

Fenton-Like Oxidation of Polycyclic Aromatic Hydrocarbons in Soils Using Electrokinetics

Krishna R. Reddy¹ and Kalyan S. Chandhuri²

Abstract: An integrated electrochemical oxidation process that utilizes electrokinetics (EK) to deliver the oxidant (5–10% hydrogen peroxide, H₂O₂) and chelant [40 mM of ethylenediaminetetraacetic acid (EDTA) or diethylenetriaminepentaacetic acid (DTPA)] or iron chelate (1.4 mM Fe-EDTA or Fe-DTPA) to oxidize polycyclic aromatic hydrocarbons (PAHs) in soils was investigated. Batch and bench-scale EK experiments were conducted using: (a) kaolin, a low permeability clayey soil, spiked with phenanthrene at 500 mg/kg, and (b) former manufactured gas plant (MGP) soil, a high buffering silty soil, contaminated by a variety of PAHs (1493 mg/kg). Batch experiments showed that chelant solutions dissolve native iron minerals to form soluble Fe-chelates that remain available even at higher pH conditions of soil for the Fenton-like oxidation of the PAHs. In EK experiments, a 5–10% H₂O₂ solution was delivered from the anode and a chelant solution or iron-chelate was delivered from the cathode. Preflushing of soil with 5% ethanol and ferrous sulfate (1.4 mM) prior to oxidant delivery was also investigated. An electric potential of 2 VDC/cm was applied in all tests to induce electroosmotic flow for 5–8 days for kaolin and 25 days for the MGP field soil. In the absence of any chelating agent, phenanthrene oxidation was catalyzed by native iron present in kaolin soil, and 49.8–82.3% of phenanthrene was oxidized by increasing H₂O₂ concentration from 5–10%. At 5% H₂O₂ concentration, phenanthrene oxidation was not increased by using 40 mM EDTA, 40 mM DTPA or 1.4 mM Fe-DTPA, but it increased to 70% using 1.4 mM Fe-EDTA. Maximum phenanthrene oxidation (90.5%) was observed by 5% ethanol preflushing and then treating with 5% H₂O₂ at the anode and 1.4 mM Fe-EDTA at the cathode. However, preflushing with 1.4 mM ferrous sulfate did not improve phenanthrene oxidation. The results with the MGP field soil indicated that delivery of 5% H₂O₂ alone resulted in oxidation of 39.8% of total PAHs (especially 2- and 3-ring PAHs). The use of EDTA and Fe-EDTA did not increase PAHs oxidation in this soil. Overall, the results reveal that an optimized in situ combined technology of EK and Fenton-like process has the potential to oxidize PAHs in low permeability and/or high buffering soils.

DOI: 10.1061/(ASCE)GT.1943-5606.0000109

CE Database subject headings: Electrokinetics; Hydrocarbons; Soil pollution; Clays; Remediation; Organic compounds; Oxidation.

Introduction

The contamination of subsurface soils with biorefractory organic chemicals such as polycyclic aromatic hydrocarbons (PAHs) is a widespread problem. PAHs are relatively stable fused, ringed compounds found in the heavier fractions of petroleum and as products of combustion. They exhibit strong carcinogenic and toxic properties (Keith and Telliard 1979). Former manufactured gas plant (MGP) sites are a main source of PAH contamination. Soils at these MGP sites are often difficult to treat because of high concentrations of PAHs, long-chain aliphatics, and phenolics (Bogan et al. 2003). Common remediation techniques available currently for PAHs contaminated soils such as incineration, thermal desorption, and soil washing are ineffective and/or costly in treating heterogeneous subsurface environments that contain clayey and/or organic soils with low permeability (Lagadec et al.

2000). These soils cause difficulty in the delivery of treatment reagents that decrease the effectiveness of existing treatments. PAHs that are greater than four rings are also highly hydrophobic and therefore, strongly sorbed to soils.

In situ chemical oxidation processes have the potential to provide an effective means of rapidly treating contaminated soils with efficient process control. Numerous previous studies reveal the strong reactivity of Fenton's reagent with hazardous compounds present in soil and groundwater, resulting in effective contaminant destruction (Gates and Siegrist 1995; Arnold et al. 1995; Pignatello and Day 1996; Chen and Pignatello 1997; Hislop and Bolton 1999; Goldstein and Meyerstein 1999; Watts et al. 1999). A conventional Fenton's reaction involves catalytic decomposition of hydrogen peroxide (H₂O₂) with iron to yield free hydroxyl radicals as shown in the following reaction:



The resultant hydroxyl radical ($\bullet\text{OH}$) is the prime oxidizing species, which nonselectively reacts with many organic compounds (Haag and Yao 1992). An effective treatment stoichiometry for in situ Fenton's oxidation is influenced by variables such as pH, contaminant concentration, and total organic carbon (TOC) of the soil being treated. A pH range of 3.0–4.0 has been described as ideal for hydroxyl radical generation (Kremer 1999).

In cases of high acid buffering soil, it is often impractical to reduce the pH of the soil-water system in order for standard Fenton's oxidation of organic compounds to occur. In such cases,

¹Professor, Dept. of Civil and Materials Engineering, Univ. of Illinois at Chicago, 842 West Taylor St., Chicago, IL 60607 (corresponding author). E-mail: kreddy@uic.edu

²Graduate Research Assistant, Dept. of Civil and Materials Engineering, Univ. of Illinois at Chicago, 842 West Taylor St., Chicago, IL 60607.

Note. This manuscript was submitted on August 25, 2007; approved on March 3, 2009; published online on March 5, 2009. Discussion period open until March 1, 2010; separate discussions must be submitted for individual papers. This paper is part of the *Journal of Geotechnical and Geoenvironmental Engineering*, Vol. 135, No. 10, October 1, 2009. ©ASCE, ISSN 1090-0241/2009/10-1429-1439/\$25.00.

Table 1. Properties of Clean Kaolin Soil and Contaminated Field Soil

Property	Test method	Kaolin soil	Field soil
Water content	ASTM D2216	35.0%	14.0%
Specific gravity	ASTM D854	2.60	2.63
Grain size distribution	ASTM D422	% gravel=0 % sand=4 % fines=96	% gravel=0 % sand=84 % fines=16
Atterberg limits	ASTM D4318	Liquid limit=50% Plastic limit=27%	Nonplastic
Hydraulic conductivity	ASTM D2434	1.0×10^{-8} cm/s	1.6×10^{-4} cm/s
pH	ASTM D4972	4.9	7.05
Organic content	ASTM D2974	~0	11.10%
USCS classification	ASTM D2488	Silty clay, CL	Organic silty sand, SM

Fenton-like oxidation that involves using iron native in the soil as a catalyst to decompose H_2O_2 to generate free radicals is advantageous (Watts et al. 1990; Tyre et al. 1991; Ravikumar and Gurol 1994; Watts et al. 1997). The native iron available as a catalyst in soil-water systems occurs as iron oxide (Fe_2O_3) or iron oxyhydroxide phases ($FeOOH$) (Hofstetter et al. 2003). Recently, remediation of contaminants using Fenton-like catalysis by these iron phases or minerals was employed to avoid the precipitation of iron (Miller and Valentine 1995; Valentine and Wang 1998; Kwan and Voelker 2003). Another modification is the use of soluble organo-iron complexes that contain carboxylate ligands to catalyze the decomposition of H_2O_2 (Rush and Koppenol 1987; Sun and Pignatello 1992; Voelker and Sulzberger 1996; Voelker et al. 1997). These modifications prevent the precipitation of iron and enhance catalysis under neutral to alkaline pH.

The polyaminocarboxylate chelates, such as ethylenediaminetetraacetic acid (EDTA) and diethylenetriaminepentaacetic acid (DTPA), can be used to form soluble complexes with free metal ions in the solution (Nowack 2002). In addition, they dissociate exchangeable cations attached to mineral surfaces and also dissolve soil minerals. The dissolution of iron phases by uncomplexed chelating agents, in particular EDTA, has been studied extensively (Hill and Evans 1965; Lindsay 1979; Chang and Matijevic 1983; Rueda et al. 1985; Stumm and Morgan 1996; Nowack and Sigg 1997). Numerous studies have shown that in solutions with near neutral pH, the rate of the reaction of Fe(II)-polyaminocarboxylate complexes with H_2O_2 is greater by orders of magnitude than the reaction of Fe(II) as its aquo-complexes with H_2O_2 (Rush et al. 1990).

