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Chemical Oxidation of Volatile and Semi-Volatile Organic Compounds in Soil

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INTRODUCTION

Subsurface contamination with fuel hydrocarbons or chlorinated hydrocarbons is prevalent throughout the Department of Energy (DOE) complex and in many sites managed by the Environmental Protection Agency (EPA) Superfund program. The most commonly reported chlorinated hydrocarbons (occurring > 50% of DOE contaminated sites) were trichloroethylene (TCE), 1,1,1,-trichloroethane (TCA), and tetrachloroethylene (PCE) with concentrations in the range of 0.2 μg/kg to 12,000 mg/kg. The fuel hydrocarbons most frequently reported as being present at DOE sites include aromatic compounds and polyaromatic compounds such as phenanthrene, pyrene, and naphthalene. The primary sources of these semi-volatile organic compounds (SVOCs) are coal waste from coal fired electric power plants used at many of these facilities in the past and gasoline spills and leaks.

Dense non-aqueous phase liquids (DNAPLs) can migrate within the subsurface for long periods of time along a variety of pathways including fractures, macropores, and micropores. Diffusion of contaminants in the non-aqueous, aqueous, and vapor phase can occur from the fractures and macropores into the matrix of fine-textured media. As a result of these contamination processes, removal of contaminants from the subsurface and the delivery of treatment agents into and throughout contaminated regions are often hindered, making rapid and extensive remediation difficult.

With *in situ* physical/chemical treatment processes, the treatment goal is to manipulate the chemistry of the subsurface environment in such a manner that the contaminants of interest are destroyed and/or rendered non-toxic. Chemical properties that can be altered include pH, ionic strength, oxidation/reduction potential, and chemical equilibria. *In situ* contaminant destruction processes, such as chemical oxidation, alter or destroy contaminants in place and are typically applied to compounds that can be either converted to innocuous species such as CO_2 and water or can be degraded to species that are non-toxic or amenable to other *in situ* processes (i.e., bioremediation).

Hydrogen peroxide oxidation of organic compounds

Due to its widespread availability and acceptance in the water and wastewater treatment field, hydrogen peroxide (H_2O_2) has emerged as an attractive oxidant for contaminated soils. Hydrogen peroxide reacts with iron (both ferrous and ferric) in natural soils or amendments in a variety of competing reactions[1]:

$$H_2O_2 + Fe^{2+} \rightarrow OH\cdot + OH^- + Fe^{3+} \tag{1}$$
$$H_2O_2 + Fe^{3+} \rightarrow HO_2\cdot + H^+ + Fe^{2+} \tag{2}$$
$$OH\cdot + Fe^{2+} \rightarrow OH^- + Fe^{3+} \tag{3}$$
$$HO_2\cdot + Fe^{3+} \rightarrow O_2 + H^+ + Fe^{2+} \tag{4}$$
$$H_2O_2 + OH\cdot \rightarrow H_2O + HO_2\cdot \tag{5}$$

The hydroxyl free radicals formed during the iron catalyzed decomposition of hydrogen peroxide in acidic soils ($pH < \sim 6$) are speculated as being the primary oxidizing species. This reaction of hydrogen peroxide with iron to yield free radicals is commonly referred to as Fenton's process.

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Hydrogen peroxide has been used to destroy a variety of organic contaminants in soil including creosote[2], coal tar[3], pentachlorophenol (PCP)[1,4,5,6] , TCE[4,7,8], trifluralin[1], hexadecane[1], dieldrin[1], and PCE[9]. Several of these authors treated contaminated soils with H_2O_2 alone[7,8] while others supplemented their treatment systems with iron[4,6,9] or combined chemical oxidation with biological treatment[2,3]. Often the pH of the H_2O_2-soil treatment system was adjusted to 3 or less in order to achieve the optimum pH (pH = 3) reported for Fenton's reagent treatment[1].

Watts, Chen and Kenny[10] evaluated catalyzed hydrogen peroxide treatment of contaminated soil to determine if contaminant degradation occurs in the sorbed or aqueous phase. One gram quantities of hematite (α-Fe_2O_3) contaminated to 0.1 mmole/kg with chlorinated benzene compounds were treated with 30 mL of 0.1, 1.2, and 5% H_2O_2. All experiments were conducted at a pH of 3 with no iron supplementation. The authors propose that contaminant-oxidant interactions involve several complex mechanisms. These mechanisms include contaminant desorption and aqueous destruction via a hydroxyl free radical mechanism and surface catalyzed destruction of contaminants at highly oxidized surface sites. They suggest that contaminant destruction may depend on the nature of the contaminant and the availability of surface sites.

Potassium permanganate oxidation of organic compounds

Weber[11], reviewed the application of potassium permanganate ($KMnO_4$) in water treatment and noted that $KMnO_4$ is useful as a water treatment oxidant because it is a powerful oxidizer of many water impurities including phenols, Fe_2, S_2, and taste and odor producing compounds (typically unspecified organic compounds). Permanganate's attack on organic compounds is described as an oxidative attack of the functional groups and multiple bonds of organics, with the possibility of some cleavage of benzene rings.

Ladbury and Cullis[12] discuss several proposed mechanisms for permanganate oxidation in aqueous media. These mechanisms include hydrogen-atom abstraction processes where hydrogen atoms are removed from the organic compounds by hydroxyl radicals formed by permanganate via the following reaction:

$$MnO_4^- + H_2O \rightleftarrows MnO_4^{2-} + OH\cdot + H^+ \tag{6}$$

Aqueous permanganate oxidation reactions are reported as being pH dependent, with hydroxyl radical formation being favored at alkaline pH values and direct oxidation by permanganate or other ionic compounds containing Mn(III) or Mn(IV) occurring in acid or neutral solutions.

