



Effect of contaminant hydrophobicity on hydrogen peroxide dosage requirements in the Fenton-like treatment of soils

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Received 18 March 2003; received in revised form 19 June 2003; accepted 20 June 2003

Abstract

A homologous series of *n*-alcohols was used as model contaminants to investigate the effect of hydrophobicity on the hydrogen peroxide concentration necessary in Fenton-like treatment for near-complete (>99%) destruction of compounds sorbed to soil. These probe compounds were selected because they exhibit equal reactivities with hydroxyl radicals, but have varied hydrophobicities. The standard Fenton reaction was first used to confirm equal hydroxyl radical reactivity for the *n*-alcohols. Central composite rotatable design experiments were then used to determine the conditions in an iron(III)–hydrogen peroxide system that resulted in 99% degradation of each of the probe compounds when sorbed to soil. The hydrogen peroxide concentrations required for 99% destruction of the sorbed compounds increased with probe compound hydrophobicity. Furthermore, hydrogen peroxide concentration requirements were directly proportional to the log octanol–water partition coefficients ($\log K_{OW}$) of each probe compound. This quantitative relationship may not be directly applicable to other organic contaminants, but a strong correlation between $\log K_{OW}$ and hydrogen peroxide requirements for other contaminants will likely be found. These results confirm that hydrogen peroxide requirements for soil treatment increase as a function of contaminant hydrophobicity and provide a basis for the development of an algorithm for hydrogen peroxide requirements when modified Fenton's reagent is used for in situ chemical oxidation (ISCO).

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Keywords: Fenton's reagent; Hydrogen peroxide; Hydroxyl radical; In situ chemical oxidation; Octanol–water partition coefficient

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1. Introduction

Soils and subsurface systems contaminated with organic compounds, such as polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs), represent a significant environmental concern. These chemicals not only result in ecotoxicity, but are also carcinogens and endocrine disrupters [1]. Many of these contaminants are characterized by high hydrophobicity, with log octanol–water partition coefficients ($\log K_{OWs}$) in the range of 4–9. As a result, nearly all of the contaminant is present in the sorbed phase and desorption rates are often negligible. Nearly all soil and groundwater treatment processes are effective only for aqueous phase contaminants, because the reactive species (e.g. enzymes, hydroxyl radicals $[OH^\bullet]$, solvated electrons) are generated and reactive only in the aqueous phase [2–4]. Desorption rates of hydrophobic contaminants are often much slower than their transformation rates, and therefore limit their rates of treatment.

Modified Fenton's reagent has been effective in degrading contaminants significantly more rapidly than their corresponding gas-purge or fill-and-draw desorption occurs. This process is based on the standard Fenton's reaction, in which dilute hydrogen peroxide is slowly added to a rapidly-stirred solution containing excess iron(II). Modifications of Fenton's reaction for environmental applications include the use of high concentrations of hydrogen peroxide and iron chelates and iron oxides as catalysts. Using such Fenton-like reactions, Watts et al. [5] demonstrated that hexachlorobenzene sorbed to silica sand was degraded more rapidly than it was lost by gas-purge desorption. Similar results were documented for TCE [6], hexadecane [7], and benzo[*a*]pyrene [8]. A common theme in these studies has been the high hydrogen peroxide concentrations used, particularly for the hyper-hydrophobic compound hexadecane ($\log K_{OW} = 9.1$). Watts et al. [9] found that in Fenton's reactions using hydrogen peroxide concentrations >300 mM, a non-hydroxyl radical species was generated that was responsible for the rapid degradation of sorbed hexachloroethane and hexachlorocyclopentadiene.

High hydrogen peroxide concentrations in modified Fenton's reactions promote propagation reactions that result in non-hydroxyl radical transient oxygen species, including perhydroxyl radical (HO_2^\bullet), superoxide radical anion ($O_2^{\bullet-}$), and hydroperoxide anion (HO_2^-) [10]:



Because these non-hydroxyl radical species are produced in greater amounts as the hydrogen peroxide concentration is increased, the degree of treatment of sorbed hydrophobic contaminants in modified Fenton's reactions may be a function of the hydrogen peroxide concentration. Based on this hypothesis, the objective of this study was to use a suite of probe compounds with equal rates of reaction with hydroxyl radicals to investigate the

relationship between contaminant hydrophobicity and hydrogen peroxide dosage in the Fenton-like treatment of contaminated soils.

