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APPLICATION OF FENTON'S REAGENT AS A PRETREATMENT STEP IN BIOLOGICAL DEGRADATION OF POLYAROMATIC HYDROCARBONS

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ABSTRACT

Fenton's reagent (H_2O_2 and Fe^{++}) has been used for chemical oxidation of numerous organic compounds in water treatment schemes. In this study, the Institute of Gas Technology (IGT) applied Fenton's treatment to polynuclear aromatic hydrocarbons (PAHs) and PAH-contaminated soils. Fenton's treatment was very reactive with PAHs, causing rapid modification of the parental compounds to oxidized products and complete degradation to CO_2. This treatment was more effective on chemically reactive PAHs, such as benzo(a)pyrene and phenanthrene. Important parameters and conditions for Fenton's treatment of PAHs in solution and soil matrices have been identified. As much as 99% of the PAHs on soil matrices can be removed by treatment with Fenton's reagent.

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INTRODUCTION

Organopollutants are a serious concern in the environment, and biological degradation (bioremediation) is often thought of as a permanent solution to these problems. In many cases, bioremediation is very effective and the most economical process, but is not very predictable when applied to complex and mixed wastes in a traditional fashion.(2,24) Bioremediaton alone is often inefficient and ineffective because of mass transfer problems -- when waste material is unavailable to microbes, or because of the toxic nature of the hazardous substances.(14,15, 23,24) An integrated chemical and biological treatment process might be able to overcome the limitation of some of the existing remedial techniques.

Chemical oxidation, involving the use of chemical oxidants for the degradation of organic compounds such as peroxide (H_2O_2), chlorine, potassium permanganate, chlorine dioxide, ozone (O_3), and ultraviolet light (UV), has been used for many years for disinfection and treatment of organic contaminants in groundwater and wastewaters. However, some problems have been encountered with the use of some of these chemical oxidants. Using chlorine may lead to the formation of volatile organics (for example, chloroform) and chlorinated phenolics when treating phenols. Although these treatments are very clean processes, they are limited in both the number of compounds and the types of waste streams that they can treat.

The recent use of UV light-catalyzed O_3 plus H_2O_2 (UV/ oxidation) for water treatment (1,8,10,12,16,18,22) overcomes some of these limitations. UV/oxidation, however, has high capital and operating costs, due to limited ozone solubility in water and the required tailgas scrubbing to treat unreacted O_3. More important to the remediation of contaminated soils, the use of UV/oxidation in soil or soil slurries will probably be limited because of the optical properties of the reaction media. UV/ oxidation systems appear to be restricted to 1% or lower levels of toxic compounds.(38) Therefore, this system is not amenable to bulky wastes.

A review of the literature reveals a number of basic studies using Fenton's reagent or Fenton-like reactions on organic compounds.(6,17,19,25,26,28) Examples of the use of Fenton's reagent or Fenton-like reactions in wastewater treatment are also numerous.(4,9,11,27) They have been used to oxidize phenol and other benzene derivatives and can also be used to reduce chemical oxygen demand (COD) and biological oxygen demand (BOD) in wastewaters from a number of industries.(2,5,7,11) In one study, a biologically treated waste stream was chemically treated using Fenton's reagent to reduce COD levels and then biologically treated again.(2) These studies show that no additional pollution results from the Fenton's reagent process itself, and capital equipment costs for Fenton's reagent treatment are low.

The Institute of Gas Technology (IGT) has been investigating the feasibility of chemically treating polynuclear aromatic hydrocarbons (PAHs) present on soils with a Fenton's-type reaction. These questions must be answered in this research: How effective is this chemical treatment in removing and degrading PAHs, and how does the presence of other organic materials affect the ability of this chemical treatment to react with PAHs?

Fenton's reagent appears to be an effective means of treating PAHs in solution and on soils. The presence of other organic material appears to have minimal effect on PAH degradation by this reagent. Important parameters and conditions for Fenton's treatment of PAHs have been identified. Kinetics and possible treatment endpoints have been determined for several PAHs. The degradation of as much as 99% of the PAHs on soils has been demonstrated.

MATERIALS AND METHODS

Chemical Treatment

^{14}C-labelled PAHs in 10 ml of water or buffer with 10 mM $FeSO_4$ were added to a 125-ml flask sealed with a flushing stopper (Figure 1). H_2O_2 was added to the flask via a syringe. The flask was shaken at 150 rpm typically for 3 hours.

CO_2 Trapping

Flasks with Fenton's reagent-treated PAHs were flushed with air for 20 to 30 minutes at a flow rate of 10 ml/min. The $^{14}CO_2$ was trapped in Carbosorb (TM, Packard Instrument Company), combined with Permafluor V (TM, Packard Instrument Company), and counted in a liquid scintillation counter (LSC). Replicates of three were used to get statistically acceptable data. A "no treatment control" was run for comparison.

Volatile Organic Trapping

An Amberlite (XAD-4) column was used to trap volatile compounds. The volatile trap consists of approximately 2 g of clean resin packed in a glass tube with glass wool plugs on either end. At the end of, or at various time intervals during, the experiment the columns were eluted with either a CH_2Cl_2 or Permafluor V scintillant and counted by an LSC.

Residual Organic Determination

After the reaction flask headspace was flushed, the residual organic material was extracted with 30 ml of dichloromethane.

