed/dissolved and oxidized in a single physiochemical process (i.e., a combined soil washing–oxidation process). Modified Fenton's reactions, in which reductants as well as hydroxyl radicals are generated, may provide a universal treatment matrix in which contaminants are desorbed from solids and mineralized through coexisting oxidations and reductions.

4. Summary and conclusions

The potential for catalyzed H_2O_2 (i.e., modified Fenton's reagent) to mineralize BaP sorbed on soils was investigated. Fenton-like treatments were conducted in silica sand and a Palouse loess soil spiked with 0.1 mmol/kg BaP, and were complete within 24 h. Confirmation of degradation was accomplished using ^{14}C -labeled BaP and recovering evolved ^{14}C - CO_2 . Experimental procedures incorporating central composite rotatable experimental designs were used to determine the most effective treatment conditions. The effects

of H_2O_2 concentration, slurry volume, and iron(II) concentrations were investigated in the silica sand. In the Palouse loess soil, the variables included H_2O_2 concentration, slurry volume, and pH with Fenton-like reactions catalyzed by iron oxyhydroxides present in the soil.

Vigorous conditions (i.e., high H_2O_2 concentrations) were required to oxidize BaP in silica sand, which was likely related to the requirement of overcoming sorption. Under optimum conditions, 59% of the ^{14}C -BaP was recovered as ^{14}C - CO_2 within 24 h using 12,300 mM H_2O_2 , a slurry volume of $0.3 \times$ the sand field capacity, and an iron(II) concentration of 6.6 mM. In the Palouse loess soil, 85% of the BaP was oxidized to CO_2 and H_2O using 14,000 mM H_2O_2 , a slurry volume of $20 \times$ field capacity, and a pH of 8.0. The oxidation stoichiometry was highly sensitive to slurry volume and less sensitive to H_2O_2 concentration, with more efficient oxidation occurring when the Fenton's reagents were in direct contact with the sorbed contaminants. In addition, mineral-catalyzed Fenton-like reactions at neutral pH were found to promote greater BaP mineralization than the same reactions conducted at acidic pH regimes. Gas-purge measurements confirmed negligible desorption of BaP over 5 d in the absence of treatment.

The radiolabeled carbon that was not mineralized (15–41%) remained with the soil fraction in the form of BaP; none was found in the aqueous phase, suggesting that the contaminant was degraded through enhanced desorption/dissolution with subsequent rapid degradation in the aqueous phase. The results show that under conditions of high H_2O_2 concentration, Fenton-like reactions can enhance desorption and NAPL dissolution while simultaneously mineralizing the contaminant.

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References

- [1] Sullivan JB, Krieger GR. Hazardous materials toxicology. Baltimore, MD: Williams and Wilkins, 1992.
- [2] Michelcic JR, Luthy RC. Degradation of polycyclic aromatic hydrocarbon compounds under various redox conditions in soil-water systems. Appl Environ Microbiol 1988;54:1182–7.

