PROCESS CONDITIONS FOR THE TOTAL OXIDATION OF HYDROCARBONS

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16. ABSTRACT

The use of Fenton's reagent for completely oxidizing hexadecane and benzo[*a*]pyrene (BAP) to their thermodynamic endpoints, carbon dioxide and water, was investigated. Confirmation of oxidation was determined by using ^{14}C-labeled compounds and recovering the evolved $^{14}CO_2$. Experimental design procedures incorporating factorial matrices were used to determine optimal treatment conditions based on three variables at five levels. Oxidative treatments were conducted in silica sand and a Palouse Loess soil. Silica sand experiments investigated the effects of slurry volume, hydrogen peroxide concentration, and iron (II) concentrations. In the Palouse soil systems, the variables investigated included slurry volume, hydrogen peroxide concentration, and pH.

Aggressive conditions were required for oxidizing hexadecane and benzo[*a*]pyrene in silica sand, which were related to their slow rates of desorption. Under optimal conditions, 74% of the hexadecane and 73% of the benzo[*a*]pyrene were oxidized to CO_2 and H_2O. In both cases, optimal treatment conditions entailed the use of 14,700 mM hydrogen peroxide. Treatment conditions differed in that slurry volumes of 4.0 x F.C. and an iron (II) concentration of 25 mM were required for hexadecane oxidation while slurry volume of 0.25 x F.C. and an iron (II) concentration of 5 mM were required for the oxidation of benzo[*a*]pyrene.

In soils, the presence of organic matter and other species that compete for and quench hydroxyl radicals require additional reagents to promote oxidative treatment. Under optimal conditions, 67% of the hexadecane and 78% of the benzo[*a*]pyrene were oxidized to CO_2 and H_2O. The optimal conditions, 67% of the two compounds was found at the same treatment conditions. These conditions consisted of 14,700 mM hydrogen peroxide, a slurry volume of 20 x field capacity and a pH of 8.0. More importantly, the ability of mineral catalyzed hydrogen peroxide for oxidizing contaminants at a neutral pH was documented.

The results show that hydrocarbons common to diesel, motor oil, and other refractory petroleum products may be oxidized to CO_2 and H_2O using Fenton's reagent.

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"Process Conditions for the Total Oxidation of Hydrocarbons"

PROCESS CONDITIONS FOR THE TOTAL OXIDATION OF HYDROCARBONS

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STUDY SUMMARY

The use of Fenton's reagent for completely oxidizing hexadecane and benzo[*a*]pyrene (BAP) to their thermodynamic endpoints, carbon dioxide and water, was investigated. Confirmation of oxidation was determined by using ^{14}C-labeled compounds and recovering the evolved $^{14}CO_2$. Experimental design procedures incorporating factorial matrices were used to determine optimal treatment conditions based on three variables at five levels. Oxidative treatments were conducted in silica sand and a Palouse Loess soil. Silica sand experiments investigated the effects of slurry volume, hydrogen peroxide concentration, and iron (II) concentrations. In the Palouse soil systems, the variables investigated included slurry volume, hydrogen peroxide concentration, and pH.

A principal concern among regulatory agencies, such as the U.S. Environmental Protection Agency and the Washington State Department of Ecology, is that the contaminants are not transformed into undegradable or toxic intermediates. If the contaminants are transformed to carbon dioxide and water, their thermodynamically stable, nontoxic end points, then confirmation of the safety of the process can be proven.

The only proven method to document the conversion of organic carbon to carbon dioxide is through the use of radiolabelled compounds, most commonly ^{14}C. This radioisotope is a ß-emitting (electron-emitting) substance, and the ß-particles are easily measured using a liquid scintillation counter. As a ^{14}C-labelled compound, such as ^{14}C-hexadecane, is oxidized completely (i.e., is mineralized), the ^{14}C originally contained in the contaminant is caught in a gas trap as ^{14}C-carbon dioxide.

Aggressive conditions were required for oxidizing hexadecane and benzo[*a*]pyrene in silica sand, which were related to their slow rates of desorption. Under optimal conditions, 74% of the hexadecane and 73% of the benzo[*a*]pyrene were oxidized to CO_2 and H_2O. In both cases, optimal treatment conditions entailed the use of 14,700 mM

hydrogen peroxide. Treatment conditions differed in that slurry volumes of 4.0 x F.C. and an iron (II) concentration of 25 mM were required for hexadecane oxidation while a slurry volume of 0.25 x F.C. and an iron (II) concentration of 5 mM were required for the oxidation of benzo[*a*]pyrene.

In soils, the presence of organic matter and other species that compete for and quench hydroxyl radicals require additional reagents to promote oxidative treatment. Under optimal conditions, 67% of the hexadecane and 78% of the benzo[*a*]pyrene were oxidized to CO_2 and H_2O. The optimal treatment of the two compounds was found at the same treatment conditions. These conditions consisted of 14,700 mM hydrogen peroxide, a slurry volume of 20 x field capacity and a pH of 8.0. More importantly, the ability of mineral catalyzed hydrogen peroxide for oxidizing contaminants at a neutral pH was documented.

The results show that hydrocarbons common to diesel, motor oil, and other refractory petroleum products may be oxidized to CO_2 and H_2O using Fenton's reagent.

CONCLUSIONS AND RECOMMENDATIONS

This research utilized factorial experimental designs to determine conditions for completely oxidizing (i.e., mineralizing) hexadecane and benzo[*a*]pyrene in silica sand and a Palouse loess soil. Experimental design techniques allowed for a thorough evaluation of Fenton's reagent for the complete oxidation of the hexadecane and benzo[*a*]pyrene to CO_2 and H_2O using ^{14}C labeled compounds. Whereas conventional experimental procedures entail altering a single variable while holding all others constant, experimental design allowed the investigation of three variables simultaneously. This methodology allows for not only the determination of effects caused by the variables themselves but also interactions occurring between variables. In addition, using factorial experimental designs allows for the evaluation of each experiment based upon statistical validity which is often not possible with conventional experimental procedures.

The oxidation of hexadecane and benzo[*a*]pyrene in silica sand utilized standard hydrogen peroxide reactions catalyzed by iron (II). Differences in treatment conditions for the two compounds were found based on the experimental data. While both compounds required high concentrations of hydrogen peroxide for effective mineralization, hexadecane oxidation was promoted by high concentrations of iron (II) and large slurry volumes (i.e., peroxide to soil ratio) while benzo[*a*]pyrene required low iron (II) concentrations and small slurry volumes. These data suggest that hexadecane requires more aggressive conditions for mineralization. The larger slurry volumes required by hexadecane utilizes the pool of reagents to increase the reaction time. Small volumes were optimal for benzo[*a*]pyrene oxidation because the compound is more dense than water and hydroxyl radical production away from the bottom of the reaction vial were quenched in other reactions.

Hexadecane and benzo[*a*]pyrene were mineralized in a Palouse loess soil utilizing mineral-catalyzed hydrogen peroxide. While treatment conditions for optimal destruction were the same for both compounds, the interaction of the three variables differed.

Increases in hexadecane oxidation was influenced by hydrogen peroxide concentration as the dosing parameter while benzo[*a*]pyrene required increases in slurry volume as a dosing parameter. One important discovery is that the previously documented pH of 2.0 to 3.0 for parent compound degradation was not necessarily optimal for its complete mineralization. Hexadecane required pH above 5.0 for significant amounts of mineralization to occur. Benzo[a]pyrene oxidation was characterized by a more complex relationship with pH. At $pH < 4.0$, effective oxidation was achieved using low slurry volumes but at $pH > 4.0$, increased oxidation occurred at high slurry volumes. These data suggest that at low pH, where hydrogen peroxide is more stable, reaction times were longer which resulted in more sustained oxidations. At high volumes there were additional reagents available to maintain the reaction for sufficient time at high pH's, resulting in increased oxidations.

This research investigated the ability of catalyzed hydrogen peroxide to completely destroy (i.e., mineralize) two common petroleum constituents, benzo[*a*]pyrene and hexadecane. Hexadecane is a straight chain C_{16} hydrocarbon with a high log K_{ow}, of 9.07 and low water solubility, of 0.00045 mg/l. Benzo[a]pyrene is five-ring polycyclic aromatic hydrocarbon (PAH) that also has a high log K_{ow} of 5.38 and low water solubility of 0.0026 mg/l. Benzo[*a*]pyrene is biorefractory and, like hexadecane, is difficult to remove by most on site or in situ remedial technologies. Benzo[*a*]pyrene is of high regulatory importance due to its carcinogenic characteristics.

Most importantly, this research confirmed that Fenton's reagent has the ability to completely oxidize contaminants to their thermodynamic endpoints, CO_2 and H_2O. One advantage of investigating the oxidation of hexadecane and benzo[*a*]pyrene is that these compound lie at the extreme end of the spectrum of petroleum hydrocarbons with respect to difficulty in soil remediation. Nearly all constituents of petroleum exhibit lower K_{ow} and higher solubilities which favor efficient treatment with Fenton's reagent. For most petroleum products treatment efficiencies would be increased significantly with complete oxidation occurring at much lower costs.

We recommend that Fenton's reagent can be used for the treatment of contaminated soils. The process converts typical petroleum hydrocarbon contaminants to carbon dioxide and water; therefore, it may be used without concern of toxic byproducts.

INTRODUCTION

RESEARCH OBJECTIVES

The objective of this research was to determine the effectiveness of catalyzed hydrogen peroxide for the complete destruction of hexadecane and benzo[*a*]pyrene. To achieve this objective the following tasks were completed.

1. The development of an experimental design for the determination of the optimal treatment conditions and the detection of interactions between variables.
2. Laboratory scale experiments were conducted using ^{14}C labeled hexadecane and benzo[*a*]pyrene to determine the extent of contaminant oxidation to CO_2 in silica sand and soils.

THE PROBLEM

Since the industrial revolution there has been a dramatic increase in the quantity of chemicals refined and produced synthetically. Over 500 million gallons of motor fuels are currently consumed in the United States on a yearly basis (1). Until the late 1970's, there was little concern over pollution due to the widespread belief that the earth has the ability to detoxify wastes through the phenomenon of dilution. During this period there was widespread surface dumping and waste storage in unlined pits, ponds, and lagoons. While these practices have been significantly reduced, present and future contamination exists through accidental spills and leaking storage tanks. Approximately 1.4 million underground storage tanks have been installed in the United States and an estimated 438,000 are leaking (2). Accidental spills and leaking underground storage tanks (UST's) produce widespread soil contamination as well as the potential for future ground water contamination. A recent General Accounting Office survey identified UST's as the most predominant sources of ground water contamination (3).

The Resource Conservation and Recovery Act (RCRA) has provided a regulatory mechanism for controlling the management of hazardous wastes (4). Through RCRA, entities that deal with hazardous wastes became accountable for their actions. The Resource Conservation and Recovery Act was enacted to prevent future uncontrolled dumping, provide an avenue for assigning responsibility for future spills and mishaps, and made all parties which deal with hazardous wastes responsible from reception until final disposal. Additional legislation, the Comprehensive Environmental Response Compensation and Liability Act (CERCLA), was enacted to deal with past problems through the provision of public resources for cleaning up contaminated areas (4). This legislation also provides an avenue for recovering resources from potentially responsible parties (PRP), who may be held responsible for acts that were committed decades earlier and can be required to assist in repairing the damage. The ultimate goal of clean up operations entails the reduction of contaminants to undetectable levels but the costs for such extensive remediation are often prohibitive. More common procedures include treating the waste to negotiated levels or to below permissible levels previously determined by regulatory agencies. For instance, the action limit for the heavier fractions of petroleum is 200 ppm, which was set by the Washington State Department of Ecology. Another important regulatory consideration is that the remedial technology does not transform the wastes into compounds that are more dangerous. The best method for achieving this reduction in hazard is to completely destroy (i.e., mineralize) the contaminants to their thermodynamic endpoints, CO_2 and H_2O.