Recently, electrokinetic (EK) remediation has shown great potential to remediate soils under low permeability and heterogeneous conditions (Acar et al. 1992; Eykholt and Daniel 1994; Reddy and Chinthamreddy 2004; Reddy and Saichek 2004; Saichek and Reddy 2005). EK remediation is a technique where electrodes are placed across the soil mass to employ a very low DC electric potential to transport the contaminants into electrodes. If the contaminants are ionic compounds, they can be transported to the oppositely charged electrode by electromigration. In addition, electroosmotic flow (EO flow) provides the driving force for the movement of contaminants. Therefore, soluble contaminants may be removed by EO flow. EK has been investigated to solubilize and remove PAHs from soils using surfactants and cosolvents (Li et al. 2000; Reddy and Saichek 2004; Saichek and Reddy 2005). Recently, EK has been investigated as a method to deliver nutrients for enhanced bioremediation (Thevanayagam and Rishindran 1998; Reddy et al. 2003). Studies have also demonstrated electrochemical redox of contaminants

such as naphthalene and chromium (Pamukcu et al. 2004; Goel et al. 2003).

This paper presents the feasibility of employing integrated electrochemical oxidation (IECO) to low permeability and/or high buffering soils that are contaminated with PAHs. Normally, during the EK process, the pH at the anode would decrease to around 3 and the pH at the cathode would increase to around 11 (Acar et al. 1992; Eykholt and Daniel 1994; Reddy and Saichek 2004). For the Fenton process to be effective, a pH of 3 is required (Kremer 1999). Thus, low pH conditions generated at the anode and the EO flow induced by the application of a low electric potential will favor delivering H_2O_2 solution from the anode. In addition, chelate solutions or a Fe-chelate solution can be electromigrated into the soil from the cathode to overcome the effect of the high pH conditions to effectively catalyze H_2O_2 solutions to generate the free hydroxyl radicals that in turn react with PAHs to oxidize them to form nontoxic end products (e.g., carbon dioxide and water). Notably, the chelant solutions (EDTA and DTPA) electromigrate into the soil as a result of their negative charge and solubilize the native iron of the soil to form soluble Fe chelates that have greater stability at the high solution pH. To investigate the feasibility of IECO, a series of laboratory experiments was conducted using kaolin (a low permeability clayey soil) spiked with phenanthrene and a PAH-contaminated MGP soil (a high buffering silty soil). The delivery of oxidant using EK for Fenton-like oxidation of the contaminants (mainly PAHs) using native and chelated iron in the soils was investigated.

Materials and Methods

Soil Characterization

The study used two types of soils: clean kaolin and contaminated field soil. Kaolin is a low permeability clayey soil obtained from EM Science (CAS 1332-58-9). The field soil was a high buffering silty soil obtained from a former MGP site near Chicago. The soils were analyzed for physical and chemical parameters. All physical parameters of both soils were determined according to the ASTM standard methods and are listed in Table 1. The organic content of clean kaolin soil was insignificant. An acid digestion procedure followed by a metal determination using atomic absorption spectrophotometer (AAS) show that kaolin contains appreciable amounts of aluminum and calcium (>3,500 mg/kg each), and lesser amounts (250 to 1,000 mg/kg each) of other metals such as iron, magnesium, sodium, and zinc (Saichek and Reddy 2003). The MGP field soil was analyzed

Table 2. Initial Concentrations of PAHs in the MGP Field Soil

PAH	Concentration (mg/kg dry soil)
2-methylnaphthalene	230
Acenaphthene	25–40
Acenaphthylene	84–120
Anthracene	69–92
Benz(a)anthracene	66–82
Benzo(a)pyrene	59–62
Benzo(b)fluoranthene	31–33
Benzo(g,h,i)perylene	4.8–33
Benzo(k)fluoranthene	23–30
Chrysene	39–75
Dibenz(a,h)anthracene	9.1
Dibenzofuran	7.7
Fluoranthene	92–130
Fluorene	92
Indeno(1,2,3-cd)pyrene	12–21
Naphthalene	600
Phenanthrene	260–350
Pyrene	130–210

Note: Chemicals for which measured concentrations were below detection limits are not listed.

according to EPA method SW 6020 for metals and EPA method SW 8170 (SIM) for PAHs. The total organic content of this soil was 11.1%. The soil contained 42,720 mg/kg of total organics, including PAHs (1,493 mg/kg). Total PAHs contamination is comprised of 2-ring PAHs, 659 mg/kg; 3-ring PAHs, 329 mg/kg; 4-ring PAHs, 383 mg/kg; 5-ring PAHs, 89 mg/kg; and 6-ring PAHs, 33 mg/kg. The main metals determined in MGP soils are Fe, 15,000 mg/kg; Ca, 38,000 mg/kg; Mg, 15,000 mg/kg; and Mn, 440 mg/kg. Table 2 lists the PAH compounds and their respective concentrations present in homogenized MGP field soil. Buffering capacity of the soils was determined by titration analysis using soil slurry (20 g of soil in 200 mL of deionized water) and 2 M nitric acid as titrant solution. The acid buffering capacity of kaolin was found to be insignificant, while the buffering capacity of the MGP soil was found to be 3.7 eq/kg (dry soil) at the inflection point of the titration curve (pH 6.2), which indicates that the MGP soil possesses high acid buffering capacity.

Batch Experiments

Batch experiments were conducted using soil slurry samples prepared with 25 g of dry soil and 100 mL aqueous solution in a conical flask. Stock solutions of sodium salts of EDTA ($\text{Na}_4\text{-EDTA}$) and DTPA ($\text{Na}_5\text{-DTPA}$) were prepared. $\text{Na}_4\text{-EDTA}$ and $\text{Na}_5\text{-DTPA}$ were provided by Akzo Nobel (Chicago, IL). The pH of the stock solution was adjusted to that of the soil using dilute NaOH and HCl. Batch tests were conducted with aqueous concentrations ranging from 5 to 40 mM of $\text{Na}_4\text{-EDTA}$ and $\text{Na}_5\text{-DTPA}$. The batch test samples were covered and shaken for 24 h on a reciprocating shaker. The final pH of the slurry samples was determined and then the slurry samples were centrifuged. The supernatant was analyzed for Fe, Ca, Mg, and Mn using an atomic absorption spectrophotometer (Video 22) and for alkalinity using electronic titrator (Titronic 96) and for p^{H} using a pH meter (Thermo Orion model 720 A). Control batch experiments were also conducted with deionized water and soil.

Electrokinetic Test Setup

Fig. 1 shows a schematic diagram of the laboratory set-up used for all the IECO tests conducted in this study. It consists of an anode reservoir, an EK cell, a cathode reservoir, a power source, and a multimeter. The EK cell was made of Plexiglas and it had an outside diameter of 3.9 cm, inside diameter of 3.1 cm, and a total length of 12.9 cm. Each electrode compartment included a valve to control the flow into the cell, a slotted graphite electrode, and a porous stone. Graphite electrodes were selected because they are inert and corrosion-resistant. Small holes in the electrode compartment contained the electrode pins and filter paper was placed between the soil sample and the electrode. The pins were used as connectors for power supply. The electrode reservoirs constructed from 1.0-cm inner diameter Plexiglas tubes were connected to the electrode compartments using Tygon tubing. Thin tubes attached to exit ports in the electrode compartments allowed gas and condensate to escape. Any condensate from these tubes was redirected to the reservoir. A power source was used to apply a constant voltage to the electrodes and a multimeter was used to monitor the voltage and measure the current through the soil sample during the testing.

Soil Preparation

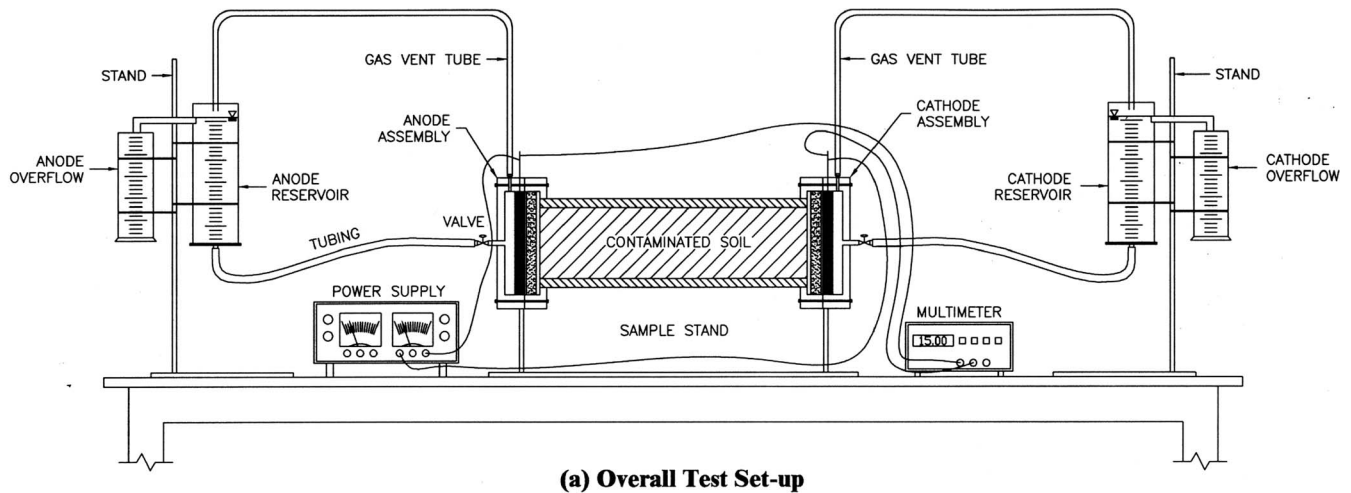
The initial set of tests was conducted on kaolin spiked with phenanthrene as a single PAH. Phenanthrene was chosen because it represents one of the commonly detected contaminants in soils. Kaolin was spiked with phenanthrene with a target concentration of 500 mg per kg dry soil (mg/kg). To spike the soil, 100% ethyl alcohol (Fisher Scientific, NJ) was used to dissolve solid phenanthrene (Aldrich Chemical Company, Milwaukee, WI). After spiking with phenanthrene, the soil was allowed to equilibrate in a hood for several days until the soil was completely dry. The dry soil was then mixed with 35% deionized water to simulate typical field moisture content and was compacted into the EK cell in uniform layers using a handheld compactor. After packing the cell, filter paper, graphite electrodes, and porous stones were placed on both sides of the cell along with electrode compartments. The weight of all cell components was taken before and after packing the wet spiked soil.

