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A foundation for the risk-based treatment of gasoline-contaminated soils using modified Fenton's reactions

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Abstract

The relative oxidation of representative aromatic and aliphatic hydrocarbons found in gasoline was evaluated to provide the foundation for risk-based treatment of petroleum-contaminated soils and groundwater using modified Fenton's reagent (catalyzed hydrogen peroxide). Aromatic components of gasoline are considered more hazardous than the aliphatic fractions due to their higher mobility in the subsurface and their higher acute and chronic toxicities. Benzene, toluene, and mixed xylenes (BTX) were selected as aromatic compounds representative of unleaded gasoline, while nonane, decane, and dodecane (NDD) were used as model aliphatic compounds. The effects of hydrogen peroxide (H_2O_2) concentration, iron catalyst concentration, and pH on the degree of treatment of the model compounds were investigated using central composite rotatable experimental designs. Oxidation of the aromatic compounds required less iron and less H_2O_2 than did oxidation of the aliphatic compounds, while proceeding more effectively at near-neutral pH. Greater than 95% of the BTX was treated at near-neutral pH using 2.5% H_2O_2 and 12.5 mM iron (III), while only 37% nonane, 7% decane, and 1% dodecane oxidation was achieved under the same conditions. The results show that the more toxic and mobile aromatic fraction was more effectively oxidized using less H_2O_2 and more economical conditions, including near-neutral pH, compared to the aliphatic fraction. A process design based on treating only the aromatic fraction of petroleum may provide significantly lower costs when using

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modified Fenton's reagent for the treatment of contaminated soils and groundwater. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

The contamination of soils and groundwater by toxic and biorefractory organic compounds remains a widespread problem, even after 2 decades of remediation efforts. One of the most common sources of soil and groundwater contamination has been leaking underground storage tanks (USTs), which often result in the release of gasoline or other chemicals to the soil surrounding the tank. Hundreds of thousands of USTs are located at gasoline stations and distribution installations throughout the US [1]. Current permits for the installation of USTs mandate the use of multiple-wall tanks, corrosion-resistant materials, and leak detection systems; however, more than 250,000 tanks may eventually leak at gasoline stations alone, posing a significant threat to public health and the environment [2].

Although natural attenuation and bioremediation are considered the most economical approaches for the treatment of petroleum-contaminated soils, advanced oxidation processes may be necessary when time constraints or other logistics require consideration. The catalyzed decomposition of hydrogen peroxide (H_2O_2) by iron (II) to form hydroxyl radicals ($\text{OH}\cdot$), commonly known as Fenton's reagent [3], is an advanced oxidation process that has been applied to the treatment of surface soils, subsurface soils, and groundwater.



Hydroxyl radicals are strong oxidants that react with most organic contaminants at near diffusion-controlled rates of 10^9 – $10^{10} \text{ M}^{-1} \text{ s}^{-1}$ [4,5]. The most common mechanism for oxidation by hydroxyl radicals is electrophilic addition to alkenes or aromatic rings, while hydrogen abstraction often occurs with saturated compounds [6].

Modified Fenton's reactions have been used in a number of environmental applications, including the pretreatment of industrial wastewaters [7,8], the treatment of water containing dilute concentrations of xenobiotics [9,10], and the remediation of soils and groundwater [11,12]. Although the standard Fenton's process uses dilute H_2O_2 with an excess of iron (II) catalyst, several modifications have been developed for specific environmental applications, including catalysis by iron chelates to promote reactions at near-neutral pH [13,14], catalysis by iron oxyhydroxides in soils [15–18], and high H_2O_2 concentrations to promote contaminant desorption from soils [19,20].

Fenton-like reactions have been investigated specifically for the treatment of petroleum fractions and related compounds in soils and groundwater. Watts [21] demonstrated that a pH of 2–3 was most effective for the treatment of a diesel-contaminated site due to the need for reducing conditions and accompanying maintenance of iron solubility. Yeh and Novak [22] used a modified Fenton's reaction to pretreat methyl *tert*-butyl ether (MTBE) in groundwater prior to biological treatment of the degradation products. Watts

and Dilly [23] determined that iron (III) is a more effective catalyst than iron (II) for the treatment of diesel-contaminated soils by Fenton-like reactions because it does not place an immediate demand on the H_2O_2 in the system. Spencer et al. [24] evaluated different Fenton's process modifications, and found that the most economical conditions consisted of low concentrations of H_2O_2 and large slurry volumes, with reactions occurring over weeks. The oxidation of specific components of petroleum by Fenton-like reactions has also recently been investigated by Kakarla and Watts [25] and Watts and Stanton [26]. The results of both studies showed that high concentrations of H_2O_2 were necessary to overcome sorption in the treatment of hexadecane.

Common contaminant measurements used in the cleanup of petroleum-contaminated soils and groundwater have been total petroleum hydrocarbon (TPH) analyses, which are often mandated by regulatory agencies. A fundamental problem with TPH data is that they do not correlate with the toxicity or mobility of specific fractions of petroleum; rather, all constituents of petroleum are given equal consideration. However, the hundreds of hydrocarbons found in petroleum exhibit widely differing toxicity and mobility characteristics and, consequently, differing human and ecological health risks. Compounds that are more mobile are characterized by higher water solubilities and lower octanol–water coefficients, and are thus more likely to migrate through groundwater and less likely to sorb to soils at the source of contamination and as they migrate away from the source. Examination of gasoline components in relation to their relative health risks reveals two dominant groups of hydrocarbons: monocyclic aromatic hydrocarbons (e.g. benzene, toluene, and xylenes — BTX) and C_5 – C_{12} aliphatic hydrocarbons [1]. Aromatic compounds (BTX and other alkylbenzenes) account for 10–59% of gasoline (mass/mass), while aliphatic hydrocarbons comprise 41–62% [27]. Monocyclic aromatic hydrocarbons are generally more toxic than aliphatic compounds of the same carbon number and are more mobile in water [28,29]; their water solubilities are three to five orders of magnitude higher (Table 1). Monocyclic aromatic hydrocarbons are also more mobile in soil–water systems than aliphatic hydrocarbons, with octanol–water partition coefficients two to four orders of magnitude lower than aliphatic hydrocarbons

