

Evaluation of iron catalysts for the Fenton-like remediation of diesel-contaminated soils

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Abstract

The treatment of a diesel-contaminated soil with hydrogen peroxide catalyzed by six iron compounds and by naturally-occurring minerals in which the hydrogen peroxide is stabilized by phosphate was investigated using central composite rotatable experimental designs. Iron (III) perchlorate and iron (III) nitrate with 1.5 M hydrogen peroxide promoted > 99% oxidation of 1000 mg kg⁻¹ diesel in a Palouse loess soil. Other iron catalysts (iron (III) sulfate, iron (II) sulfate, iron (II) perchlorate) provided 70–80% diesel oxidation under similar reaction conditions. The oxidation reactions were complete within one hour and minimal desorption occurred over 90 h, suggesting that the diesel was oxidized, at least in part, in the sorbed phase. Iron (II) compounds were less effective catalysts than iron (III) species owing to the initial loss of hydrogen peroxide in oxidizing iron (II) to iron (III). The effectiveness of the iron catalysts also correlated with the lowest rates at which their anionic component quenches hydroxyl radicals. Monobasic potassium phosphate was also investigated as a mechanism to enhance the mineral-catalyzed Fenton-like remediation of diesel in the Palouse loess, but resulted in only 40% diesel loss. A central composite design used to investigate the effect of hydrogen peroxide volume on the Fenton-like remediation of the diesel-contaminated Palouse loess showed that a solution sufficient to saturate the soil (3.5 ml (5 g soil)⁻¹) provided the optimum volume. Based on these optimization results, the estimated chemical cost for the remediation of 1000 mg kg⁻¹ diesel in the Palouse loess was \$52 (907 kg)⁻¹ (ton).

Keywords: Advanced oxidation process; Chemical oxidation; Fenton's reagent; Hydrogen peroxide; Petroleum contaminated soil; Soil remediation

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1. Introduction

The contamination of surface soils with hazardous organic wastes is a widespread problem requiring effective remediation processes. Modifications of Fenton's reagent, in which the decomposition of hydrogen peroxide is catalyzed by iron (II) to form hydroxyl radicals ($\text{OH}\cdot$), has recently been applied to the remediation of contaminated soils:



Hydroxyl radicals are capable of oxidizing a range of contaminants because they react with most organic compounds in solution at near-diffusion controlled rates [1]. Hydroxyl radicals react with organic substrates (R) by addition and hydrogen abstraction reactions:



A number of competing reactions are involved in Fenton's systems including the production of perhydroxyl ($\text{HO}_2\cdot$) radical 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 . These competing reactions in the Fenton's process include:



The use of Fenton's reagent for oxidizing biorefractory organic compounds in aqueous solutions and industrial waste streams has been studied extensively. Bowers et al. [2] used Fenton's reagent to oxidize 2,4-dichlorophenol, 4,6-dinitro-*o*-cresol, and a phenolic wastewater to decrease toxicity prior to biological treatment. Barbeni et al. [3] investigated the mineralization of chlorophenols, which was confirmed by stoichiometric chloride recovery, and Sedlak and Andren [4] documented partial mineralization of chlorophenol and chlorobenzene. Lipczynska et al. [5] determined reaction rate constants for the oxidation of 4-chlorophenol using Fenton's reagent.

In contrast to water-soluble compounds, contaminants in soils are usually sorbed or present as nonaqueous phase liquids (NAPLs), which can have significant effects on Fenton's process chemistry. Fenton-like oxidations in soils have focused on the process chemistry that most effectively destroys and mineralizes biorefractory contaminants. Watts et al. [6] first reported using Fenton-like reactions for soil remediation and showed that pentachlorophenol (PCP) in silica sand was destroyed at a slurry pH of 2–3. Their results also confirmed that when high concentrations of peroxide are used for soil remediation, which is often necessary to oxidize contaminants in a complex matrix such as soils, soluble iron concentrations decline rapidly over the first 30 min of the reaction with subsequent formation of an amorphous iron floc over the following 3 h. Soil–water slurries containing the iron floc were characterized by inefficient treatment stoichiometries of up to 50,000 mole H_2O_2 per mole contaminant oxidized. Tyre et al. [7] used Fenton's reagent to oxidize PCP, trifluralin, hexadecane, and dieldrin in soils and found

that iron oxyhydroxides effectively catalyze Fenton-like reactions. Watts et al. [8] subsequently documented that the most efficient oxidation of soluble PCP in silica sand was catalyzed by naturally-occurring iron oxyhydroxides; however, sorbed PCP was not oxidized with goethite as the only Fenton's catalyst. The results provided by Tyre et al. [7] and Watts et al. [8] suggest that naturally-occurring iron oxyhydroxides serve as an effective Fenton's catalyst. A possible mechanism for mineral-catalyzed Fenton's reactions has been proposed by Kitajima et al. [9]:



where S is the mineral surface and S^+ is an oxidized region on the mineral. These heterogeneous mineral catalysts are effective because of their conservative nature and consistent rates of hydroxyl radical generation when high concentrations of hydrogen peroxide are used.