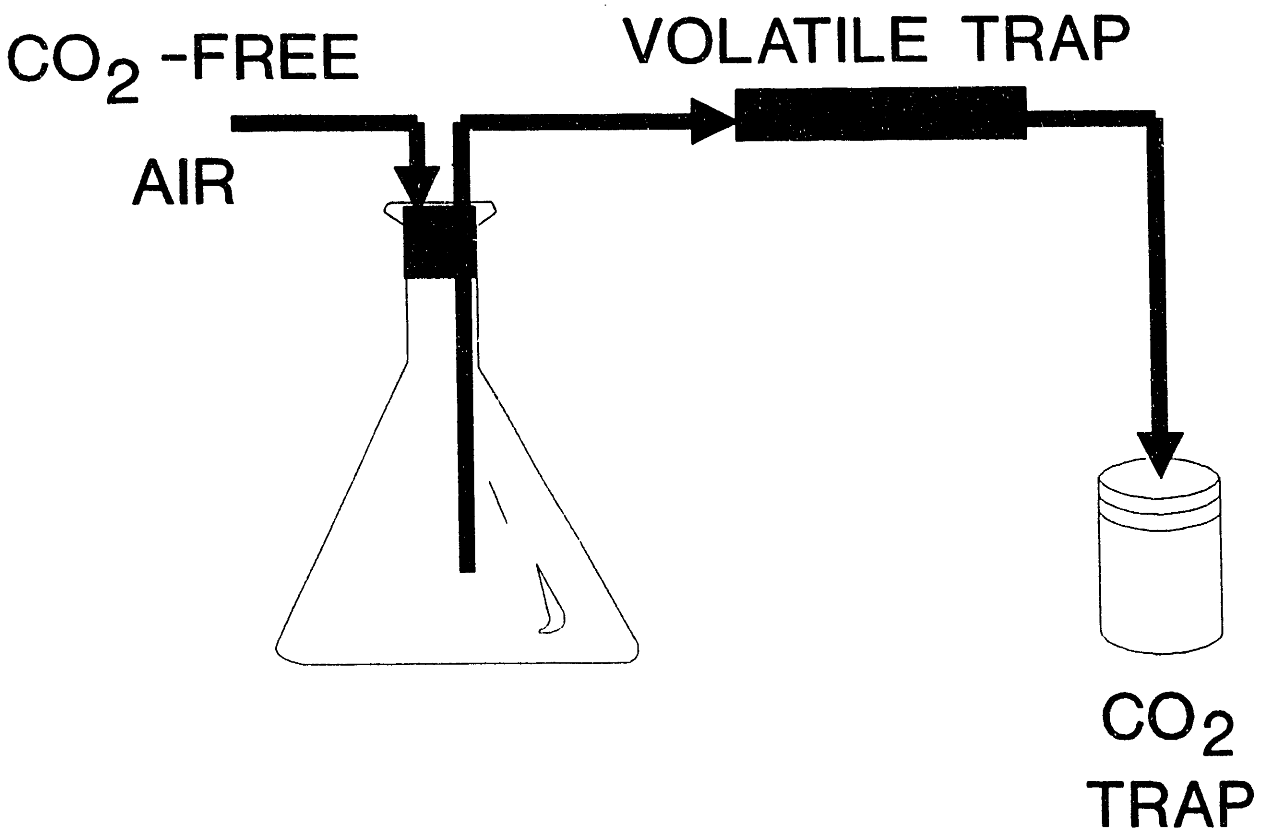


Figure 1. FLUSHING MANIFOLD

Two ml of the dichloromethane layer was combined with 10 ml of Permafluor V and counted in an LSC. Triplicate determinations were used to get statistically acceptable data.

C_{18}-Reverse Phase HPLC

Differentiation of parent and transformed products was determined by C_{18}-reverse phase HPLC. Following EPA method 8310, an 100% acetonitrile mobile phase at 1.5 ml/min and an Adsorbosphere C_{18} 5µ (150 mm x 4.6 mm) was used to separate PAHs and oxidative products.

GC/MS Analysis

Contaminated and decontaminated soils were extracted by EPA Method 3540. Hydrocarbon concentrations in the soil Soxhlet extracts were determined by capillary column GC/MS analyses (EPA Methods 8100 and 8270). For screening tests, extraction efficiencies were not determined for all contaminants but only for representative contaminants present in high concentrations. To ensure data reliability, replicate tests were conducted in all extraction and separation test groups.

Liquids containing waste materials were extracted using EPA Method 3510 followed by GC/MS analysis. The concentration of waste organics in the extract was measured by capillary GC/MS of replicate samples by the most appropriate method for the waste.

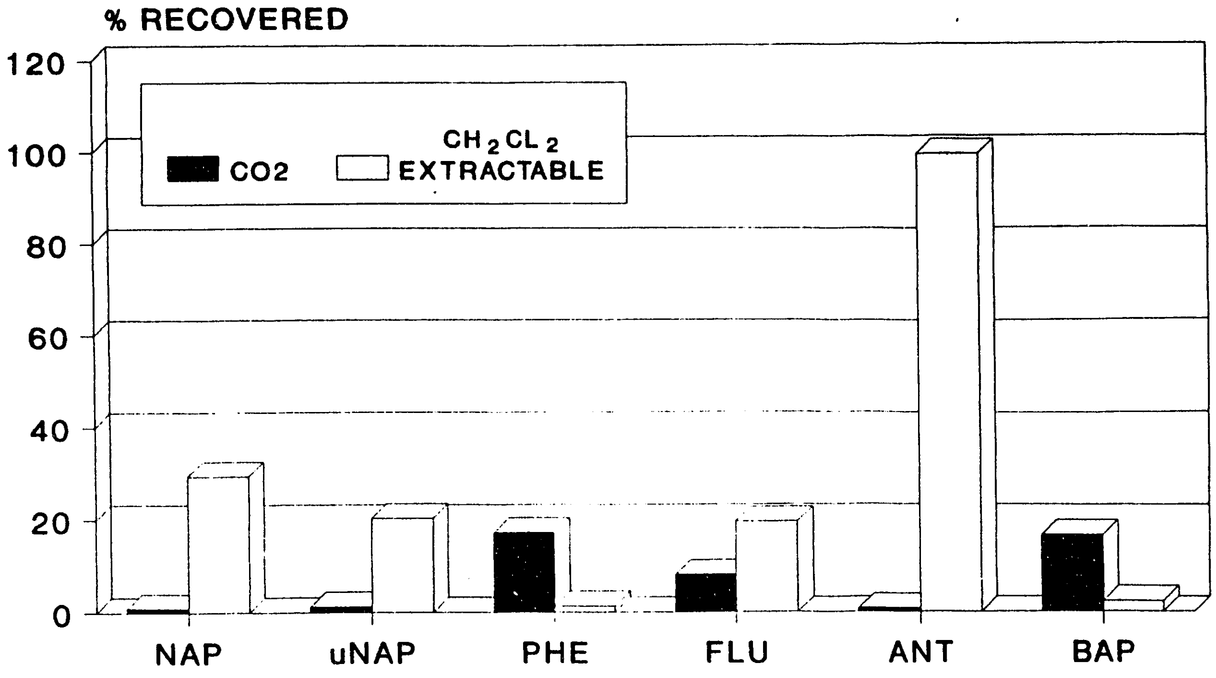
RESULTS

Important Parameters and Conditions for Fenton's Treatment of PAHs

Mineralization of various PAHs by Fenton's reagent was determined with 5% H_2O_2 and 10 mM $FeSO_4$ after 3 hours of reaction time, as depicted in Figure 2. The amount of methylene chloride extractable is also shown. Benzo(a)pyrene (BaP) and phenanthrene (PHE) had similar reactivities with Fenton's reagent, as judged by total destruction to CO_2. However, the Fenton's reagent is also reactive with other PAHs, such as NAP and ANT. C_{18}-reverse phase HPLC analysis indicates that products more polar than the parent compound are being produced with both NAP and ANT. These products are probably oxidative products, and because some of them are water-soluble, they would be amenable to rapid biological degradation. The effect of H_2O_2 concentration on BaP mineralization by Fenton's reagent is shown in Figure 3. The amount of mineralization increased linearly with the amount of H_2O_2 added, following first-order kinetics. Up to 43% of the BaP is recovered as CO_2 with 10% H_2O_2. Several experiments were conducted to determine more precisely the kinetics of the oxidation of PAHs by Fenton's reagent. Figure 4 indicates that the majority of CO_2 production from ^{14}C-BaP occurs between 10 minutes and 1 hour; however, significant activity occurs between 1 and 5 hours.