Spicher and Skrinde[13], and Cherry[14], discuss laboratory and field studies conducted using $KMnO_4$ to treat domestic water supplies. The primary objectives of these treatments were to remove taste and odor producing compounds from the drinking water, prior to distribution. Both Spicher and Cherry conducted optimimization experiments and determined the optimum pH for permanganate oxidation to be between pH 7.6 and 7.8.

Vella et al.[15], demonstrated the ability of $KMnO_4$ to oxidize phenols in an industrial wastewater to levels below regulatory limits ($< 19\ \mu g/L$) in laboratory and field scale studies.

Vella observed the formation of manganese dioxide (MnO_2) as a reaction by-product and noted the impact of MnO_2 formation on effluent turbidity. Vella et al. compared $KMnO_4$ and H_2O_2 oxidation of phenolic wastewaters and observed that $KMnO_4$ was as effective of an oxidizer and easier to handle than H_2O_2.

OBJECTIVES

Laboratory bench-scale experiments were conducted to provide a better understanding of the *in situ* chemical oxidation process. While previous work has yielded promising results regarding the successful use of H_2O_2 for treatment of organic compounds in soil, this study was conducted to evaluate other chemical oxidants such as $KMnO_4$ in addition to H_2O_2. The primary objectives of these experimental studies were to:

- compare hydrogen peroxide and potassium permanganate as chemical oxidants,
- determine the effect of soil properties, particularly pH, on *in situ* chemical oxidation treatment efficiency, and
- determine whether *in situ* chemical oxidation can effectively treat VOC and SVOC compounds similar to those reported at contaminated sites.

MATERIALS AND METHODS

Zero headspace extraction vessels

The laboratory experiments were conducted in batch mode in 130 mL zero-headspace extraction vessels (ZHEs). These reaction vessels were used to minimize the losses of the volatile and semi-volatile contaminants during treatment. The use of these apparatus to evaluate the chemical oxidation of contaminated soil is described in detail elsewhere [16,17]. In summary, artificially contaminated soil slurries were placed in the reaction vessels. Chemical oxidants were injected in the reaction vessels under gas-tight conditions, and the soils were treated for a period of either 24 h (VOC-contaminated soil) or 48 h (SVOC-contaminated soil). After treatment, samples were extracted and analyzed for contaminant concentration.

Study soils

Soil from two different DOE facilities was used in the laboratory studies. The first soil was collected from the Hanford site in Richland, WA. This soil is representative of Pasco Basin sand on which much of the DOE Hanford facility is located. This study soil was collected from the subsurface at a depth of at least 6 m to minimize the amount of humic material in the sample and is classified as a sandy soil. The second soil was collected from a DOE facility in Portsmouth, Ohio. This soil was collected from a depth of 1-3 m, and is classified as a clayey soil. The composition of the two study soils is summarized in Table 1.

Reagents

Baker Analyzed reagent grade hydrogen peroxide was purchased at a concentration of 30% and diluted with deionized (DI) water (Milli-Q Water System) to the concentrations required for treatment. Reagent grade EM Science crystalline potassium permanganate was used to prepare $KMnO_4$ solutions in DI water at least 16 h prior to use. All organic contaminants including TCE, PCE, TCA, naphthalene, phenanthrene, and pyrene were purchased as reagent grade compounds and used without further purification. The hexane used for the posttreatment organic extractions was chromatography grade.

Soil Contamination

Soil samples were contaminated under controlled conditions prior to each experimental run. It was recognized that the behavior and treatability of some organics in soils can vary depending on duration of exposure to contamination. For the purposes of this study, controlled contamination was deemed necessary and appropriate, to enable replicated experimental runs.

Prior to initiating the VOC and SVOC removal studies, ancillary studies were completed to determine the most appropriate contaminant spiking method for the study soils. These experiments revealed that an contamination time of 24 h was sufficient for VOC spiking of both soils and 16 h was sufficient time to allow the volatilization of the acetone used to prepare the SVOC spiking solutions. The contaminant equilibration studies also revealed that unacceptably high SVOC losses would occur if the equilibration time was too long or if the reaction vessels were not properly covered. In order to minimize SVOC losses the ZHEs were covered with parafilm during the contaminant equilibration period.

VOC contamination. A slurry was made from the study soils prior to contamination with VOCs (TCE, PCE, and TCA). Slurries were prepared by adding 15 and 5 mL of DI water to 15 g of dried, sieved (#10) clay and sandy soil, respectively. Larger quantities of water were required for the clay soil slurries to ensure that a homogenous, easy to mix slurry was formed. After the soil slurries were formed, VOC spiking was acheived by adding 4 mL of an aqueous VOC spiking solution. Pretreatment VOC concentration of 120, 130, and 30 mg/kg (dry wt. basis) of TCA, TCE, and PCE, respectively were achieved using this method. Immediately after VOC spiking, the reaction vessels were sealed and the contents were mixed for a period of 24 h.