The field soil obtained from a PAH-contaminated MGP site was also tested. It was mixed with 15% deionized water to simulate field moisture conditions at the site and was compacted into the EK cell. The packing and test assembly procedures were all identical to those followed for the kaolin soil.

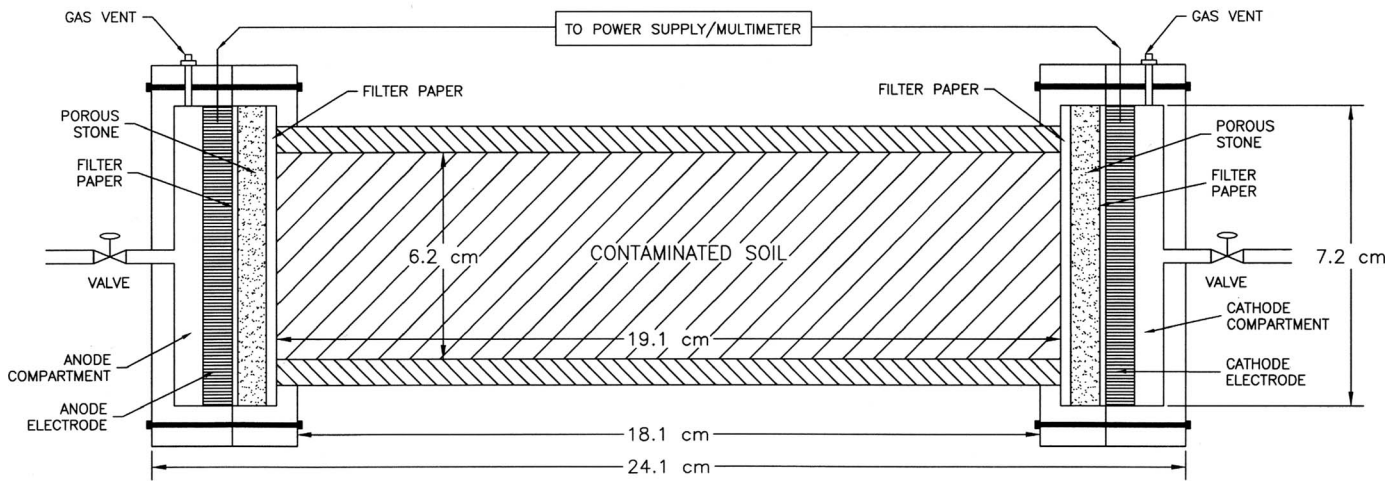
Operating Conditions and Variables

Detailed experimental conditions and variables used for 13 different IECO tests are summarized in Table 3. As seen in this table, the first ten tests (KHP1–KHP10) were performed using kaolin soil and additional three tests (DHP1–DHP3) were performed using MGP field soil. Each test setup was connected to a power supply and a constant voltage gradient of 2 VDC/cm was applied across the soil specimen. A higher voltage gradient of 2 VDC/cm was selected in this study to induce faster EO flow so that the hydrogen peroxide is rapidly introduced into the soil. The test duration was 5–8 days for the spiked kaolin soil and 25 days for the MGP field soil.

Baseline test KHP1 was carried out for the comparison between IECO process and EK process alone. KHP2 and KHP3 were performed to optimize the effect of H_2O_2 concentration for



(a) Overall Test Set-up



(b) Cell Details

Fig. 1. Schematic of EK test setup

phenanthrene oxidation. KHP4 and KHP5 were performed to determine the effect of EDTA and DTPA on both native Fe solubilization under the EK condition and subsequent catalytic decomposition of H_2O_2 by Fe-EDTA and Fe-DTPA formed within the system. KHP6 and KHP7 were performed to compare the catalytic efficiency of Fe-EDTA and Fe-DTPA solutions flushed by EK process to the process of forming Fe chelates by flushing the system with EDTA and DTPA solutions in KHP4 and KHP5. Important, the pH of all the chelant and Fe-chelate solutions were kept to that of soil pH.

KHP8 was carried out to determine the effect of Fe-EDTA on kaolin soil that was preflushed with 5% ethanol (cosolvent) solution. KHP9 and KHP10 were performed to analyze the effect of preflushing by ethanol and ferrous sulfate (standard Fenton's catalyst), respectively, in the absence of any chelant. Ethanol was selected as cosolvent in this study because it is shown to be effective for solubilization of phenanthrene and it is also environmentally benign and practical to use for in situ application (Saichek and Reddy 2004).

DHP1–DHP3 were performed on the MGP field soil for 25 days under similar operational conditions. Cathode solution was the only variable altered in these field soil tests. In test DHP1, the anode reservoir was filled with 5% H_2O_2 while the cathode res-

ervoir was filled with deionized water. Tests DHP2 and DHP3 were identical to DHP1 except that the cathode reservoir was filled with aqueous solutions of chelating agent (EDTA) and Fe chelates (Fe-EDTA), respectively.

Testing Procedures

Equal liquid level within the cathode and anode reservoirs was maintained to avoid the development of a hydraulic gradient across the soil sample in all kaolin and field soil tests. During the application of electric potential, the current and the EO flow were measured regularly. At the end of each test, aqueous solutions from the anode and cathode reservoirs were collected separately and the volumes were measured. The soil specimen was extruded and divided into four sections using a mechanical extruder. Each section was weighed and placed in a separate glass jar. From each soil section, 10 g of soil was shaken with 10 mL of deionized water by a reciprocating shaker and the solids were allowed to settle for an hour and pH was measured (ASTM D4972). The soil sections were also analyzed using the EPA method SW 8170 (SIM) for PAHs [U.S. Environmental Protection Agency (USEPA) 1986]. Chemical analyses were performed in duplicate.

Table 3. Experimental Program Using Kaolin and MGP Field Soil

Test	Soil	Phenanthrene or total PAHs concentration (mg/kg) ^a	Voltage gradient (VDC/cm)	Anode solution	Cathode solution	Oxidant delivery duration (days) ^b	Special pretreatment
KHP1	Kaolin	500	2	Deionized water	—	7	—
KHP2	Kaolin	500	2	5% H ₂ O ₂	—	7	—
KHP3	Kaolin	500	2	10% H ₂ O ₂	—	7	—
KHP4	Kaolin	500	2	5% H ₂ O ₂	40-mM DTPA	7	—
KHP5	Kaolin	500	2	5% H ₂ O ₂	40-mM EDTA	6	—
KHP6	Kaolin	500	2	5% H ₂ O ₂	1.4-mM Fe-DTPA	7	—
KHP7	Kaolin	500	2	5% H ₂ O ₂	1.4-mM Fe-EDTA	7	—
KHP8	Kaolin	500	2	5% H ₂ O ₂	1.4-mM Fe-EDTA	7	Preflushed with 5% ethanol alone for 11 days (≈1 pore volume) prior to oxidant injection
KHP9	Kaolin	500	2	5% H ₂ O ₂	—	8	Preflushed with 5% ethanol alone for 9 days (≈1.5 pore volumes) prior to oxidant injection
KHP10	Kaolin	500	2	5% H ₂ O ₂	—	5	Preflushed with 1.4 mM ferrous sulfate alone for 1 day (≈0.6 pore volume) prior to oxidant injection
DHP1	MGP soil	1493	2	5% H ₂ O ₂	—	25	—
DHP2	MGP soil	1493	2	5% H ₂ O ₂	40 mM EDTA	25	—
DHP3	MGP soil	1493	2	5% H ₂ O ₂	1.4 mM Fe-EDTA	25	—

^aKaolin spiked with phenanthrene alone at target initial concentration of 500 mg/kg.