2. Materials and methods

2.1. Materials

1-Hexanol (98%), 1-heptanol (99%), 1-octanol (99%), 1-nonanol (98%), 1-decanol, and iron(II) perchlorate (99%) were purchased from Sigma (Milwaukee, WI). Pentane was purchased from J.T. Baker (Phillipsburg, NJ) and mixed hexanes and iron(III) sulfate were obtained from Fisher Scientific (Pittsburgh, PA). Hydrogen peroxide was provided gratis by Solvay Interlox (Deer Park, TX). All aqueous solutions were prepared with deionized water, which was purified to $>18\text{ M}\Omega\text{ cm}$ using a Barnstead Nanopure II deionizing system. The soil used was a grayish-brown gravelly loamy sand, mixed, mesic Torriothentic Haploxeroll, sampled from an alluvial fan above Carson Valley, NV. It was characterized for particle size distribution by the pipette method [11]. Organic carbon was determined by combustion at $900\text{ }^{\circ}\text{C}$ with evolved CO_2 trapped in KOH and measured by back-titration of unreacted KOH [12]. Cation exchange capacity was established by saturation with sodium acetate at pH 8.2 [13]. Crystalline and amorphous iron and manganese oxyhydroxides were determined by citrate–bicarbonate–dithionite extraction [14]. The soil characteristics are listed in Table 1.

2.2. Confirmation of equal reactivity of probe compounds with hydroxyl radicals

A series of *n*-alcohols was chosen for use as probe compounds. Rate constants for 1-hexanol, 1-heptanol, 1-octanol, 1-nonanol, and 1-decanol with hydroxyl radicals were determined using an optimized Fenton's procedure that produces a maximum stoichiometric yield of hydroxyl radicals [15]. Reactions for each probe compound were carried out in triplicate in 250 ml Erlenmeyer flasks containing 50 ml of a 0.2 mM probe and 30 mM iron(II) perchlorate solution, which was nitrogen purged for 10 min prior to starting the reaction. The probe concentration of 0.2 mM was based on the water solubility of 1-decanol,

Table 1
Characteristics of the Carson Valley soil

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

the least water soluble of the probe compounds. Hydrogen peroxide (0.5 mM) was added to the rapidly-stirred probe-iron(II) solution at a rate of 1 ml min⁻¹. Aliquots were collected at 1 min intervals, extracted with mixed hexanes, and analyzed by gas chromatography. Control experiments were conducted in parallel using deionized water in place of hydrogen peroxide. The data were analyzed by normalizing the concentration for dilution and then plotting the normalized concentration as a function of hydrogen peroxide (mol) added per mol of probe compound degraded.

2.3. Experimental design

Central composite rotatable experimental designs [16] were used to determine the optimum concentrations of hydrogen peroxide and iron(III) for degradation of probe compounds sorbed to Carson Valley soil. Iron(III) was chosen for this system rather than iron(II) because, with the relatively high concentrations of H₂O₂ used, iron(II) is rapidly oxidized to iron(III) with a resulting initial demand on the H₂O₂ in the system [17]. Therefore, the more efficient perhydroxyl-driven initiation reaction was used to initiate the Fenton's process chemistry:



Hydrogen peroxide concentrations ranged from 7 to 442 mM and iron(III) sulfate concentrations ranged from 1.5 to 7 mM. The central composite matrix was characterized by five center points and four star points, or vertices, set at a factor of ± 1.4142 on the far ends of the coded scale to achieve complete rotatability [16]. Linear regression using least squares analysis was used to derive regression equations from the experimental data. A single sided *t*-distribution ($\alpha = 0.10$) was used to evaluate each term in the regression equation; the terms that were not significant at the 90% interval were eliminated. Correlation (R^2) values were determined by comparing experimental values to values calculated using the regression equations. Corresponding three-dimensional response surfaces, representing the effect of hydrogen peroxide and soluble iron concentration on probe compound degradation in the soil slurries, were generated from the regression equations using SYSTAT[®] software.