Petroleum products are the most widely used class of chemicals, and as a result, are found at many contaminated sites. Petroleum fractions are comprised of an wide range of chemical compounds; including paraffins, cycloparaffins, and aromatics. The size of these molecules can range from four carbons to lengthy chains and multi-ring structures with greater than 50 carbons. This complex mixture of chemicals presents difficulties when designing soil remediation systems, and improved processes for their remediation are necessary for easily-treated compounds as well as some which are strongly adsorbed, non-volatile, and biorefractory.

The strategy most commonly used in experimental research is to hold all variables constant except one, which is varied until the desired result is found. Using this point, the procedure is repeated for a second variable until its result is determined. This changing of one-variable-at-a-time strategy is then repeated until the information under consideration is found for each of the variables. Such a method for either the optimization or mechanistic experimental investigation of several variables is inefficient, time consuming, and can be expensive in terms of number of experiments conducted. More importantly, it negates the possibility of detecting interactions among variables.

The experimental matrix used for determining optimal conditions for contaminant mineralization was a central composite rotatable design using the concept of response surfaces. This experimental design procedure was advantageous because it statistically showed interactions between experimental variables, unlike the one-variable-at-a-time strategy, and additionally cut down the ultimate number of experiments conducted while still keeping a high degree of statistical significance in the results.

The purpose of this research was to document that Fenton's reagent actually works, and to confirm that hydrocarbons are mineralized (i.e., oxidized completely) to carbon dioxide and water, and that no toxic intermediates are formed or are terminal end products. Such information is necessary for process approval from regulatory agencies. Practical applications dealing with process engineering are provided in the companion document "On Site Treatment of Contaminated Soils Using Catalyzed Hydrogen Peroxide" (T9234-06).

REVIEW OF CURRENT PRACTICE

FENTON'S REAGENT

The process of hydrogen peroxide catalysis by iron (II) has been well documented in the fundamental chemistry literature. In 1894, H.J.H. Fenton (5) discovered that when hydrogen peroxide and iron (II) are mixed, a vigorous reaction was initiated. The primary reaction involves the catalysis of H_2O_2 by iron (II) to yield iron (III), hydroxyl radical ($OH\bullet$), and hydroxide (OH^-) (6).

$$H_2O_2 + Fe^{2+} \text{-------------}> Fe^{3+} + OH\bullet + OH^- \qquad (1)$$

Hydroxyl radical is a highly reactive species which reacts rapidly with most organic compounds at rates of 10^7-10^{10} $M^{-1}s^{-1}$ (7).

In addition, reactions occur during Fenton's reagent that quench the hydroxyl radicals which are produced in equation 1 (6).

$$OH\bullet + OH\bullet \text{-------------}> H_2O_2 \qquad (2)$$

$$OH\bullet + H_2O_2 \text{-------------}> H_2O + HO_2\bullet \qquad (3)$$

$$OH\bullet + Fe^{2+} \text{-------------}> Fe^{3+} + OH^- \qquad (4)$$

Hydroxyl radicals react with $OH\bullet$, Fe^{2+}, and H_2O_2 at rates of $5x10^9$, 4×10^8, and $1.2x10^7$ $M^{-1}s^{-1}$, respectively (8).

In addition to the formation of hydroxyl radicals, other radicals are produced such as perhydroxyl radicals ($HO_2\bullet$) (equation 3) and organic radicals (equation 5) (9).

$$OH\bullet + R \text{-------------}> \bullet ROH \qquad (5)$$

$$\bullet ROH + Fe^{3+} \text{-------------}> ROH + Fe^{2+} + H^+ \qquad (6)$$

Where R is an organic compound and $\bullet ROH$ is an organic radical. The organic radical can then enter into reactions reducing iron (III) to iron (II) as in reaction 6, providing additional iron (II) to catalyze H_2O_2 (6).

$$HO_2\bullet + H_2O_2 \text{-------------}> O_2 + H_2O + OH\bullet \qquad (7)$$

Perhydroxyl radicals react with excess hydrogen peroxide to create additional hydroxyl radicals as shown in equation 7 as well as the potential for direct oxidation of highly labile compounds (10).

The chemistry of Fenton's reagent has received extensive attention and several hypotheses have been presented. These hypotheses are quite complex with literally hundreds of equations required to quantify the chemistry. The most effective use of Fenton's reagent will require the minimization of hydroxyl radical quenching while generating the most hydroxyl radicals.

AQUEOUS WASTE TREATMENT

The application of Fenton's reagent in treating aqueous compounds and industrial wastes has been studied extensively (11)(12)(13)(14). These studies have focused on the oxidation of highly soluble compounds such as phenols, chlorophenols, and substituted benzene compounds (11)(12). Industrial waste streams containing formaldehyde, dichlorophenol, phenol have also been treated using Fenton's reagent (13)(14)(15).

Incomplete oxidation of the parent compound that results in daughter products was often reported (11)(12). The oxidation of nitrophenol produced the oxidation products 1,2,4-trihydroxybenzene, hydroquinone, and *p*-benzoquinone(12). The formation of chloroaliphatic compounds after the oxidation of chlorine-substituted phenols suggested that the benzene ring had been opened through hydroxyl radical attack although these daughter compounds were not readily degraded (11). The complete degradation of 2,4-D resulted in only partial formation of CO_2 which suggested that highly oxygenated species resistant to hydroxyl radical attack were created (16). On the other hand, the oxidation of a waste stream containing formaldehyde resulted in complete stoichiometric recovery of CO_2 (13).

The use of Fenton's reagent for treating aqueous wastes and industrial wastes has been documented with the parent compound being degraded while in most instances, complete oxidation does not occur.

SOIL TREATMENT

Fenton's reagent has been extended to the treatment of soils based on the potential for inexpensively and rapidly remediating contaminated sites. Hydrogen peroxide has been used extensively as a method for removing organic carbon from soil prior to mineralogical analysis (17). More recently, application of catalyzed H_2O_2 to the oxidation of contaminated soils has been investigated (18)(19)(20)(21).

The use of high concentrations of hydrogen peroxide for the removal of organic carbon from soils often results in the formation of various products, including n-alkanes, aliphatic acids, and phenolic acids (17). This suggests that the organic carbon as well as the degradation by-products must be oxidized to completely mineralize contaminants .

Studies conducted in silica sand have shown that the use of iron (II) catalyzed hydrogen peroxide has the ability to completely destroy pentachlorophenol and perchloroethylene (18) (20). Complete compound destruction was confirmed by stoiciometric recovery of CO_2 and Cl^-. The destruction of compounds in silica sand was optimal at a pH ranging from 2.0-3.0 when soluble iron was used as a catalyst (18). The oxidation of pentachlorophenol, octachlorodibenzo-*p*-dioxin, hexadecane, trifluralin, and dieldrin in natural soils was also documented (18) (19) (21). Tyre *et al.* (19) investigated the Fenton's reagent treatment of a three dimensional matrix consisting of four soils of varying organic contents (0.4%, 0.7%, 1%, and 1.6%) x four contaminants (pentachlorophenol, trifluralin, hexadecane, and dieldrin) x three iron (II) amendments (0, 240 mg l^{-1}, and 400 mg l^{-1}). They found that, although contaminant oxidation was significantly more rapid in the systems with iron amendments, the efficiency (i.e., the moles contaminant treated per mole of H_2O_2 consumed) was noticeably more inefficient. This was probably due to the precipitation of soluble iron as ferrihydrite, which is an ineffective Fenton's catalyst. Visual inspection of the reactions has shown that, as the ferrihydrite precipitated over the first three hours, oxygen evolution increased significantly. The corresponding minimal contaminant oxidation after three hours confirms that ferrihydrite is an ineffective catalyst for the production of hydroxyl radicals. Unexpectedly, Tyre et al. (19) found that the systems without iron amendment (which were considered control systems) were characterized by significant contaminant degradation, although the rate was slower than in the soluble iron systems. They also found that the hydrogen peroxide consumption rate was extremely low, and the resulting treatment stoichiometry was nearly an order of magnitude more efficient than the soluble iron systems. Because soluble iron concentrations were negligible during the reactions, the authors hypothesized that naturally occurring crystalline iron oxides may be capable of catalyzing Fenton-like reactions. Mineral-catalyzed Fenton-like oxidations may occur by at least two mechanisms: 1). mineral dissolution with release of soluble iron which then catalyzes hydrogen peroxide decomposition and 2). heterogeneous catalysis on mineral surfaces. The oxidation of pentachlorophenol and trifluralin in soils proceeded readily while dieldrin and hexadecane resisted oxidation (19). Dieldrin and hexadecane may have resisted degradation due to their highly hydrophobic nature and low solubilities. In addition, degradation efficiencies decreased as a function of soil organic carbon which would suggest that the existing organic matter must be oxidized as well as the compounds of interest. The oxidation of octachlorodibenzo-*p*-dioxin was achieved by the addition of a small amount of high concentration hydrogen peroxide and GC/MS revealed no detectable organics remaining (22). The degradation of particulate PCP and soluble PCP was compared with more aggressive conditions being required to oxidized particulate PCP (21). This suggests that to oxidize particulate or sorbed compounds aggressive oxidations must be used due to mass transfer limitations.

Research to date suggests that while compounds can be completely mineralized in soil slurries, there may be compounds which resist degradation due to their particulate or sorbed nature. The effectiveness of catalyzed hydrogen peroxide for remediating contaminate soil appears to depend on a complex matrix of variables such as organic carbon content, compound characteristics, pH, and hydrogen peroxide dosages.

EXPERIMENTAL METHODOLOGY

MATERIALS

A Palouse loess soil was obtained from an eastern Washington wheat field and was characterized before use. Its particle size distribution was determined by the pipette method (23). Organic carbon was determined by combustion at 900 °C with evolved CO_2 trapped in KOH and measured by back titration of unreacted KOH (24). Amorphous and crystalline iron and manganese oxyhydroxides were determined by citrate-bicarbonate-dithionite extractions (25). Cation exchange capacity was established by saturation with sodium acetate at pH 8.2 (26). The soil characteristics are shown in Table 1. Radiolabeled hexadecane and benzo[*a*]pyrene were purchased from Sigma Chemical Co. The ^{14}C labeled hexadecane and benzo[*a*]pyrene had a specific activity of 2.2 mCi $mmole^{-1}$ and 10.7 mCi $mmole^{-1}$, respectively. Hydrogen peroxide was provided by Solvay Interox. Ferrous sulfate ($FeSO_4{\cdot}7H_2O$), ethyl acetate ($CH_3COCH_2COOC_2H_5$), pentane ($CH_3(CH_2)_3CH_3$), sulfuric acid (H_2SO_4), phosphoric acid (H_3PO_4), and Scintallene scintillation cocktail were obtained from Fisher Scientific Co. Carbo-Sorb and Scint-A XF were obtained from Packard Scientific. All solutions used water from a Barnstead Nanopure II deionizing system.