^bDuration decided based on the observed results (e.g., current and flow).

Results and Analysis

Batch Test Results

Based on the batch tests, the leachable amount of iron from kaolin and MGP field soil with varying concentrations of EDTA and DTPA was determined. As seen from the results shown in Fig. 2, leaching of iron increased with an increase in chelant concentration. Kaolin soil showed a high amount of iron (nearly 100 mg/kg) leached with a low concentration of chelant in comparison to MGP field soil. This may be attributed to limited amounts of iron sorbed to the kaolin surfaces, whereas in the MGP field soil iron

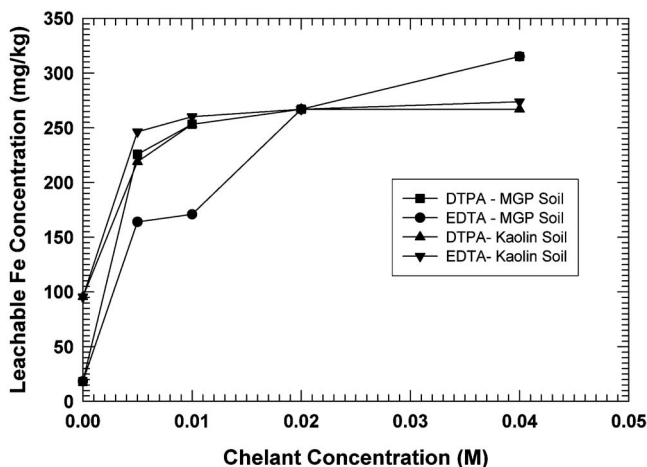


Fig. 2. Effect of chelant on leachate native iron in kaolin and MGP field soil

oxide and hydroxide phases may be present which are not easily soluble. At higher chelant concentrations, iron leaching in kaolin soil increases and reaches a plateau. Conversely, MGP soil shows increasing iron leaching with increase in chelant concentration. These findings show that an appreciable amount of iron can be leached from both kaolin and MGP soil to form stable Fe chelate at slightly acidic (pH 4.9) to neutral pH (pH 7.05) conditions.

Table 4 shows that the aqueous concentrations of Fe, Ca, Mg, and Mn increase with chelate concentration in MGP soil. Thus, in the lower concentration range of chelates, the aqueous concentration of Fe-DTPA is greater than that of Fe-EDTA. The aqueous Fe concentration ranges from 0.27 to 1.4 mM for the EDTA systems, and from 0.51–1.33 mM for the DTPA systems for the investigated chelate concentration range (5–40 mM). Results show that aqueous concentrations of metals decrease as Ca > Mg > Fe

Table 4. Effect of Chelant on Leachable Metals in MGP Soil

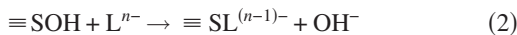
Chelant	Fe	Ca	Mg	Mn
DTPA (mM)				
40	2.0%	14.0%	2.3%	22.6%
20	1.6%	9.5%	1.3%	15.9%
10	1.0%	6.0%	1.6%	13.2%
5	0.8%	3.2%	2.4%	12.3%
EDTA (mM)				
40	2.1%	14.7%	4.9%	23.5%
20	1.2%	8.5%	1.3%	17.3%
10	0.8%	5.2%	1.8%	13.2%
5	0.4%	3.0%	2.1%	12.0%
Control (without chelant)				
	0.1%	0.1%	0.3%	0.0%

Note: Percentages are of total concentration present.

> Mn for all chelant concentrations. A similar leaching trend was also observed in the control test with no chelate. The mass transfer from soil into aqueous phase decreases in the order Mn > Ca > Mg > Fe for the investigated chelate concentration range. Despite its low concentration in the soil relative to the other three metals, the mass transfer is greatest for Mn. Mn was absent in the control tests. In general, the final pH of batch experiments increases with chelant concentration and ranges from 7.8–8.3. The carbonate alkalinity of the supernatant also increases with chelate concentration and can be up to 50 times that of the control.

The results of the batch leaching experiments indicate that carbonate phases in soil dissolve and increase bicarbonate alkalinity. The dissolution of carbonate phases also accounts for the aqueous Ca and Mg activity. The high affinity of EDTA and DTPA for Mn in soils is consistent with the findings of others (Norvell and Lindsay 1969, 1972). The lower solution concentration of Fe relative to Ca and Mg may be attributed to both the lower Fe-mineral content of MGP soil relative to carbonates and lower chelate solubility of Fe-oxyhydroxide phases relative to that of carbonates (Hill and Evans 1965). In general, chelation of iron from soil by EDTA and DTPA strongly depends upon the concentrations of Ca and Mg (Lindsay 1979). Ca and Mg at high solution concentrations compete with Fe for chelates (Hill and Evans 1965). Because of its greater stability constant, the stability of Fe-DTPA is less affected by the presence of Ca and Mg than that of Fe-EDTA (Stumm and Morgan 1996). Increasing the concentration of the chelant solution can further enhance the stability of the Fe-EDTA and Fe-DTPA. For this reason, as shown in Fig. 2, maximum leaching of iron was observed at high chelant concentration.

Dissolution of mineral phases by chelating agents can be attributed to ligand exchange reactions (Stumm 1997) because chelates themselves adsorb onto surfaces. As a result, metal-oxygen bonds on the surface are weakened upon adsorption of the ligand, and the release of metal ions from the surface to the adjacent solution is promoted by the following complexation reaction



where $\equiv\text{SOH}$ =surface site, in our studies Fe minerals, and L is the added chelating agent. The formation of these nonsorbing aqueous metal complexes or direct competition for surface sites can decrease metal adsorption. Ligand can increase metal adsorption through changes in the electrostatic properties of the interface by the following two reactions:



Eq. (3) shows the formation of a ternary surface complex in which metal forms a bridge between the surface and the ligand, while Eq. (4) represents the formation of surface complexes in which the ligand forms a bridge between metal and surface. The latter complexes show a decrease in adsorption behavior at a higher pH and that metal-ligand complex (or Fe-EDTA) remains in the solution to act as a catalyst. Overall, batch leaching studies with spiked kaolin soil and MGP field soil demonstrate substantial availability, stability, and concentration of iron (bound as Fe-EDTA or Fe-DTPA) to catalyze Fenton's oxidation of PAHs.

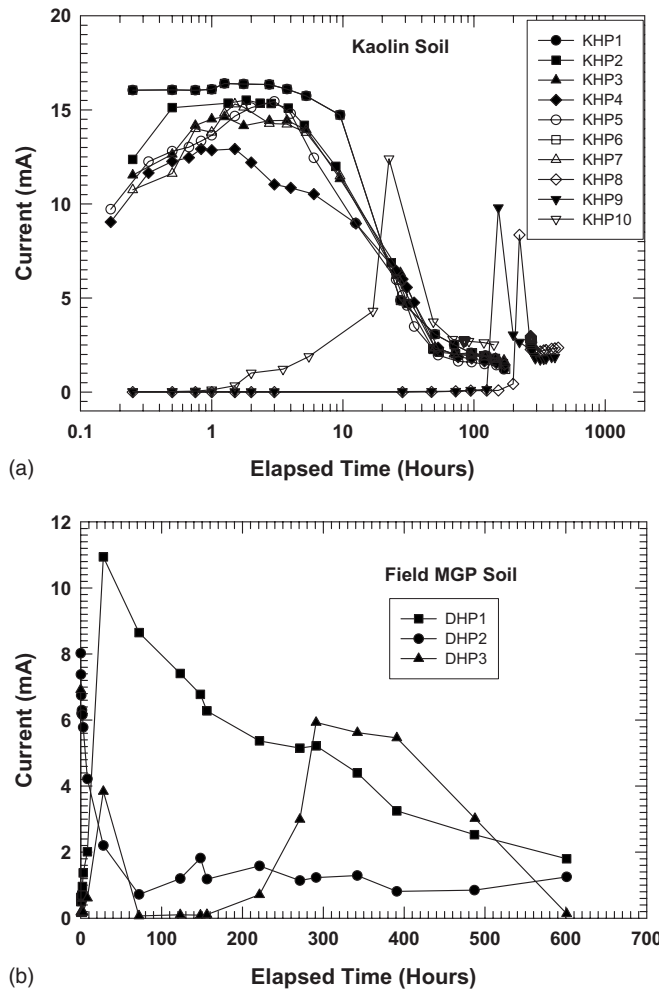


Fig. 3. Comparison of current versus elapsed time for tests with (a) Kaolin; (b) MGP field soil

Integrated Electrochemical Oxidation Test Results

Electric Current

Figs. 3(a and b) show the current values for all the integrated electrochemical oxidation (IECO) tests conducted using kaolin and field soil, respectively. For spiked kaolin soil [Fig. 3(a)], the trend of electric current remained almost the same except for the two tests with ethanol preflushing (KHP8 and KHP9). Generally, the current increased rapidly during the first few hours, then decreased over a period of time. KHP6 (conducted with 5% H_2O_2 and 1.4-mM Fe-DTPA solution) recorded the high current value of 16.4 mA. Compared to other tests, the trend for electric current in preflushed tests is slightly different. For ethanol preflushed tests (KHP8 and KHP9), the electric current was very low during the ethanol flushing stage and then it increased as soon as the injection of oxidant started and later decreased and finally stabilized at approximately 2 mA. Ferrous sulfate preflushed test (KHP10) show a trend of increasing current in the first few days, followed by a rapid decrease and then remained constant around 3 mA. Of all the three preflushed tests, the ferrous sulfate preflushed test (KHP10) showed the maximum current.