Table 1

Second-order hydroxyl radical rate constants ($k_{\text{OH}\cdot}$), mean water solubilities, and octanol–water partition coefficients (K_{ow}) for BTX and NDD

Compound	$k_{\text{OH}\cdot}$ ($\text{M}^{-1} \text{s}^{-1}$)	Water solubility (mg/l) ^a	$\log K_{\text{ow}}^{\text{a}}$
Benzene	$7.8 \times 10^{9\text{b}}$	1760	2.12
Toluene	$3.0 \times 10^{9\text{b}}$	532	2.73
Xylenes	$(6.7\text{--}7.5) \times 10^{9\text{b}}$	163–185	2.95–3.26
Nonane	$3.6 \times 10^{9\text{c}}$	0.122	4.67
Decane	$4.0 \times 10^{9\text{c}}$	0.021	6.69
Dodecane	$4.7 \times 10^{9\text{c}}$	0.005	7.24

^aFrom Watts [1].

^bFrom Buxton et al. [50].

^cCalculated using regression equation ($\log k_{\text{OH}\cdot}(\text{water}) = -1.45 + 1.12 \log k_{\text{OH}\cdot}(\text{air})$) provided by Atkinson [51] and hydroxyl radical rate constants in air from Buxton et al. [50].

with corresponding carbon numbers (Table 1). The lower the octanol–water coefficient of a compound, the less likely it is to sorb to the organic carbon content of soils. Therefore, the monocyclic aromatic hydrocarbons not only tend to be more chronically toxic, but are also more likely to migrate through the subsurface to water supply wells.

Because non-specific TPH analyses do not provide a measure of the risk from petroleum contamination, the use of risk-based corrective actions (RBCAs) has recently been proposed as an approach for determining the remediation end point for contaminated sites [30]. RBCAs for different petroleum fractions are based on the specific mobilities and toxicities of the individual compounds that are characteristic of each fraction. Similar initiatives have also been proposed by states; for example, the Massachusetts Department of Environmental Protection has initiated a risk-based TPH procedure that emphasizes the presence of the more toxic and mobile aromatic compounds over aliphatic species [31]. The fractions of gasoline are quantified by gas chromatography with flame ionization detection (GC/FID) in series with photoionization detection (GC/PID); the masses of these fractions are then normalized by relative risk and summed to obtain an adjusted TPH value. This method designates the risk of aromatic compounds as 2 to 200 times that of aliphatic compounds of equal carbon numbers based on established reference doses (RfDs) and slope factors (SFs), providing a more accurate quantification of the risk of petroleum-contaminated sites relative to non-specific TPH analyses. An RfD is a regulatory parameter used for quantifying the toxicities of non-carcinogens, and is based on no observed adverse effect levels; an SF is a regulatory parameter used to describe the carcinogenicities of cancer-causing compounds [1].

The low correlation between non-specific TPH and risk to public health and the environment suggests that RBCAs for site assessments and cleanup will become more commonplace. The adoption of risk-based TPH analyses may have a significant impact on the process design of technologies used to treat petroleum-contaminated sites, favoring process dynamics that target the most toxic and mobile fractions of petroleum. Results from previous studies on the Fenton-like treatment of contaminated soils [23,24] suggest that the aromatic compounds in gasoline may be more readily oxidized than the aliphatic compounds, indicating that modified Fenton's reagent may be a technology that targets the higher risk aromatic fraction of gasoline. Therefore, the purpose of this research was to examine the comparative effectiveness of the Fenton-like oxidation of selected aromatic and aliphatic compounds typically found in gasoline as a basis for developing a more economical process design using risk-based methodology.

2. Materials and methods

2.1. Materials

Benzene, toluene, and mixed (*-o*, *-m*, and *-p*) xylenes (BTX) were used as representative aromatic compounds, and *n*-nonane, *n*-decane, and *n*-dodecane (NDD) were selected as common aliphatic components of gasoline. Benzene, toluene, xylenes, and *n*-decane (> 99% purity) were purchased from Fisher Scientific, while *n*-nonane and

n-dodecane (> 99% purity) were obtained from Sigma and Aldrich, respectively. Physical constants of the model contaminants are listed in Table 1. Unleaded gasoline was obtained from Cenex (St. Paul, MN).

Although the most common form of iron used in laboratory studies of Fenton's reagent is $\text{Fe}(\text{ClO}_4)_2$, $\text{Fe}_2(\text{SO}_4)_3$ (purchased from Sigma) was used in this study because it is commercially available in large quantities and does not pose a threat to public health, as perchlorate does [29]. In addition, iron (III) was chosen rather than iron (II) because, with the high concentrations of H_2O_2 used in modified Fenton's reactions, iron (II) is rapidly oxidized to iron (III) with a resulting initial demand on the H_2O_2 in the system [23]. Stock hydrogen peroxide (50%) was provided gratis by Solvay Interlox. The deionized water used in the controls and stock solutions was purified to greater than 18 $\text{M}\Omega \cdot \text{cm}$ with a Barnstead NANOpure II deionizing system. The soil used was a sandy loam collected from an alluvial fan above the Carson Valley, NV. It was characterized for particle size distribution by the pipette method [32]. Organic carbon was determined by combustion at 900°C with evolved CO_2 trapped in KOH and measured by back-titration of unreacted KOH [33]. Cation exchange capacity was established by saturation with sodium acetate at pH 8.2 [34]. Crystalline and amorphous iron and manganese oxyhydroxides were determined by citrate–bicarbonate–dithionite extraction [35]. The soil characteristics are listed in Table 2.