Iron complexes have also been studied to catalyze the Fenton-like oxidation of pesticides. Sun and Pignatello [10] screened iron complexes for their potential to promote the oxidization of pesticides by Fenton-like reactions. Nitrilotriacetic acid (NTA), tetrahydroxy-1,4-quinone (THQ), and hexaketocyclohexane (HKCH) were most effective. The primary advantage of the iron complexes is the potential for effective generation of hydroxyl radicals at near-neutral pH.

Diesel is commonly used as an engine fuel and refuelling facilities are common throughout the world; therefore, spills and leaking storage facilities result in a need for the remediation of diesel-contaminated soils. Spencer et al. [11] found that the most efficient Fenton's treatment conditions for diesel-contaminated soils included 30 mM hydrogen peroxide and thirty times the field capacity of the soil with four weeks required for the reaction to reach completion. Although such large volumes of dilute peroxide were effective in oxidizing diesel in a surface soil (by a coupled desorption–mineral-catalyzed oxidation mechanism), the system will likely be impractical in the field. For example, > 9.5 l (2.5 gal) would be required to treat 1 kg (2.2 lb) of contaminated soil using the process conditions developed by Spencer et al. [11]. An alternative process condition developed by Spencer et al. [11] is the mineral-catalyzed use of aggressive Fenton-like reactions using low slurry volumes ($0.5\text{--}3.0 \times$ the soil field capacity) and high hydrogen peroxide concentrations (3 to 9 M). Using these process conditions, diesel in a natural surface soil was oxidized more rapidly than it was desorbed, suggesting the potential for the Fenton-like oxidation of sorbed contaminants.

Watts et al. [12] investigated another set of process conditions to promote the catalyzed hydrogen peroxide treatment of hexachlorobenzene-contaminated soils. They used hydrogen peroxide concentrations ranging from 3 to 300 mM catalyzed by iron (II) rather than the natural iron oxyhydroxides used by Spencer et al. [11]. Watts et al. [12] found that oxidation of sorbed hexachlorobenzene was effective using hydrogen peroxide concentrations as low as 30 mM if catalysis is promoted by soluble iron rather than natural iron oxyhydroxides. Because of the high relative concentration of the iron mineral catalysts in a slurry with a low volume ratio of liquid to soil, the hydrogen peroxide decomposition is potentially rapid, i.e., < 8 h. Therefore, the use of soluble iron to catalyze the Fenton-like oxidation of sorbed contaminants may provide more economical and effective process conditions than the criteria developed by Spencer et al.

[11]. The remediation of contaminated soil systems with soluble iron addition and moderate hydrogen peroxide (0.1 to 2.0 M) concentrations with low slurry volume may provide more economical process conditions.

Based on the results of previous Fenton-like soil remediation studies with multiple forms of iron catalysts, the purpose of this research was to compare iron catalysts and optimize the Fenton-like remediation of diesel-contaminated soil based on: (1) the species of the iron catalyst, (2) the hydrogen peroxide concentration, and (3) the slurry volume.

2. Materials and methods

2.1. Materials

Diesel fuel was obtained from Cenex (St. Paul, MN). Diesel, which is a composite of alkanes, isoalkanes, cycloalkanes, and polycyclic aromatic hydrocarbons of carbon length C_{15} to C_{25} [13], is a realistic model contaminant for remediation studies because of its widespread use and chemical variability.

Hydrogen peroxide was provided by Solvay Interlox (Deer Park, TX). Iron (III) sulfate, iron (III) nitrate, and nitrilotriacetic acid were purchased from Sigma. Iron (II) perchlorate and iron (III) perchlorate were obtained from Aldrich and iron (II) sulfate, pentane, and ethyl acetate were purchased from J.T. Baker. Water was purified to greater than $17\text{ M}\Omega$ with a Barnstead NANOpure II deionizing system.

A silty loam soil (Palouse loess) was sampled from a wheat field near Pullman, WA. Particle size distribution was determined by the pipette method [14]. Organic carbon was measured by combustion at 900°C with CO_2 trapped in KOH and back titrated with unreacted KOH [15]. Cation exchange capacity was determined by sodium acetate saturation at pH 8.2 [16]. Amorphous and crystalline iron and manganese concentrations were quantified by citrate–bicarbonate–dithionite extractions [17]. The soil characteristics are listed in Table 1.

Table 1
Characteristics of the Palouse loess soil

Characteristic	Value
Organic carbon (%)	0.33
Sand (%)	18.4
Silt (%)	58.8
Clay (%)	22.8
CEC (cmol kg^{-1})	19.1
Crystalline Fe (mg kg^{-1})	30390
Crystalline Mn (mg kg^{-1})	690
Amorphous Fe (mg kg^{-1})	38.3
Amorphous Mn (mg kg^{-1})	30.4
pH	6.2
Field Capacity (ml g^{-1})	0.318

2.2. Sample preparation

Diesel, dissolved in pentane, was applied to 500 g of soil to obtain a final concentration of 1000 mg kg^{-1} diesel. The pentane was allowed to evaporate and $5 \pm 0.01 \text{ g}$ soil was placed in 40 ml borosilicate vials with Teflon-lined caps. Oxidation studies were conducted using four replicate vials and initial diesel concentrations were verified by the analysis of at least eight replicates.