For MGP soil [Fig. 3(b)], test DHP1 used only 5% H_2O_2 at the anode and deionized water at the cathode. The current gradually

increased to reach a value of 11 mA after 1 day and then decreased over a period of time until the end of the experiment. For test DHP2, the current rapidly increased to 8 mA, then decreased rapidly and remained stabilized at 1.5–1.7 mA through most of the test duration. Finally, test DHP3 showed a different trend when compared to the other two tests. At the beginning, current increased to approximately 4 mA, but dropped rapidly and then gradually increased to approximately 6 mA and finally decreased gradually to 0.07 mA at the end of testing. The variable current variations in tests DHP2 and DHP3 may be attributed to the introduction of EDTA or Fe-EDTA at the cathode and the extent of their migration into the soil, forming surface reactions and dissolution of minerals.

In general, the higher current values are due to high concentration of ions in the pore water as a result of dissolution of salts attached with the dry soil particles (Mitchell 1993). As the ions electromigrated toward the electrodes, their concentration in pore water decreases resulting in a decreased current of the tested system. In the ethanol preflushed tests, lower current is resulted due to lower amount of ion dissociation during the ethanol flushing stage. However, current is increased during the oxidant and chelant delivery stage due to higher amount of ion dissociation. These tests indicate that current generated under a constant voltage gradient is a function of time and the type of electrode solutions used.

Electro-Osmotic Flow

Figs. 4(a and b) show the cumulative EO flow for all tests conducted using kaolin and field soil, respectively. Experimental results showed that in all tests, the EO flow occurred from anode to cathode. In all tests except the ethanol preflushed tests (KHP8 and KHP9), the EO flow rate initially increased and then decreased with a maximum EO flow of 287 and 184 mL (or 4 and 2.6 pore volumes, respectively) for tests KHP2 and KHP7, respectively; this correlates with the relatively higher electrical current values measured for these tests [Fig. 3(a)]. In comparison, the EO flow in ethanol preflushed tests (KHP8 and KHP9) remained low for the first 100–200 h, which may be due to low electric current and low dielectric constant of ethanol. After the preflushing stage, EO increased during the subsequent hydrogen peroxide delivery stage due to increase in electric current, resulting in total cumulative flow of 374 and 265 mL (or approximately 5 and 3.6 pore volumes) in tests KHP8 and KHP9, respectively. The first test with MGP soil (DHP1) demonstrated the maximum EO flow of 261-mL volume [Fig. 4(b)]. For the other two tests (DHP2 and DHP3) using EDTA and Fe-EDTA as the cathode solution, respectively, the EO flow was similar for the entire test period; their maximum cumulative volumes were 71 and 89 mL, respectively.

The EO flow is proportional to the electrical gradient, zeta potential of the soil, and dielectric constant of pore fluid; the flow is inversely proportional to the viscosity of pore fluid (Saichek and Reddy 2003). The zeta potential (surface charge) of the soil is changed due to changes in soil pH and the ion and chelate adsorption as well as mineral dissolution in the regions of both low and high pH. The changes in zeta potential and pore fluid properties (such as dielectric constant and viscosity) influence the EO flow. Additionally, the electrical gradient may not be uniform throughout the soil; hence, the EO flow is generally not uniform spatially or temporally (Eykholt and Daniel 1994; Saichek and Reddy 2003). Thus, the observed differences in EO flow in different tests are attributed to varying physicochemical changes that

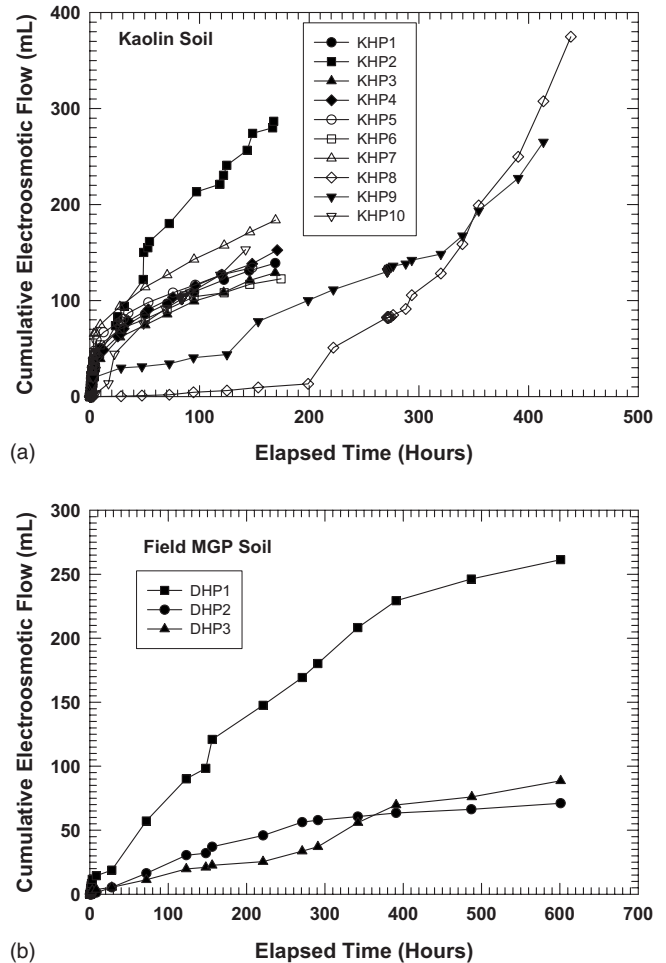


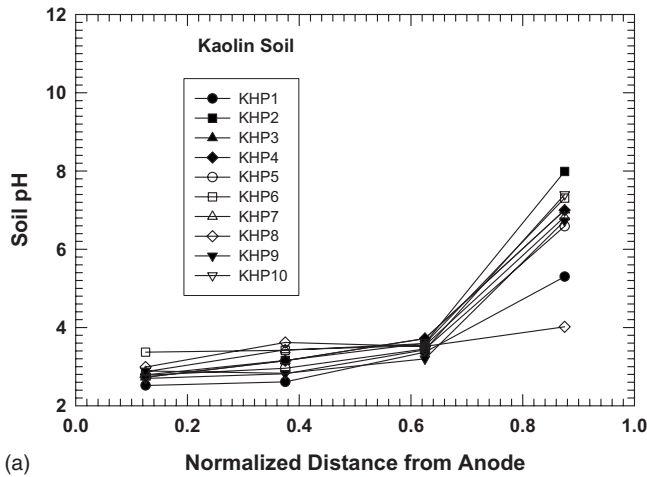
Fig. 4. Comparison of cumulative EO flow versus elapsed time for tests with (a) kaolin; (b) MGP field soil

exist in soils under different operating conditions selected for this study.

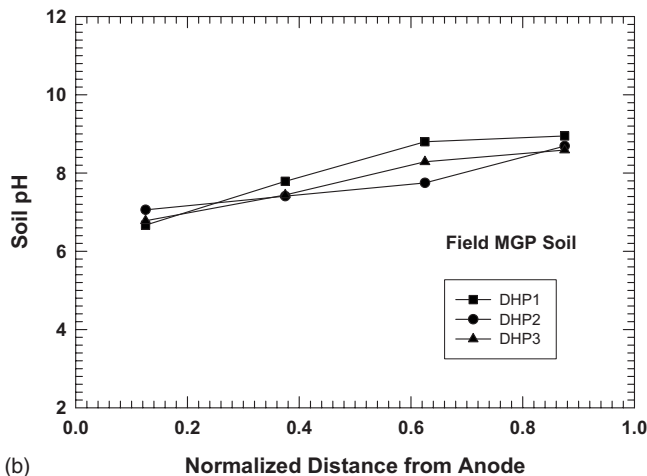
Soil pH

During the EK process, electrolysis reactions produce hydrogen ions at anode and hydroxyl ions at cathode, creating respective acidic and alkaline conditions. Generally, the resulting acid front migrates toward cathode under the influence of bulk water flow and high ionic mobility of H^+ . Dissolved cations are free to move through the soil, ideally to the cathode reservoir where they can be removed (Roach 2002). The measured pH values of soil sections are plotted with normalized distance from the anode in Figs. 5(a and b) for kaolin and field soil, respectively. The normalized distance from the anode is defined as the distance to the center of the soil section from the anode divided by the total length of soil sample. In the present study, the pH drift for all the kaolin tests remained almost the same, except near the cathode where pH ranged from 4–8 depending on the test conditions. A uniform pH ranging from 3.0–4.0 was observed only in KHP8 test in which ethanol was flushed first followed by the use of H_2O_2 at the anode and Fe-EDTA at the cathode.