Table 1. Soil Characterization of Palouse Loess

Characteristic	Value
Organic C content (%)	0.11
Sand (%)	20.4
Clay (%)	18.8
Silt (%)	60.8
Crystalline Fe oxides ($\mu g\ g^{-1}$)	33540
Amorphous Fe oxides ($\mu g\ g^{-1}$)	22.5
Crystalline Mn oxides ($\mu g\ g^{-1}$)	7126
Amorphous Mn oxides ($\mu g\ g^{-1}$)	35.5
Cation exchange capacity ($cmol_c\ kg^{-1}$)	22.5
pH	6.4

EXPERIMENTAL DESIGN

This research utilized a central composite experimental design to determine the optimal treatment conditions as well as to elicit any interactions between the variables investigated. The design incorporated three variables at five levels with five center points for statistical validity (27). Figure 1 shows a three dimensional graphical representation of the experimental design with the black dots representing points where experiments were conducted. The six star points which lie outside of the boxed region were calculated using a factor of 1.680 to achieve complete rotatability. Rotatability is defined as achieving complete symmetry for the variables investigated at all levels.

The data collected from this experimental matrix were used to develop a regression equation which quantitatively described the system of interest using the method of least squares. Equation validation was achieved by evaluating each term based on the 90% interval of a single sided *t*-distribution and eliminating all terms which did not meet this criterion. Additionally, the data fit was evaluated based on the R^2 of the final regression equation. The resulting regression equation was then used to develop contour plots through the use of a SYSTAT software package.

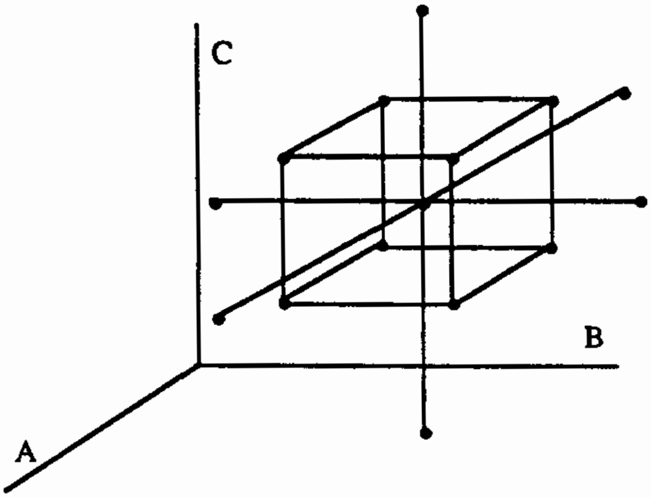

Figure 1. Three dimensional representation of the central composite experimental procedure.

EXPERIMENTAL PROCEDURE: SILICA SAND

Experiments were conducted in batch reactors containing 0.5 grams of silica sand contaminated with hexadecane at a concentration of 0.1 mmole kg^{-1} and an activity of 112.6 µCi. Hexadecane was introduced to the silica sand by adding 1 ml of a 1000 mM (millimoles/L) solution of hexadecane and pentane. The pentane was then allowed to evaporate leaving hexadecane remaining on the silica sand. Benzo[*a*]pyrene was introduced to the sand with the same method but with an activity of 547.6 µCi. The experimental matrix used for the factorial design included three variables; hydrogen peroxide concentration, slurry volume, and iron (II) concentration. Hydrogen peroxide concentrations ranged from 1000 mM to 15,000 mM. Slurry volume was based on the field capacity (x F.C.) of silica sand which was previously determined to be 0.44 ml per 1.0 g. (Field capacity is the volume of water held by the soil under the force of gravity). The slurry volume varied between 0.25 x F.C. and 4.0 x F.C. Iron (II) was used at concentrations from 5 mM to 25 mM. Initially, hydrogen peroxide was added to the silica sand and the pH was adjusted to 3.0 with 40 µl of 0.05 N H_2SO_4. Iron (II) was then added to the system with 40 µl of a stock solution. Reactions were allowed to proceed until completion, which was determined by undetectable H_2O_2 concentrations. Control experiments were conducted with deionized water in place of H_2O_2.

EXPERIMENTAL PROCEDURE: SOILS

Palouse loess was spiked with hexadecane by the method described in the previous section. The variables that were investigated included hydrogen peroxide concentration, slurry volume, and pH. Hydrogen peroxide concentrations ranged from 1500 to 15,000 mM. (For H_2O_2, mg/L = mM x 34 mg/mmole; e.g., 1,500 mM = 51,000 mg/L). The slurry volume ranged from 1 x F.C. to 20 x F.C. (F.C.= 0.356 ml g^{-1}). The slurries were adjusted to pH 2, 3.2, 5, and 8 with 1 N H_2SO_4 or 1 N NaOH. All experiments were allowed to proceed until H_2O_2 dropped to undetectable levels. Parallel control experiments were conducted with deionized water in place of H_2O_2.

^{14}C RECOVERY

In order to document hexadecane oxidation during Fenton-like remediations, the experiments were repeated in a closed system consisting of a reaction vial and a trap for collecting evolved $^{14}CO_2$. Gas collection was accomplished by 0.18 mm diameter fused silica capillary tubing. Figure 2 shows the system used for ^{14}C analysis. The evolved CO_2 was trapped in 10 ml of a 20% (v/v) solution of Carbo-sorb in S¢int-A XF Scintillation cocktail. As the experiments proceeded, the trapping vials were exchanged daily in order to ensure adequate trapping capacity. All reaction vials were then extracted with 10 ml of ethyl acetate; 5 ml of the extract was added to a scintillation vial containing 5 ml of Scintilene counting cocktail. Extractable organic concentrations were determined by shake extraction with ethyl acetate (19). A materials balance was then constructed with the ^{14}C recovered from the two phases.

ANALYSIS

Concentrations of hydrogen peroxide as experiments progressed were determined by iodiometric titration with sodium thiosulfate (28). Isotope analysis was performed on a Packard 2200LL scintillation counter. A quench curve was developed from standards supplied by Packard.

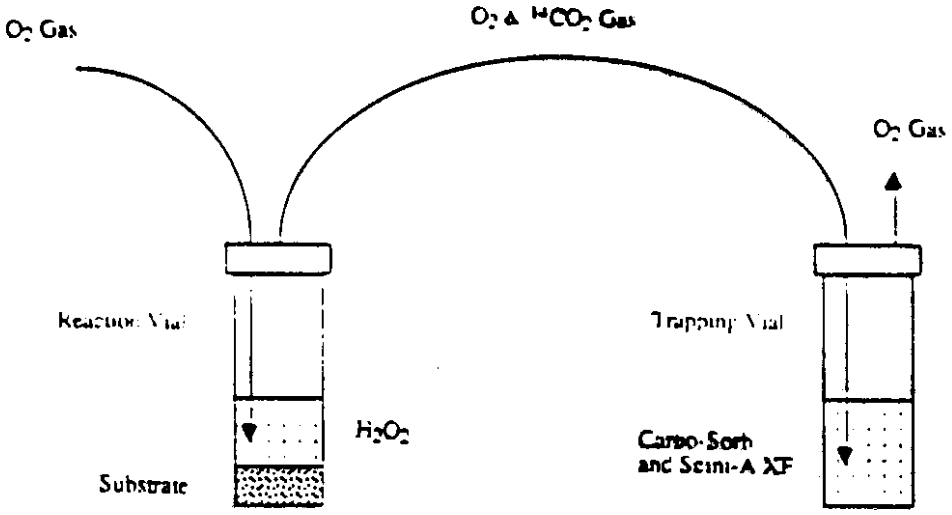

Figure 2. Apparatus for Determining ^{14}C Mass Balances

DISCUSSION

HEXADECANE IN SILICA SAND

Experimental Design Results

The experimental data for ^{14}C recovery were entered and subjected to multilevel regression analysis using SYSTAT to develop regression equations and surface responses. Hexadecane oxidation to $^{14}CO_2$ in silica sand was described by:

$$^{14}CO_2\ (\%) = 26.04 - 1.30 \times 10^{-3}(H_2O_2) - 8.59(\mathrm{VOLUME}) - 3.13 \times 10^{-2}(\mathrm{IRON})^2 + 8.20 \times 10^{-4}(H_2O_2)(\mathrm{VOLUME}) + 1.05 \times 10^{-4}(H_2O_2)(\mathrm{IRON}) + 3.45 \times 10^{-1}(\mathrm{VOLUME})(\mathrm{IRON}) \quad (8)$$

Treatment efficiency in mmoles of CO_2 per mole of hydrogen peroxide consumed is quantified by:

$$\mathrm{Efficiency}\ (\mathrm{mmole}\ ^{14}C\text{-}CO_2\ \mathrm{mole}^{-1}\ H_2O_2) = 1.05 \times 10^{-1} - 3.62 \times 10^{-6}(H_2O_2) - 5.90 \times 10^{-2}(\mathrm{VOLUME}) + 9.50 \times 10^{-3}(\mathrm{VOLUME})^2 + 1.05 \times 10^{-6}(H_2O_2)(\mathrm{VOLUME}) \quad (9)$$

where

H_2O_2 = hydrogen peroxide concentration (mM)
VOLUME = slurry volume (x F.C.)
IRON = iron (II) concentration (mM)

The regression equations had an R^2 of 0.92 and 0.83, with all terms lying within the 90% confidence interval of a single sided *t*-distribution with 10 and 15 degrees of freedom, respectively. The materials balance accounted for 99% of the hexadecane in the silica sand systems.

Treatment Results

The optimal conditions for hexadecane mineralization (14,700 mM hydrogen peroxide, a slurry volume of 4.0 x F.C., and a iron (II) concentration of 25 mM) provided 74% oxidation to CO_2 in silica sand as noted in the upper right hand portion of the figure. The remaining 26% of the ethyl acetate-extractable ^{14}C residue may include organic acids, alcohols, and unreacted hexadecane. Most research to date has proposed that hydroxyl radical mediated reactions occur in only the aqueous phase (29), and that sorbed and particulate materials are not available for OH• attack. Hexadecane is highly hydrophobic (log Kow = 9.07) and exhibits low water solubility (0.00045 mg l^{-1}), and as a result, occurs primarily in the particulate and sorbed states. Therefore, aggressive oxidation conditions were required to oxidize particulate and sorbed species because phase boundaries must be crossed. Less aggressive conditions resulted in reduced conversion to CO_2.

The oxidation of hexadecane in silica sand is shown in Figure 3 as a function of hydrogen peroxide concentration and slurry volume when an iron (II) concentration of 25 mM was used as a catalyst. Treatment effectiveness measured by the conversion of ^{14}C-hexadecane to ^{14}C-CO_2 increased as hydrogen peroxide dosages (i.e., volume and H_2O_2 concentration) increased. At H_2O_2 concentrations of less than 5000 mM, the slurry volume had little affect on the mineralization of hexadecane. These data suggest that the Fenton-like reactions characteristic of lower hydrogen peroxide concentrations are not aggressive enough to mineralize hexadecane; furthermore, increases in slurry volume resulted in inefficient use of H_2O_2. At high H_2O_2 concentrations, (e.g., 14,700 mM), additional slurry volumes enhanced the mineralization of hexadecane. This result was most likely due to a combination if aggressive reaction conditions and a significant pool of reactants.