2.3. Experimental procedures

The gas purge desorption procedure [18] was used on the spiked samples to determine the rate of diesel volatilization. To determine the duration of the Fenton-like reactions, parallel experiments were analyzed hourly for residual hydrogen peroxide. These data were used to evaluate the extent to which desorption controls the Fenton-like oxidation of diesel.

To investigate the most effective form of iron catalysts, six iron species were added to the Palouse loess to promote the Fenton-like oxidation of diesel upon the addition of hydrogen peroxide. In addition, monobasic potassium phosphate was investigated for its potential to stabilize hydrogen peroxide as a basis for enhancing the native mineral-catalyzed oxidation of diesel. Central composite rotatable experimental designs were used, which describe the combined effect of n variables on an $n + 1$ component. The data from central composite designs were used to establish direct and interactive effects of the variables through an n -dimensional response equation. Three-dimensional response surfaces representing the effect of hydrogen peroxide and soluble iron concentrations on diesel oxidation were generated by evaluation of the regression equations.

Iron (III) perchlorate, iron (III) nitrate, iron (III) sulfate, iron (II) perchlorate, iron (II) sulfate, and iron (III)-NTA were used to catalyze slurries containing 5 g of soil and 5 ml of hydrogen peroxide. Iron concentrations ranged from 5 to 25 mM and hydrogen peroxide concentrations were varied from 0.15 to 1.5 M. Iron (III)-NTA was prepared by dissolving NTA in deionized water with concentrated NaOH prior to combining with equimolar iron (III) perchlorate in deionized water followed by pH adjustment to 6.0 with NaOH [4]. The final iron complex concentrations in the slurries ranged from 2.5 mM to 25 mM. Central composite designs for the potassium phosphate addition used 5 ml hydrogen peroxide ranging from 0.15 to 1.5 M in conjunction with monobasic potassium phosphate (KH_2PO_4) concentrations from 5 to 75 mM. Upon addition of reagents, the vials were mixed using a vortex to ensure homogeneity of the iron catalyst and hydrogen peroxide. The reactions were allowed to proceed until the hydrogen peroxide was consumed (2 h). The entire vial contents were then extracted and analyzed for residual total petroleum hydrocarbons (TPH).

Using the most effective catalyst and its optimum concentration, a subsequent central composite design was used to investigate the interactive effect of slurry volume and hydrogen peroxide concentration. The catalyst [iron (III) perchlorate] at a fixed concentration of 25 mM was used with hydrogen peroxide concentrations from 0.15 to 1.5 M and liquid volumes from 1.5 to 5 ml per 5 g soil. The reaction proceeded until the hydrogen peroxide decomposed to undetectable levels. The samples were then extracted and analyzed for residual TPH.

2.4. Analysis

Soil slurries were brought to a normalized volume of 20 ml with deionized water and shake extracted for 12 h with ethyl acetate. The samples were then analyzed using a Hewlett Packard 5890A gas chromatograph with flame ionization detector and 30 m \times 0.32 mm DB-1 capillary column. Chromatographic conditions included an initial oven temperature of 100°C, final temperature of 240°C, program rate of 15°C min⁻¹, injector temperature of 250°C, and detector temperature of 280°C. Peak integrations were summed and compared to a standard curve of diesel prepared in ethyl acetate.

3. Results and discussion

3.1. Contaminant desorption

The results of the gas-purge desorption procedure showing residual diesel as a function of time for the 1000 mg kg⁻¹ diesel-spiked soil are illustrated in Fig. 1. Diesel desorption from the Palouse loess soil over 90 h was negligible, which demonstrates that the diesel was strongly sorbed to the soil. Diesel is composed of hydrocarbons ranging from C₁₅ to C₂₅ [13], which are characterized by high octanol–water partition coefficients. Karickhoff et al. [19] documented that sorption of organic compounds in soils is directly proportional to the octanol–water partition coefficient; therefore, the data of Fig. 1 are expected based on the hydrophobicity of the C₁₅ to C₂₅ hydrocarbons. The effect of sorption on soil remediation processes has been well documented. Chemicals that are sorbed are often considered to have reduced reactivity with most species used to promote remediation, such as hydroxyl radicals, aqueous electrons, or microorganisms.