For MGP soil [Fig. 5(b)], the pH distribution within the DHP1 test varied from pH 6.6 near the anode to pH 8.9 near the cathode. The relatively higher pH values near anode as compared to that of



(a)



(b)

Fig. 5. Comparison of soil pH versus normalized distance from anode for tests with (a) kaolin; (b) MGP field soil

kaolin tests are attributed to the high acid buffering capacity of the field soil due to high carbonate and organic content of this soil. In DHP2, pH distribution ranged from pH 7.0–8.6 from anode to cathode, respectively. Similarly, in DHP3, the pH varied from pH 6.7–8.5 from anode to cathode. Since the initial pH of the soil was 6.9, higher values of pH suggest the migration of OH^- from the cathode was more effective than the migration of H^+ ions from the anode.

Contaminant Oxidation

The anode and cathode solutions collected after the completion of testing for all kaolin tests did not contain detectable levels of phenanthrene. Fig. 6 shows the residual phenanthrene concentration with normalized distance from anode after the treatment of spiked kaolin soil. The calculated percent reductions of phenanthrene in soil for each test are shown in Table 5. The test conducted with deionized water (KHP1) shows the highest phenanthrene concentration through most of the soil as compared to all other tests that used hydrogen peroxide. The phenanthrene concentration decreased in the first section near the anode and increased in the second section, indicating that slight migration occurred toward the cathode. There is no significant solubilization and migration of phenanthrene near the cathode. Phenanthrene has very low solubility and such observed migration behavior is

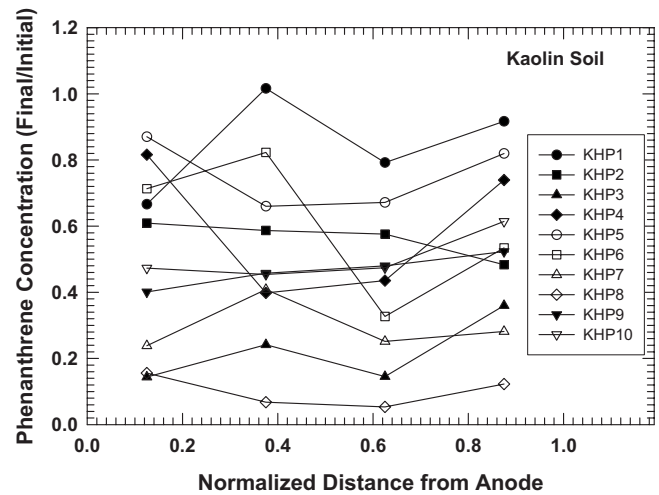


Fig. 6. Residual phenanthrene in kaolin soil

expected. The tests with 5 and 10% H_2O_2 solutions that did not utilize any externally provided iron catalyst oxidized 49.8 and 82.3% of phenanthrene, respectively. This indicates that the native iron of kaolin soil can effectively catalyze the oxidation of phenanthrene under operating conditions. The soil pH was slightly higher in KHP2 test with 5% H_2O_2 which resulted in approximately double the EO flow as compared to KHP3 test with 10% H_2O_2 . However, the higher concentration of H_2O_2 in KHP3 increases the stability of the hydroxyl radicals generated, resulting in significant increase in oxidation of phenanthrene. Furthermore, soil pH in test KHP3 was low as compared to test KHP2 that increases desorption of metals, including native iron that remains available for the decomposition of H_2O_2 . These findings are in agreement with the study of Watts et al. (1994) for the oxidation of hexachlorobenzene from soil. They also reported that high H_2O_2 concentration is needed to promote a combined desorption-oxidation process for the destruction of hydrophobic contaminants (Watts et al. 1994); the same aggressive oxidation conditions may also be effective in mineralizing the intermediates formed in the treatment process.

Tests conducted with 40 mM DTPA and EDTA (KHP4 and KHP5) showed 44.0 and 27.6% oxidation of phenanthrene, respectively. The difference in oxidation efficiency may be attributed to the differences in the stability of metal-ligand complexes formed in the H_2O_2 -DTPA and H_2O_2 -EDTA tests and also to the interfering metals (e.g., Ca, Mg, and Mn) simultaneously competing with iron for the available binding sites of the chelates. DTPA forms more stable complexes as compared to EDTA resulting in the higher oxidation of phenanthrene. It can also be seen that the test conducted with 40-mM DTPA (KHP4) showed slightly higher soil pH value and higher EO flow as compared to the test conducted with 40-mM EDTA (KHP5) resulting in higher oxidation of phenanthrene. The KHP2 and KHP3 tests conducted with H_2O_2 alone without chelants (EDTA or DTPA) resulted in higher amounts of phenanthrene oxidation, demonstrating that native iron in kaolin soil was available for reaction and it is not necessary to use any chelants.

In contrast, tests KHP6 and KHP7 conducted using iron chelates, 1.4-mM Fe-DTPA and 1.4-mM Fe-EDTA, respectively, at the cathode showed different results than those obtained in corresponding tests using chelates alone, DTPA and EDTA (KHP4 and KHP5). With Fe-EDTA, almost 70% of the phenanthrene was oxidized; while with Fe-DTPA, only 40.8% of phenanthrene was

Table 5. Comparison of Total Flow and Phenanthrene or Total PAHs Oxidized in Tests with Kaolin and MGP Field Soil

Test	Oxidant delivery duration (days)	Total flow during oxidant delivery (mL)	Oxidant pore volume collected	Phenanthrene or total PAHs oxidized ^a (%)
KHP2	7	287	4.0	49.8
KHP3	7	129	1.8	82.3
KHP4	7	152	2.1	44.0
KHP5	6	134	1.9	27.6
KHP6	7	122	1.7	40.8
KHP7	7	184	2.6	70.0
KHP8	7	293	4.0	90.5
KHP9	8	154	2.1	58.0
KHP10	5	109	1.5	49.0
DHP1	25	261	6.4	39.8
DHP2	25	71	1.7	30.2
DHP3	25	89	2.2	33.7

^aKaolin contained only phenanthrene.

oxidized using the same 5% concentration of H₂O₂. In Fe-EDTA test (KHP7), EO flow was found to be significantly higher than Fe-DTPA test (KHP6). It can be seen from Fig. 6 that in Fe-EDTA test, there was substantial and uniform phenanthrene oxidation throughout the soil, while in Fe-DTPA test residual phenanthrene concentrations were low near the cathode and high near the anode, indicating that significant phenanthrene oxidation occurred near the cathode. It is possible that Fe-DTPA was transported only to limited extent into the soil. This limited transport of Fe-DTPA combined with low EO flow caused overall low phenanthrene oxidation. In general, the low soil pH and high EO flow favors the stability of the Fe chelates to catalyze the H₂O₂ to generate hydroxyl radicals for the oxidation of phenanthrene.

Test KHP8 was conducted using 1.4-mM Fe-EDTA at cathode after preflushing the soil with approximately one pore volume of 5% ethanol (cosolvent). This test resulted in a maximum phenanthrene oxidation of 90.5%. When the soil is preflushed with ethanol, the phenanthrene dissolution is enhanced and more aqueous phase phenanthrene is readily available for oxidation. KHP9 is conducted similar to KHP8, but without using Fe-EDTA at the cathode and it shows that 58% of phenanthrene is oxidized. Comparison of KHP8 and KHP9 test results reveal that the transport of Fe-EDTA into the soil enhanced the catalytic oxidation of phenanthrene significantly. Test KHP10 was conducted by preflushing of 1.4-mM ferrous sulfate prior to the delivery of oxidant (5% H₂O₂) and it showed oxidation of 49% phenanthrene.

The tests with 5 and 10% H₂O₂ solutions that did not utilize an iron catalyst oxidized 49.8 and 82.3% of phenanthrene, respectively. This indicates that the native iron of kaolin soil can catalyze the oxidation of phenanthrene under operating conditions. With 5% H₂O₂ at anode and 1.4-mM Fe-EDTA at cathode in test KHP7 shows the increase in phenanthrene oxidation to 70%. This may be due to the fact that Fe-EDTA is more stable under oxidizing conditions than Fe-aquo-complexes. However, if preflushing with 5% ethanol (solvent), the phenanthrene oxidation can be increased from 70–90.5%.