2.4. Procedures

Reactions were conducted in batch reactors consisting of 30 ml borosilicate vials fitted with PTFE-lined caps. All reactions were conducted in triplicate. Each vial contained 5 ± 0.01 g of Carson Valley soil to which a probe compound was added in pentane. The pentane was allowed to evaporate, resulting in a probe concentration of 0.25 mmol kg⁻¹. The reactions were conducted using reagent volumes of 1.2 times the soil field capacity. The pH was adjusted to pH 3 using 0.1N solutions of NaOH or H₂SO₄. Upon addition of reagents and adjustment of pH, the vials were mixed at 26.2 rad s⁻¹ on an orbital shaker to ensure homogeneity of the catalyst and hydrogen peroxide. The reactions were allowed to proceed until the hydrogen peroxide was consumed (9–30 h). The entire vial contents were then extracted with mixed hexanes and analyzed by gas chromatography. The extraction efficiencies for 1-hexanol, 2-heptanol, 3-octanol, 4-nonanol, and 5-decanol into ethyl acetate

were 84, 85, 87, 87 and 89%, respectively. Control reactions were conducted in parallel using deionized water in place of hydrogen peroxide.

2.5. Analysis

Probe compound residuals were determined using a Hewlett-Packard 5890 Series II gas chromatograph fitted with a Supelco SPB-5 0.53 mm i.d. \times 15 m fused silica capillary column and flame ionization detector. The injector port and detector port temperatures were 280 and 300 °C, respectively. The initial temperatures were 45 °C for 1-hexanol, 55 °C for 1-heptanol, 75 °C for 1-octanol, 90 °C for 1-nonanol, and 105 °C for 1-decanol. The program rate was 15 °C min⁻¹ for hexanol and 20 °C min⁻¹ for all other probe compounds; the final temperature was 280 °C.

Hydrogen peroxide concentrations >100 mg l⁻¹ were determined by iodometric titration with 0.1N sodium thiosulfate [18]. Hydrogen peroxide concentrations <100 mg l⁻¹ were determined by complexation with TiSO₄ followed by spectrophotometric quantitation of the complex using a Genesys Spectronic 20 [19].

3. Results

3.1. Reactivity of hydroxyl radicals with probe compounds

In order to isolate the effect of contaminant hydrophobicity on hydrogen peroxide dosage requirements in modified Fenton's treatment of sorbed compounds, probe compounds must be used that have varying hydrophobicities but equal or near-equal rates of reaction with hydroxyl radicals. The *n*-alcohols 1-hexanol, 1-heptanol, 1-octanol, 1-nonanol, and 1-decanol should have near-equal reactivity with hydroxyl radicals; however, available second-order rate constants for the alcohols were obtained under varying conditions, and could not be compared directly. Therefore, the standard Fenton's reaction was used to verify that the five *n*-alcohols are oxidized at near-equal rates. The oxidation of the probe compounds in a standard Fenton's system is shown in Fig. 1; the results of analysis of variance (ANOVA) performed on the slopes of the treatment reactions as well as the control reactions are summarized in Table 2. Based on the ANOVA, no significant difference ($\alpha = 0.05$) was found between rates of oxidation of the five probe compounds by hydroxyl radicals. Therefore, any differences found in hydrogen peroxide requirements for the treatment of sorbed *n*-alcohols may be attributed to hydrophobicity rather than reactivity with hydroxyl radicals.

3.2. Evaluation of optimum hydrogen peroxide dosages for probe oxidation

Experiments with two-level central composite rotatable designs were used to determine the hydrogen peroxide and iron requirements for degradation of the five probe compounds. These designs are multivariable, multilevel experimental procedures that are used to produce regression equations describing the interactive effects between variables, which are then illustrated graphically using three-dimensional response surfaces [20]. In central composite