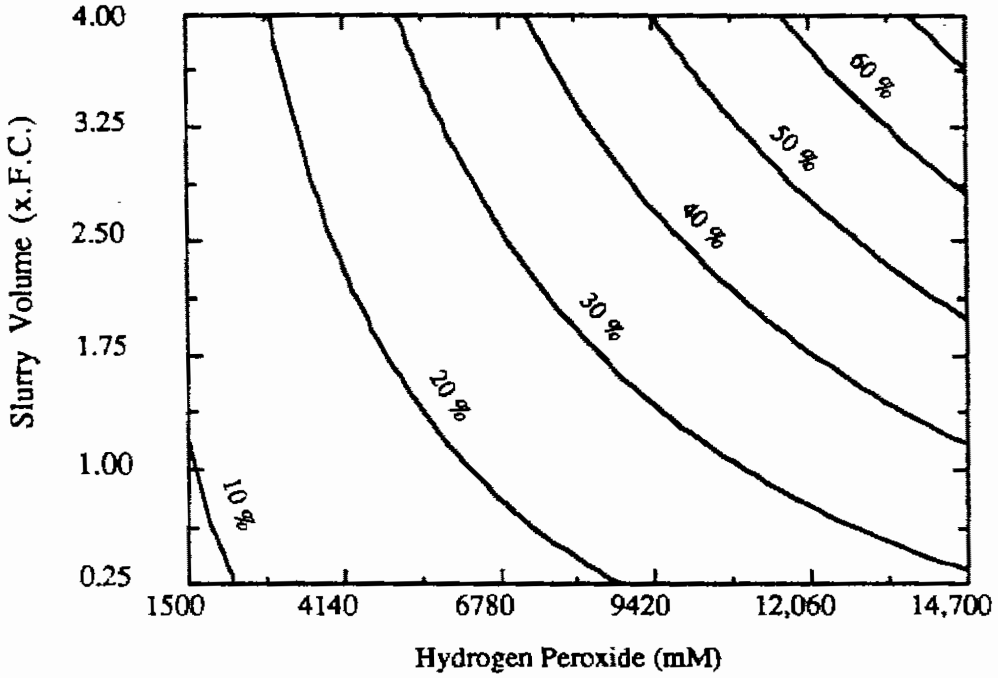

Figure 3. Hexadecane oxidation in silica sand as a function of hydrogen peroxide concentration and slurry volume at an optimal iron (II) concentration of 25 mM.

The concentration of iron (II) has a significant role in the ability of Fenton-like reactions to mineralize hexadecane. The response surface for the interaction between hydrogen peroxide concentration and iron (II) concentration is shown in Figure 4. At all H_2O_2 concentrations, increased mineralization occurred as iron (II) concentrations increased from 5 mM to 25 mM, even though the increased benefit was determined at 20-25 mM iron (II). . At H_2O_2 concentrations less than 5000 mM, iron (II) concentrations greater than 17 mM resulted in no increase in hexadecane mineralization. These data suggest that additional iron may be quenching hydroxyl radicals and oxidized ferric species may be reducing hydrogen peroxide (30). With H_2O_2 concentrations greater than 10,000 mM, CO_2 evolution continued to increase with higher iron (II) concentrations. Therefore, higher iron (II) concentrations may have the potential of greater mineralization of hexadecane.

The surface response for iron (II) concentration and slurry volume is shown in Figure 5. The interaction between iron (II) concentration and slurry volume is analogous to the interaction between iron (II) concentration and hydrogen peroxide concentration, although instead of being a cause (e.g., creates aggressive oxidation conditions) it is an effect (e.g., provides a reservoir of reagent for highly aggressive conditions to be sustained). At high concentrations of iron (II) aggressive conditions exist, and additional hydrogen peroxide is available for generating additional hydroxyl radicals if the slurry volume (i.e., the multiple of field capacity) is increased. Regardless of the H_2O_2 concentration, it is more effective and efficient to increase iron (II) concentration than to increase the slurry volume as long as iron concentrations do not increase to the point where the iron (II) results in quenching with coincidental decreases in the promotion of mineralization.

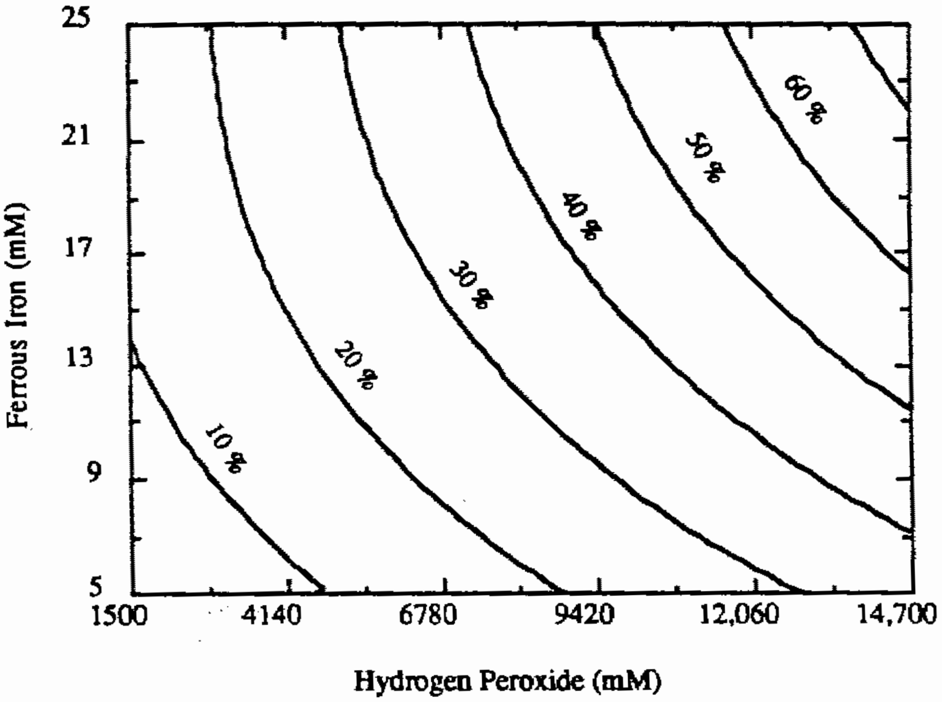

Figure 4. Hexadecane oxidation in silica sand as a function of hydrogen peroxide concentration and iron (II) concentration at an optimal slurry volume of 4.0 x F.C.

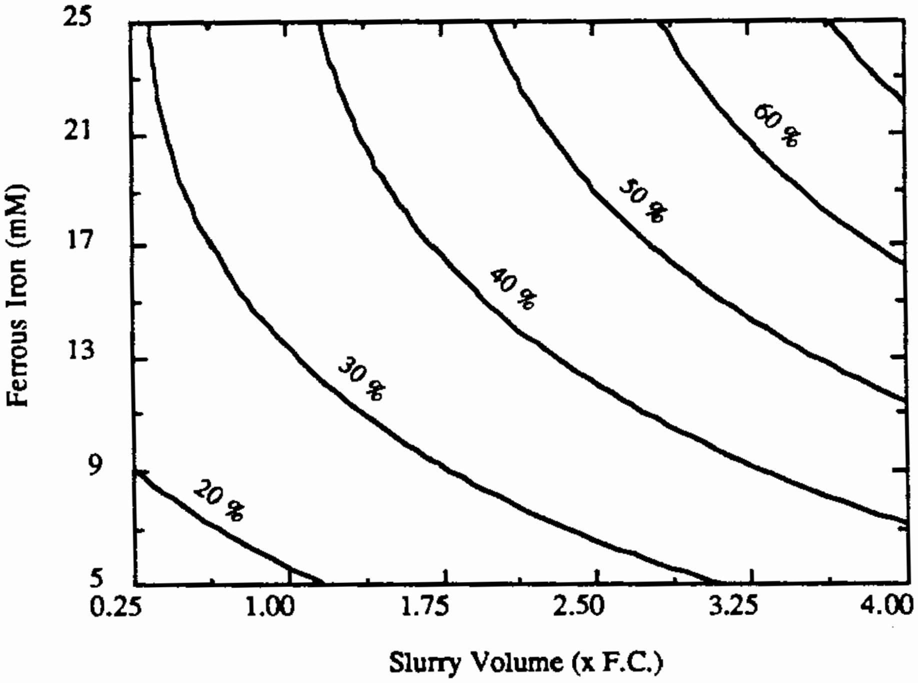

Figure 5. Hexadecane oxidation in silica sand as a function of slurry volume and ferrous iron concentration at an optimal hydrogen peroxide concentration of 14,700 mM.

Treatment stoichiometries (mmoles of CO_2 per mole of hydrogen peroxide consumed) for the mineralization of hexadecane in silica sand are shown in Figure 6. The stoichiometry was most efficient at low slurry volume, however, a lower relative degree of treatment was found in this region. For 60% oxidation, 0.126 mmoles of CO_2 were recovered for every mole of hydrogen peroxide with treatment conditions consisting of a slurry volume of 4.0 x F.C., 14,700 mM hydrogen peroxide, and an iron (II) concentration of 25 mM.

Conclusion

The oxidation of hexadecane in silica sand requires aggressive treatment conditions utilizing high concentrations of hydrogen peroxide and iron (II). The slurry volume is critical since increased oxidation is obtained by adding additional reagents. For example, oxidation of hexadecane is increased from 30% to 70% by using a slurry volume of 4.0 instead of 0.25 x F.C. Most importantly the hexadecane can be completely oxidized to CO_2 and H_2O using Fenton's reagent in a silica sand slurry.

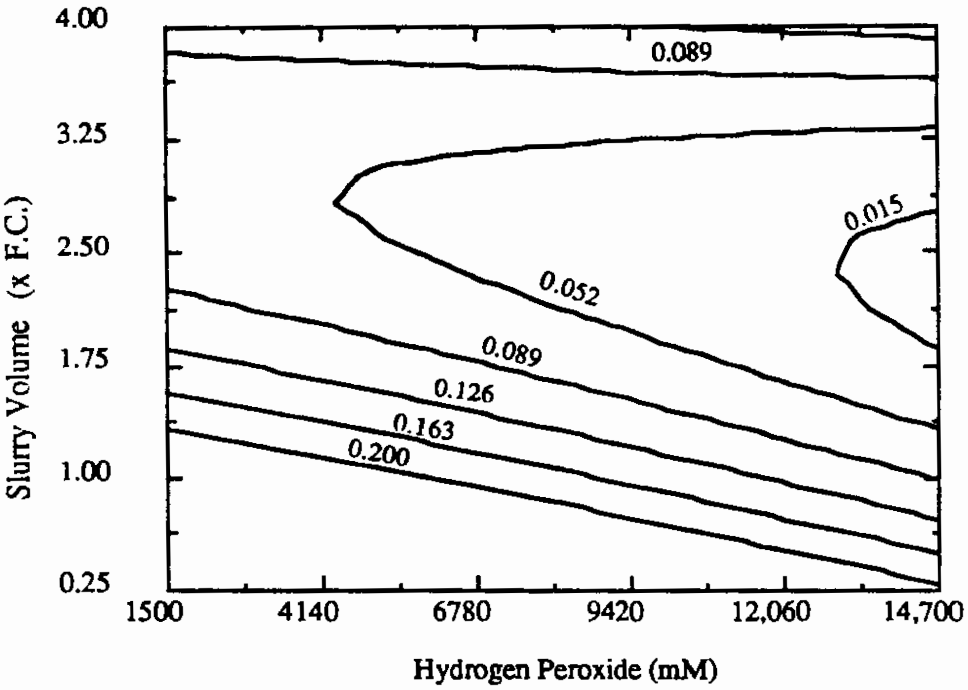

Figure 6. Hexadecane treatment efficiencies in silica sand as a function of hydrogen peroxide concentration and slurry volume in terms of mmole CO_2 per mole of hydrogen peroxide consumed.