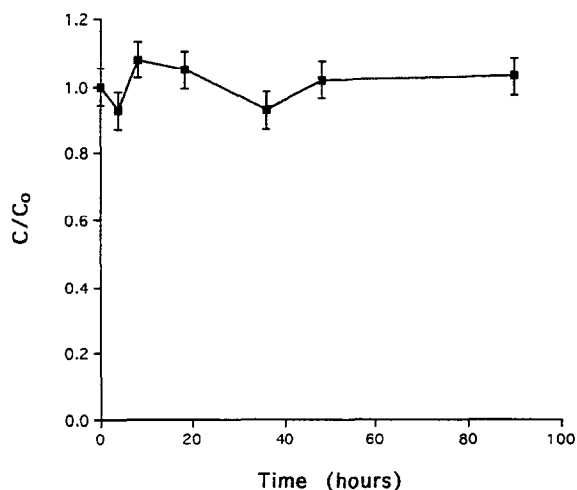


Fig. 1. Desorption of 1000 mg kg⁻¹ diesel from the Palouse loess soil.

Sheldon and Kochi [20] stated that for reactive species that are generated in the aqueous phase of two-phase systems (e.g., a water–NAPL slurry or water–solids with a sorbed substrate), the NAPL or sorbed species is not usually available to react with the species present in the aqueous phase. The principles proposed by Sheldon and Kochi [20] have been confirmed by Sedlak and Andren [21] for chemical processes and Weber et al. [22] and Ogram et al. [23] for enzymatic processes. However, if Fenton-like oxidations can proceed more rapidly than desorption, at least partial oxidation may be occurring in the sorbed phase; furthermore, time requirements for soil remediation can be reduced dramatically.

The rate of Fenton-like reactions in soils is proportional to the concentration ratios of peroxide to catalyst and inversely proportional to the volume ratio of peroxide to catalyst [11], i.e., soil systems containing a low soluble iron catalyst concentration and a large volume of hydrogen peroxide solution will be characterized by a slow rate of reaction. Using a 1:1 mass ratio of soil-to-hydrogen peroxide volume and the lowest soluble iron concentration (5 mM), the peroxide decomposed rapidly and reached undetectable concentrations within 1 h. Because desorption was negligible, if diesel oxidation proceeded within these 1 h reactions, then Fenton-like processes will have overcome the controlling influence of sorption.

3.2. Comparison of iron species in Fenton-like soil remediation

Regression equations derived from the data of central composite experiments that evaluated the six iron species are listed in Table 2. The regression data were then plotted as three-dimensional response surfaces (Figs. 2–6), which show the effects of H_2O_2 and iron on the percentage removal of diesel for iron amendments ranging from 5 to 25 mM and hydrogen peroxide concentrations from 0.15 to 1.5 M (with the exception of KH_2PO_4 addition which covered a range from 5 to 75 mM). The trends for each response surface were similar: the per cent loss of diesel increased as a function of catalyst concentration and hydrogen peroxide concentration. The results also show that more aggressive Fenton-like reactions were necessary to oxidize diesel over the 1 h time period.

The data of Figs. 2–6 show that Fenton-like reactions catalyzed by iron (III) species were more effective than reactions catalyzed by iron (II) species. Nearly 80% oxidation of the diesel was found using 25 mM iron (III) sulfate and 1.5 M hydrogen peroxide as shown in Fig. 4, while the use of iron (II) sulfate additions promoted less than 70% diesel oxidation under the same conditions. Results of central composite analyses using iron (III) and iron (II) perchlorate as Fenton's catalysts showed the same trend with > 99% diesel oxidation using iron (III) and 90% diesel oxidation under optimum conditions using iron (II) perchlorate. In the standard Fenton's procedure, dilute hydrogen peroxide is slowly added to a deoxygenated iron (II)-substrate solution. Such a system provides near-stoichiometric generation of hydroxyl radicals and minimizes the autooxidation of iron (II) to iron (III). However, modified Fenton-like systems are characterized by aggressive conditions promoted by the use of higher hydrogen peroxide concentrations to oxidize sorbed contaminants [12]. Dilute hydrogen peroxide is normally used in Fenton's systems to minimize the oxidation of iron (II) to iron (III). With

Table 2

Regression equations for the Fenton-like oxidation of 1000 mg kg⁻¹ diesel in the Palouse loess soil using six iron catalysts and KH₂PO₄ as a stabilizer