We have examined the effects of pH on the Fenton's reagents degradation of PAHs, as indicated in Figure 5. Degradation of BaP by Fenton's reagent is greatest under acidic conditions (pH ~4.0). However, recovery of CH_2Cl_2 extractable organics increased at a higher pH. The reason for this is unclear. The effect of temperature on BaP mineralization by Fenton's reagent is shown in Figure 6. As expected for an exothermic reaction, mineralization is favored at lower temperatures. Interestingly, at 4°C, mineralization is inhibited, but considerable modification of the parent compound is evident by the loss of approximately 55% of the extractable parent BaP. The effect of different catalytic salts on BaP mineralization by Fenton's reagent is shown in Figure 7. Cu^{++} is described in the literature as an alternative salt to Fe^{++} in the Fenton's reaction.(28) Our results show that, by itself, Cu^{++} is not effective but in combination with Fe^{++} it enhances mineralization by 2% to 3% over Fe^{++} alone, which is not statistically significant.

The effect on the mineralization of BaP of other organic material, such as glucose, cellulose, or lignin (a humic material), was also examined, as shown in Table 1. Interference



BAP = Benzo(a)pyrene; NAP = Naphthalene; u = Uniformly labelled; FLU = Fluorene; ANT = Anthracene; PHE = Phenanthrene

Figure 2. MINERALIZATION OF VARIOUS PAHs BY FENTON'S REAGENT (5% H_2O_2; 3 Hours)

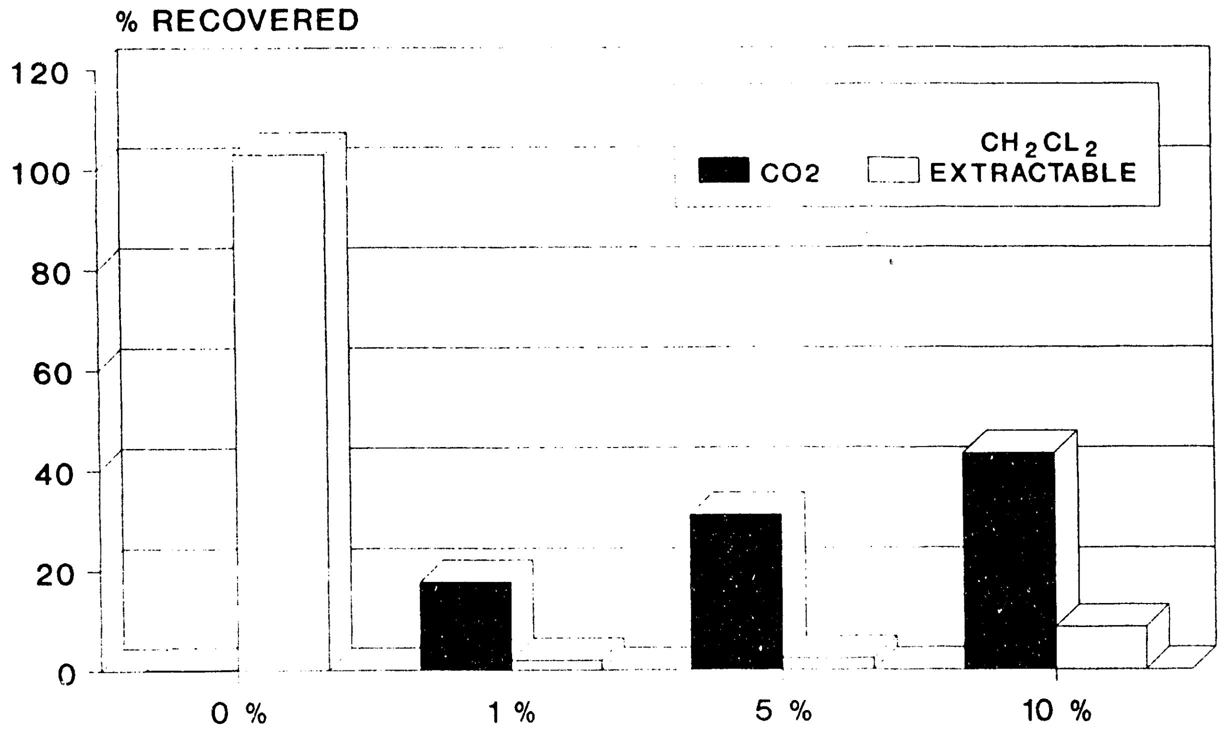


Figure 3. THE EFFECT OF H_2O_2 CONCENTRATION ON BENZO(A)PYRENE MINERALIZATION BY FENTON'S REAGENT (3 Hours)