2.2. Sample preparation

A mass of 20 ± 0.01 g of soil was weighed into 40-ml borosilicate vials fitted with PTFE-lined caps. The soil was spiked with either BTX or NDD; equimolar concentrations of each of the three model contaminants in pentane were added to a final soil concentration of 15 mmol/kg total BTX or total NDD. These concentrations of the model contaminants exceeded their water solubilities and insured that some of each compound was sorbed or present as a non-aqueous phase liquid (NAPL). The vials were hand-shaken to uniformly coat the soil and the pentane was allowed to evaporate prior to reagent addition. All reactions were conducted in triplicate and control reactions were performed in parallel using deionized water in place of H_2O_2 . Control reactions

Table 2
Characteristics of the Carson Valley soil

Organic carbon content (%)	0.5
Sand (%)	86.5
Silt (%)	11
Clay (%)	2.5
Crystalline Fe oxides (mg/kg)	4400
Crystalline Mn oxides (mg/kg)	100
Amorphous Fe oxides (mg/kg)	4400
Amorphous Mn oxides (mg/kg)	100
Cation exchange capacity (cmol/kg)	4.28
pH	6.4

contained the expected levels of all probe compounds, indicating that no significant loss of the more volatile benzene occurred during soil spiking and evaporation.

2.3. Measurement of desorption

The maximum rate of contaminant desorption was measured using the gas purge (GP) procedure, which was described by Karickhoff and Morris [36] for quantifying desorption rates of hydrophobic contaminants in soil–water systems. The GP procedure, in which a slurry is purged with an inert gas, is based on the rapid loss of desorbed organic compounds from the aqueous phase by volatilization. Volatile organic analysis vials (40 ml) containing 20 ml deionized water and 10 g of soil spiked with BTX or NDD were purged with nitrogen gas at a flow rate of 80 ml/min. Originally, hydrocarbon concentrations were measured on the soil, in the aqueous phase, and in the off gas (trapped in Supelco ORBO-32 adsorbent tubes). No hydrocarbon was detected in the aqueous phase, and the residual on the soil correlated with the mass collected on the gas adsorbent tubes. Therefore, subsequent GP analyses relied on quantifying the residual sorbed on the Carson Valley soil. Residual sorbed contaminants were quantified over 48 h and compared to the degree of treatment by Fenton-like reactions.

2.4. Experimental design and procedures

Central composite rotatable experimental designs were used to investigate the effects and interactions between three treatment parameters. Central composite rotatable designs are multivariable, multilevel experimental procedures that analyze the interactions between variables and produce response equations [37,38]. If only two variables are evaluated and represented on the x and y axes of a coordinate system, the results may be described by a response surface, a planar description of experimental data including the maxima, minima, and interactions, which may be visualized by folds and shifts in a surface plane. Three variables (H_2O_2 concentration, iron (III) sulfate concentration, and pH) were investigated in the Fenton-like oxidation of the BTX- and NDD-spiked soils using two-level central composite design experiments. Hydrogen peroxide concentration and iron (III) concentration were varied for each chemical class at both acidic and near-neutral pH regimes. Concentrations of H_2O_2 were varied from 0.5% to 3% for the BTX and from 1 to 10% for the NDD. The Fenton's catalyst, iron (III), was added in concentrations ranging from 0 to 25 mM for both the aromatic and aliphatic compounds. The liquid-to-soil ratio (L:S) was maintained at 1.0 ml/g. Two pH conditions were also evaluated: an acidic pH regime (pH 3) and a near-neutral pH regime (~ 6.5), which was governed by the buffering capacity of the soil and the concentration of weakly acidic iron (III) sulfate. Adjustment to pH 3 was accomplished by the addition of 4.5 M sulfuric acid. Following the addition of reagents, the vials were tightly capped and mixed to ensure homogenous contact of both hydrogen peroxide and the catalyst. The reactions were allowed to proceed until the H_2O_2 was consumed (~ 2 h). The entire vial contents were then shake-extracted on a wrist-action shaker for 24 h; n -decane was used to extract the BTX samples and ethyl acetate was used to extract the NDD samples. The vials were then centrifuged and analyzed for each set of contaminants by GC.

2.5. Treatment of unleaded gasoline

Using the optimum Fenton's conditions established for the degradation of BTX, the Carson Valley soil was spiked with 1000 mg/kg unleaded gasoline and treated to evaluate the effectiveness of the risk-based procedure. The soil was spiked by adding 1.0 g of the gasoline to 1.0 kg of the soil and agitating it in a closed 2-l borosilicate glass container until the gasoline was equally distributed. The L:S used was 0.3 ml/g, which was found to be optimal for the Fenton-like treatment of the Carson Valley soil [23,39]. The soil (10 g) was then treated in 40 ml batch reactors by adding 3 ml of reagent with varying concentrations of H_2O_2 , 12.5 mM iron (III) sulfate, and a near-neutral pH. After the H_2O_2 decomposed to an undetectable concentration, the reactor contents were shake-extracted with pentane and the extracts were analyzed by GC/FID and GC/PID.

2.6. Analysis

Both BTX and NDD were analyzed on a Hewlett-Packard 5890A gas chromatograph fitted with a flame ionization detector and a 30 m \times 0.32 mm Supelco 2-4044 fused silica capillary column with a film thickness of 0.25 mm. Chromatographic conditions included initial oven temperature of 40°C, program rate of 8°C/min, and final oven temperature of 150°C. The injector temperature was 160°C and the detector temperature was 200°C. The gasoline residual extracted from the Carson Valley soil was analyzed by both GC/FID and GC/PID using the same column and temperature conditions as for BTX and NDD.