Compound	Regression equation	R ²	Equation number
Iron (III) perchlorate	Diesel degradation (%) = 33.2 + 18.6(C _{cat}) + 16.3(C _{H₂O₂) + 8.2(C_{cat}) (C_{H₂O₂) + 3.3(C_{cat})² + 1.5(C_{H₂O₂)²}}}	0.91	(7)
Iron (III) nitrate	Diesel degradation (%) = 32.5 + 20.4(C _{cat}) + 16.5(C _{H₂O₂) + 4.6(C_{cat}) (C_{H₂O₂) + 4.6(C_{cat})² + 1.7(C_{H₂O₂)²}}}	0.88	(8)
Iron (III) sulfate	Diesel degradation (%) = 43.0 + 13.0(C _{cat}) + 14.8(C _{H₂O₂) + 1.6(C_{cat}) (C_{H₂O₂) - 1.9(C_{cat})² - 0.7(C_{H₂O₂)²}}}	0.85	(9)
Iron (II) perchlorate	Diesel degradation (%) = 42.9 + 6.4(C _{cat}) + 10.6(C _{H₂O₂) + 7.9(C_{cat}) (C_{H₂O₂) - 0.02(C_{cat})² + 2.2(C_{H₂O₂)²}}}	0.88	(10)
Iron (II) sulfate	Diesel degradation (%) = 36.5 + 10.4(C _{H₂O₂) + 14.5(C_{cat}) + 4.5(C_{H₂O₂) (C_{cat}) - 2.5(C_{H₂O₂)² - 3.1(C_{cat})²}}}	0.90	(11)
Iron (III)-NTA chelate	Diesel degradation (%) = 46.5 + 10.4(C _{cat}) + 9.4(C _{H₂O₂) + 5.3(C_{cat}) (C_{H₂O₂) + 1.9(C_{cat})² - 3.9(C_{H₂O₂)²}}}	0.83	(12)
Monobasic potassium phosphate	Diesel degradation (%) = 38.9 + 5.9(C _{Stab}) + 7.5(C _{H₂O₂) + 0.5(C_{Stab}) (C_{H₂O₂) - 3.2(C_{Stab})² - 4.7(C_{H₂O₂)²}}}	0.86	(13)

C_{H₂O₂} = Hydrogen peroxide concentration (M)

C_{cat} = Catalyst concentration (mM)

C_{Stab} = Stabilizer concentration (mM)

the high hydrogen peroxide concentrations necessary to desorb contaminants, iron (II) is rapidly oxidized to iron (III), resulting in an immediate demand on the hydrogen peroxide residual (equation 4). Iron (III) is a more effective catalyst because it does not

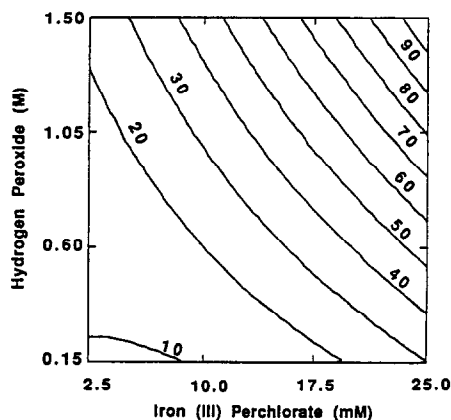


Fig. 2. Response surface for diesel degradation as a function of hydrogen peroxide and iron (III) perchlorate concentration. Isoconcentration lines represent percent diesel degraded.

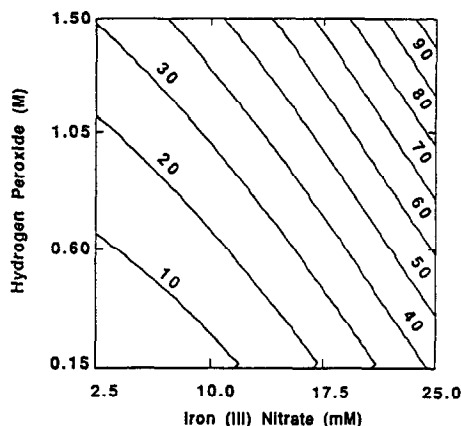


Fig. 3. Response surface for diesel degradation as a function of hydrogen peroxide and iron (III) nitrate concentration. Isoconcentration lines represent percent diesel degraded.

place an immediate demand on the hydrogen peroxide; i.e., equation 4 becomes negligible. Murphy et al. [24] described similar results in oxidizing formaldehyde solutions with Fenton-like reactions. Iron (II) oxidation to iron (III) was suggested as a cause of the loss of stoichiometric efficiency in formaldehyde oxidation and two iron (II) oxidation pathways were proposed. The results shown in Figs. 2–6 are in agreement with the stoichiometry of Fenton's chemistry (Eqs. (1)–(6)) and the results reported by Murphy et al. [24].

The effectiveness of different iron salts for catalyzing Fenton's reactions in aqueous solution has been well documented (Table 3). Based on these results, the most effective iron salt catalysts are



The data of Figs. 2–6 are in agreement with the relative quenching rates listed in Eq.

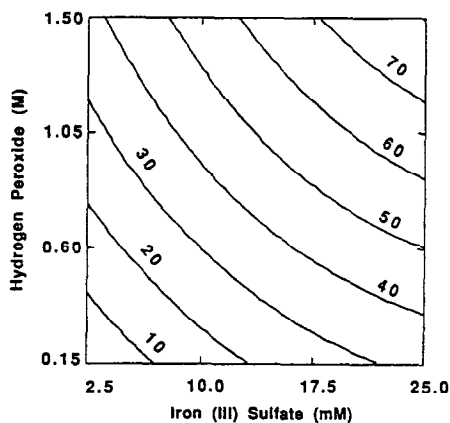


Fig. 4. Response surface for diesel degradation as a function of hydrogen peroxide and iron (III) sulfate concentration. Isoconcentration lines represent percent diesel degraded.