HEXADECANE IN SOILS

Experimental Design Results

Based on statistical analyses and surface response development, the empirical equation describing hexadecane oxidation in the Palouse loess soil is:

$$CO_2\ (\%) = 38.59 - 2.00 \times 10^{-3}(H_2O_2) - 3.524(\text{VOLUME}) + 1.00 \times 10^{-7}(H_2O_2)^2 + 6.83 \times 10^{-2}(\text{VOLUME})^2 - 4.129 \times 10^{-1}(pH)^2 + 3.43 \times 10^{-4}(pH)(H_2O_2) + 4.06 \times 10^{-1}(\text{VOLUME})(pH) \quad (10)$$

Treatment efficiency (mmole of CO_2 per mole of H_2O_2 consumed) is:

$$\text{Efficiency (mmole } {}^{14}C\text{-}CO_2 \text{ mole}^{-1}\ H_2O_2) = 1.49 \times 10^{-1} - 2.28 \times 10^{-6}(H_2O_2) - 1.86 \times 10^{-2}(\text{VOLUME}) + 6.74 \times 10^{-4}(\text{VOLUME})^2 \quad (11)$$

The $R^2 = 0.84$ for equation 10 and $R^2 = 0.75$ for equation 11 with all terms lying within the 90% confidence interval of a one-sided *t*-distribution with 12 and 16 degrees of freedom, respectively. The materials balance accounted for the ^{14}C in the Palouse loess.

Treatment Results

Hexadecane oxidation as a function of hydrogen peroxide concentration and slurry volume at an optimal pH of 8.0 is shown in Figure 7. In a soil with organic matter and other inorganic species (e.g., trace metals, carbonates) the H_2O_2 may be reduced to other transient species than $OH\bullet$, resulting in ineffective treatment . Under treatment conditions consisting of 14,700 mM hydrogen peroxide, a slurry volume of 20 x F.C., and a pH of 8.0, 67% of the hexadecane was oxidized to CO_2. As with the oxidation of hexadecane in silica sand, increases in hydrogen peroxide concentrations resulted in higher CO_2 evolution. Higher peroxide concentrations appear to result in more aggressive treatment conditions, while increased volume provides an additional pool of reagents.

Initial research determined that the optimal pH for Fenton's reagent in soils was in the range of 2.0 to 3.0, and this pH range has been well documented as the optimal for aqueous systems which were amended with soluble iron (II) (18). This research has shown that the complete oxidation of hexadecane at higher pH's was more effective, which is perhaps a function of mineral-catalyzed reactions; possibly even a different mechanism. Figure 8 shows the response surface for the interaction of hydrogen peroxide concentration and pH at a slurry volume of 20 x F.C. At all H_2O_2 concentrations, increased mineralization was achieved by increasing the pH, which may be due to an increase in reaction aggressiveness which is witnessed by exothermic and mixing vigorousness. Low concentrations of hydrogen peroxide exhibit less dramatic increases in hexadecane oxidations as pH is increased than at high H_2O_2 concentrations. Reactions conducted at pH 8 and 2 at a concentration of 7500 mM and a slurry volume of 10 x F.C. resulted in different reaction periods. At pH 8.0, the reaction was 90 % completed after 2 days while at pH 2.0 it required 6 days until 90 % of the reaction was completed. An important result is that at a high pH, treatment could be conducted rapidly while achieving complete contaminant oxidation.

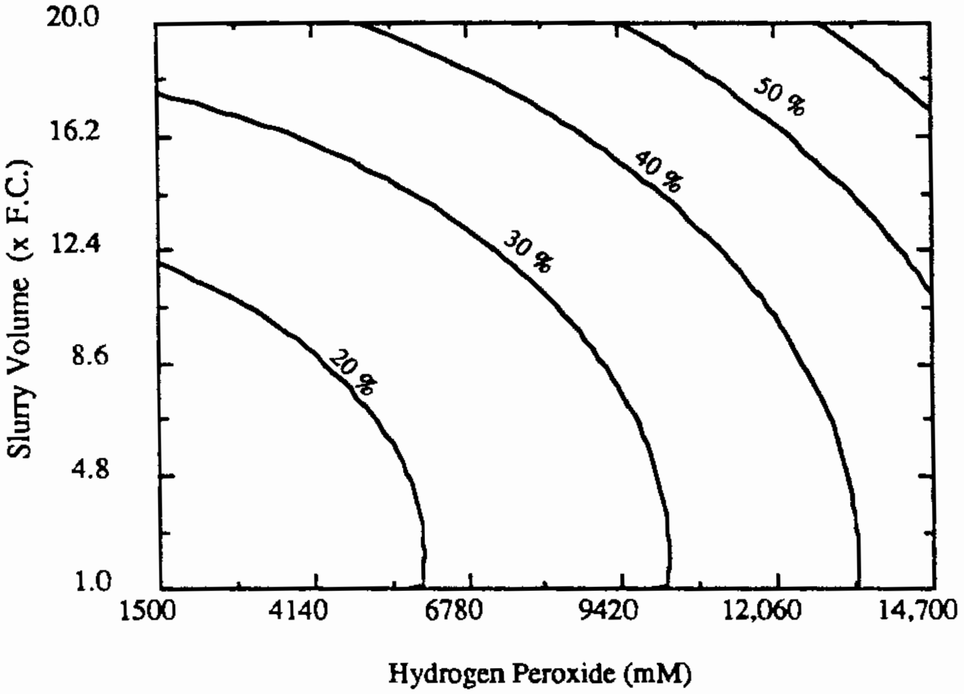

Figure 7. Hexadecane oxidation in Palouse loess as a function of hydrogen peroxide concentration and slurry volume at a optimal pH of 8.0.

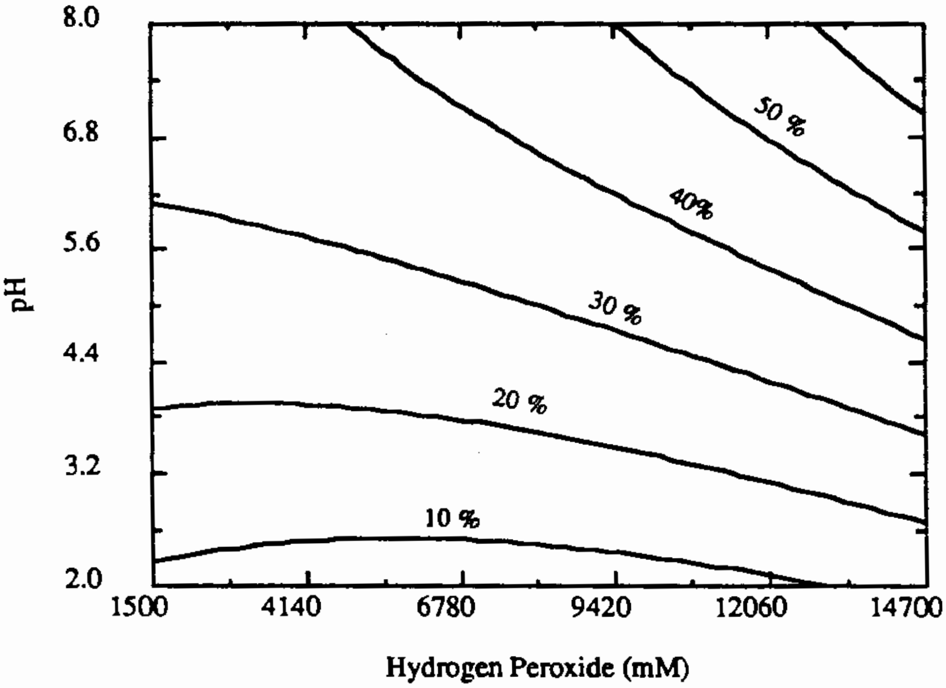

Figure 8. Hexadecane oxidation in Palouse loess as a function of hydrogen peroxide concentration and pH at an optimal slurry volume of 20 x F.C.

The response surface for the interaction of slurry volume and pH is shown in Figure 9. The results of Figures 7 and 8 show that high slurry volumes oxidize more hexadecane, however, the data of Figure 9 show that increased slurry volume resulted in a decrease in hexadecane mineralization. This phenomenon, may be due to a change in the reaction mechanism as the pH increases; in addition, particulate hexadecane may float to the surface of the slurry (sp. gr.= 0.77) where it is unavailable for mineral catalyzed reactions. At a low slurry volume more hexadecane oxidation may have occurred due to the slower reaction rate at a low pH and because there was only a limited amount of reagent present.

Figure 10 shows the response surface for treatment efficiency for hexadecane mineralization in the Palouse loess soil. At low slurry volumes, increases in hydrogen peroxide concentration resulted in additional hexadecane oxidation with insignificant change in the treatment efficiency. As the slurry volume increased the treatment efficiency decreases rapidly until a slurry volume of greater than approximately 15 x F.C. is reached. At this point efficiency of treatment increased which can be contributed to the oxidation at lower hydrogen peroxide concentrations.

Conclusion

Hexadecane was completely oxidized in soils using naturally occurring iron minerals as the catalyst for Fenton-like oxidations. Similar to the treatment in silica sand, aggressive oxidation conditions resulted in the highest conversion to $^{14}C-CO_2$. The most important results is the previously documented optimal pH for treatment, pH 2.0-3.0, may not be appropriate in all cases. The mineralization of hexadecane in Palouse loess soil was optimal at pH 8, which is important for the process engineering of catalyzed soil treatment, because for compounds with similar characteristic (e.g., alkanes), pH adjustment of the soils may not be necessary.

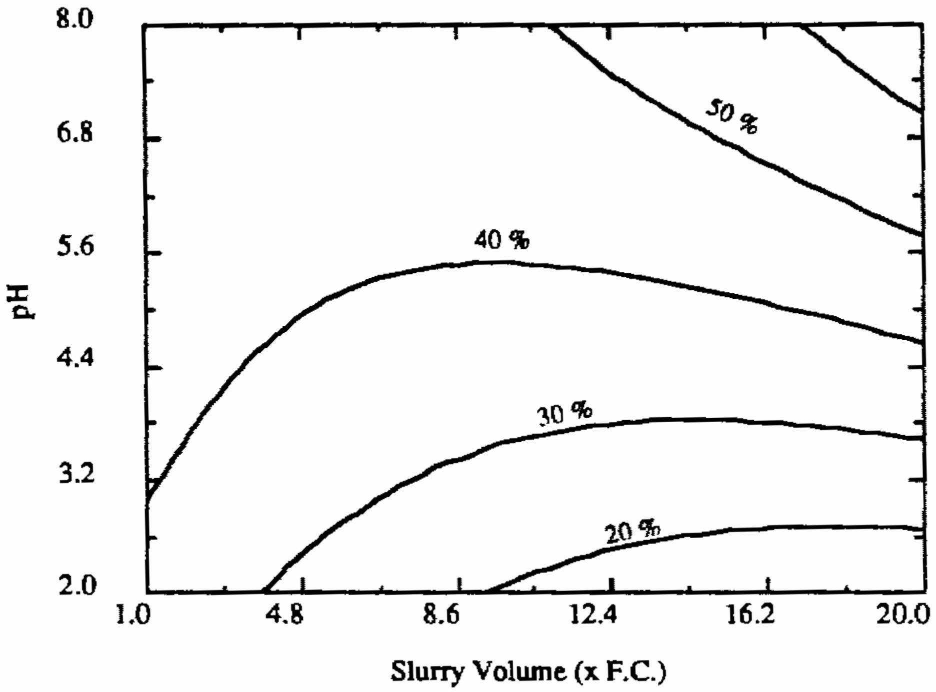

Figure 9. Hexadecane oxidation in Palouse loess as a function of slurry volume and pH as at an optimal hydrogen peroxide concentration of 14,700 mM.