3. Results and discussion

3.1. Desorption of BTX and NDD

The results of the GP desorption analysis for Carson Valley soil samples spiked with 15 mmol/kg of each of BTX and NDD are shown in Fig. 1. Approximately 20% of the NDD desorbed over 48 h, while BTX desorption was nearly complete in 32 h. During the 2 h reaction time used for oxidative treatments, < 1% of NDD desorbed, while 38%,

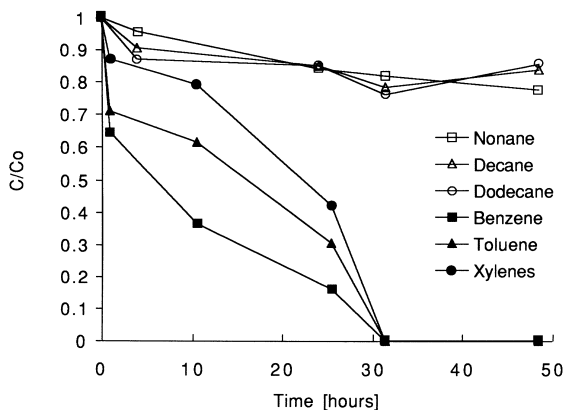


Fig. 1. Desorption of 15 mmol/kg BTX and NDD from the Carson Valley soil.

34%, and 18% of the benzene, toluene, and xylenes desorbed, respectively. Desorption is often the rate-controlling mechanism in the treatment of contaminated soils [40,41]. When contaminants desorb into the aqueous phase, their subsequent transformation creates a gradient for further desorption and then further transformation. If the contaminant is degraded as soon as it is desorbed, the rate of treatment then equals the rate of desorption. However, if the rate of treatment exceeds the natural maximum desorption rate, then the rate of contaminant desorption is enhanced by the treatment process. Therefore, the rate of Fenton-like oxidations relative to the rate of GP desorption provides a measure of the ability of this oxidative soil treatment to overcome the rate-limiting step of desorption.

3.2. Oxidation of BTX and NDD at pH 3

The procedure used to compare the effectiveness of the Fenton-like treatment of the six different hydrocarbons was to investigate two variables at one time (i.e., to vary the H_2O_2 concentration and the iron (III) amendment while holding pH constant), and then compare the degradation of each compound at that fixed level through a central composite two-level experimental design [37]. Relative degradation of each hydrocarbon was obtained by normalizing treatment data to controls using deionized water in place of H_2O_2 ; regression equations (listed in Table 3) were then developed from the experimental data using the procedure described by Box and Draper [38] and Diamond [37]. SYSTAT[®] software was used to generate response surfaces from the regression equations. Response surfaces for the Fenton-like oxidation of BTX and NDD as a function of H_2O_2 concentration and iron (III) concentration at pH 3 are shown in Figs. 2a–c and 3a–c, with isoresponse lines representing percent hydrocarbon oxidation. For the majority of conditions tested, degradation of BTX and NDD surpassed their natural desorption rates as determined by GP analysis, indicating that enhanced desorption occurred. Recent work by Watts et al. [42] has shown that the enhanced desorption found in vigorous Fenton-like reactions ($\text{H}_2\text{O}_2 > 1\%$) is mediated by a non-hydroxyl radical mechanism that involves a reducing species. For a given iron concentration, higher H_2O_2 concentrations generally resulted in greater contaminant degradation. Significant degradation occurred for most contaminants even with zero added iron; this was likely due to catalysis by naturally occurring iron minerals in the soil [15–18].

Inspection of Fig. 2a–c indicates that, for equal amendments of H_2O_2 and iron (III), more benzene was oxidized, followed by toluene and xylenes. Because loss of xylenes controlled the treatment of the aromatic fraction, the minimum H_2O_2 and iron (III) concentrations necessary for 99% degradation of xylenes were determined using a sensitivity analysis. The analysis showed that, at the optimum condition of 2.8% H_2O_2 and 6.5 mM iron (III), > 99% treatment of the xylenes was achieved, with corresponding > 99% treatment of the benzene and toluene. Using Eqs. (3)–(6) of Table 3, the corresponding degrees of aliphatic treatment at this condition of optimum aromatic treatment (2.8% H_2O_2 and 6.5 mM iron (III)) were only 86%, 66%, and 20% for nonane, decane, and dodecane, respectively. These results show that the aromatic fraction found in unleaded gasoline is treated more effectively than aliphatic compounds in Fenton-like reactions. The most commonly used regulatory cleanup standard for

Table 3

Regression equations for the Fenton-like oxidation of BTX and NDD as a function of H₂O₂ concentration, iron (III) concentration, and pH

Compound	Regression equation	pH	Equation number
Benzene	%Degradation = 41.2 + 11.7(H ₂ O ₂) + 3.9(Fe) - 1(H ₂ O ₂)(Fe) + 5.2(H ₂ O ₂) ² - 0.11(Fe) ²	3	1
Toluene	%Degradation = 19.8 + 18.7(H ₂ O ₂) + 4.3(Fe) - 1(H ₂ O ₂)(Fe) + 4.7(H ₂ O ₂) ² - 0.13(Fe) ²	3	2
Xylenes	%Degradation = 9.1 + 16(H ₂ O ₂) + 4.2(Fe) - 0.85(H ₂ O ₂)(Fe) + 5.5(H ₂ O ₂) ² - 0.14(Fe) ²	3	3
Nonane	%Degradation = 94.0 + 9.1(H ₂ O ₂) + 0.6(Fe) - 7.6(H ₂ O ₂)(Fe) + 1.0(H ₂ O ₂) ² + 2.3(Fe) ²	3	4
Decane	%Degradation = 75.9 + 10.0(H ₂ O ₂) + 4.2(Fe) - 3.9(H ₂ O ₂)(Fe) - 2.8(H ₂ O ₂) ² + 5.9(Fe) ²	3	5
Dodecane	%Degradation = 21.7 + 14.1(H ₂ O ₂) + 1.9(Fe) + 15.7(H ₂ O ₂)(Fe) - 3.0(H ₂ O ₂) ² + 7.2(Fe) ²	3	6
Benzene	%Degradation = 40.32 + 50.52(H ₂ O ₂) + 0.94(Fe) + 0.086(H ₂ O ₂)(Fe) - 12.02(H ₂ O ₂) ² - 0.034(Fe) ²	Near neutral	7
Toluene	%Degradation = 22.74 + 49.64(H ₂ O ₂) + 2.67(Fe) - 0.19(H ₂ O ₂)(Fe) - 9.79(H ₂ O ₂) ² - 0.09(Fe) ²	Near neutral	8
Xylenes	%Degradation = 6.7 + 57.5(H ₂ O ₂) + 2.6(Fe) - 0.72(H ₂ O ₂)(Fe) - 9.7(H ₂ O ₂) ² - 0.065(Fe) ²	Near neutral	9
Nonane	%Degradation = 43.8 + 17.5(H ₂ O ₂) + 11.7(Fe) - 1.0(H ₂ O ₂)(Fe) + 0.4(H ₂ O ₂) ² + 2.6(Fe) ²	Near neutral	10
Decane	%Degradation = 18.1 + 15.9(H ₂ O ₂) + 8.1(Fe) + 7.9(H ₂ O ₂)(Fe) + 0.7(H ₂ O ₂) ² + 4.8(Fe) ²	Near neutral	11
Dodecane	%Degradation = 3.5 + 5.1(H ₂ O ₂) + 1.7(Fe) + 7.0(H ₂ O ₂)(Fe) + 2.0(H ₂ O ₂) ² + 12.2(Fe) ²	Near neutral	12