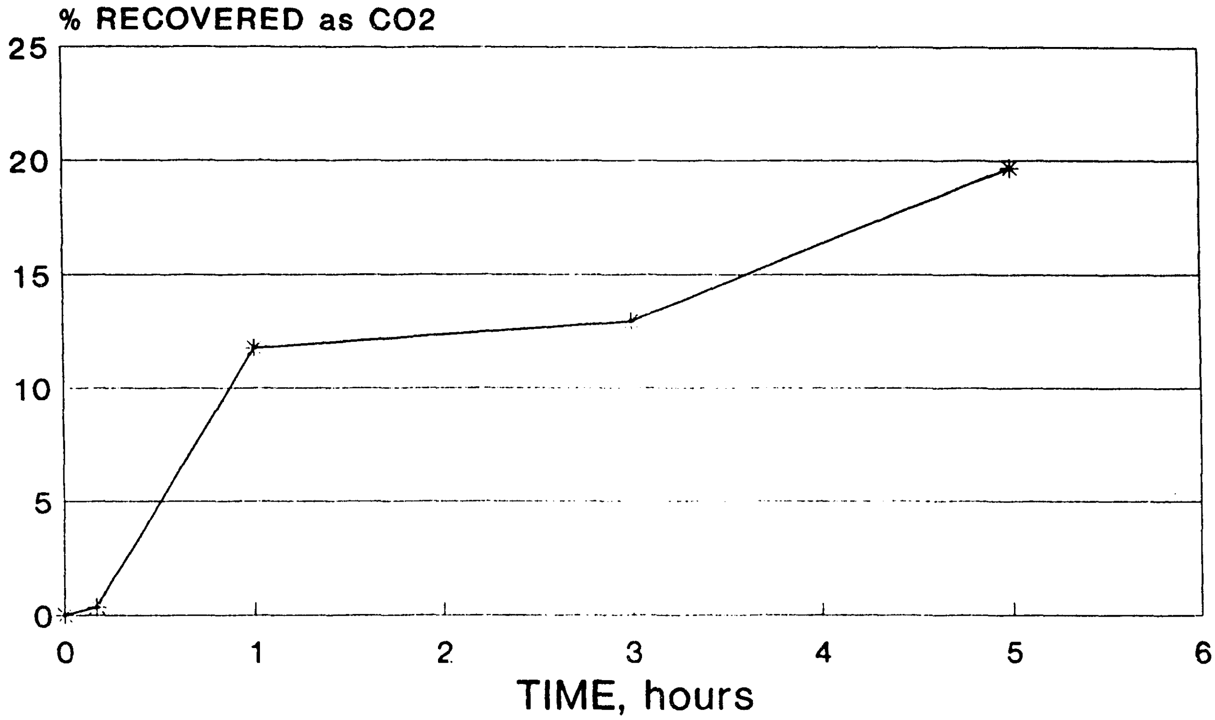


Figure 4. KINETICS OF MINERALIZATION OF BENZO(A)PYRENE BY FENTON'S REAGENT (5% H_2O_2; pH = 4)

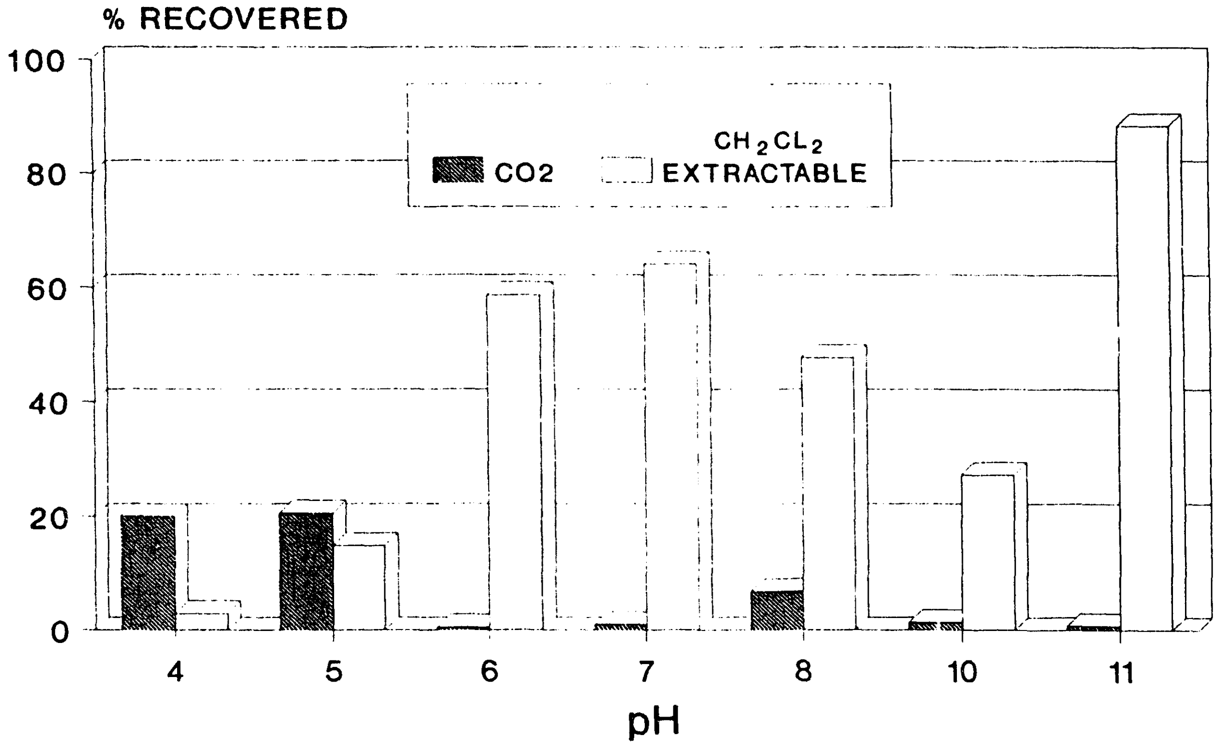


Figure 5. THE EFFECT OF pH ON MINERALIZATION OF BENZO(A)PYRENE BY FENTON'S REAGENT (5% H_2O_2; 3 hours)

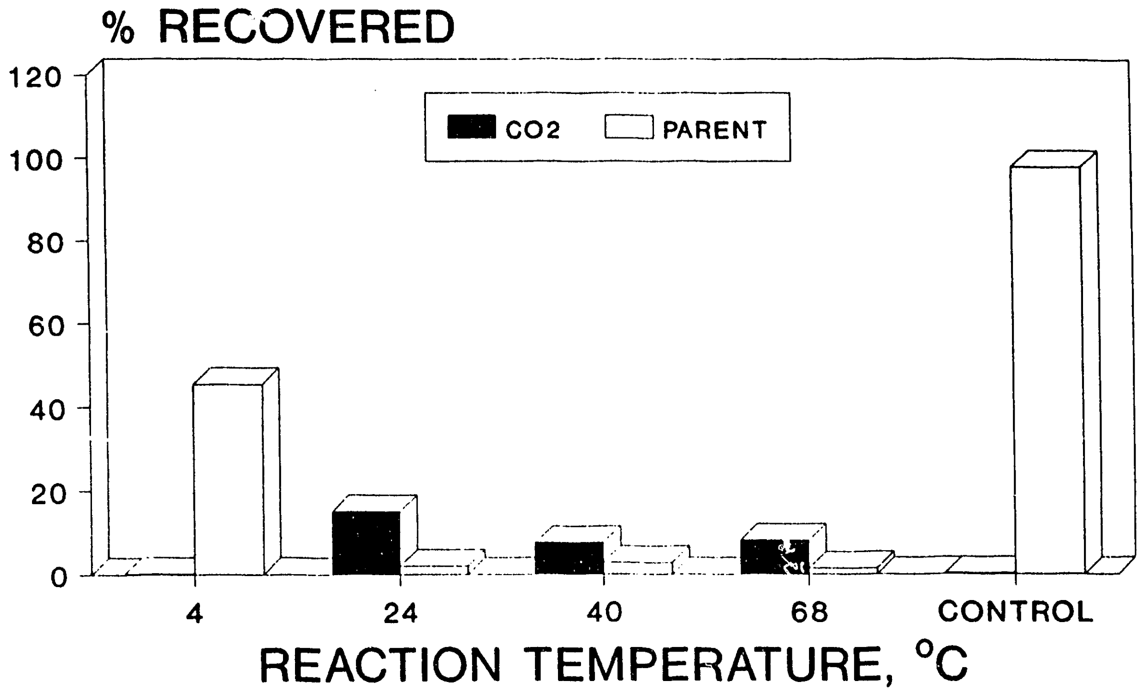


Figure 6. THE EFFECT OF TEMPERATURE ON BENZO(A)PYRENE MINERALIZATION BY FENTON'S REAGENT (5% H_2O_2; 3 hours)