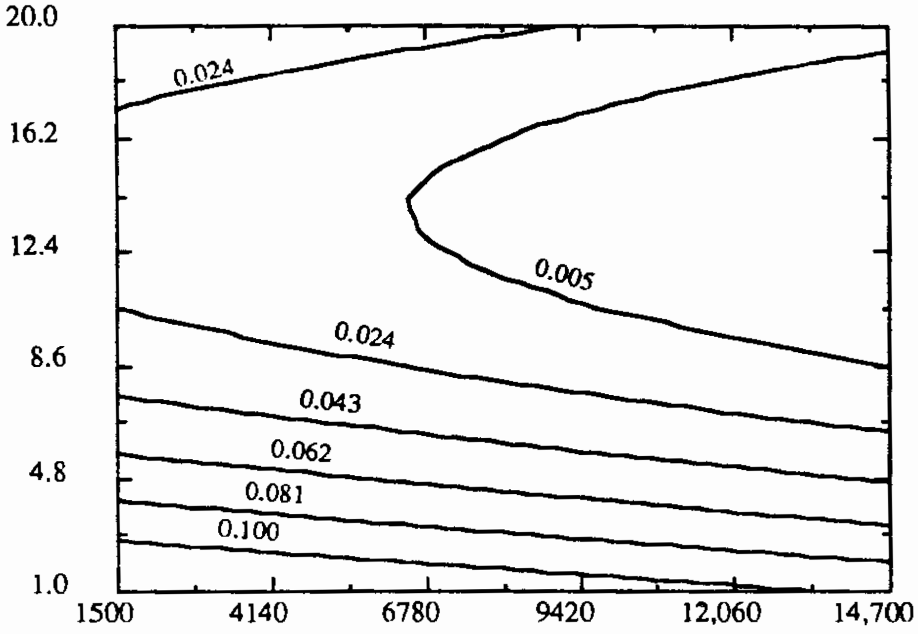

Figure 10. Hexadecane treatment efficiencies in Palouse loess as a function of hydrogen peroxide concentration and slurry volume at an optimal pH of 8.0.

BENZO[*a*]PYRENE IN SILICA SAND

Experimental Design Results

Based on statistical analysis of the experimental data, benzo[*a*]pyrene (BAP) oxidation in silica sand is described by:

$$CO_2\ (\%) = 40.65 + 1.47 \times 10^{-3}(H_2O_2) - 3.40(\mathrm{VOLUME}) - 2.33(\mathrm{IRON}) + 1.07 \times 10^{-7}(H_2O_2)^2 + 3.00 \times 10^{-2}(\mathrm{VOLUME})^2 + 4.58 \times 10^{-1}(\mathrm{VOLUME})(\mathrm{IRON}) \quad (12)$$

Treatment stoichiometries in terms of mmoles of CO_2 per mole of hydrogen peroxide consumed is quantified by:

$$\mathrm{Efficiency}\ (\mathrm{mmole}\ ^{14}C\text{-}CO_2\ \mathrm{mole}^{-1}\ H_2O_2) = 1.197 - 3.705 \times 10^{-5}(H_2O_2) - 6.41 \times 10^{-1}(\mathrm{VOLUME}) + 1.013 \times 10^{-1}(\mathrm{VOLUME})^2 + 9.62 \times 10^{-6}(H_2O_2)(\mathrm{VOLUME}) \quad (13)$$

The regression equations have an R^2 of 0.88 and 0.91, with all terms lying within the 90 % confidence interval of a single sided *t*-distribution with 13 and 15 degrees of freedom, respectively. The materials balance accounted for 86 % of the 14C in silica sand.

Treatment Results

Benzo[*a*]pyrene was mineralized up to 73% in silica sand using Fenton's reagent. The optimal treatment conditions consisted of 14,700 mM hydrogen peroxide, a slurry volume of 0.25 x F.C., and an iron (II) concentration of 5 mM, which resulted in 73% benzo[*a*]pyrene mineralization. Like hexadecane, benzo[*a*]pyrene required high hydrogen peroxide concentrations, but unlike hexadecane, small slurry volumes and low iron concentrations resulted in the most effective CO_2 evolution.

Benzo[*a*]pyrene oxidation in silica sand as a function of hydrogen peroxide concentration and slurry volume at an optimal iron (II) amendment of 5 mM is shown in Figure 11. Slurry volume had little significance in hexadecane mineralization while hydrogen peroxide concentration produced a nearly linear relationship. The lack effect with slurry volume may have been due to the density of benzo[*a*]pyrene, which is higher than water (sp. gr. = 1.35) and the contaminant equilibrates at the bottom of the slurry. At high slurry volumes in which the reaction is taking place throughout the slurry volume, the reagents are wasted in the aqueous phase since no BAP exists there. The linear increase in oxidation as a function of H_2O_2 concentration may be due to the successively more aggressive reaction conditions.

Figure 12 shows the oxidation of benzo[*a*]pyrene as a function of hydrogen peroxide concentration and iron (II) concentration at an optimal slurry volume of 0.25 x F.C. Benzo[*a*]pyrene mineralization increases as a function of H_2O_2 concentration and were inversely proportional to iron (II) amendment, which may be due to the increase in reaction time and steady state hydroxyl radical production at low iron (II) concentrations. Unlike hexadecane in which extremely aggressive conditions were required for oxidation, BAP (which equilibrates at the bottom of the slurry and is characterized by a water solubility an order of magnitude higher), appears to require milder oxidation conditions.

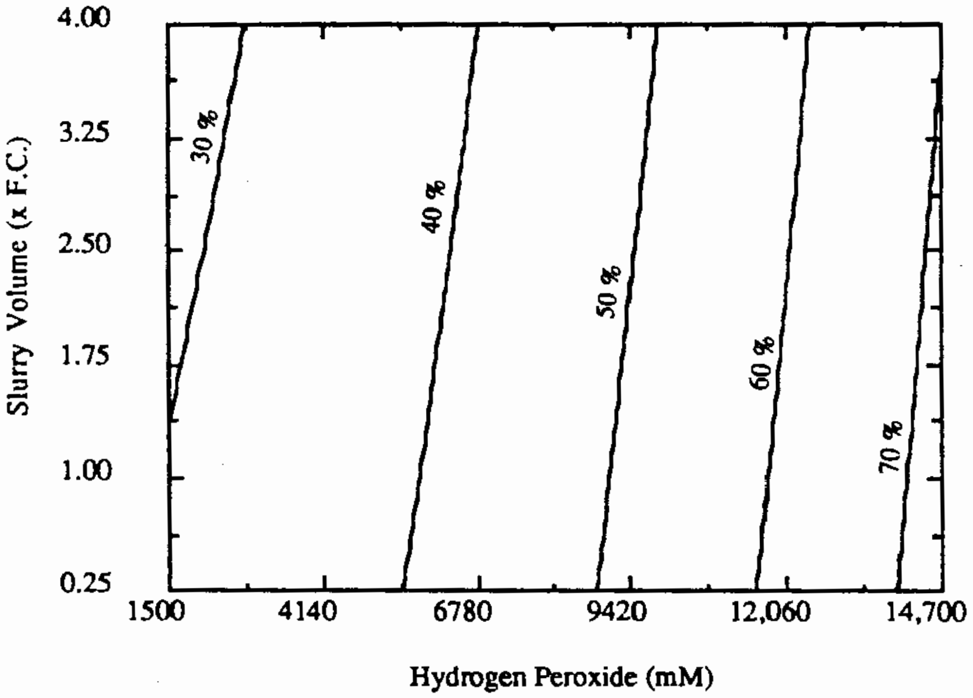

Figure 11. Benzo[*a*]pyrene oxidation in silica sand as a function of hydrogen peroxide concentration and slurry volume at an optimal iron (II) concentration of 5 mM.

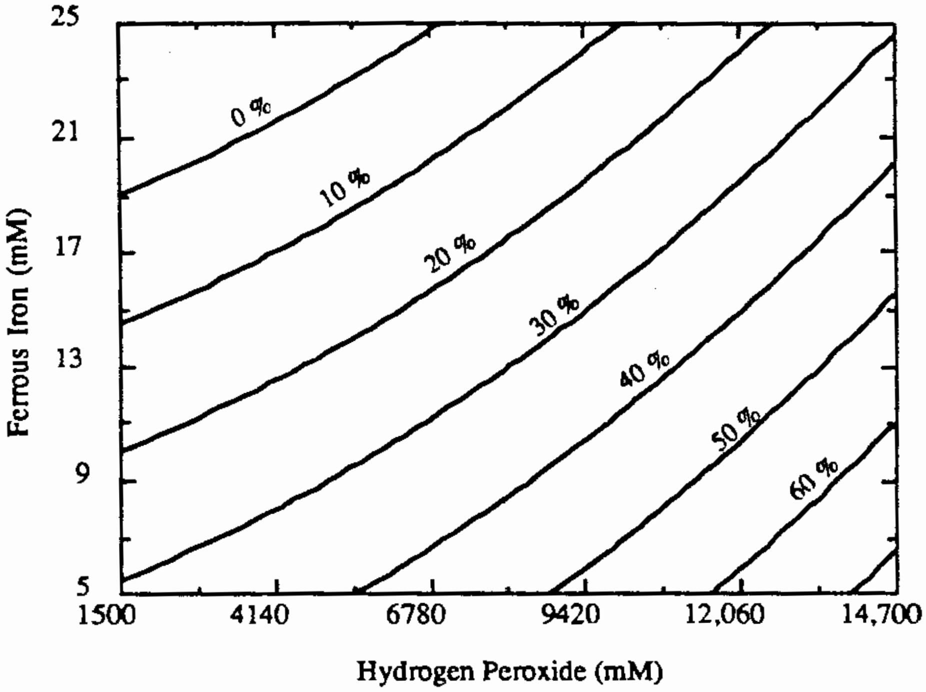

Figure 12. Benzo[*a*]pyrene oxidation in silica sand as a function of hydrogen peroxide concentration and iron (II) concentration at an optimal slurry volume of 0.25 x F.C.