gasoline, 100 mg/kg TPH, would not be met using Fenton's conditions of 2.8% H₂O₂ and 6.5 mM iron (III) at pH 3, even though > 99% destruction of the more toxic aromatic fraction was achieved.

Sorption of contaminants to soils has been shown to significantly retard contaminant degradation through both biotic and abiotic processes. Tyre et al. [15] found that hydrophobic contaminants were degraded more slowly than water-soluble compounds by Fenton-like reactions in soils, and Weber et al. [43] reported that sorption of 2,4-D and other pesticides to organic matter and clays limited their bioavailability in soil–water systems. The kinetics and stoichiometry of Fenton-like reactions in soils are likely a function of both the rates of reaction of hydroxyl radicals with the contaminants and the availability of the contaminants [19,41]. The second-order hydroxyl radical rate constants, mean water solubilities, and log octanol–water partition coefficients for BTX and NDD (Table 1) document that the six hydrocarbons investigated react with hydroxyl radicals at nearly the same rate; however, the NDD compounds are significantly more hydrophobic and less soluble in water than the BTX compounds. Comparison of the oxidation of the BTX and NDD components with their GP desorption rates and the data of Table 1 suggests that the degree of enhanced desorption and degradation in Fenton-like reactions may be proportional to the natural desorption rate and inversely

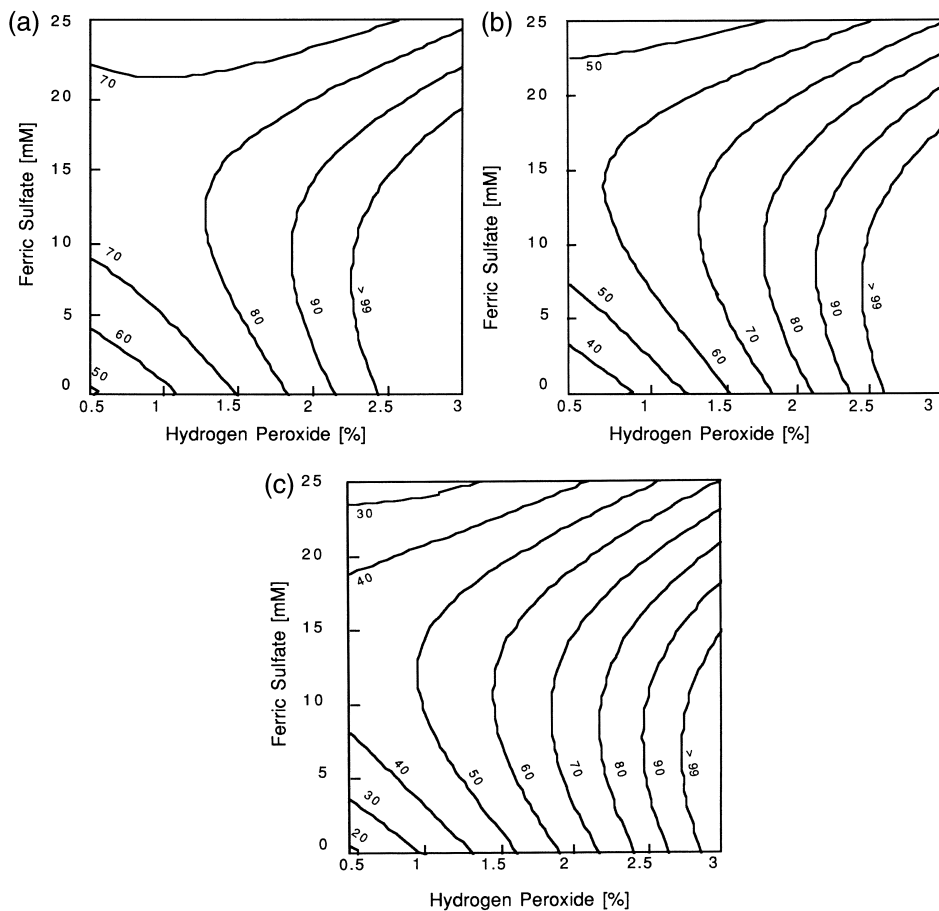


Fig. 2. (a) Response surface for the Fenton-like oxidation of benzene at pH 3. Isoresponse lines represent percent oxidation. (b) Response surface for the Fenton-like oxidation of toluene at pH 3. Isoresponse lines represent percent oxidation. (c) Response surface for the Fenton-like oxidation of xylenes at pH 3. Isoresponse lines represent percent oxidation.

proportional to the octanol–water partition coefficients. The less effective treatment of NDD (Fig. 3a–c) compared to BTX (Fig. 2a–c) was likely a function of its higher degree of sorption to the soil. Therefore, the higher water solubility and lower sorptivity that make the aromatic fractions of gasoline more hazardous also serve to facilitate their treatment by Fenton-like reactions.