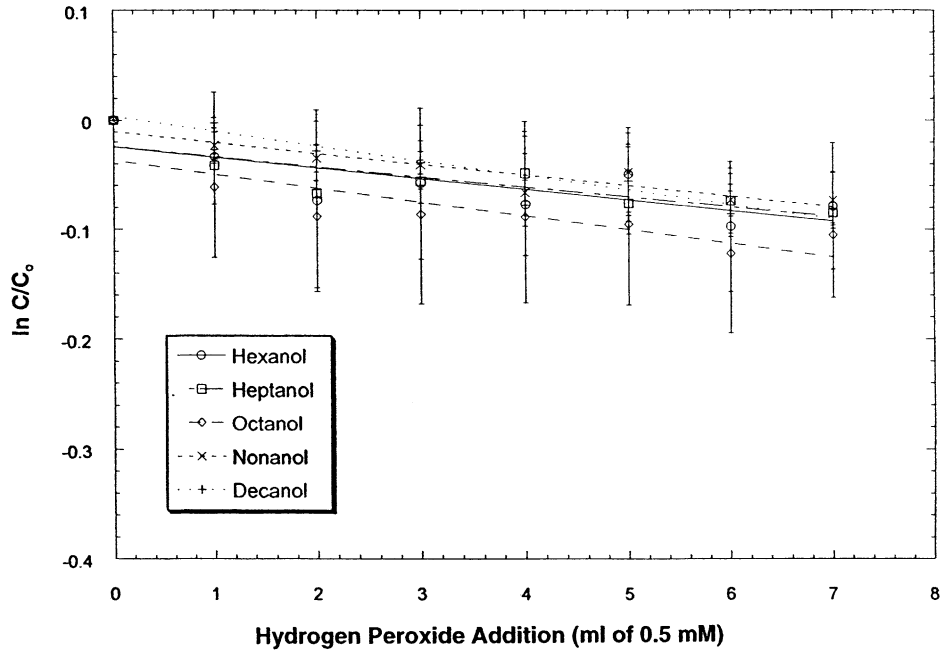


Fig. 1. Oxidation of *n*-alcohols in a standard Fenton's system.

designs, the range of each variable is chosen to achieve complete rotatability around the central point of a two-level matrix. Using such matrix designs, all of the vertices within the experimental boundaries are tested, and interpolation anywhere within the two-dimensional space is valid [16]. The regression equations developed from the experimental data and their coefficients of correlation (R^2) with the experimental data are listed in Table 3, and the corresponding response surfaces for the oxidation of the five *n*-alcohols are shown in Figs. 2–6. The concentric response lines in each of the response surfaces indicate that hydro-

Table 2
Analysis of variance from the standard Fenton's system

Source of variation	d.f.	Sum of squares	Mean square	f^a
Treatments				
Treatments	4	2.574×10^{-4}	6.435×10^{-5}	1.046
Error	10	6.150×10^{-4}	6.154×10^{-5}	
Total	14	8.728×10^{-4}		
Controls				
Treatments	4	1.307×10^{-3}	3.267×10^{-4}	0.199
Error	10	1.640×10^{-2}	1.640×10^{-3}	
Total	14	1.771×10^{-2}		

^a Values are valid because f of 2.61 using $d f_1/d f_2$ of 4/10 was not exceeded.

Table 3
Regression equations

Probe	Regression equation ^a	R ^{2b}
1-Hexanol	$87.5 + 12.6(\text{iron}) + 9.21(\text{H}_2\text{O}_2) - 1.96(\text{iron})(\text{H}_2\text{O}_2) - 2.80(\text{iron})^2 - 3.33(\text{H}_2\text{O}_2)^2$	0.90
1-Heptanol	$90.3 + 7.03(\text{iron}) + 14.0(\text{H}_2\text{O}_2) - 2.58(\text{iron})(\text{H}_2\text{O}_2) - 1.93(\text{iron})^2 - 7.22(\text{H}_2\text{O}_2)^2$	0.92
1-Octanol	$96.8 + 7.60(\text{iron}) + 8.97(\text{H}_2\text{O}_2) - 5.23(\text{iron})(\text{H}_2\text{O}_2) - 4.0(\text{iron})^2 - 6.63(\text{H}_2\text{O}_2)^2$	0.95
1-Nonanol	$88.9 + 8.19(\text{iron}) + 13.6(\text{H}_2\text{O}_2) - 5.24(\text{iron})(\text{H}_2\text{O}_2) - 1.01(\text{iron})^2 - 6.36(\text{H}_2\text{O}_2)^2$	0.88
1-Decanol	$87.4 + 10.5(\text{iron}) + 12.5(\text{H}_2\text{O}_2) - 5.6(\text{iron})(\text{H}_2\text{O}_2) - 7.1(\text{iron})^2 + 2.61(\text{H}_2\text{O}_2)^2$	0.87

^a Iron and H₂O₂ are coded terms [16] for ferric sulfate concentration and hydrogen peroxide concentration, respectively.