The mineralization of BAP in silica sand as a function of slurry volume and iron (II) amendment at an optimal hydrogen peroxide concentration of 14,700 mM is shown in Figure 13. Benzo[*a*]pyrene oxidation was inversely proportional to the iron (II) amendment, suggesting that at low iron concentrations reaction times increased which resulted in additional oxidation. At high slurry volumes this relationship was not evident, which may be due to the additional pool of reagents allowing radical production to be sufficient even though reaction times were shorter at high iron (II) concentrations.

Treatment efficiency for BAP in silica sand is shown in Figure 14. Under treatment conditions consisting of 14,700 mM hydrogen peroxide, a slurry volume of 0.25 x F.C., and a iron (II) concentration of 5 mM, 70% of the benzo[*a*]pyrene was oxidized with stochiometries of 0.50 mmoles CO_2 for every mole of hydrogen peroxide consumed. The most efficient treatment required low slurry volumes because it appears that increased slurry volumes were characterized by reactions occurring away from the bottom of the slurry where BAP resides.

Conclusion

Benzo[*a*]pyrene was effectively mineralized in silica sand to 73% CO_2. Unlike hexadecane, the treatment was most effective at low slurry volumes with low iron (II) concentrations. This suggests that a steady state reaction where hydroxyl radicals are continually produced in close proximity to the benzo[*a*]pyrene was most effective for treatment.

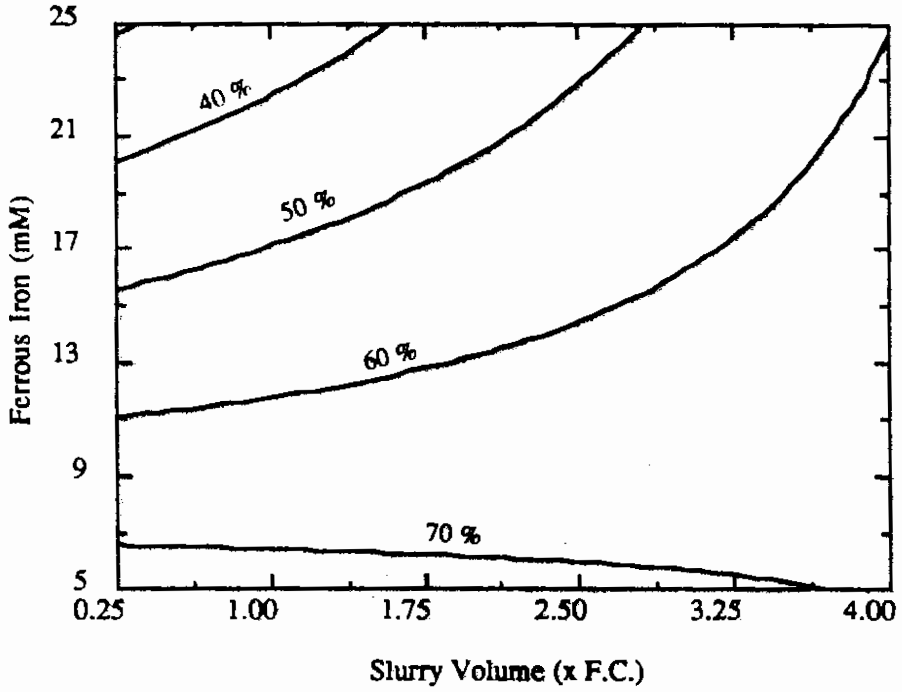

Figure 13. Benzo[*a*]pyrene oxidation in silica sand as a function of slurry volume and iron (II) concentration at an optimal hydrogen peroxide concentration of 17,400 mM.

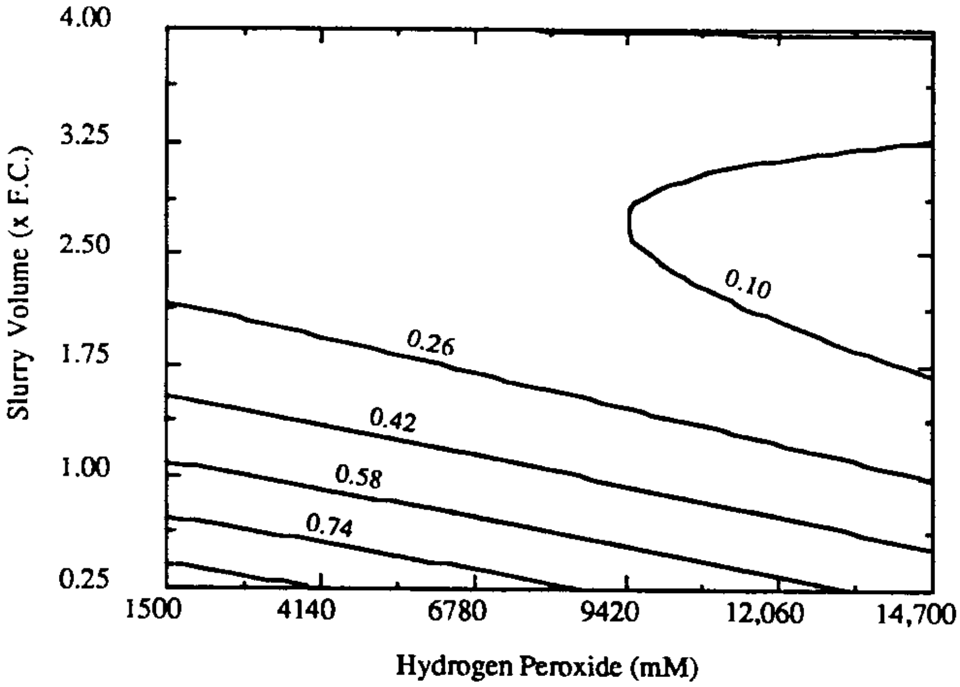

Figure 14. Benzo[a]pyrene treatment efficiencies in silica sand as a function of hydrogen peroxide concentration and slurry volume in terms of mmoles CO_2 per mole of hydrogen peroxide consumed.

BENZO[*a*]PYRENE IN SOILS

Experimental Design Results

Statistical analyses of the experimental data showed that benzo[*a*]pyrene oxidation in Palouse loess soil may be quantified by:

$$CO_2\ (\%) = 53.05 + 1.13 \times 10^{-3}(H_2O_2) - 5.79(pH) - 1.22 \times 10^{-1}(VOLUME)^2 - 3.60 \times 10^{-1}(pH)^2 + 8.38 \times 10^{-1}(VOLUME)(pH) \tag{14}$$

Treatment efficiency for the oxidation of benzo[*a*]pyrene in Palouse loess is:

$$\text{Efficiency (mmole } {}^{14}C\text{-}CO_2 \text{ mole}^{-1} H_2O_2) = 4.18 \times 10^{-1} - 3.25 \times 10^{-5}(H_2O_2) - 2.90 \times 10^{-2}(VOLUME) + 1.42 \times 10^{-9}(H_2O_2)^2 + 6.53 \times 10^{-4}(VOLUME)^2 - 2.09 \times 10^{-3}(pH)^2 + 1.63 \times 10^{-3}(VOLUME)(pH) \tag{15}$$

The regression equations had a R^2 of 0.89 and 0.84, with all terms lying within the 90% confidence interval of a one sided t-distribution with 14 and 13 degrees of freedom, respectively. The materials balance accounted for 73% of the ^{14}C in the system.

Treatment Results

Under optimal treatment conditions consisting of 14,700 mM hydrogen peroxide, a slurry volume of 20 x F.C., and a pH of 8.0, 86% of the benzo[*a*]pyrene was oxidized in the Palouse loess soil. Treatment conditions were significantly different from those required for hexadecane oxidation. Although optimal mineralization occurred under nearly equal conditions of hydrogen peroxide concentration and slurry volumes, contours describing the interactions were completely different. Hydrogen peroxide concentration has the most influence on the mineralization of hexadecane and slurry volume was most significant for benzo[*a*]pyrene mineralization.

Figure 15 shows the degradation of BAP as a function of hydrogen peroxide concentration and slurry volume at pH 8. The relationship for benzo[*a*]pyrene mineralization between hydrogen peroxide and slurry volume, was linear, and was most sensitive to slurry volume. These data suggest that milder conditions could be utilized for BAP oxidation unlike the conditions required for hexadecane mineralization. Small slurry volumes were not effective at a pH 8, which may be due to the rapid H_2O_2 decomposition at high pH. Larger slurry volumes provided a pool of reagents and provided longer reaction times at high pH regimes.

The oxidation of benzo[*a*]pyrene in the Palouse loess soil as a function of hydrogen peroxide and pH at an optimal slurry volume of 20 x F.C. is shown in Figure 16. The treatment was affected more by pH than hydrogen peroxide concentration. For example, if hydrogen peroxide concentration was increased from 1500 mM to 14,700 mM at a pH of 5.0, BAP oxidation would increase from 53% to 67%, whereas if pH was increased from 2.0 to 8.0 at a hydrogen peroxide concentration of 8100 mM, BAP oxidation would increased from 34% to 78%. With most soils having a natural pH of 5.5 to 7.5, mineralization of BAP may be effective with no pH adjustment.

Figure 17 shows the oxidation of benzo[*a*]pyrene in the Palouse loess soil as a function of slurry volume and pH at an optimal hydrogen peroxide concentration of 14,700 mM. These data show that while the optimal oxidation occurs at a pH of 8.0 and a slurry volume of 20 x F.C., at low slurry volume significant oxidations occur at low pH regimes. This phenomenon may be due to the high stability of hydrogen peroxide reactivity at low pH and possibly alternative mechanisms. Additionally, with this lowering in reactivity the length of the reactions increases allowing additional hydroxyl radical production and more efficient stoichiometry.

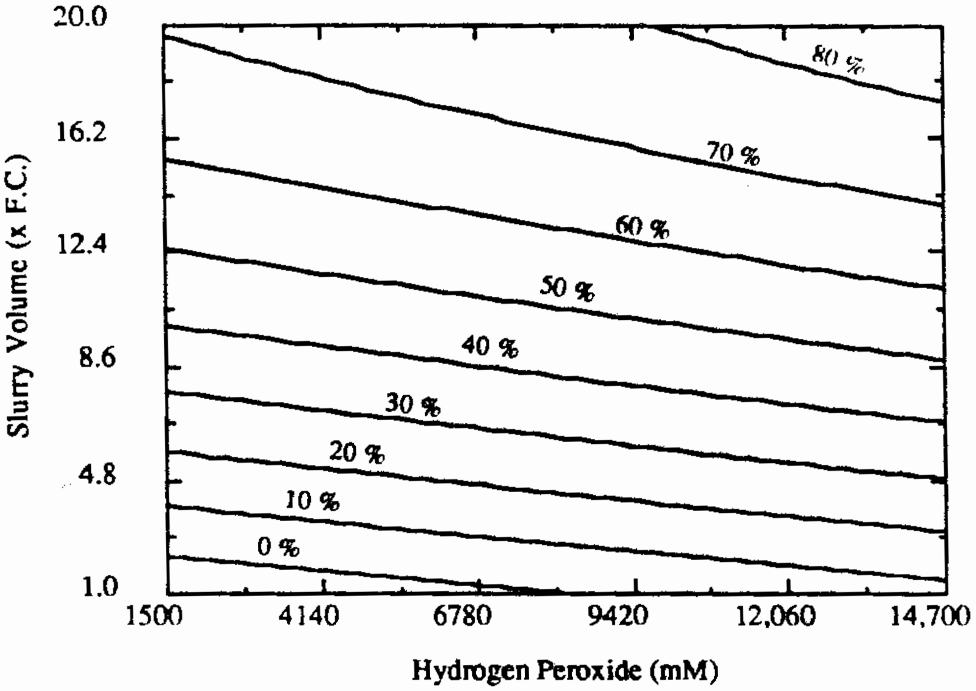

Figure 15. Benzo[*a*]pyrene oxidation in Palouse loess as a function of hydrogen peroxide concentration and slurry volume at an optimal pH of 8.0.