3.3. Oxidation of BTX and NDD at near-neutral pH

The response surfaces for BTX and NDD oxidation at near-neutral pH as a function of H_2O_2 concentration and iron (III) amendment are shown in Figs. 4a–c and 5a–c, respectively. The optimum treatment conditions for maximum BTX degradation were determined using Eqs. (7)–(10) of Table 3 in a sensitivity analysis in which the

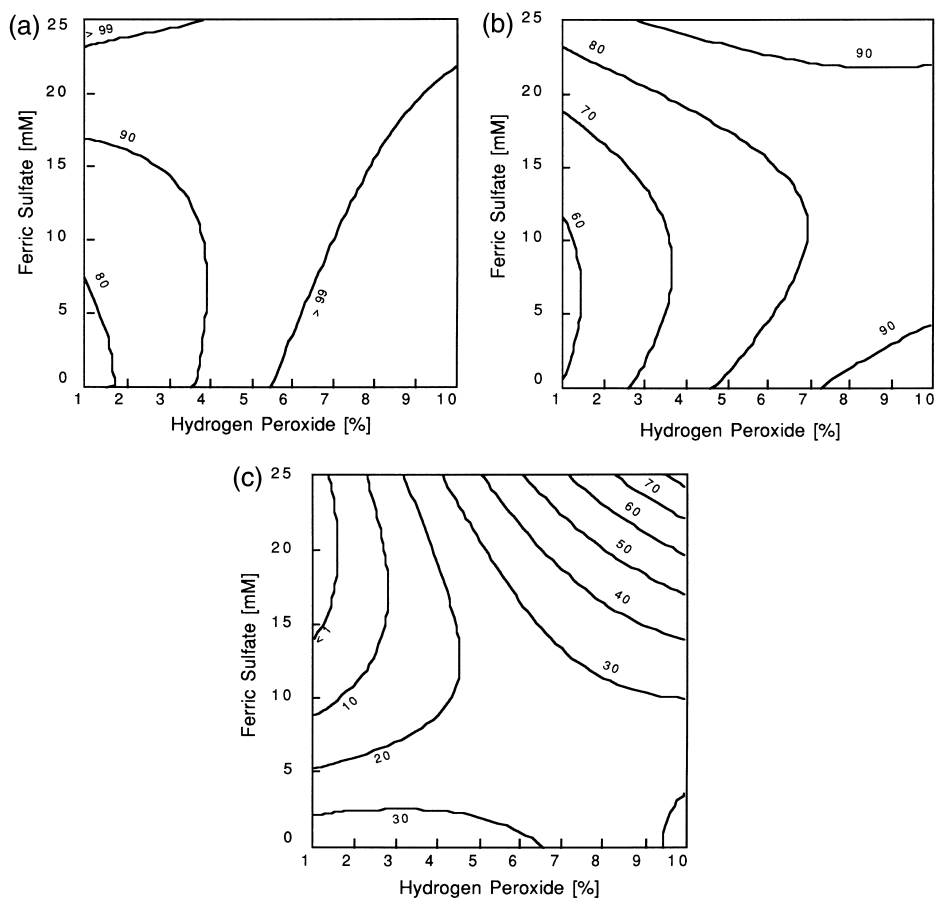


Fig. 3. (a) Response surface for the Fenton-like oxidation of nonane at pH 3. Isoresponse lines represent percent oxidation. (b) Response surface for the Fenton-like oxidation of decane at pH 3. Isoresponse lines represent percent oxidation. (c) Response surface for the Fenton-like oxidation of dodecane at pH 3. Isoresponse lines represent percent oxidation.

treatment was controlled by xylenes. The sensitivity analysis showed that the most effective condition for the degradation of BTX at near-neutral pH was 2.5% H_2O_2 and 12.5 mM iron (III). Under these conditions, the maximum treatment attained for benzene, toluene, and xylenes was >99%, 99%, and 90%, respectively. The corresponding treatment of the aliphatic fraction was 31%, 7%, and 1% for nonane, decane, and dodecane, respectively. The difficulty of oxidizing hydrophobic aliphatic hydrocarbons was previously documented by Kakarla and Watts [25] and Watts and Stanton [26], who found that H_2O_2 concentrations in the range of 15–45% are necessary to oxidize sorbed hexadecane in soils.

Most Fenton's reactions have been conducted at acidic pH, a practice that maintains iron solubility in the system. The higher degradation rate of the contaminants (NDD in particular) under the low pH regime, compared to the near-neutral pH regime, may have