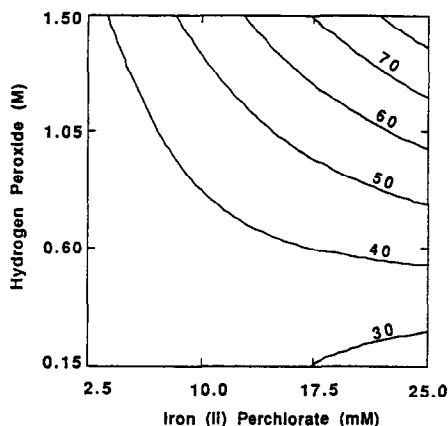


Fig. 5. Response surface for diesel degradation as a function of hydrogen peroxide and iron (II) perchlorate concentration. Isoconcentration lines represent percent diesel degraded.

(14). Perchlorate and nitrate salts quench hydroxyl radicals at the lowest rates and, therefore, provide the highest degree of oxidation in TPH-contaminated soils. Iron sulfates provided intermediate diesel oxidation, while potassium phosphate was least efficient in promoting the oxidation of diesel in the Palouse loess. Although phosphate was added as KH_2PO_4 , at pH 6, both H_2PO_4^- and HPO_4^{2-} would be present in the system. Therefore, the quenching of hydroxyl radicals by phosphate species is a function of relative concentrations of H_2PO_4^- (with $k_{\text{OH}\cdot} < 1.2 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$) and HPO_4^{2-} (with $k_{\text{OH}\cdot} = 7.9 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$).

The higher hydrogen peroxide concentrations required to oxidize diesel-contaminated soil are comparable to the results of previous Fenton-like soil remediation studies. Watts et al. [12] found that $\geq 0.1 \text{ M}$ hydrogen peroxide with soluble iron oxidized sorbed

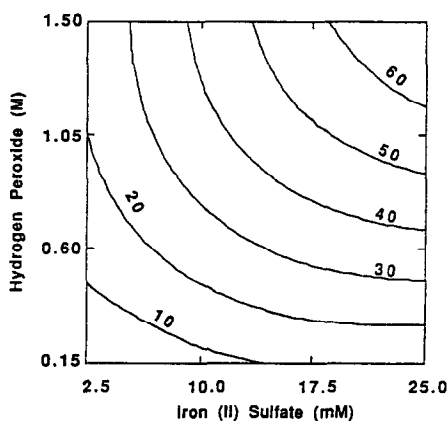


Fig. 6. Response surface for diesel degradation as a function of hydrogen peroxide and iron (II) sulfate concentration. Isoconcentration lines represent percent diesel degraded.

Table 3
Oxidation rate constants of selected anions with hydroxyl radicals [25]

Anion	$k_{OH} \cdot (M^{-1} s^{-1})$	pH
NO_3^-	5×10^5	9
SO_4^{2-}	1.6×10^6	7
$H_2PO_4^{1-}$	$< 1.2 \times 10^7$	~ 7
HPO_4^{2-}	7.9×10^5	9
PO_4^{3-}	$< 10^7$	–

hexachlorobenzene, while oxidation with lower concentrations of hydrogen peroxide was controlled by the desorption rate. Spencer et al. [11] determined that 3 to 9 M hydrogen peroxide was required to oxidize sorbed diesel using iron oxyhydroxides as the only source of iron catalysts. They also documented that, by promoting a combined desorption–oxidation mechanism using lower concentrations of peroxide, four weeks were required for diesel to desorb coupled with oxidation by mineral-catalyzed Fenton-like reactions. Because diesel did not desorb during the 1 h time period of the Fenton-like reactions of this study (Fig. 1), moderate concentrations of hydrogen peroxide (~ 1.5 M) and soluble iron were capable of destroying diesel at the soil surface. Although not as efficient as the desorption–oxidation mechanism described by Spencer et al. [11], the use of moderate concentrations of hydrogen peroxide (~ 1.5 M) catalyzed by soluble iron appears to be the most effective process condition for the oxidation of sorbed hydrocarbons.

Pignatello and Baehr [26], in studying the Fenton-like oxidation of herbicides catalyzed by iron complexes, found that some of the complexes were more effective than iron (III) perchlorate, particularly at neutral pH. To determine the potential of an iron chelate to oxidize diesel under near-neutral pH conditions, an iron (III)–NTA complex was investigated under similar conditions to the systems catalyzed by iron salts. Eq. (12) listed in Table 2 describes the experimental data, and the response surface showing the effects of hydrogen peroxide and iron (III)–NTA concentrations is shown in Fig. 7. The maximum diesel loss under these conditions (approximately 80%) was comparable to that attained using the iron (II) perchlorate or iron (III) sulfate. However, the advantage of the iron (III)–NTA complex as a catalyst for Fenton-like reactions is the potential for conducting the reaction at near-neutral pH. The soil pH in the iron (III)–NTA system was 5.7, and the pH of the iron (III) perchlorate systems was 3.6 with an iron (III) amendment of 20 mM, which provided an equal degree (80%) of diesel oxidation. Therefore, the iron complex was equally effective as iron (II) perchlorate and has the advantage of promoting Fenton-like oxidations at near-neutral pH.