SVOC contamination. Because the target SVOCs (naphthalene, phenanthrene and pyrene) were insoluble in H_2O, the study soils were contaminated with SVOC spiking solutions prepared in acetone prior to forming a slurry from the soils. After the SVOC spiking solutions were added to the study soils, the reaction vessels were covered with parafilm which was perforated in several places. The reaction vessels were placed in a fume hood overnight to allow the acetone to evaporate prior to slurry formation. Pretreatment levels of 330 mg/kg of naphthalene, phenanthrene and pyrene were achieved using this method. Soil slurries were then prepared by adding DI water to the SVOC contaminated soil using the same liquid to solid ratios used in the preparation of the VOC contaminated soil slurries.

Soil Treatment

Soil treatment was accomplished by adding 6 mL of the desired oxidant solution to the contaminated soil slurries. Oxidant solutions were injected through gas-tight fittings in the reaction vessels to avoid non-oxidative losses of the contaminants of interest. H_2O_2 solutions of 8.5 weight percent and $KMnO_4$ solutions of 5 weight percent were used for all of the chemical oxidation studies reported herein. These oxidant doses yielded $KMnO_4$ and H_2O_2 loadings of 20 and 40 g oxidant/kg soil, respectively. Control samples were also prepared and had 6 mL DI water injected instead of oxidant solutions. After oxidant addition, the reaction vessels were mixed by rotating end-over-end at 30 rpm for 24 h (VOCs) or 48 h (SVOCs), prior to sample extraction.

In order to improve H_2O_2 contaminant destruction, iron supplementation and/or pH adjustment were included as part of the soil treatment in several experiments. Iron supplementation was achieved by adding 1 mL $FeSO_4$ solution to achieve a pretreatment aqueous iron (Fe^{2+}) concentration of 5 mM. A pretreatment pH of 3 was obtained by adding 1 mL of 1 M HCl to the reaction vessels before the H_2O_2 was injected.

Sample Extraction

Hexane was added directly to the reaction vessels to extract any organics remaining after chemical oxidation treatment. One extraction using 50 mL of hexane and an extraction period of 2 h was used for the VOC studies, while two extractions of 30 and 20 mL each and a total extraction period of 20 h was used for the SVOC studies. After the extraction period, the hexane was collected and stored at 4° C in glass sample vials with teflon lined caps. All samples were analyzed for VOCs or SVOCs within 48 h of collection.

Analysis

VOCs. VOCs were analyzed by gas chromatography with a Hewlett Packard 5890 Series II gas chromatograph equipped with an electron capture detector and a Hewlett Packard HP-5 capillary column (50 m x 0.32 mm diam. x 0.52 μm df). At least one hexane blank and VOC standard (calibration check) were analyzed each analysis day. Samples were analyzed using a 1.0 μL direct injection.

SVOCs. A Shimadzu GC9a gas chromatograph equipped with a Hewlett Packard HP-1 (50 m x 0.2 mm diam. x 0.11 μm df) cross-linked methyl silicone capillary column was used for SVOC analysis. Samples were injected in 1 μL volumes by autosampler using a splitless program with a 0.5 minute split time.

Oxidants. Hydrogen peroxide concentrations were measured by idometric titration, while $KMnO_4$ concentrations were measured by arsenious trioxide titration[18]. All solutions used during the oxidant analysis were prepared with reagent grade chemicals.

RESULTS

The ability of the experimental apparatus to maintain gas-tight conditions was verified in a series of experiments with SVOCs where 97.5% recovery of dosed SVOC was observed after a period of 48 h. Duplicate experiments were conducted with both VOCs and SVOCs, and in all cases close agreement was found in the results. These findings led to the conclusion that the experimental method was valid, and the results obtained were assumed to adequately reflect the oxidant-contaminant interactions that occurred during treatment in the apparatus used. For both the VOC and SVOC studies, contaminant reduction percentages were determined by comparing contaminant concentrations in control and treated reaction vessels.

Chemical oxidation of VOCs

In Figs. 1 and 2, the VOC reduction achieved with chemical oxidation treatment is given for the clay and sandy soils. The greatest TCE and PCE reductions were observed in the soils treated with $KMnO_4$. TCE removals of 99% and 98% and PCE removals of 90% and 93% were observed in the clay and sandy soils treated with $KMnO_4$, respectively. Lower TCE and PCE removals were observed in the soils treated with H_2O_2 or H_2O_2 supplemented with iron. In the clay soil, iron supplementation (5 mM Fe^{2+}) increased TCE removal by 12% (from 76 to 86%) and PCE removal by 82% (from 12 to 68%) compared to soil treated with H_2O_2 alone. In the sandy soil, very little TCE or PCE removal (0 and 12%, respectively) was achieved with H_2O_2 alone. Iron supplementation increased TCE and PCE removals to 61 and 32%. Very little destruction of TCA was observed with either of the oxidants evaluated.

During one series of experiments (using only the clay soil) the initial TCE concentration was increased over three orders of magnitude, from 9 to 8000 mg/kg TCE, to evaluate the effect of initial contaminant concentration on chemical oxidation treatment efficiency (Figs. 3 and 4). With $KMnO_4$ treatment, the TCE removal was the same (~95%) for all of the initial TCE levels evaluated. With H_2O_2, the TCE removal was the same (~89%) for the three lower initial TCE concentrations. A decrease in TCE removal efficiency to 74% was observed at the highest TCE concentration evaluated.