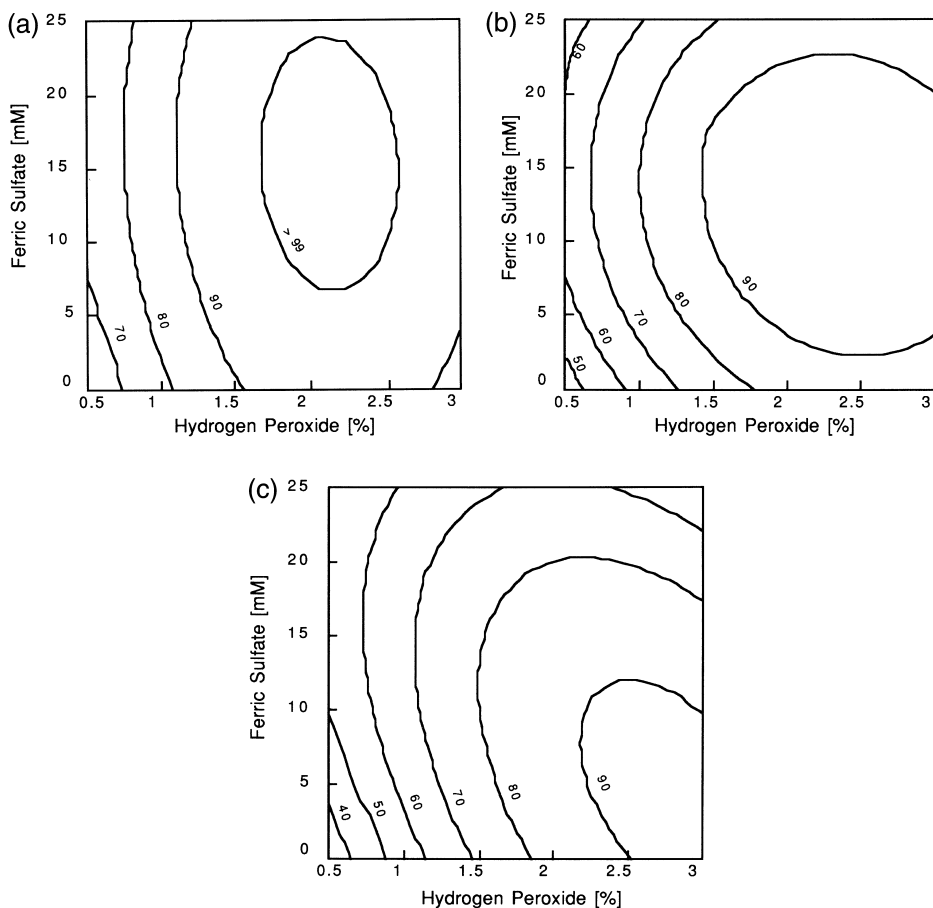


Fig. 4. (a) Response surface for the Fenton-like oxidation of benzene at near-neutral pH. Isoresponse lines represent percent oxidation. (b) Response surface for the Fenton-like oxidation of toluene at near-neutral pH. Isoresponse lines represent percent oxidation. (c) Response surface for the Fenton-like oxidation of xylenes at near-neutral pH. Isoresponse lines represent percent oxidation.

been due to the high reducing conditions. The initiating Fenton's reaction (Eq. (1)) is highly redox sensitive, and its rate increases significantly under reducing conditions [44]. Bielski [45] also found that low pH conditions favored the oxidation of organic compounds, and hypothesized that $\text{Fe}(\text{OH})^+$, formed at a pH range of 2–4, has a higher activity than Fe^{2+} in Fenton reactions and leads to the improved compound destruction in this pH range.

However, low pH conditions severely limit the usefulness of Fenton-like reactions for soil remediation because of the need to acidify large volumes of soil [46]. The results of Figs. 4a–c and 5a–c show that, if only the aromatic fractions are targeted for oxidation by Fenton-like reactions, the treatment proceeds effectively at near-neutral pH regimes. Such a neutral pH process design would improve the logistics of ex situ soil treatment

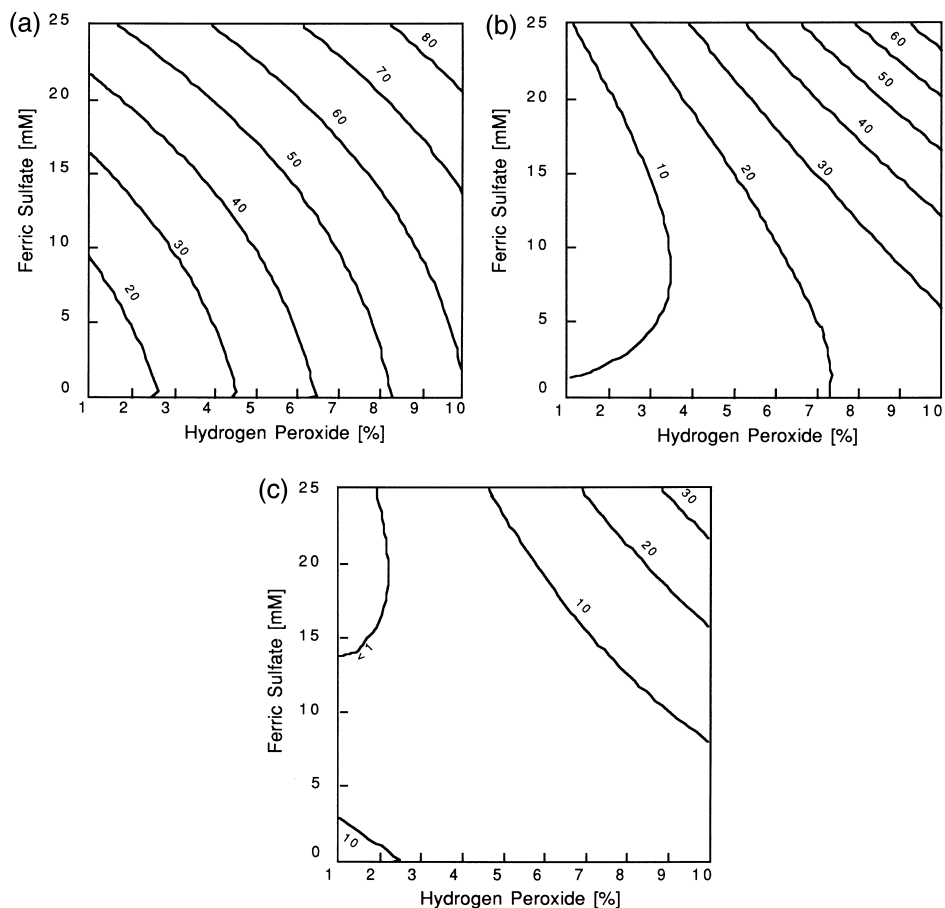


Fig. 5. (a) Response surface for the Fenton-like oxidation of nonane at near-neutral pH. Isoresponse lines represent percent oxidation. (b) Response surface for the Fenton-like oxidation of decane at near-neutral pH. Isoresponse lines represent percent oxidation. (c) Response surface for the Fenton-like oxidation of dodecane at near-neutral pH. Isoresponse lines represent percent oxidation.

and greatly enhance the potential for the in situ injection of reagents to treat deeply contaminated soils and groundwater.