Similar to kaolin tests, PAHs were not detected in any of the anode or cathode solutions collected for all the MGP field soil tests. Based on the residual PAH concentrations, Figs. 7(a and b) show the percent oxidation of the total PAHs with normalized distance from anode and PAHs grouped according to the number of benzene rings in the structure from MGP field soil. The total PAHs reduction was highest for the test DHP1 with 39.8% oxidation, followed by a 33.7% oxidation for the DHP3 test and a

30.2% oxidation for the DHP2 test (Table 5). The total PAHs reduction was relatively uniform across the soil specimens for DHP1 and DHP3. However, in test DHP2, the total PAH oxidized decreased at the anode from approximately 29% (remaining in three sections from the anode) to 5% in the section close to the cathode. EO flow was reduced when EDTA or Fe-EDTA was used

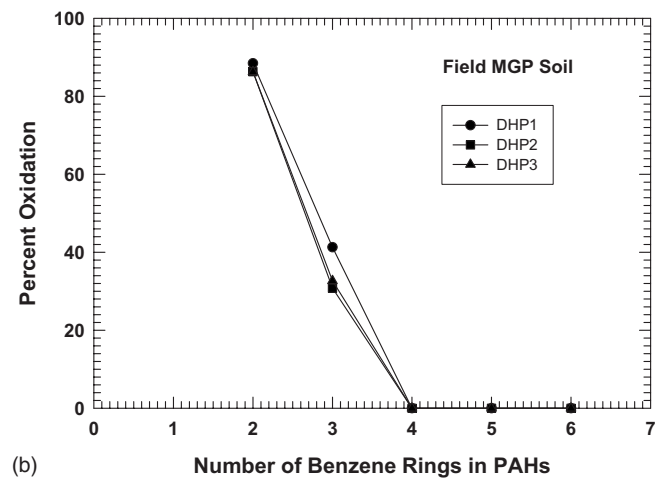
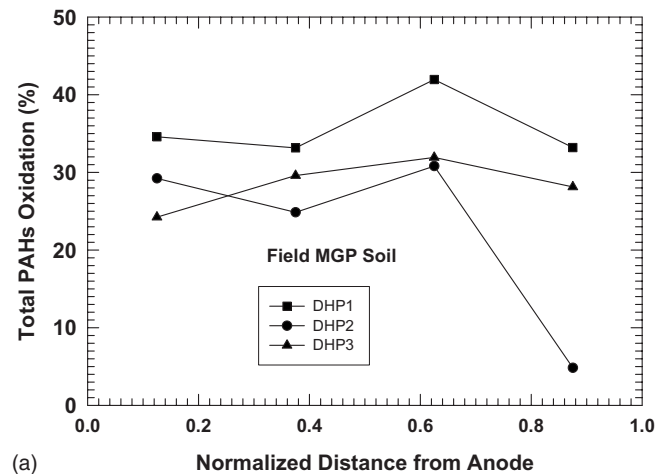


Fig. 7. PAHs oxidation with (a) normalized distance from anode; (b) number of benzene rings in MGP soils

and overall phenanthrene oxidation was lower as compared to the test that uses H_2O_2 alone without any chelant. This demonstrates that native iron present in the soil can catalyze H_2O_2 for phenanthrene oxidation. Fig. 7(b) suggests that two-ring PAHs are almost completely oxidized (90%) and that oxidation decreases for PAHs with higher ring number (i.e., hydrophobicity).

Overall, the results with kaolin soil show that phenanthrene oxidation by IECO technique is possible and that the extent of phenanthrene oxidation significantly depends on the native iron content of soil and the concentration of H_2O_2 and chelating agents. In the absence of any chelating agent, phenanthrene oxidation is catalyzed by native iron present in the soil and can be promoted by increasing H_2O_2 concentration (removal was increased from 49.8–82.3% by increasing H_2O_2 concentration from 5–10%). These results also confirm that the native iron is not a limiting factor for Fenton-like oxidation when a higher concentration of H_2O_2 is employed. The use of chelating agents (EDTA and DTPA) and Fe-DTPA in the cathode did not enhance the degradation of phenanthrene, but the use of Fe-EDTA in the cathode improved the oxidation of phenanthrene. Preflushing of kaolin with 5% ethanol increased the soluble phenanthrene and subsequent use of 5% H_2O_2 at the anode and 1.4-mM Fe-EDTA at the cathode anode resulted in a maximum phenanthrene oxidation (90.5%). However, preflushing with 1.4-mM ferrous sulfate did not significantly enhance phenanthrene oxidation.

The results with the MGP field soil indicate that delivery of H_2O_2 into high buffering soil is feasible. Test DHP1 demonstrates the effectiveness of the Fenton-like oxidation as considerable amount of PAHs was oxidized. Results show that 2–4 ringed PAHs are more rapidly oxidized than higher ringed PAHs. This test results also indicates that iron amendments were not required to reach high removal efficiencies, which suggests that sufficient native iron was present in the MGP field soil to support the Fenton-like oxidation of PAHs. This conclusion is supported by the tests with EDTA and Fe-EDTA (i.e., tests DHP2 and DHP3) which resulted in low oxidation of PAHs. Thus, this study demonstrates that IECO has the potential to remediate PAH-contaminated soils effectively rather than using EK or Fenton-like oxidation methods individually.

Conclusions

Based on this study, the following conclusions can be drawn:

- When EK was coupled with the Fenton process that uses the native iron of kaolin soil to catalyze 5% H_2O_2 , 49.8% oxidation of phenanthrene resulted. The increased H_2O_2 concentration of 10% resulted in the increased oxidation of phenanthrene to 82.3% due to the formation of more stable hydroxyl radicals. The pretreatment of kaolin soil with a standard $FeSO_4$ catalyst did not significantly affect the oxidation efficiency of phenanthrene.
- The use of Fe-EDTA was found to be more effective than using chelant solutions (DTPA and EDTA) alone or Fe-DTPA. Fewer disturbances in the soil with Fe-EDTA resulted in the enhanced EO flow and 70% phenanthrene oxidation. Pretreatment with 5% ethanol increased the phenanthrene oxidation from 70–90%.
- In the aged contaminated field soil, oxidation of PAHs was dependent on the presence of soil organic matter and reactivity of the PAHs. The field soil contained sufficient native iron to be used as a catalyst for the 5% H_2O_2 decomposition for oxidation of 39.8% of PAHs. The use of chelant (EDTA) or iron

chelant (Fe-EDTA) did not improve remedial effectiveness.

- Among several PAHs present in the field soil, only 2–4 ringed PAHs were more rapidly oxidized than higher ringed PAHs. It is believed that longer duration and a higher applied voltage gradient may result in better PAHs oxidation efficiency. Electroosmosis is the major transport mechanism for the delivery of H_2O_2 ; higher EO flow leads to better efficiency for the oxidation of PAHs.

Acknowledgments

This project was funded by the Technology Challenge Grant from the State of Illinois. The writers are thankful to Surendra Kumar, Craig Chawla, Saurabh Sharma, and Andreas Jazdanian for their assistance in this project.

References

- Acar, Y. B., Li, H., and Gale, R. J. (1992). "Phenol removal from kaolinite by electrokinetics." *J. Geotech. Engrg.*, 118, 1837–1852.
- Arnold, S. M., Hickey, W. J., and Harris, R. F. (1995). "Degradation of atrazine by Fenton's reagent: Condition optimization and product quantification." *Environ. Sci. Technol.*, 29, 2083–2089.
- Bogan, B. W., Trbovic, V., and Paterek, J. R. (2003). "Inclusion of vegetable oils in Fenton's chemistry for remediation of PAH-contaminated soils." *Chemosphere*, 50, 15–21.
- Chang, H.-C., and Matijevic, E. (1983). "Interactions of metal hydrous oxides with chelating agents." *J. Colloid Interface Sci.*, 92(2), 479–488.
- Chen, R., and Pignatello, J. J. (1997). "Role of quinone intermediates as electron shuttles in Fenton and photoassisted Fenton oxidations of aromatic compounds." *Environ. Sci. Technol.*, 31, 2399–2406.
- Eykholt, G. R., and Daniel, D. E. (1994). "Impact on system chemistry on electroosmosis in contaminated soils." *J. Geotech. Engrg.*, 120, 797–815.
- Gates, D. D., and Siegrist, R. L. (1995). "In-situ chemical oxidation of trichloroethylene using hydrogen peroxide." *J. Envir. Engrg. Div.*, 121, 639–644.
- Goel, R. K., Flora, J., and Ferry, J. (2003). "Mechanisms for naphthalene removal during electrolytic aeration." *Water Res.*, 37(4), 891–901.
- Goldstein, S., and Meyerstein, D. (1999). "Comments on the mechanism of the 'Fenton-like' reaction." *Acc. Chem. Res.*, 32, 547–550.
- Haag, W. R., and Yao, C. (1992). "Rate constants for reaction of hydroxyl radicals with several drinking water contaminants." *Environ. Sci. Technol.*, 26, 1005–1013.
- Hill, W. E., and Evans, D. E. (1965). "Solubility of twenty minerals in selected versene (EDTA) solutions." *Kansas State geological survey, Lawrence, Kan., Bulletin No. 175, Part 3, 22.*
- Hislop, K. A., and Bolton, J. R. (1999). "The photochemical generation of hydroxyl radicals in the UV-vis/ferrioxalate/ H_2O_2 system." *Environ. Sci. Technol.*, 33, 3119–3126.
- Hofstetter, T. B., Schwarzenbach, R. P., and Haderlein, S. B. (2003). "Reactivity of Fe(II) species associated with clay minerals." *Environ. Sci. Technol.*, 37, 519–528.
- Keith, L. H., and Telliard, W. A. (1979). "ES&T special report: Priority pollutants: I—A perspective view." *Environ. Sci. Technol.*, 13, 416–423.
- Kremer, M. L. (1999). "Mechanism of the Fenton reaction: Evidence for a new intermediate." *Physiol. Chem. Phys.*, 1, 3595–3607.
- Kwan, W. P., and Voelker, B. M. (2003). "Rates of hydroxyl radical generation and organic compound oxidation in mineral-catalyzed Fenton-like systems." *Environ. Sci. Technol.*, 37, 1150–1158.
- Lagadee, A. J. M., Miller, D. J., Like, A. V., and Hawthorne, S. B. (2000). "Pilot-scale subcritical water remediation of polycyclic aromatic hydrocarbon- and pesticide-contaminated soil." *Environ. Sci.*