The TCE residual concentrations (Fig. 4) observed during the initial concentration study, were representative of the VOC residuals measured during the treatment efficiency study. For the soils treated with $KMnO_4$, experimental runs with > 90% TCE and PCE removal percentages had residual TCE concentrations in the range of 0.3 to 9.1 mg/kg and PCE concentrations in the range of 0.8 to 6.9 mg/kg. TCA residual concentrations were in the range of 58.2 to 120 mg/kg since $KMnO_4$ was not an effective oxidant for this compound. The slightly greater TCE and PCE residual concentrations (11.3 to 43.2 mg/kg TCE and 4.5 to 21.4 mg/kg PCE) measured in the soils treated with H_2O_2 solutions were not unexpected since the VOC removal percentages (see above) were lower for these oxidants.

Chemical oxidation of SVOCs

The trends observed during the treatment of the SVOC contaminated soils were similar to those observed with the VOC contaminated soil, with the exception of H_2O_2 treatment in the sandy soil. The SVOC reductions observed in the clay and sandy soils treated with H_2O_2 and $KMnO_4$ are given in Figs. 5 and 6. Complete reduction of the three SVOCs was observed in both the clay and sandy soils treated with $KMnO_4$. The H_2O_2 treatments were more successful in the clay soil where total SVOC removals of 47 and 98% were achieved with the H_2O_2 and $H_2O_2 + Fe^{2+}$, respectively. Lower SVOC treatment efficiencies were observed in the sandy soil with the H_2O_2 treatments.

An additional experiment was conducted to determine if adjusting the system pH to 3, in addition to adding supplemental iron, would improve H_2O_2 efficiency in the sandy soil. Although the results of this test were inconclusive (Fig. 7), the results indicate that pH adjustment did improve SVOC removal efficiency significantly.

DISCUSSION

For both contaminant groups and soil types evaluated, $KMnO_4$ effectively removed over 90% of the contaminants, with the exception of TCA. H_2O_2 destruction of the contaminants was more variable and appeared to be dependent on iron concentration, pH, and perhaps initial contaminant concentration. TCA appears to be resistant to oxidative destruction with the oxidants evaluated. This may be because the carbon-carbon bond is saturated, and the initiation step for the expected chain organic destruction reactions may not be thermodynamically favorable.

Effect of iron addition of H_2O_2 treatment efficiency

With iron addition, the H_2O_2 contaminant destruction efficiency improved in both of the study soils. Although contaminant destruction improved with iron supplementation of H_2O_2, greater contaminant destruction was observed with $KMnO_4$ treatment for both soils and contaminants groups, with the exception of the naphthalene in clay soils. In the clay soil, iron supplementation increased the H_2O_2 treatment efficiency to within an average 8% of the treatment efficiencies achieved in the clay soils treated with $KMnO_4$. However, even with iron supplementation there was a considerable difference between the H_2O_2 and $KMnO_4$ treatment efficiencies (average difference = 65%) in the sandy soils. The sandy soil had the lowest initial Fe level (1,900 mg/kg free Fe oxides) of the soils treated, and if contaminant destruction requires the formation of Fenton's reagent, the native Fe levels in the soil plus the supplemental Fe may have been insufficient. Other factors in addition to iron concentration, such as pH, may also have affected H_2O_2 treatment efficiency in the sandy soil.

Effect of pH

The optimum pH range for chemical oxidation is considerably different for the two oxidants evaluated. While $KMnO_4$ has an alkaline optimum pH in the range of 7.6-7.8, Fenton's reagent has an acidic optimum pH of ~ 3. The effect of the two oxidants on the pH of the treatment systems was monitored to determine if the optimum pH for contaminant destruction was achieved after oxidant addition. The addition of $KMnO_4$ to the clay and sandy soil slurries reduced the pH to 5.0 and 7.4, respectively, from original values of pH 5.5 and 8.7. The $KMnO_4$-sandy soil slurries closely approached the optimum pH, while the system pH was lower than desired in the clay soil. *In situ* treatment with $KMnO_4$ may not require pH adjustment, since high contaminant reductions were achieved with $KMnO_4$ in soils that in some cases had pH's lower than the optimum pH.

H_2O_2 addition reduced the pH of clay and sandy soil to 5.7 and 8.6 respectively. In both soils, H_2O_2 was unable to reduce to pH of the soil slurries to within the optimum range for H_2O_2 treatment. The addition of 5 mM iron also did not reduce the pH to the desired range either. H_2O_2 treatment of some contaminants in alkaline soils may require pH adjustment to achieve high contaminant reductions.

Effect of initial contaminant concentration

The experimental results indicate while $KMnO_4$ contaminant reduction appears to be independent of initial contaminant concentration, H_2O_2 contaminant destruction may be affected by the initial contaminant concentration. Previously, it had been reported that the *in situ* chemical oxidation of TCE with H_2O_2 was independent of initial TCE concentration.[8] The rationale for this hypothesis was that contaminant particles were oxidized incidentally as the non-specific hydroxyl radicals (OH•) randomly oxidized any material, including soil organic matter, that was available for reaction. The current data suggest that this hypothesis may only apply when the soil organic content far exceeds the contaminant concentration, and an upper limit may exist beyond which treatment efficiency may depend on initial contaminant concentration. Further studies would need to be conducted to determine the effect of contaminant concentration on chemical oxidation destruction efficiency at higher contamination levels.

