Integrated Electrochemical Remediation of Mixed Contaminants in Subsurface

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Abstract

This paper presents the laboratory evaluation of the integrated electrochemical remediation (IECR) for kaolin soil spiked with mixed contaminants: phenanthrene as representative polycyclic aromatic hydrocarbon (PAH) and nickel as representative heavy metal. Batch experiments showed that significant oxidation of phenanthrene can be achieved using hydrogen peroxide (H_2O_2) as an oxidizer. Using 5% and 30% H_2O_2, 75% and 85% of phenanthrene was oxidized, respectively. Electrokinetic experiments conducted using H_2O_2 at different concentrations with 1 VDC/cm voltage gradient showed that with increase of concentration of oxidant, increased oxidation of phenanthrene could be achieved. Contrary to batch experiments, using 5% and 30% H_2O_2 resulted 27% and 56% oxidation of phenanthrene in the soil, respectively. In all electrokinetic experiments, nickel migrated towards the cathode, but it precipitated as nickel hydroxide near the cathode due to high pH conditions. The residual leachable native iron in the soil was significant indicating that native iron was not a limiting factor for the catalytic reaction of H_2O_2 to oxidize phenanthrene.

Introduction

Numerous studies have been performed in order to characterize, assess, and remediate the contaminated sites with either heavy metals or organic compounds or in some cases, with radionuclides (USEPA, 1997). Numerous technologies have been developed which could effectively treat the contaminants individually both under in-situ and ex-situ conditions (Sharma and Reddy, 2004). However, very limited research has been conducted to remediate mixed contaminants in the subsurface. Many technical issues arise when dealing with mixed contaminants due to the distinctly different characteristics of the contaminants and the complex synergistic interactions between the soil constituents and the contaminants.

The problem of mixed contaminants and the lack of effective remediation technologies for low permeability soils have necessitated development of new and effective remediation technologies. The specific goal of this research is to develop an integrated electrochemical remediation (IECR) of low permeability soils contaminated with heavy metals and PAHs. This remediation process aims at simultaneous oxidation of organic contaminants and removal of heavy metals. Fenton's reagent, consisting of hydrogen peroxide (H_2O_2) and native iron catalyst, is utilized for chemical oxidation. Essentially, this remediation processes combines chemical oxidation and electrokinetic remediation technologies that have been used for the remediation of organic contaminants and heavy metals, respectively (ITRC, 2005;

5th ICEG Environmental Geotechnics, Thomas Telford, London 2006.

Acar et al., 1995; Reddy and Chinthamreddy, 2003; Reddy et al., 2003). The specific objectives of this research are to: (1) evaluate the Fenton-like oxidation of PAHs in mixed contaminated clayey soils utilizing native soil iron as catalyst; (2) assess the extent of oxidant (H_2O_2) delivery using electroosmosis and consequent Fenton-like oxidation of PAHs in mixed contaminated clayey soils; (3) determine the transport and removal of heavy metals while the Fenton-like oxidation of PAHs in clayey soils taking place under applied electric potential; (4) optimize system variables such as oxidant concentration and applied electric potential, and (5) investigate the synergistic effects of PAHs and heavy metals on remediation.

The research objectives are being addressed by performing a series of batch and bench-scale electrokinetic experiments on different spiked and field contaminated soils. This paper presents the results from the first phase of this research program, completed using a spiked soil system. Kaolin was used as a model low permeability soil and it was spiked with both nickel and phenanthrene to represent typical mixed contamination found at contaminated sites. Batch experiments conducted using different H_2O_2 concentrations helped to assess the extent of PAHs oxidation and utilization of natural iron. Bench-scale electrokinetic experiments using H_2O_2 at different concentrations helped to assess the oxidant delivery, transport and Fenton-like oxidation of PAHs, and transport and removal of heavy metals.

Materials and Methods

The commercially available laboratory grade kaolin soil, obtained from VWR Scientific Products and manufactured by EM Science was used for the experiments. Kaolin was selected as the model soil because of its low permeability. The composition and properties of kaolin are summarized in Reddy and Saichek (2004).