Results of a central composite analysis for the addition of monobasic potassium phosphate (5 to 75 mM) and hydrogen peroxide (0.15 to 1.5 M) are shown in Fig. 8 based on Eq. (13) of Table 2. These data show a consistent increase in diesel oxidation with KH_2PO_4 up to 40 mM and hydrogen peroxide concentrations up to 0.8 M. Higher concentrations of both reagents were ineffective in increasing diesel oxidation above 40%. This modification of the soil treatment process also required 8 h for 90% decomposition of the hydrogen peroxide. The ability of phosphate to stabilize hydrogen

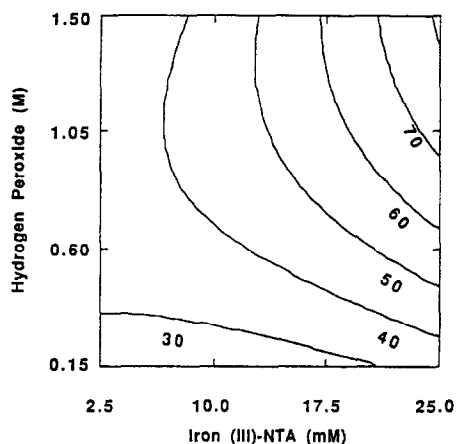


Fig. 7. Response surface for diesel degradation as a function of hydrogen peroxide and Iron (III)-NTA chelate concentration. Isoconcentration lines represent percent diesel degraded.

peroxide is well documented [27]. Most forms of phosphate (H_2PO_4^- , HPO_4^{2-} , triphosphate) complex multivalent cations, such as iron and other transition metals, lowering their activity as Fenton's catalysts. As a result, phosphates tend to decrease rates of soluble Fenton's reactions; however, phosphates appear to increase the rate of mineral-catalyzed Fenton-like reactions [28]. The rate of Fenton-like reactions is proportional to the system reducing potential [20] and phosphate exchanged at the mineral surface may lower the surface oxidation-reduction potential to increase rates of mineral-catalyzed Fenton-like reactions. Addition of phosphate as a stabilizer has potential for enhancing the mineral-catalyzed Fenton-like oxidation of contaminated soils using longer reaction times, but does not appear to provide process conditions that

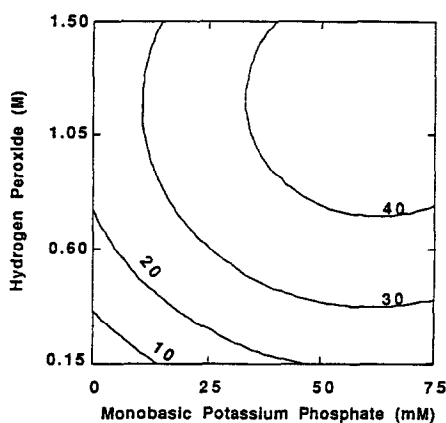


Fig. 8. Response surface for diesel degradation as a function of hydrogen peroxide and monobasic potassium phosphate concentration. Isoconcentration lines represent percent diesel degraded.

promote the oxidation of sorbed contaminants [12]. Therefore, the lower diesel oxidation found with phosphate addition may be related to minimal presence of the diesel components in the soil solution and negligible desorption over the 8 h time period of the reactions.

3.3. Effect of slurry volume

The regression equation derived from the experimental data of the central composite experiment that evaluated slurry volumes from 1.5 to 5 ml per 5 g soil and hydrogen peroxide concentrations from 0.15 to 1.5 M with 25 mM iron (III) perchlorate as the catalyst is:

$$\text{Diesel Degradation}(\%) = 51.7 + 7.9(V) + 10.6(C_{\text{H}_2\text{O}_2}) + 1.74(V)(C_{\text{H}_2\text{O}_2}) - 5.8(V) - 2.0(C_{\text{H}_2\text{O}_2})^2, \quad (15)$$

where

$C_{\text{H}_2\text{O}_2}$ = Hydrogen Peroxide Concentration (M),

V = Volume $[\text{ml} (5\text{g soil})^{-1}]$.