CONCLUSIONS

The results of these experiments demonstrate that the chemical oxidation of VOCs and SVOCs in contaminated soils can be achieved using $KMnO_4$ or H_2O_2 solutions. VOCs require less time for removal than SVOCs. Of the two oxidant solutions evaluated $KMnO_4$ was found to have the highest overall treatment efficiency for both the VOC and SVOC compounds treated. $KMnO_4$ treatment efficiency appeared to be unaffected by the soil composition or the initial contaminant concentration. Hydrogen peroxide treatment efficiency, in contrast, appeared to be dependent on soil properties including the soil iron content and pH. Supplementing the H_2O_2 solutions with Fe^{2+} (5 mM) or adjusting the pH to <3 improved the contaminant reduction achieved with H_2O_2.

While the present research has demonstrated that the oxidants of interest are applicable to relevant waste streams, further research is required before this technology can be widely applied as an *in situ* remediation technique. Studies should be conducted to optimize the chemical oxidant dose and to evaluate process modifications that may allow the treatment of TCA contaminated soil or improve the H_2O_2 treatment efficiency in low iron, high pH soils. Key areas for future research include the delivery and distribution of chemical oxidant solutions in the subsurface and the effect of *in situ* chemical oxidation on soil composition and structure. The persistence of chemical oxidants *in situ* may also require consideration when permitting and designing field applications. Field demonstrations conducted to date suggest that under certain conditions the injection of H_2O_2 and/or $KMnO_4$ will meet with regulatory acceptance as long as appropriate controls and monitoring are implemented.[19]

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Table 1. Composition of soils used in chemical oxidation study.

Parameter	Soil I Hanford Site	Soil II Portsmouth site
Particle Size Distribution	91% Sand 9% Silt and Clay	63% Sand 37% Silt and Clay
Cation Exchange Capacity (CEC)	2.80 meq/100g	17.47 meq/100g
Soil pH	8.7 in DI Water	5.7 in DI Water
Free Iron Oxides	1,937 mg/kg	23,311 mg/kg
Amorphous Iron Oxides	1,620 mg/kg	1,353 mg/kg
Water Content	5.2 wt%	22.3 wt%

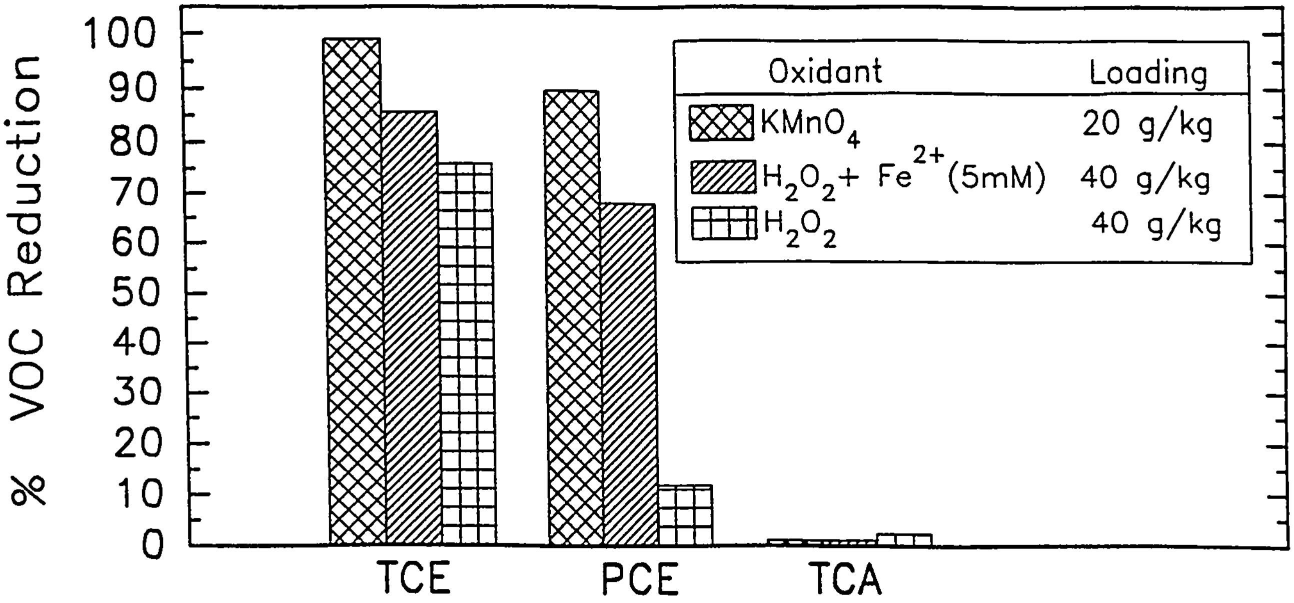

Figure 1. VOC reduction observed in clay soil treated 24 h with $KMnO_4$, H_2O_2, or H_2O_2 + iron. Initial contaminant concentrations (mg/kg): TCE=130, PCE = 30, TCA=130.