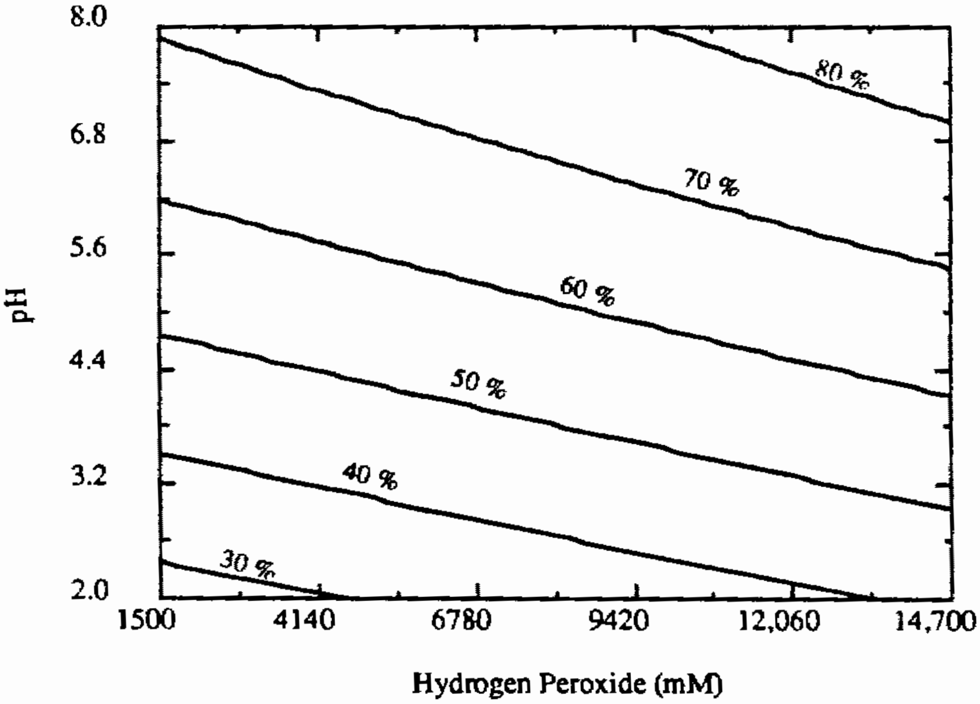

Figure 16. Benzo[*a*]pyrene oxidation in Palouse loess as a function of hydrogen peroxide concentration and pH at an optimal slurry volume of 20 x F.C.

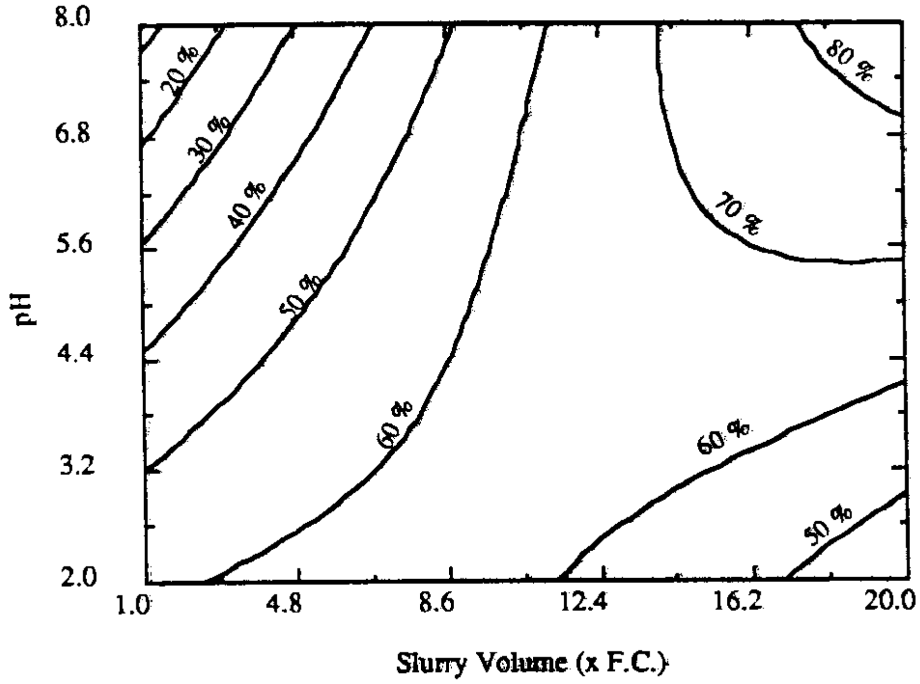

Figure 17. Benzo[*a*]pyrene oxidation in Palouse loess as a function of slurry volume and pH at an optimal hydrogen peroxide concentration of 14,700 mM.

The treatment efficiency of BAP in Palouse loess is shown in figure 18 as a function of hydrogen peroxide concentration slurry volume at a pH of 8. The most effective treatment conditions consisted of using hydrogen peroxide concentration of approximately 1500 mM at a slurry volume of 20 x F.C. which would yield 70% BAP oxidation at an efficiency of 0.200 mmole CO_2 for every mole of H_2O_2.

Conclusion

Benzo[*a*]pyrene was effectively oxidized to CO_2 and H_2O in the Palouse loess soil. Unlike the treatment of hexadecane where high hydrogen peroxide concentrations and slurry volumes were required for treatment, BAP utilized large slurry volumes but low hydrogen peroxide concentrations. Similar to hexadecane, BAP was most effectively oxidized using high pH.

Cumulative Conclusion

The purpose of this research was to document that Fenton's reagent actually works in soils and that common components of petroleum (hexadecane and benzo[*a*]pyrene) can be oxidized completely (i.e., mineralized) to carbon dioxide and water. Using statistically valid experimental design procedures (e.g. central composite rotatable designs), agressive oxidation conditions provided 70-80% contaminant mineralization. These results are similar to mineralization achieved by bioremediation. The data confirm that Fenton's reagent provides a process that oxidizes hydrocarbons to nontoxic products.

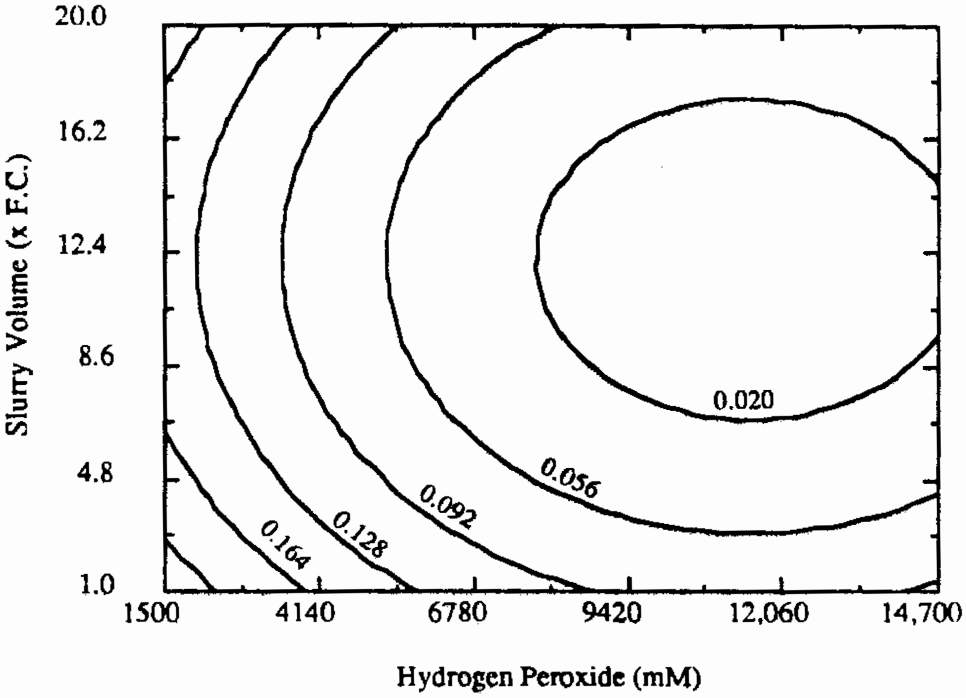

Figure 18. Benzo[*a*]pyrene treatment efficiency in Palouse loess as a function of hydrogen peroxide concentration and slurry volume in terms of moles CO_2 per mole of hydrogen peroxide consumed at an optimal pH of 8.0.

APPLICATIONS AND IMPLEMENTATION

Contaminated soil remediation may be accomplished by on-site or off-site processes. Off-site technologies, such as land filling have been widely used for solving petroleum soil contamination problems. These practices often expose the parties performing the remediation to liability for accidents in transportation or disposal and the potential for future legal responsibility for the wastes after they have been disposed. One of the advantages of off-site treatment is that site closure is rapid, because, once the contaminated soils are excavated, the site has been remediated. On-site technologies, such as bioremediation, while effective in completely remediating the site, often take long periods of time (i.e., from months to years). The use of Fenton's reagent for treating petroleum contaminated soils offers the potential for completely oxidizing the contaminants in a short period of time (i.e., as rapidly as one day).

Fenton's reagent has the potential for application as an *in-situ* and *ex-situ* treatment technology. Based on this research focusing on the complete destruction of all contaminants, an *ex-situ* technology may be required. An *in-situ* technology, based on allowing the hydrogen peroxide to percolate through the contaminated area may be applicable based on further research. Hexadecane, benzo[*a*]pyrene, and similar compounds that exhibit tendencies to sorb or exist as particulate species require aggressive treatment conditions which may be difficult to achieve *in-situ*.

The most simple method of treatment would be to treat the soil in a batch reactor. For example, quantities of soil can be treated in polyethylene barrels or bermed areas. For implementation of the process, peroxide requirements would be determined for the particular site and applied to the soil on-site. This research has shown that mineralization is favored at a pH of 6.0-7.0. Once the hydrogen peroxide was added to batch process, the reaction would be allowed to continue until completion, approximately 2 days to 2 weeks depending on treatment and soil conditions. To optimize the process using a automated control system to maintain the hydrogen peroxide concentration has the potential to enhance contaminant oxidation and reduce costs.

For more rapid treatment a mixing batch reactor (e.g., a concrete mixer) could be used with a small slurry volume and high H_2O_2 concentrations which may increase the reaction rate resulting in a shorter treatment period. If soil and H_2O_2 were added to the mixer and allowed enough time (e.g., approximately 15 min, and returned) several batches could be treated in a hour. Reaction times for treating the soils may range from approximately 10 hrs to 2 days depending on treatment and soil conditions.

The use of Fenton's reagent for treating soils on-site offers the potential for completely oxidizing the contaminants rapidly. While in some instances H_2O_2 costs may be higher than technologies such as bioremediation, the short treatment period can allow rapid site closure. In addition, the rapid treatment period allows for the use of Fenton's reagent as an immediate response tool for remediating a site before additional problems develop.

ACKNOWLEDGMENTS

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