^b Derived with 12 d.f.

gen peroxide and iron concentrations both had a significant effect on contaminant treatment. Furthermore, inspection of Figs. 2–6 shows that the hydrogen peroxide dosage required for >99% degradation increased with increasing size and corresponding hydrophobicity of the *n*-alcohol used.

The enhanced treatment of sorbed contaminants by modified Fenton's reagent requires high concentrations of hydrogen peroxide relative to those required for aqueous contaminants. Watts et al. [5] demonstrated that hexachlorobenzene sorbed on silica sand degraded significantly more rapidly than it was desorbed in Fenton-like reactions using ≥ 100 mM hydrogen peroxide. Gates and Siegrist [6] found enhanced TCE treatment in

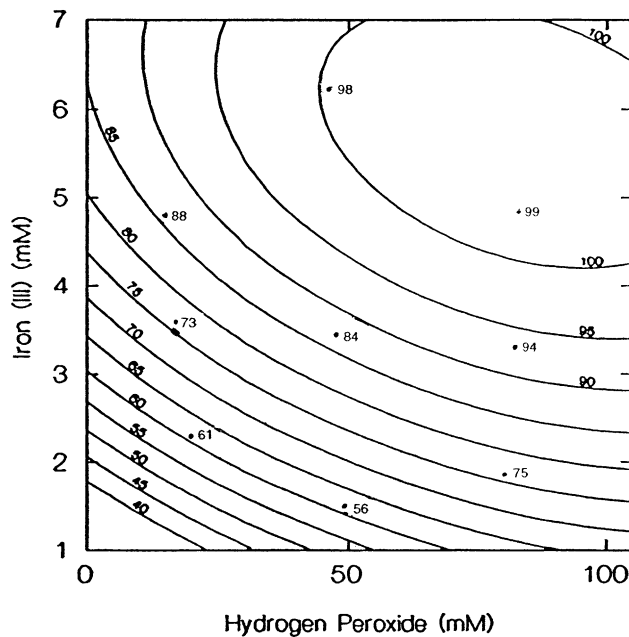


Fig. 2. Response surface for the degradation of 1-hexanol sorbed to Carson Valley soil as a function of hydrogen peroxide and iron(III) sulfate concentrations. Isoresponse lines represent percent degradation.

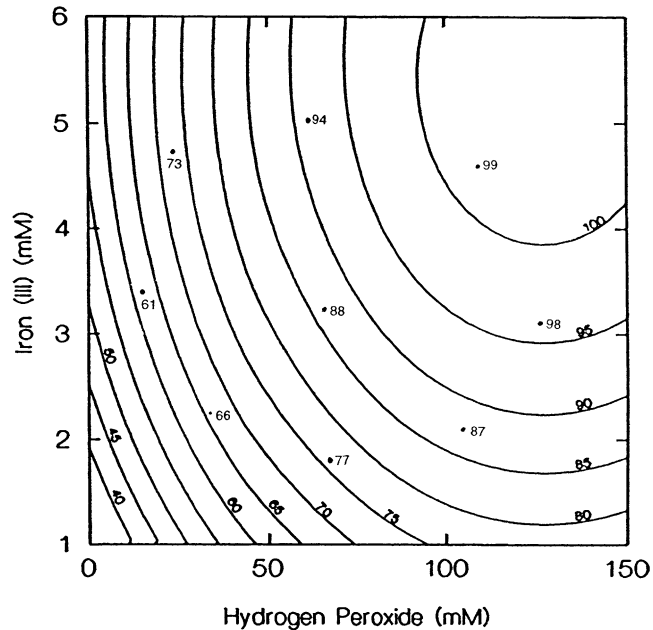


Fig. 3. Response surface for the degradation of 1-heptanol sorbed to Carson Valley soil as a function of hydrogen peroxide and iron(III) sulfate concentrations. Isoresponse lines represent percent degradation.