Phenanthrene, a neutral organic compound containing three aromatic rings, was selected as a representative PAH. It is hydrophobic in nature with an aqueous solubility of 1.1 mg/L at 25^0C. Nickel was used as representative heavy metal, and nickel chloride salt ($NiCl_2.6H_2O$) was used as source chemical for nickel.

In order to investigate the Fenton-like oxidation process, H_2O_2 was used as the oxidant in all the experiments. The H_2O_2 solutions were used at concentrations of 5%, 10%, 20% and 30%. The diluted H_2O_2 solutions were prepared from 30% H_2O_2. For the baseline experiment, deionized water was used.

All experiments in this study were performed on the kaolin soil spiked with nickel and phenanthrene. The clean kaolin soil was initially spiked with both the contaminants each at 500 mg/kg of dry soil concentration. Due to the hydrophobic nature of phenanthrene, it was mixed in hexane and the resulting solution was used to spike the soil. A known amount of clean and dry soil was taken in a glass beaker and the phenanthrene in the solvent was allowed to mix within the soil homogeneously by constant stirring with a stainless steel spoon. The mixing was carried out in a fume hood and care was taken to reduce the chances of volatilization of solvent along with phenanthrene. Once the mixing was completed, the soil in the glass beaker was kept in the same fume hood for about 3 days to dry. When the soil was completely dry, it was taken in a glass pan and mixed with nickel chloride solution to get a concentration of 500 mg/kg. Nickel chloride salt was mixed completely in known volume of water to yield initial soil moisture content of 35% by weight and the resulting solution was mixed within the soil. After mixing continuously for homogeneity, a small amount of soil was taken for analyzing the moisture content, pH, and the actual initial concentration of contaminants in the soil.