- [3] Haag WR, Yao CCD. Rate constants for reaction of hydroxyl radicals with several drinking water contaminants. *Environ Sci Technol* 1992;26:1005–13.
- [4] Dorfman LM, Adams GE. Reactivity of the hydroxyl radical in aqueous solutions. Rep. no. NSRDS-NBS-46, National Bureau of Standards, Washington, DC, 1973.
- [5] Barbeni MC, Minero C, Pelizzetti E, Borgarello E, Serpone N. Hemical degradation of chlorophenols with Fenton's reagent. *Chemosphere* 1987;16:2225–37.
- [6] Sedlak DL, Andren AW. Aqueous-phase oxidation of polychlorinated biphenyls by hydroxyl radicals. *Environ Sci Technol* 1991;25:1419–27.
- [7] Watts RJ, Udell MD, Rauch PA, Leung SW. Treatment of pentachlorophenol-contaminated soils using Fenton's reagent. *Haz Wastes Haz Mater* 1990;7:335–45.
- [8] Tyre BW, Watts RJ, Miller GC. Treatment of four biorefractory contaminants in soils using catalyzed hydrogen peroxide. *J Environ Qual* 1991;20:832–8.
- [9] Watts RJ, Udell MD, Monsen RM. Use of iron minerals in optimizing the peroxide treatment of contaminated soils. *Water Environ Res* 1993;65:839–44.
- [10] Ravikumar JX, Gurol MD. Chemical oxidation of chlorinated organics by hydrogen peroxide in the presence of sand. *Environ Sci Technol* 1994;28:394–400.
- [11] Miller CM, Valentine RL. Hydrogen peroxide decomposition and quinoline degradation in the presence of aquifer material. *Water Res* 1995;29:2353–9.
- [12] Miller CM, Valentine RL. Oxidation behavior of aqueous contaminants in the presence of hydrogen peroxide and filter media. *J Haz Mater* 1995;41:105–16.
- [13] Lin S-S, Gurol MD. Catalytic decomposition of hydrogen peroxide on iron oxide: kinetics, mechanisms, and implications. *Environ Sci Technol* 1998;32:1417–23.
- [14] Watts RJ, Udell MD, Kong S, Leung SW. Fenton-like soil remediation catalyzed by naturally occurring iron minerals. *Environ Eng Sci* 1999;16:93–103.
- [15] Valentine RL, Wang HCA. Iron oxide catalyzed oxidation of quinoline by hydrogen peroxide. *J Environ Eng* 1998;124:31–8.
- [16] Sedlak DL, Andren AW. The effect of sorption on the oxidation of polychlorinated biphenyls (PCBs) by hydroxyl radical. *Water Res* 1994;28:1207–15.
- [17] Gates DD, Siegrist RL. In-situ chemical oxidation of trichloroethylene using hydrogen peroxide. *J Environ Eng* 1995;121:639–44.
- [18] Siegrist RL. In situ chemical oxidation: technology features and applications. Abiotic in situ Technologies for Groundwater Remediation Conference, Dallas, TX, August 31–September 2, 1999.
- [19] Watts RJ, Stanton PC. Mineralization of sorbed and NAPL-phase hexadecane by catalyzed hydrogen peroxide. *Water Res* 1999;33:1405–14.
- [20] Watts RJ, Bottenberg BC, Hess TF, Jensen MD, Teel AL. The role of reductants in the enhanced desorption and transformation of chloroaliphatic compounds by modified Fenton's reactions. *Environ Sci Technol* 1999;33:3432–7.
- [21] Davidson CA, Busch AW. Catalyzed chemical oxidation of phenol in aqueous solution. *Proc Div Refin API* 1966;46:299–302.
- [22] Ronen Z, Horvath-Gordon M, Bollag JM. Biological and chemical mineralization of pyridine. *Environ Toxicol Chem* 1994;13:21–6.
- [23] Buxton GV, Greenstock CL, Helman WP, Ross AB. Critical review of rate constants for reactions of hydrated electrons, hydrogen atoms and hydroxyl radicals ($\bullet\text{OH}/\bullet\text{O}$) in aqueous solution. *J Phys Chem Ref Data* 1987;17:513–886.
- [24] Watts RJ, Foget MK, Kong S, Teel AL. Hydrogen peroxide decomposition in model subsurface systems. *J Haz Mater* 1999;B69:229–43.
- [25] Gee BW, Bauder JW. In: Klute A et al., editors. *Methods of soil analysis. Part I. Physical and mineralogical methods*. Madison, WI: American Society of Agronomy, 1986. p. 399.
- [26] Nelson DW, Summers LE. In: Page AL et al., editors. *Methods of soil analysis, part 2*. Madison, WI: ASA and SSSA, 1982. p. 579.
- [27] Jackson ML, Lim CH, Zelazny LW. In: Klute A et al., editors. *Methods of soil analysis, part 1*. Madison, WI: ASA and SSSA, 1986. p. 124.
- [28] US Soil Conservation Service. *Soil survey investigation: report 1*. US Government Printing Office, Washington, DC, 1972.
- [29] Cochran WG, Cox GM. *Experimental designs*, 2nd ed. New York: Wiley, 1992.
- [30] Diamond WJ. *Practical experiment designs for engineers and scientists*, 2nd ed. New York: Van Nostrand Reinhold, 1989.
- [31] Box GEP, Draper NR. *Empirical model-building and response surfaces*. New York: Wiley, 1987.
- [32] Brusseau ML, Jessup RE, Rao PSC. Sorption kinetics of organic chemicals: evaluation of gas-purge and miscible-displacement techniques. *Environ Sci Technol* 1990;24:727–35.
- [33] Schumb WC, Stratterfield CN, Wentworth RL. *Hydrogen peroxide*. New York: American Chemical Society, Reinhold Publishing Co., 1955.
- [34] Griffith SM, Schnitzer M. Organic compounds formed by the hydrogen peroxide oxidation of soils. *Can J Soil Sci* 1977;57:223–31.
- [35] Walling C. Fenton's reagent revisited. *Acc Chem Res* 1975;8:125–31.
- [36] Li ZM, Shea PJ, Comfort SD. Fenton oxidation of 2,4,6-trinitrotoluene in contaminated soil slurries. *Environ Eng Sci* 1997;14:55–6.
- [37] Watts RJ, Kong S, Dippre M, Barnes WT. Oxidation of sorbed hexachlorobenzene using catalyzed hydrogen peroxide. *J Haz Mater* 1994;39:33–47.
- [38] Miller CM, Valentine RL, Roehl ME, Alvarez PJJ. Chemical and microbiological assessment of pendimethalin contaminated soil after treatment with Fenton's reagent. *Water Res* 1996;30:2579–86.
- [39] Kakarla P, Watts RJ. Depth of Fenton-like oxidation in remediation of surface soils. *J Environ Eng* 1997;123:11–7.
- [40] Miller CM, Valentine RL. Mechanistic studies of surface catalyzed H_2O_2 decomposition and contaminant degradation in the presence of sand. *Water Res* 1999;33:2805–16.
- [41] Schwarzenbach RP, Gschwend PM, Imboden DM. *Environmental organic chemistry*. New York: Wiley, 1993.

- [42] Jones SH, Alexander M. Kinetics of mineralization of phenols in lake water. *Appl Environ Microbiol* 1986;51: 891–7.
- [43] Schmidt SK, Gier MJ. Dynamics of microbial populations in soil: indigenous microorganisms degrading 2,4-dinitrophenol. *Microb Ecol* 1989;18:285–96.
- [44] Scow KM, Schmidt SK, Alexander M. Kinetics of biodegradation of mixtures of substrates in soils. *Soil Biol Biochem* 1989;21:703–8.
- [45] Wayt HJ, Wilson DJ. Soil cleanup by in situ surfactant flushing. II. Theory of micellular solubilization. *Sep Sci Technol* 1989;24:905–9.
- [46] Valsaraj KT, Thibodeaux LJ. Relationships between micelle-water and octanol: water partition constants for hydrophobic organics of environmental interest. *Water Res* 1989;23:183–7.