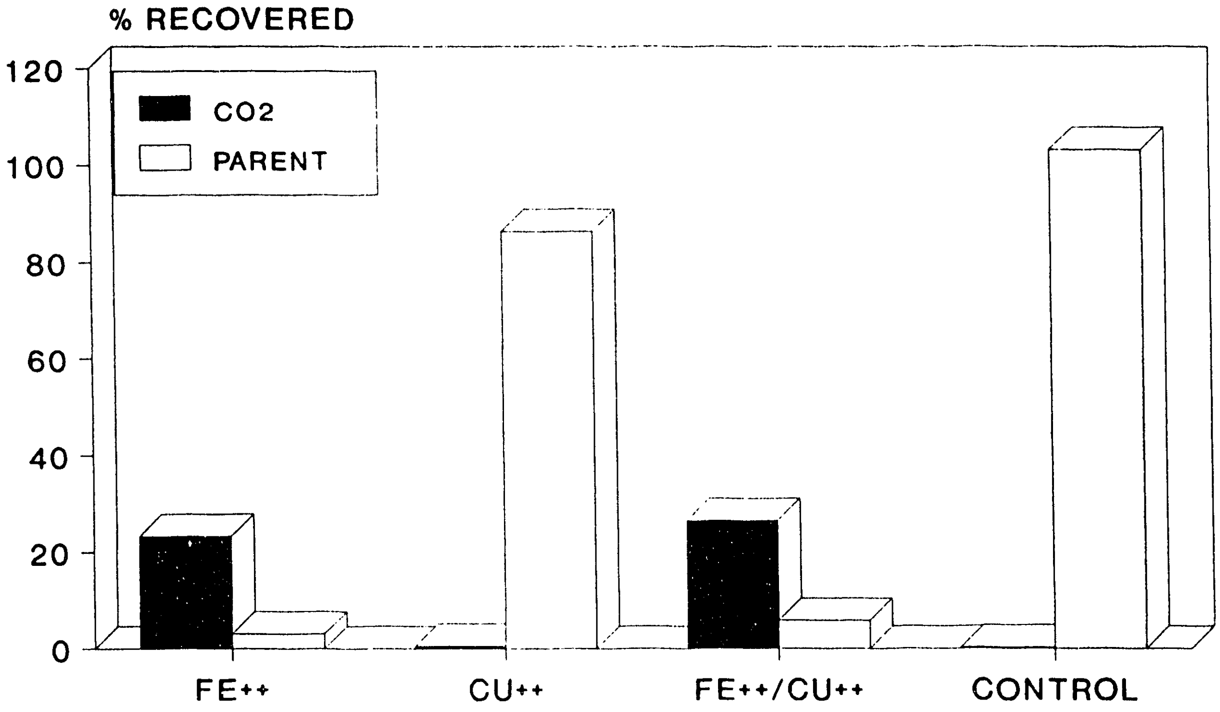


Figure 7. THE EFFECT OF CATALYTIC SALTS ON BENZO(A)PYRENE MINERALIZATION BY FENTON'S REAGENT (5% H_2O_2; 3 hours)

Table 1. THE EFFECT OF ORGANICS ON MINERALIZATION OF BENZO(A)PYRENE BY FENTON'S REAGENT*

Organic Compound	Concentration, w/v %	% Inhibition
Glucose	1	5
	5	27
	10	66
Cellulose	0.1	5
	10	68
Lignin	0.1	23
	10	70

* 5% H_2O_2 for 3 hours.

of mineralization was seen when 5% to 10% w/v of these organic materials was added. All organic material appeared to inhibit mineralization to the same extent at a concentration of 10% (w/v).

Several experiments with virgin sand laced with ^{14}C-BaP were conducted. As shown earlier, the extent of oxidation of the BaP was determined by the amount of H_2O_2 added. Figure 8 shows some characteristic results with BaP-laced sand (10 g) to which 2 ml of H_2O_2 (33% solution) was added. Typically, 25% of the PAH was recovered as CO_2, 50% as an oxidized nonpolar (methylene chloride extractable) compound, and 12% as polar (water-phase product) oxidized products. An especially surprising result was the quick and complete removal of parent PAHs from both aqueous and solid matrices. HPLC separation of Fenton's reagent-treated BaP attached to sand indicates that no ^{14}C-labelled compounds could be found to co-elute with known BaP standards. However, more polar ^{14}C-labelled compounds are seen in Figure 9. With additional oxidation steps (5% H_2O_2 per step), these oxidation products also started to disappear.

Because this treatment process will benefit from reduced H_2O_2 costs, the effect of H_2O_2 concentration in BaP degradation on sand by Fenton's reagent was studied, as shown in Figure 10. As in the liquid studies, mineralization increased linearly with increases in H_2O_2. However, a more complete material balance was achieved by extracting the sand with methylene chloride. As mineralization increased, the amount of nonpolar and polar ^{14}C-labelled compounds decreased. Additionally, the nonpolar compounds can be divided into parental and more polar compounds. As H_2O_2 concentration increased, the amount of this oxidized product increased and the parental compound decreased.