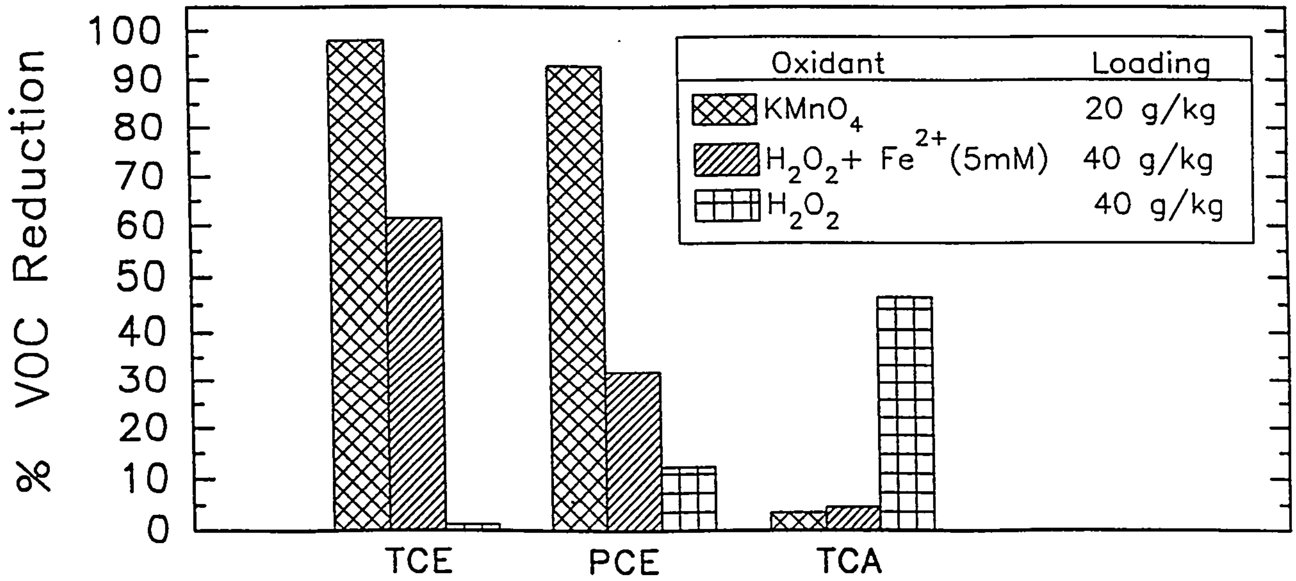

Figure 2. VOC reduction observed in sandy soil treated 24 h with $KMnO_4$, H_2O_2 + iron, or H_2O_2. Initial contaminant concentrations (mg/kg): TCE=120, PCE=30, TCA=130.

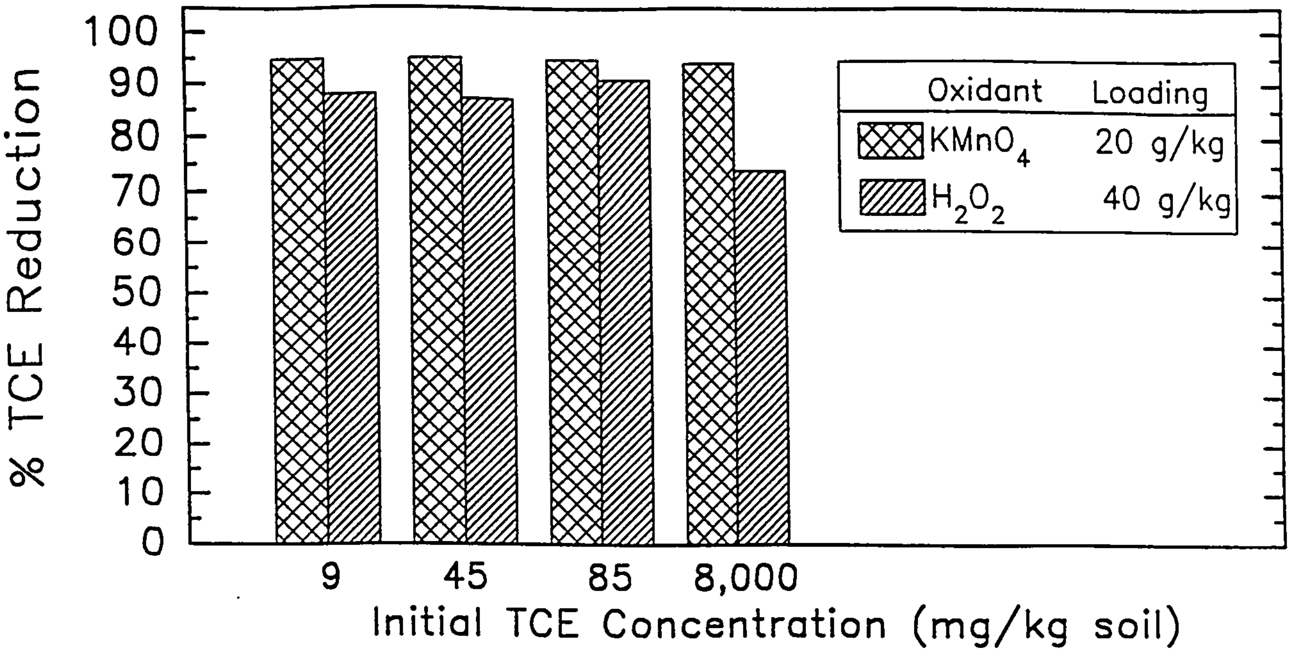

Figure 3. Effect of initial contaminant concentration on chemical oxidation treatment efficiency.