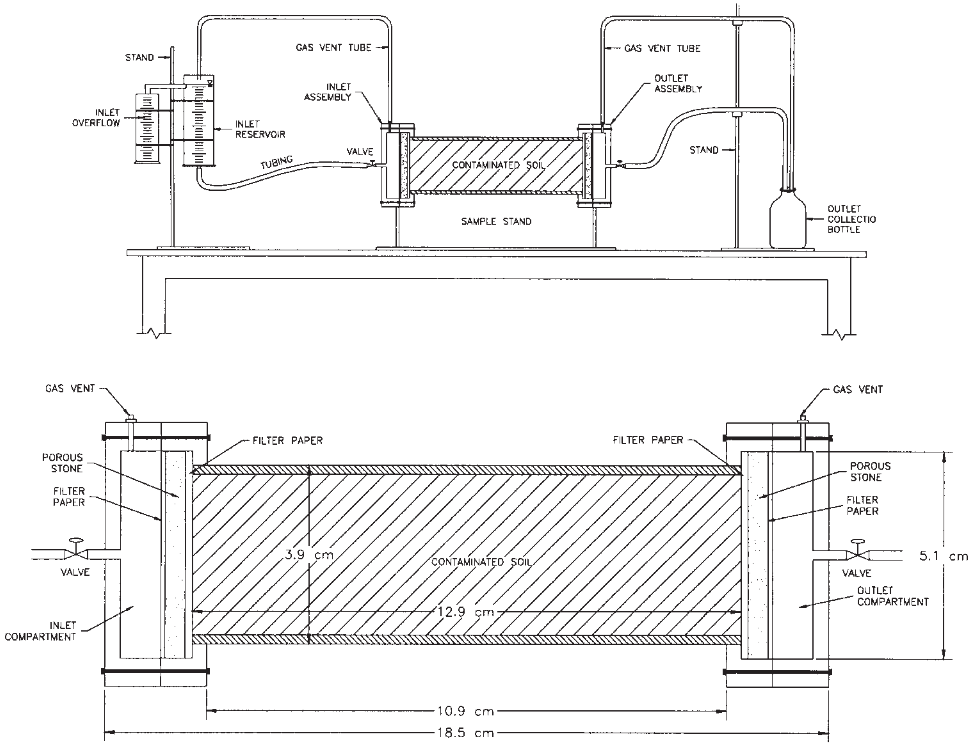

Figure 1. Bench-scale electrokinetic experimental set-up

Batch Experiments

A series of batch experiments was conducted to determine the effects of H_2O_2 concentration on phenanthrene oxidation. For each experiment, 20 grams of contaminated soil was taken in a conical flask. To the flask, about 100 mL of oxidant was added, which makes the soil to solution ratio 1:5. The selected oxidant in this case was H_2O_2 in various concentrations- 5, 10, 20 and 30%. A baseline experiment with deionized water was also conducted. Once the solutions were added to the flasks, they were sealed airtight with a laboratory film (Parafilm M). Then, the flasks were kept on a mechanical shaker. The shaking was carried out for 24 hours. At the end of 24 hours, the soil and solution were separated from each flask by centrifuging at 4000 rpm for about 30 minutes. The separated soil and solutions were then collected in different containers for phenanthrene and nickel analysis. All the experiments were performed in duplicates in order to ensure accuracy.

Electrokinetic Experiments

Figure 1 shows the complete bench-scale electrokinetic experimental set-up. A detailed description of the experiment setup is given in Reddy et al. (1997). The spiked soil was uniformly compacted in an electrokinetic cell, which is made of Plexiglas. Once the soil was packed in the cell, filter papers were attached to either ends of the cell and then the cell was closed by electrode assembly that consist of porous stone and graphite electrode on either ends. The anode reservoir was connected to the anode assembly, and a sample collection bottle was placed at the cathode outlet. Initially, H_2O_2 solution was placed in the anode reservoir and deionized water was placed in the cathode as shown in Figure 1. Pre-selected constant voltage gradient of 1 VDC/cm was applied across the soil sample. Electric current and the electroosmotic flow were measured at regular time intervals. Periodically, outflow samples were collected at the cathode, and the anode reservoir was replenished with fresh stock of solutions.

At the end of the each experiment, aqueous solutions from anode and cathode reservoirs and the electrode chambers were collected separately and the volumes were measured. The soil specimen was extruded from the electrokinetic cell and cut into five equal sections with the section close to cathode was sub-sectioned into two equal sections. Therefore, the soil specimen was divided into six sections. Each sample was taken in a glass jar and a representative sample was taken for final moisture content determination. About 10 grams of soil was taken from each sample for the determination of pH of the soil at the end of the testing period. The moisture content of the samples was determined by using the standard method ASTM D2216 and the pH of the soil was measured using ASTM D4972 (ASTM, 2004).

Chemical Analysis

To determine the concentration of phenanthrene in the soil at the end of the testing, Soxhlet extraction was performed using the USEPA test method 3540C (USEPA, 1986). The extracted solvent-phenanthrene samples were analyzed using gas chromatography. More details on the extraction procedure are given in Reddy and Saichek (2004) and Maturi (2004). Supernatant samples from batch experiments and liquid samples collected at the electrodes in electrokinetic experiments were analyzed for phenanthrene concentration by performing liquid-liquid extraction. The extractants were later analyzed using gas chromatography.

Acid digestion of soil samples was performed using the USEPA 3050 procedure (USEPA, 1986). Then the concentrations of nickel and iron were determined using atomic absorption spectrophotometry (AAS) (USEPA, 1986). In order to verify the reproducibility of the results, all the analyses were conducted in duplicates.

Results and Discussion

Batch experimental results showed that H_2O_2 is a good oxidizing agent for the oxidation of phenanthrene in the soil. The oxidation of phenanthrene increased with increased H_2O_2 concentration. With 5% H_2O_2, 76% oxidation was achieved whereas with 30% H_2O_2, about 87% oxidation was achieved. In the experiment with deionized water, phenanthrene oxidation was negligible. Hence it can be seen that Fenton-like oxidation, using H_2O_2 and native iron in the soil is able to produce the necessary hydroxyl radicals which could oxidize phenanthrene to very low levels within the soil. The Fenton-like oxidation and the subsequent reaction of PAHs with hydroxyl radicals is represented as follows (Walling 1975):

$$\begin{gathered}
Fe^{2+} + H_2O_2 \Rightarrow OH + Fe^{3+} + OH \\
Fe^{3+} + H_2O_2 \Rightarrow Fe^{2+} + OOH + H^{+} \\
RH + OH \Rightarrow H_2O + R \\
R + Fe^{3+} \Rightarrow Fe^{2+} + \text{products}
\end{gathered}$$

- R is a HOC such as Phenanthrene

From the results of final nickel concentration in the soil and the effluent, it can be concluded that although there was very low removal of nickel from the soil irrespective of concentration of oxidant, the decreased concentrations of nickel in soil with increasing concentrations of oxidant could be attributed to the pH decrease with increase in H_2O_2 concentration.