The corresponding response surface for Eq. (15) is shown in Fig. 9. The ability of Fenton-like reactions to remediate diesel-contaminated soil increased as a function of liquid volumes to a maximum at $3.5 \text{ ml} (5\text{g soil})^{-1}$. An advantage of using low volumes of hydrogen peroxide with soluble iron amendments in soil systems is a reaction in which hydroxyl radicals are generated in close proximity to the sorbed contaminants. Using volumes $< 3.5 \text{ ml}$, diesel oxidation was limited by minimal contact of the soil with the liquid. At volumes $> 3.5 \text{ ml}$, the excess hydrogen peroxide volume was not in contact with the soil, lowering the effectiveness of the reaction. The data of Fig. 9

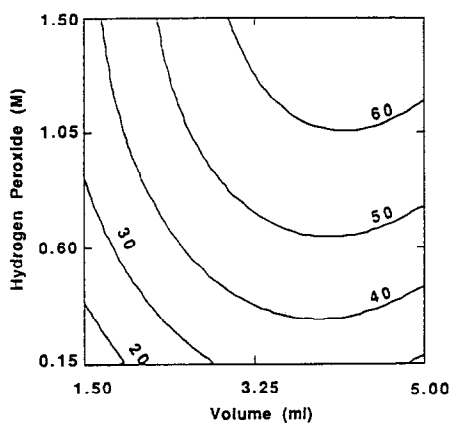


Fig. 9. Response surface for diesel degradation as a function of hydrogen peroxide concentration and volume. Isoconcentration lines represent percent diesel degraded.

predict lower diesel oxidation than the investigation with iron (III) perchlorate under similar conditions (Fig. 2). This anomaly may be a result of different effects of catalyst concentration and liquid volume on diesel oxidation, i.e., the catalyst may affect the oxidation in a manner unrelated to the increased volume.

Environmental effects and logistics may be concerns for some forms of the iron catalyst. Iron (II) and iron (III) perchlorate, the most effective species, are currently commercially unavailable in large quantities (> 1 kg), which will likely limit its use for full-scale site remediation. Iron (III) nitrate was also effective as a Fenton's catalyst. Nitrate, a primary constituent of fertilizer, is applied at rates of up to $190 \text{ kg hectare}^{-1}$ to promote crop growth and 2–10% of the nitrate leaches into the subsoil [29]. If nitrate migrates to drinking water, it may cause methemaglobonemia; however, primary drinking water standards allow a maximum contaminant level (MCL) of 10 mg l^{-1} $\text{NO}_3\text{-N}$. Although plant uptake is a removal mechanism in surface soils, threats of groundwater contamination will likely limit the use of iron (III) nitrate as a Fenton's catalyst. Iron (III) sulfate, although a less-effective Fenton's catalyst, is commonly used in fertilizer formulations and should pose no threat to public health and the environment as a catalyst for the Fenton-like remediation of contaminated soils.

The basis for an economic analysis of soil remediation systems includes capital, excavation, hauling, chemical costs, and operation and maintenance. The primary chemical cost, hydrogen peroxide, is $\$0.31 \text{ kg}^{-1}$. Based on this price and the data of Fig. 4, the hydrogen peroxide cost to remediate 1000 mg kg^{-1} diesel to below the most common regulatory standard of 100 mg kg^{-1} TPH is $\$52 (907 \text{ kg})^{-1}$ (ton). The primary advantages of the use of catalyzed hydrogen peroxide are the ease of operation and the cost of time and labor. A single application of catalyzed hydrogen peroxide oxidized diesel in the Palouse loess in 1–2 h. If such reaction rates can be achieved in the field, the process would provide lower labor and monitoring costs relative to remediation processes that are controlled by desorption.

4. Summary and conclusions

A number of iron catalysts were investigated in the remediation of a Palouse loess soil contaminated with 1000 mg kg^{-1} diesel using catalyzed hydrogen peroxide. The catalysts included iron (III) perchlorate, iron (III) nitrate, iron (III) sulfate, iron (II) perchlorate, iron (II) sulfate, and an iron (III)–NTA complex. Of the six forms of inorganic catalysts, iron (III) perchlorate and iron (III) nitrate were most effective in oxidizing diesel in the Palouse loess soil. Central composite rotatable designs were used to investigate the effects of hydrogen peroxide and iron concentrations on the Fenton-like oxidation of diesel. The reactions were complete within 1 h owing to the low volume ratio of peroxide to catalyst. Because desorption was negligible over 90 h, diesel oxidation occurred, at least in part, in the sorbed state. Iron (III) perchlorate was the most effective catalyst, but its use for full-scale soil remediation will be limited because it is commercially unavailable. Although not as effective as iron (III) perchlorate, iron (III)–NTA catalyzed up to 80% TPH oxidation at near-neutral soil pH. Amendments of potassium phosphate (KH_2PO_4) slowed the rate of Fenton's reaction in soil slurries,

probably by complexing soluble iron and other Fenton's catalysts; however, diesel oxidation was not significantly enhanced. These results are in agreement with previous studies which have shown that mineral-catalyzed Fenton-like reactions are most effective in oxidizing desorbed or soluble contaminants in the soil solution. Based on the results of this research, the chemical cost for the Fenton-like treatment of diesel-contaminated Palouse loess soil is \$52 (907 kg)⁻¹ (ton). The cost may vary in other soils depending on soil characteristics, contaminant properties, and the contaminant concentration.

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