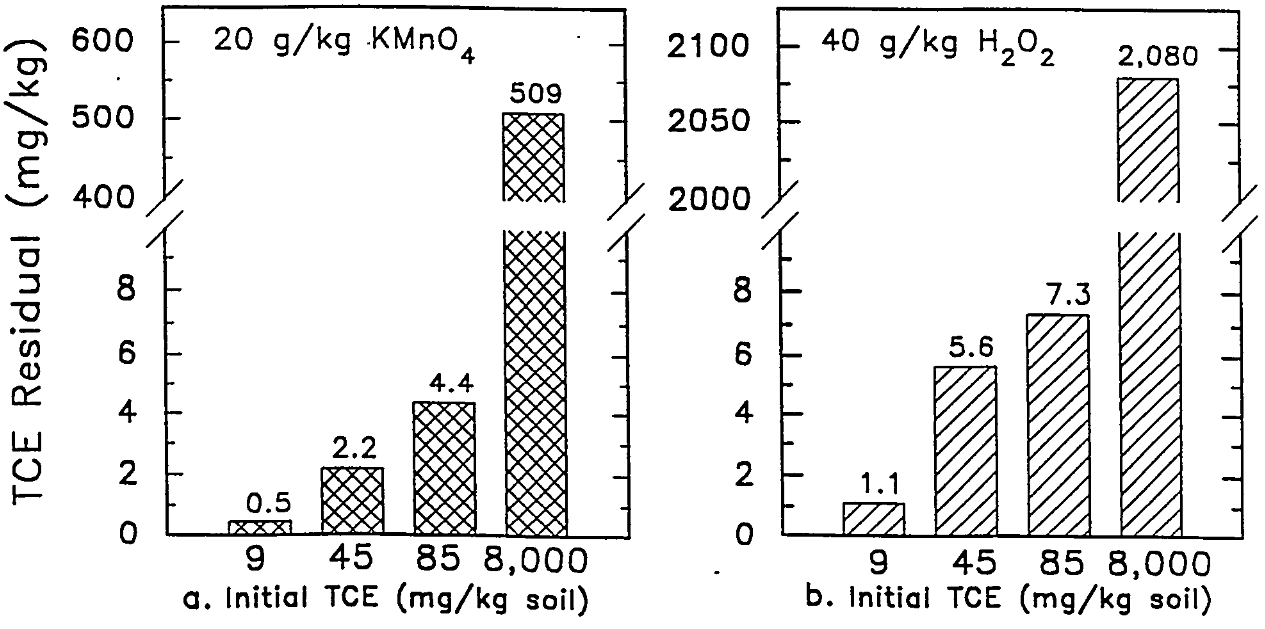

Figure 4. TCE concentration after chemical oxidation.

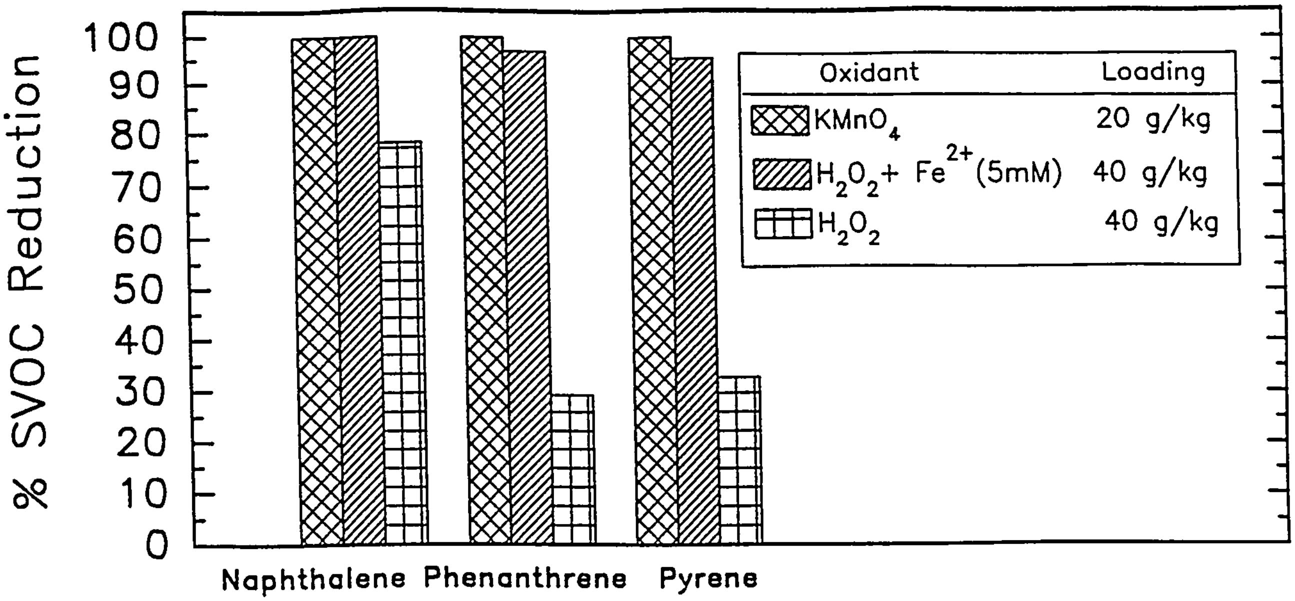

Figure 5. SVOC reduction observed in clay soil treated 48 h with $KMnO_4$, H_2O_2, or H_2O_2 + iron. Initial contaminant concentrations (mg/kg): naphthalene=330, phenanthrene=330, pyrene=330.