the vadose zone using modified Fenton's reagent with 600 mM hydrogen peroxide. Furthermore, treatment and mineralization of ^{14}C -hexadecane required >10 M hydrogen peroxide [7]. These results have suggested that the hydrogen peroxide dosages required for treatment may increase with increasing contaminant hydrophobicity. The data shown in Figs. 2–6 confirm that the destruction of sorbed *n*-alcohols of equal reactivity with hydroxyl radicals requires higher dosages of hydrogen peroxide for compounds of higher hydrophobicity.

A quantitative relationship that describes hydrogen peroxide concentrations required to treat contaminants of varying hydrophobicities would be valuable for the design of Fenton's treatment systems. The minimum H_2O_2 concentrations required to achieve 99% degradation for each probe compound were obtained by iteration using the regression equations, and are listed in Table 4. Numerous physical parameters have been used as predictors of hydrophobicity, including the octanol–water partition coefficient (K_{OW}) and water solubility (S). Because hydrophobicity appears to be the variable that controls the rate at which sorbed contaminants are treated by modified Fenton's reaction, the hydrogen peroxide concentrations required for 99% destruction of the *n*-alcohols were correlated with K_{OW} , $\log K_{\text{OW}}$, $1/S$, and $\log 1/S$. The best correlation was obtained with $\log K_{\text{OW}}$; the data of Fig. 7 show a strong correlation ($R^2 = 0.97$) between compound hydrophobicity as measured by $\log K_{\text{OW}}$ [21] and the concentration of hydrogen peroxide required to achieve 99% destruction of the probe compound. The same quantitative relationship is not likely to be identical for other contaminants; however, based on recent studies [7,8],

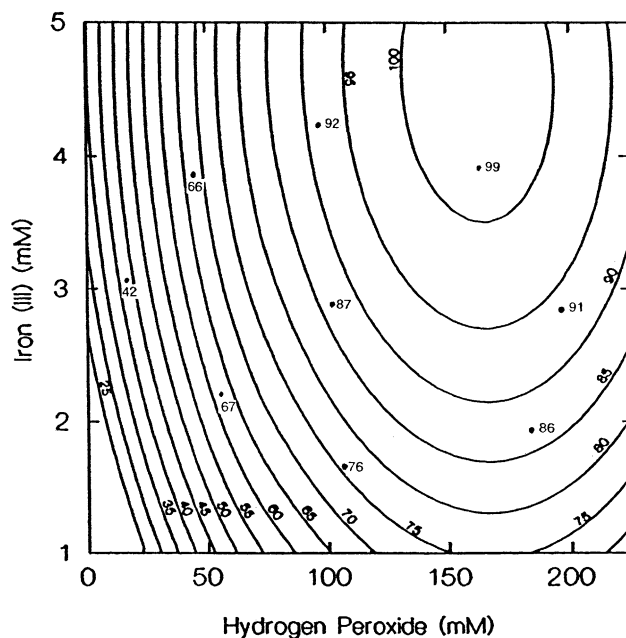


Fig. 4. Response surface for the degradation of 1-octanol sorbed to Carson Valley soil as a function of hydrogen peroxide and iron(III) sulfate concentrations. Isoresponse lines represent percent degradation.

hydrogen peroxide dosages will likely increase as a function of contaminant hydrophobicity. In addition, the soil organic carbon content may affect hydrogen peroxide requirements for a given soil; the soil organic carbon content of the Carson Valley soil was low at 0.36% and higher hydrogen peroxide dosages may be required for soils with more organic carbon.

Propagation reactions (Eqs. (2)–(5)) become dominant when hydrogen peroxide concentrations are increased in modified Fenton's reactions. For example, the reaction of hydroxyl radicals with hydrogen peroxide to generate perhydroxyl radical (Eq. (2)) is favored at higher hydrogen peroxide concentrations. Perhydroxyl radical is a weak oxidant in modified Fenton's systems, while superoxide anion is a weak reductant and nucleophile, and hydroperoxide anion is a strong nucleophile [22,23]. One or more of these species have been

Table 4

Probe characteristics and minimum H_2O_2 concentrations required for >99% degradation

Probe	$\log K_{\text{OW}}$	S (mg l^{-1})	Minimum H_2O_2 (mM)
1-Hexanol	2.03	5900	51.9
1-Heptanol	2.41	2000	95.2
1-Octanol	2.80	300	149
1-Nonanol	3.67	100	222
1-Decanol	4.11	37	398

$\log K_{\text{OW}}$: log octanol–water coefficient; S : water solubility; source: [21].