- Technol.*, 34, 1542–1548.
- Li, A., Cheung, K. A., and Reddy, K. R. (2000). “Cosolvent-enhanced electrokinetic remediation of soils contaminated with phenanthrene.” *J. Environ. Eng.*, 126(6), 527–533.
- Lindsay, W. L. (1979). *Chemical equilibria in soils*, Wiley, New York.
- Miller, C. M., and Valentine, R. L. (1995). “Hydrogen peroxide decomposition and quinoline degradation in the presence of aquifer material.” *Water Res.*, 29, 2353–2359.
- Mitchell, J. K. (1993). *Fundamentals of soil behavior*, Wiley, New York.
- Norvell, W. A., and Lindsay, W. L. (1969). “Reactions of EDTA complexes of Fe, Zn, Mn and Cu with soils.” *Soil Sci. Soc. Am. Proc.*, 33, 86–91.
- Norvell, W. A., and Lindsay, W. L. (1972). “Reactions of DTPA chelates of Fe, Zn, Cu and Mn with soils.” *Soil Sci. Soc. Am. Proc.*, 36, 778–783.
- Nowack, B. (2002). “Environmental chemistry of aminopolycarboxylate chelating agents.” *Environ. Sci. Technol.*, 36, 4009–4016.
- Nowack, B., and Sigg, L. (1997). “Dissolution of Fe(III) (hydr) oxides by metal-EDTA complexes.” *Geochim. Cosmochim. Acta*, 61(5), 951–963.
- Pamukcu, S., Weeks, A., and Wittle, J. K. (2004). “Enhanced reduction of Cr by direct current in contaminated clay.” *Environ. Sci. Technol.*, 38(4), 1236–1241.
- Pignatello, J. J., and Day, M. (1996). “Mineralization of methyl-parathion insecticide in soil by hydrogen peroxide activated with iron(III)-NTA or-HEIDA complexes.” *Hazard. Waste Hazard. Mater.*, 13, 237–244.
- Ravikumar, J. X., and Gurol, M. D. (1994). “Chemical oxidation of chlorinated organics by hydrogen peroxide in the presence of sand.” *Environ. Sci. Technol.*, 28, 394–400.
- Reddy, K. R., and Chinthamreddy, S. (2004). “Enhanced electrokinetic remediation of heavy metals in glacial till soils using different electrolyte solutions.” *J. Environ. Eng.*, 130(4), 442–455.
- Reddy, K. R., Chinthamreddy, S., Saichek, R. E., and Cutright, T. J. (2003). “Nutrient amendment for the bioremediation of a chromium-contaminated soil by electrokinetics.” *Energy Sources*, 25(9), 931–943.
- Reddy, K.R., and Saichek, R.E. (2004). “Enhanced electrokinetic removal of phenanthrene from clay soil by periodic electric potential application.” *J. Environ. Sci. Health, Part A: Toxic/Hazard. Subst. Environ. Eng.*, A39(5), 1189–1212.
- Roach, N. (2002). “Mineral structure and particle morphology of kaolin subjected to electrokinetic remediation.” MS thesis, Univ. of Illinois at Chicago, Chicago, Ill.
- Rueda, E. H., Grassi, R. L., and Blesa, M. A. (1985). “Adsorption and dissolution in the system goethite/aqueous EDTA.” *J. Colloid Interface Sci.*, 106(1), 243–246.
- Rush, J. D., and Koppenol, W. H. (1987). “Oxidizing intermediates in the reaction of ferrous EDTA with hydrogen peroxide.” *J. Inorg. Biochem.*, 29, 199–215.
- Rush, J. D., Maskos, Z., and Koppenol, W. H. (1990). “Distinction between hydroxyl radical and ferryl species.” *Methods Enzymol.*, 186, 148–156.
- Saichek, R. E., and Reddy, K. R. (2003). “Effect of pH control at the anode for the electrokinetic removal of phenanthrene from kaolin soil.” *Chemosphere*, 51, 273–287.
- Saichek, R. E., and Reddy, K. R. (2004). “Evaluation of surfactants/cosolvents for desorption/solubilization of phenanthrene in clayey soils.” *Int. J. Environ. Stud.*, 61(5), 587–604.
- Saichek, R. E., and Reddy, K. R. (2005). “Surfactant-enhanced electrokinetic remediation of polycyclic aromatic hydrocarbons in heterogeneous subsurface environments.” *J. Environ. Eng. Sci.*, 4(5), 327–339.
- Stumm, W. (1997). “Reactivity at the mineral-water interface: Dissolution and inhibition.” *Colloids Surfaces A*, 120, 143–166.
- Stumm, W., and Morgan, J. J. (1996). *Aquatic chemistry*, Wiley, N.Y.
- Sun, Y., and Pignatello, J. J. (1992). “Chemical treatment of pesticide wastes evaluation of Fe(III) chelates for catalytic hydrogen peroxide oxidation of 2,4-D at circumneutral pH.” *J. Agric. Food Chem.*, 40, 322–327.
- Thevanayagam, S., and Rishindran, T. (1998). “Injection of nutrients and TEAs in clayey soils using electrokinetics.” *J. Geotech. Geoenviron. Eng.*, 124(4), 330–338.
- Tyre, B. W., Watts, R. J., and Miller, G. C. (1991). “Treatment of four biorefractory contaminants in soils using catalyzed hydrogen peroxide.” *J. Environ. Qual.*, 20, 832–838.
- U.S. Environmental Protection Agency (USEPA). (1986). “Test methods for evaluating solid waste.” *Laboratory manual physical/chemical methods*, 3rd Ed., Vol. 1A, Office of Solid Waste and Emergency Response, Washington, D.C.
- Valentine, R. L., and Wang, H. C. A. (1998). “Iron oxide surface catalyzed oxidation by quinoline by hydrogen peroxide.” *J. Environ. Eng.*, 124(1), 31–38.
- Voelker, B. M., Morel, F. M. M., and Sulzberger, B. (1997). “Iron redox cycling in surface waters: Effects of humic substances and light.” *Environ. Sci. Technol.*, 31, 1004–1011.
- Voelker, B. M., and Sulzberger, B. (1996). “Effects of fulvic acid on Fe(II) oxidation by hydrogen peroxide.” *Environ. Sci. Technol.*, 30, 1106–1114.
- Watts, R. J., Bottenberg, B. C., Hess, T. F., Jensen, M. D., and Teel, A. L. (1999). “Role of reductants in the enhanced desorption and transformation of chloroaliphatic compounds.” *Environ. Sci. Technol.*, 33, 3432–3437.
- Watts, R. J., Jones, A. P., Chen, P. H., and Kenny, A. (1997). “Mineral-catalyzed Fenton-like oxidation of sorbed chlorobenzenes.” *Water Environ. Res.*, 69, 269–275.
- Watts, R. J., Kong, S., Dippre, M., and Barnes, W. T. (1994). “Oxidation of sorbed hexachlorobenzene in soils using catalyzed hydrogen peroxide.” *J. Hazard. Mater.*, 39, 33–47.
- Watts, R. J., Udell, M. D., Rauch, D. A., and Leung, S. W. (1990). “Treatment of pentachlorophenol-contaminated soils using Fenton’s reagent.” *Hazard. Waste Hazard. Mater.*, 7, 335–345.