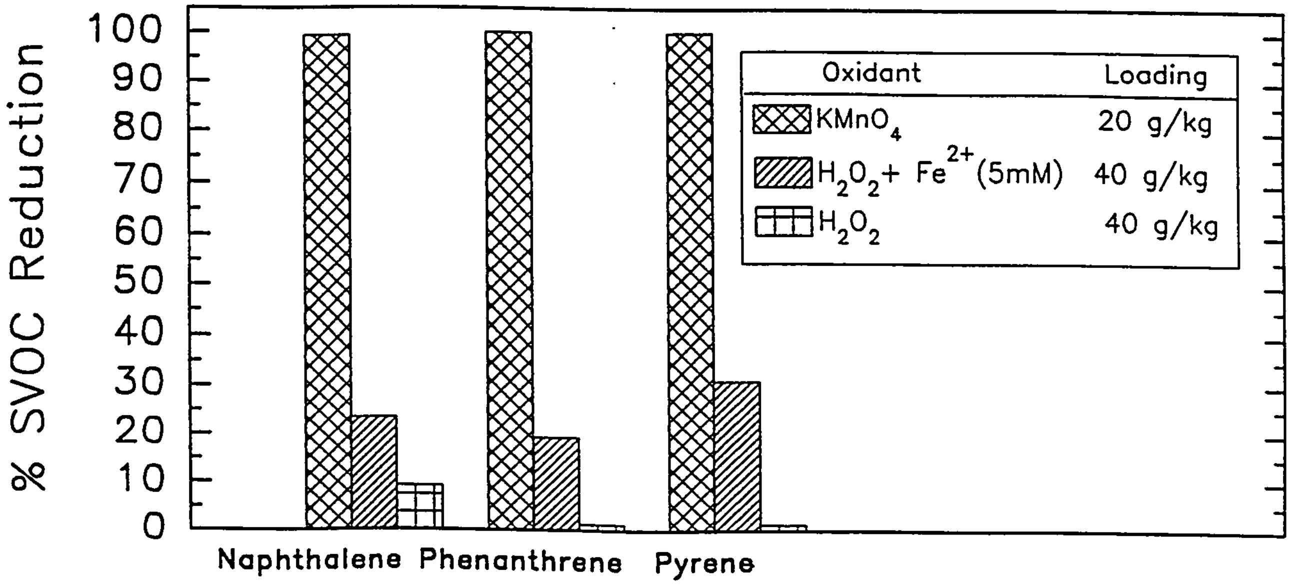

Figure 6. SVOC reduction observed in sandy soil treated 48 h with $KMnO_4$, H_2O_2 + iron, or H_2O_2. Initial contaminant concentrations (mg/kg): naphthalene=330, phenanthrene=330, pyrene=330.

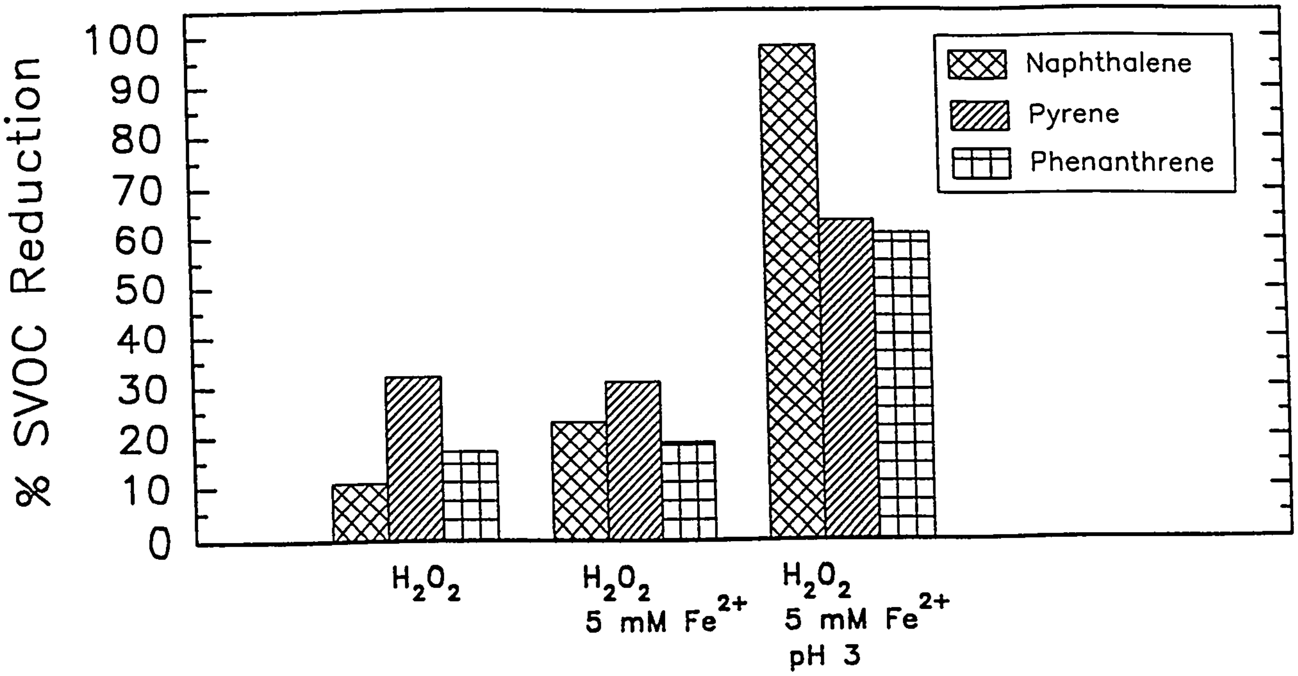

Figure 7. Effect of pH adjustment and iron supplementation on H_2O_2 treatment (30 g/kg) of SVOC contaminated sandy soil.

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