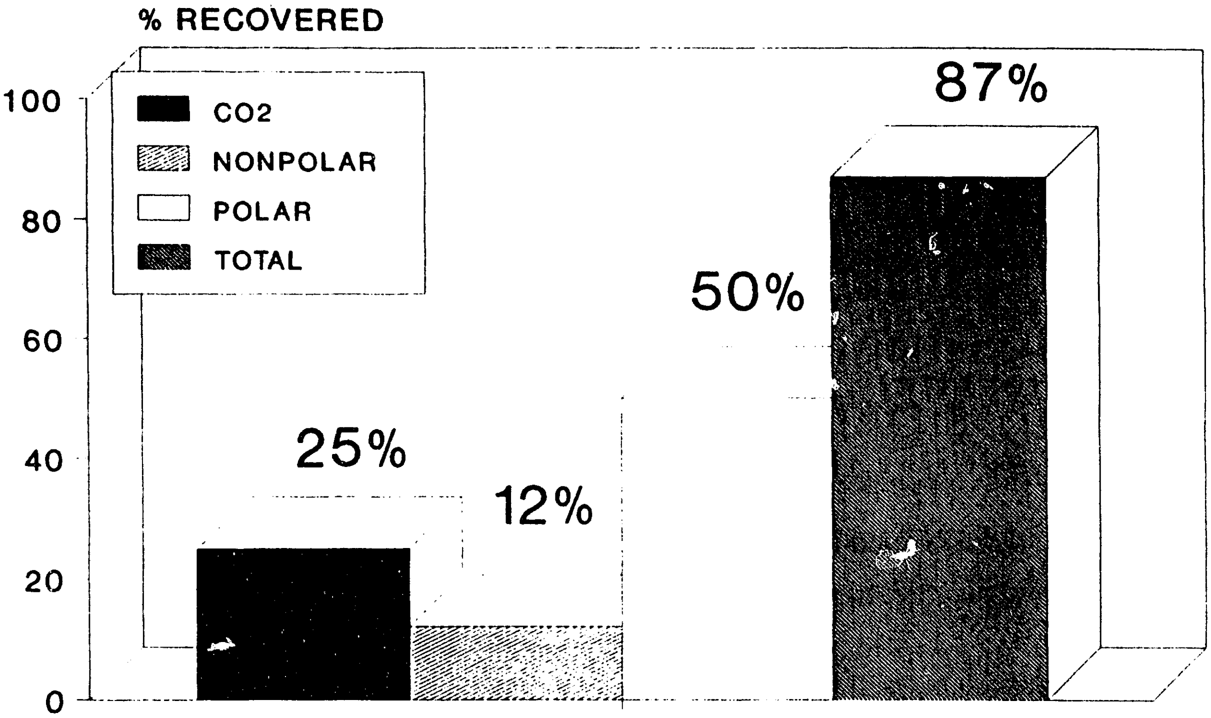


Figure 8. THE EXTENT OF OXIDATION BY FENTON'S TREATMENT OF ^{14}C-BENZO(A)PYRENE ON A SAND MATRIX (10% H_2O_2; 3 Hours)

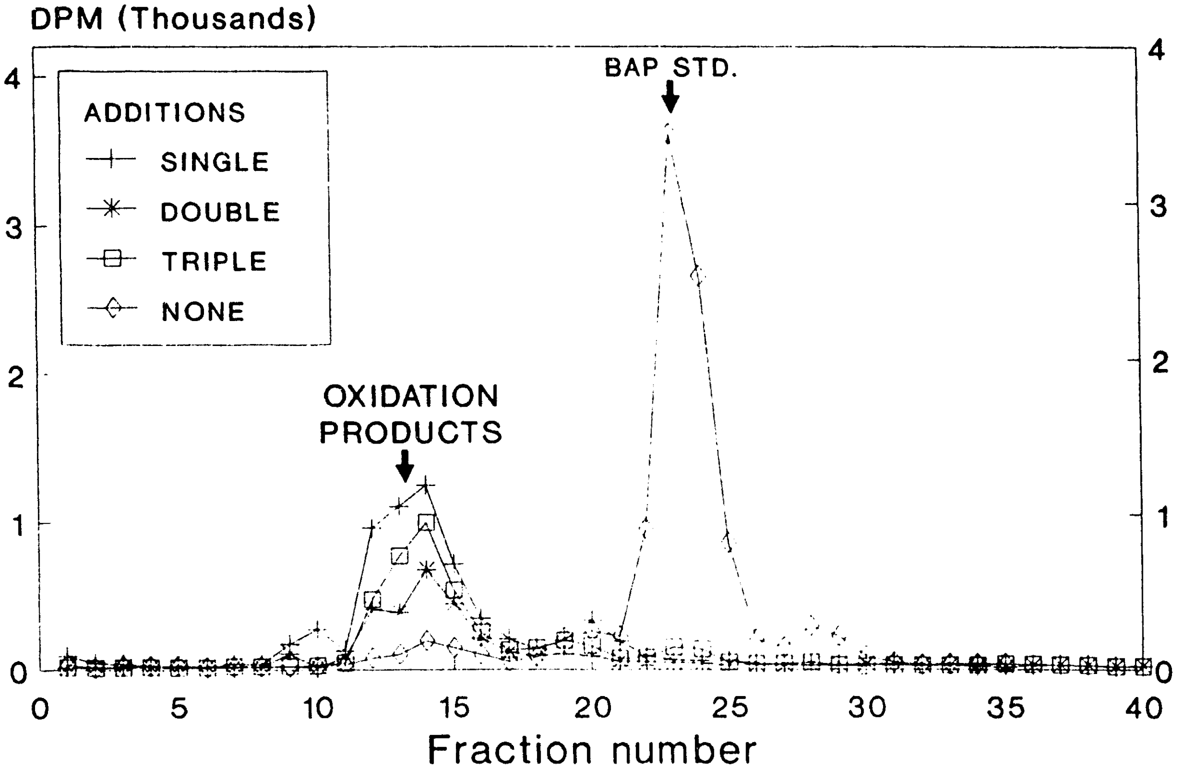
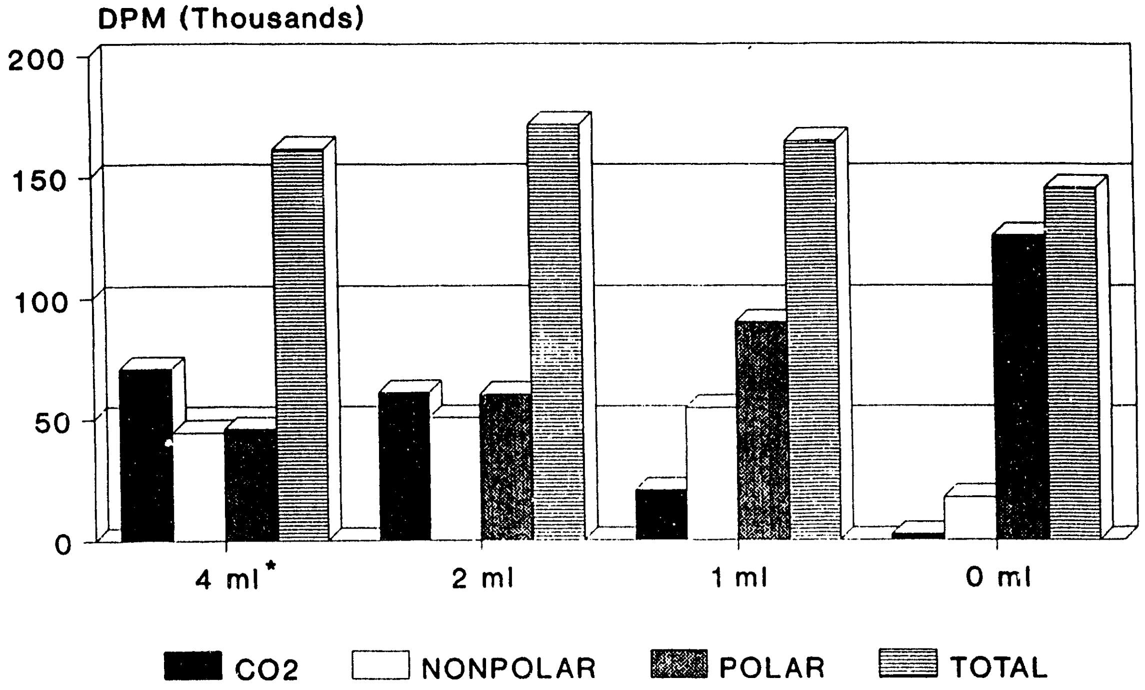