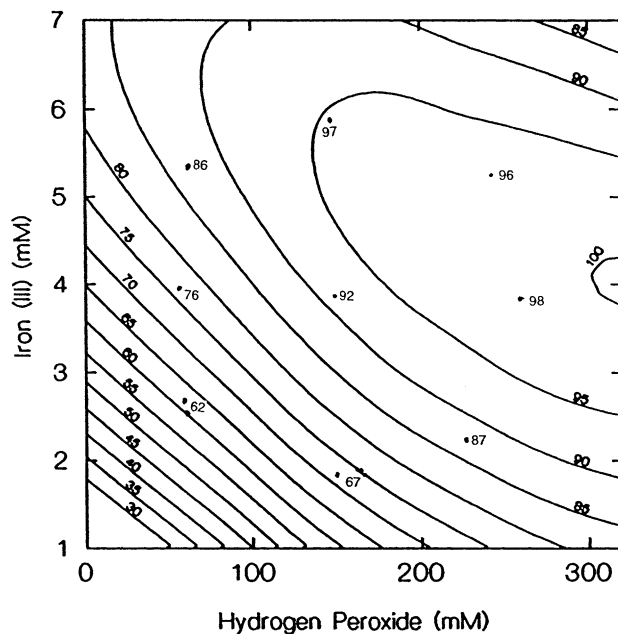


Fig. 5. Response surface for the degradation of 1-nonanol sorbed to Carson Valley soil as a function of hydrogen peroxide and iron(III) sulfate concentrations. Isoresponse lines represent percent degradation.

implicated in enhanced desorption during modified Fenton reactions and their generation likely resulted in lower total oxidation of the nonane above 300 mM H_2O_2 (Fig. 5) [9]. The correlation between increased hydrogen peroxide requirements and hydrophobicity of sorbed contaminants is likely related to the increased generation of the species (e.g. superoxide or hydroperoxide) required to desorb the increasingly hydrophobic probe compounds.

Although modified Fenton's reagent has seen increased use for in situ chemical oxidation (ISCO) over the past decade, no design criteria have been established, and no starting points for bench-scale treatability studies of full-scale application of modified Fenton's reagent have been developed. Hydrogen peroxide requirements vary substantially at full-scale Fenton's ISCO applications, often with no basis in process chemistry. Decomposition rates of hydrogen peroxide and generation rates of hydroxyl radicals and other transient oxygen species are a function of the soil mineralogy, soil organic matter content, and the dosage of catalyst added. Many contaminants of concern react with hydroxyl radicals at near diffusion-controlled rates ($>3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$); however, $\log K_{\text{OW}}$ for these contaminants range from 500 to over 10^7 , making hydrophobicity a significant variable in the Fenton-like treatment of contaminated soils and groundwater. The results of this research demonstrate a strong correlation between $\log K_{\text{OW}}$ and the hydrogen peroxide dose required to treat *n*-alcohols sorbed to the Carson Valley soil and, although an identical quantitative relationship may not be found for other classes of compounds and soils, hydrogen peroxide dosages will likely be proportional to $\log K_{\text{OW}}$. These results will provide a basis for developing structure-treatability relationships and design criteria for soil and groundwater remediation systems using modified Fenton's reactions.