3.4. Treatment of unleaded gasoline

The Carson Valley soil was spiked with 1000 mg/kg gasoline, treated with varying concentrations of H_2O_2 and approximately 12.5 mM iron (III) at near-neutral pH and an L:S of 0.3 ml/g, and analyzed by GC/FID and GC/PID after the reactions were complete. The results (Fig. 6) show that approximately 30% of the TPHs originally present were detectable by GC/PID. Although PID is not exclusively selective for aromatic compounds, it does provide an effective indicator of the aromaticity of a

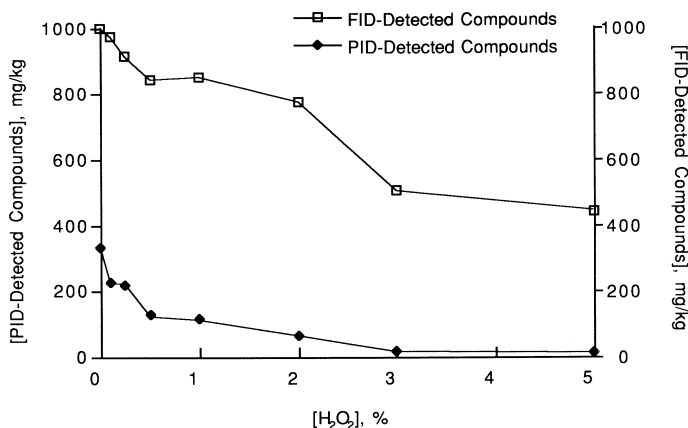


Fig. 6. Loss of FID- and PID-measured hydrocarbons in the Fenton-like treatment of 1000 mg/kg unleaded gasoline in the Carson Valley soil with a range of hydrogen peroxide concentrations at L:S = 0.3.

hydrocarbon sample [47]. The results of Fig. 6 also show that the PID-detectable fraction was degraded to an asymptotic level of 2 mg/kg with approximately 2.5% H₂O₂ and 12.5 mM iron (III). This suggests that the aromatic compounds present in gasoline, along with any aromatic degradation products, were almost entirely degraded under these Fenton's conditions. The total mass of hydrocarbons, measured by GC/FID, decreased in parallel to the GC/PID data, indicating minimal oxidation of the aliphatic fraction. These results confirm that modified Fenton's reactions preferentially treat the aromatic fractions of petroleum, and indicate that L:S ratios as low as 0.3 ml/g can provide effective, rapid, and economical treatment of the toxic and mobile aromatic fraction of gasoline.

4. Conclusions

A risk-based process design for the Fenton-like treatment of gasoline-contaminated soils was investigated using three toxic aromatic compounds (benzene, toluene, xylenes) characteristic of gasoline and three representative aliphatic compounds (nonane, decane, dodecane), which represent a significantly lower risk. A characterized soil was spiked with each of the six compounds, and treatment effectiveness was evaluated using a matrix of H₂O₂ concentrations and iron (III) amendments at either pH 3 or near-neutral pH. The results demonstrate that BTX was preferentially oxidized over NDD by modified Fenton's reaction at both pH regimes. All compounds were degraded more rapidly than their natural desorption rates under most of the Fenton's conditions used in this study. At pH 3, 2.8% H₂O₂ and 6.5 mM iron (III), > 99% degradation of BTX and 86%, 66%, and 20% degradation of nonane, decane, and dodecane were achieved. At near-neutral pH, 2.5% H₂O₂, and 12.5 mM iron (III), > 95% degradation of BTX and 31%, 7%, and 1% degradation of nonane, decane, and dodecane were attained. Under

equal reaction conditions, more BTX oxidation was found relative to NDD, which was probably due to lower degrees of sorption of the BTX compounds. Based on these results and a cost of US\$0.68/l for 50% H₂O₂ [23], a gasoline-contaminated site could be treated to > 95% oxidation of the aromatic fraction with a chemical cost of US\$34/metric ton using an L:S of 1.0 ml/g. An additional benefit of the use of modified Fenton's reagent for soil and groundwater treatment is related to its rapid cleanup time. Fenton-like treatments can be completed within hours to days compared to months to years for other processes. One reason for such rapid cleanup is the potential for displacing sorbed contaminants with subsequent degradation in the surrounding interstitial water [42].

The results obtained using the six model compounds were verified by treating a gasoline-spiked soil and monitoring the treatment of both the aromatic fraction and total hydrocarbons by GC/PID and GC/FID, respectively. At an L:S ratio of 0.3 ml/g, modified Fenton's reactions promoted the oxidation of 95% of the GC/PID-detectable compounds with a cost of US\$10/metric ton. Treatment technologies for petroleum-contaminated soils that have costs less than US\$50/metric ton are competitive with excavation and disposal. In addition, modified Fenton's reagent has an advantage over excavation and disposal, because Fenton-like treatment systems destroy most of the high-risk contaminants with a corresponding potential for economical site remediation and exemption from liability. Although natural attenuation is usually the most economical means of treating gasoline-contaminated soils, the low cost of risk-based Fenton-like treatment of contaminated sites may compete with the long term monitoring costs of natural attenuation. Furthermore, Fenton-like reactions can effectively treat petroleum-contaminated soils on the order of hours to days [21,48], while bioremediation or natural attenuation of these sites may require months to years [49]. With the trend toward risk-based TPH standards that target the aromatic fraction of petroleum, Fenton-like reactions can economically and quickly oxidize the compounds that are highly regulated using favorable process conditions such as near-neutral pH and low L:S ratios.

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