Figure 9. C_{18}-HPLC SEPARATION OF FENTON'S REAGENT-TREATED BENZO(A)PYRENE ATTACHED TO SAND



* ml of H_2O_2 added to 10 g of sand.

Figure 10. THE EFFECT OF H_2O_2 CONCENTRATION ON BENZO(A)PYRENE MINERALIZATION ON SAND BY FENTON'S REAGENT

Figure 11 shows the removal of PAHs achieved on sandy soil contaminated with town gas waste in a slurry (20% solids) of 20 mM $FeSO_4$ at pH 4.5 to which H_2O_2 was added over 16 hours, up to a final concentration of 10% by weight H_2O_2. Most PAHs were completely removed, including PAHs as large as six rings. Also, the addition of 5% (v/v) methanol dramatically enhanced the removal of PAHs.

Figure 12 shows the result of repetitive batch Fenton's reagent treatment on a contaminated sandy soil. In this treatment, H_2O_2 was added on 4 consecutive days in batch additions instead of slowly over a 16-hour period as in the previous sample. Even with four times the H_2O_2 added, 88% of the PAHs were removed, compared with 99% removal with slow, continuous addition.

Finally, Figure 13 shows the effects of Fenton's treatment on a contaminated soil that was previously subjected to biological degradation. Repetitive additions of H_2O_2 over 4 consecutive days removed an additional 6000 ppm of PAHs from this soil.

DISCUSSION

Fenton's reagent appears to be an effective means of treating PAHs in solution and on soils. This treatment rapidly oxidizes PAHs to either water-soluble compounds or methylene

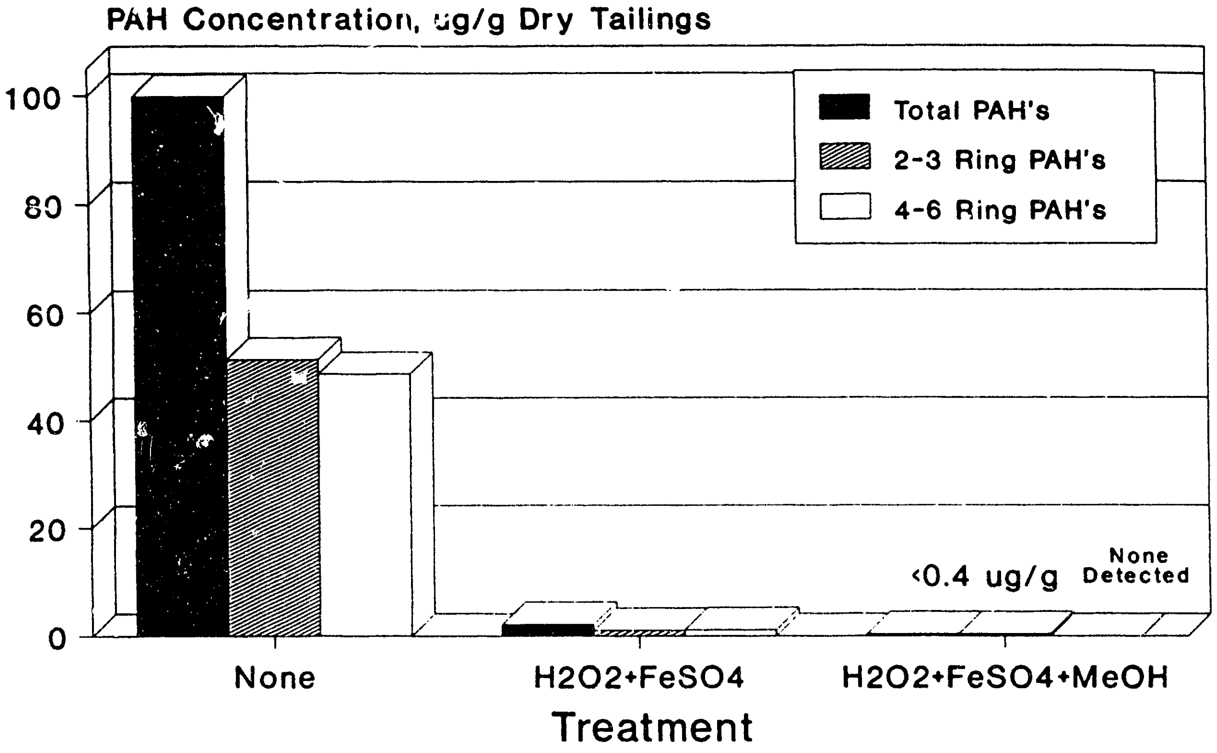


Figure 11. TREATMENT OF PAH-CONTAMINATED SOIL WITH FENTON'S REAGENT (5% H_2O_2; 16 hours)