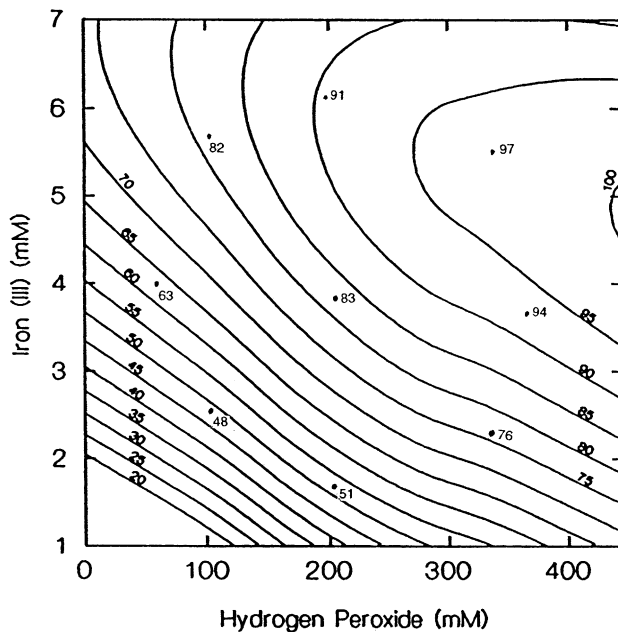


Fig. 6. Response surface for the degradation of 1-decanol sorbed to Carson Valley soil as a function of hydrogen peroxide and iron(III) sulfate concentrations. Isoresponse lines represent percent degradation.

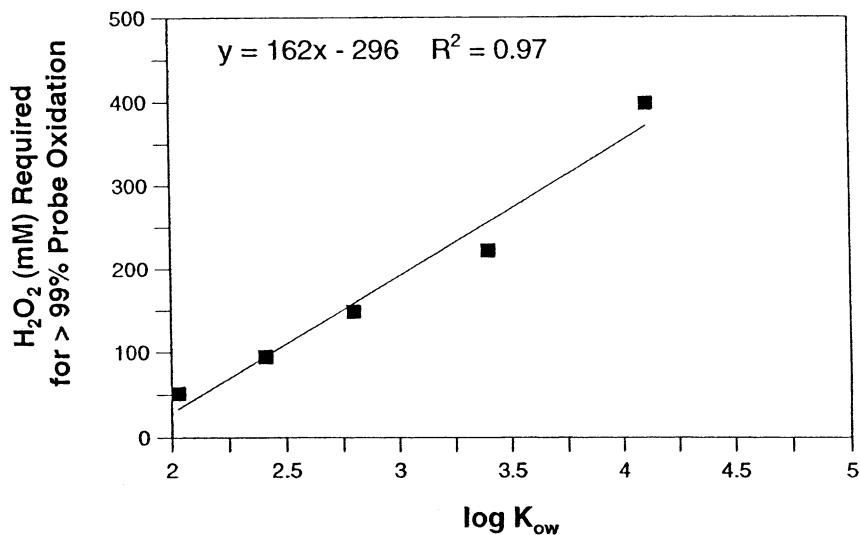


Fig. 7. Relationship between $\log K_{Ow}$ s and the minimum hydrogen peroxide concentrations required for >99% degradation of sorbed *n*-alcohols.

4. Conclusions

A homologous series of five *n*-alcohols was used as model contaminants to evaluate the relationship between contaminant hydrophobicity and dose of hydrogen peroxide required to treat contaminated soils using modified Fenton's reagent. Treatment with a standard Fenton's system confirmed that there were no significant differences ($\alpha < 0.05$) among the five probe compounds in their second-order rate constants for reaction with hydroxyl radicals. When sorbed probe compounds were treated with varying concentrations of catalyst and hydrogen peroxide, the minimum hydrogen peroxide concentration required to treat >99% of each of the *n*-alcohols increased as a function of the size of the compounds and correlated well ($R^2 = 0.97$) with their $\log K_{OW}$ s. The increased hydrogen peroxide concentration necessary for treatment of the more hydrophobic *n*-alcohols was likely due to the formation of transient oxygen species other than hydroxyl radicals, such as superoxide or hydroperoxide anion, which may be responsible for enhanced contaminant desorption. The results of this study show that a direct relationship exists between $\log K_{OW}$ and the concentration of hydrogen peroxide required in modified Fenton's reagent to treat contaminated soils and groundwater and serves as the basis for predicting hydrogen peroxide requirements.

Acknowledgements

Funding for this research was provided by the US Environmental Protection Agency (Assistance Agreement No. R826163-01) and the National Science Foundation (Grant No. BES-9613258).

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