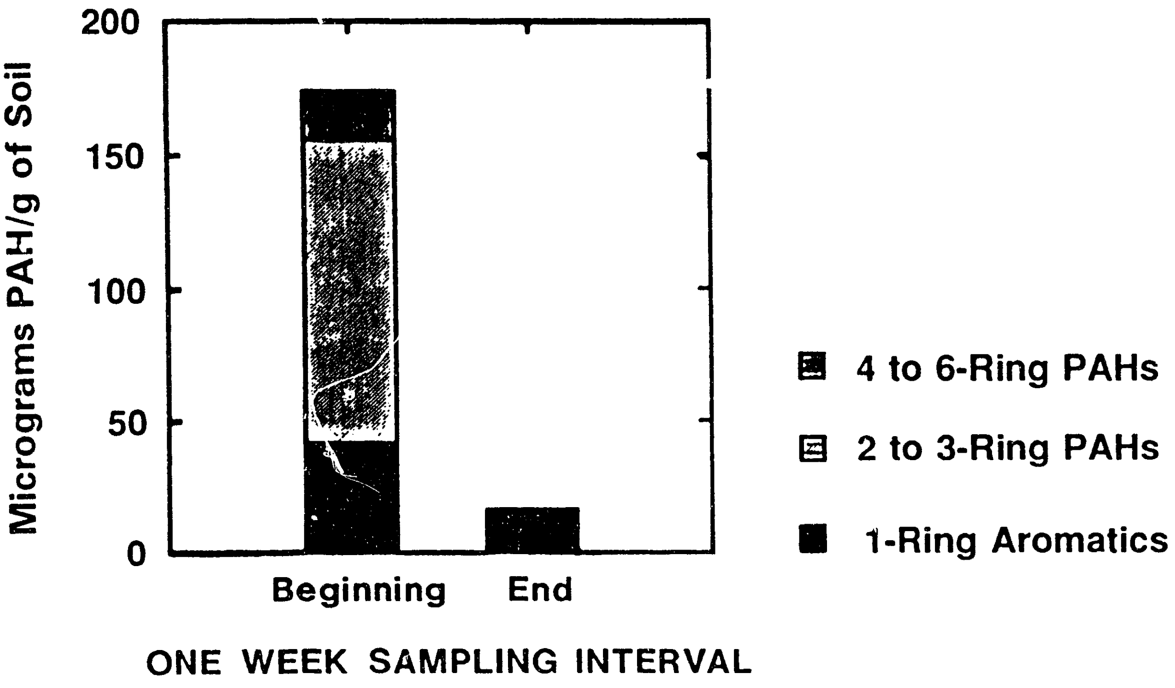


Figure 12. TOTAL PAHs [TGS-8(B) SOIL Treated With Fenton's Reagent on 4 Consecutive Days]

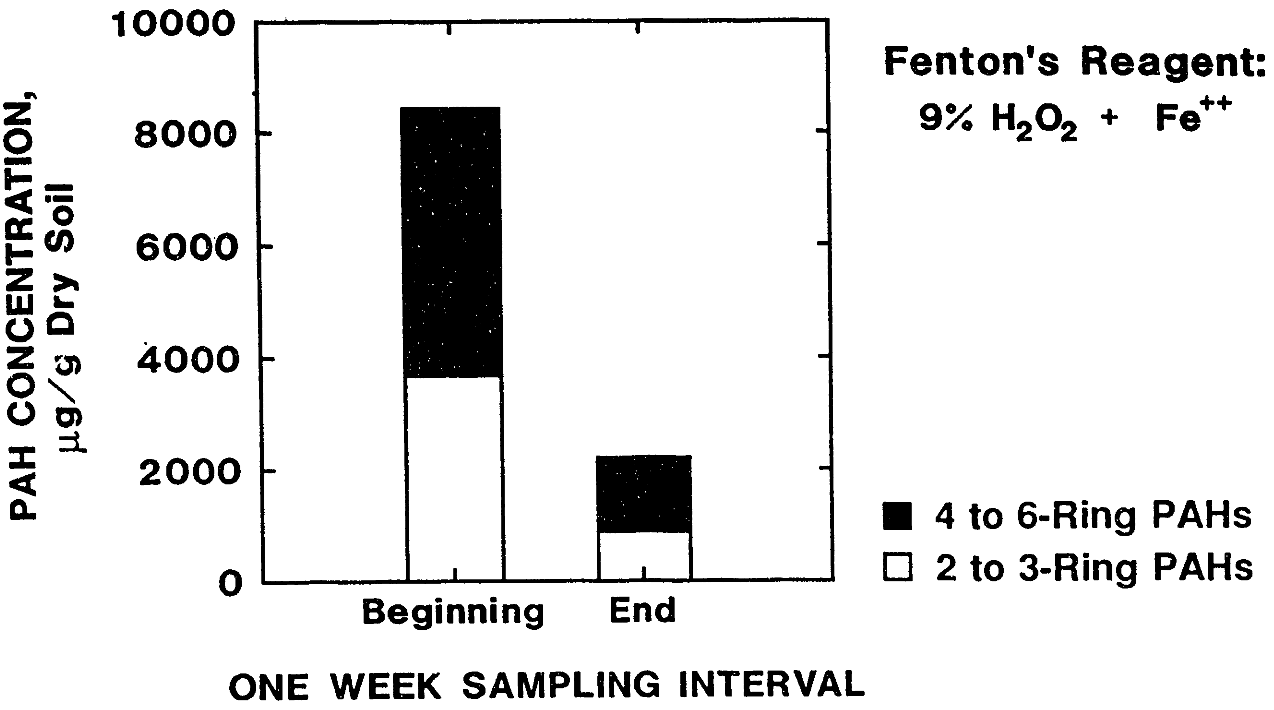


Figure 13. CHEMICAL TREATMENT OF BIOLOGICALLY TREATED TGS-7(F) SOIL USING FENTON'S REAGENT Added on 4 Consecutive Days

chloride extractable compounds that have little structural similarity to the parental PAHs. The extent of oxidation is dependent on the amount of H_2O_2 that was added. On a sand matrix with 10% H_2O_2, typically 24% of the ^{14}C-BaP was recovered as CO_2, 11% as water soluble (polar) compounds, and 50% as methylene chloride extractable (nonpolar) compound. No parental PAHs were detectable. Using 10% H_2O_2 for soil or sludge cleanup is probably uneconomical. However, the real inhibitor to mineralization by Fenton's reagent is more likely the inefficient contact between the free radicals generated by the reagent and the organic compounds. Complete oxidation of PAHs to CO_2 appeared to vary with the structure of the PAHs. BaP and PHE had similar reactivities with Fenton's reagent. Molecular orbital (MO) theory can be used to predict the chemical reactivity of PAHs and also appears to predict the carcinogenicity of these compounds.(13) The similarities between the structures at BaP and PHE would predict similar reactivities. Therefore, Fenton's reagent appears to selectively mineralize the more carcinogenic PAHs, such as BaP.

The presence of other organics appears to have minimal effect on PAH degradation by Fenton's reagent. The optimal pH is below 4 and the optimal temperature is ~20°C. Higher solids content (80% w/v) and slow addition of H_2O_2 significantly increase the removal of PAHs from solid matrices.

Fenton's reagent appears to be effective for both pre- and post-treatment of PAHs in soil and sandy matrices. As a pretreatment, Fenton's reagent's efficiency removes PAHs from the solid matrices and either degrades them to CO_2 or oxidizes them to more polar compounds, which should be more biodegradable. As a post-treatment, Fenton's reagent removes a significant number of PAHs that are resistant to biological degradation.

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