The results of the electrokinetic experiments were analyzed to assess the electric current, electroosmotic flow, pH, and contaminant transport, removal and oxidation in the soil. In all the experiments, at the beginning, current increased very rapidly to a peak value. Then it started dropping to a very low value where it stabilized within about 24 hours. After a period of about 48 hours, all the experiments showed similar values of electric current. The electroosmotic flow was observed to increase at a uniform rate until the termination of the experiments. Approximately 1.6, 1.5, 1.2 and 1.5 pore volumes were obtained in 5%, 10%, 20% and 30% H_2O_2 experiments, respectively. In the baseline experiment, about 1.0 pore volume of flow was obtained.

The soil pH increased from anode to cathode in all the experiments as shown in Figure 2. Due to the electrolysis reactions, the acidic solution generated at the anode migrates into the soil towards cathode thereby reducing the pH of soil. The OH^- ions generated at the cathode migrate from cathode to anode which is opposite to the direction of EO flow and hinder the flow by reducing the conductivity through neutralization of the H^+ ions migrating from anode.

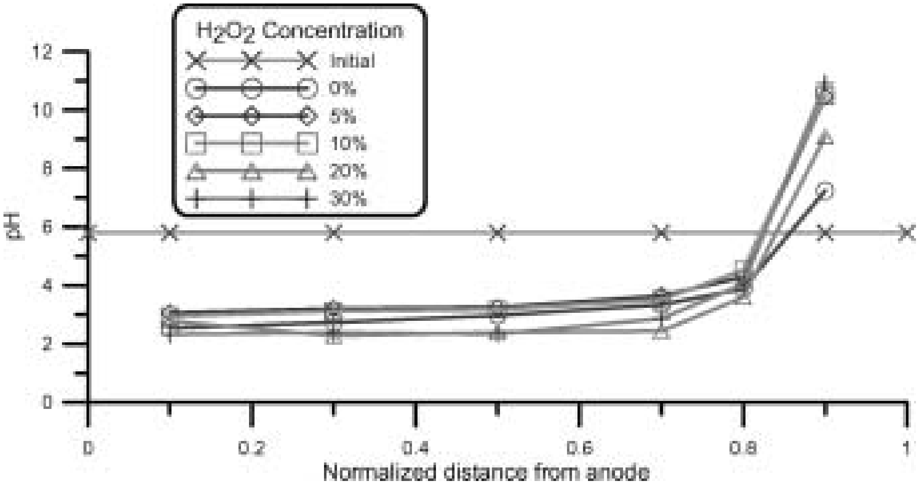

Figure 2. Effect of hydrogen peroxide concentration on pH distribution

Figure 3 shows the distribution of nickel in various sections of soil from anode to cathode at the end of electrokinetic testing. In general, the nickel concentrations were low in the sections closer to the anode and higher near the cathode. Significant mobilization of nickel occurred in all the experiments as it can be seen from the reduced concentrations near anode to highly increased concentrations at the cathode. Due to the transfer of momentum from the electrons to other ions that constitute the interconnected soil, electromigration occurs. Electromigration refers to the transport of ionic species in the pore fluid toward the oppositely charged electrodes (Reddy et al., 2003). Depending on the charge of contaminant, electromigration causes its attraction towards the respective electrode. Thus, in this case, the bivalent positively charged nickel ions migrate towards negatively charged cathode. The concentration of nickel at cathode was very high in all the experiments due to the high pH conditions existing near cathode. At high pH, nickel precipitated as nickel hydroxide (Ni $(OH)_2$) in the soil thereby reducing its removal into the cathode solution.

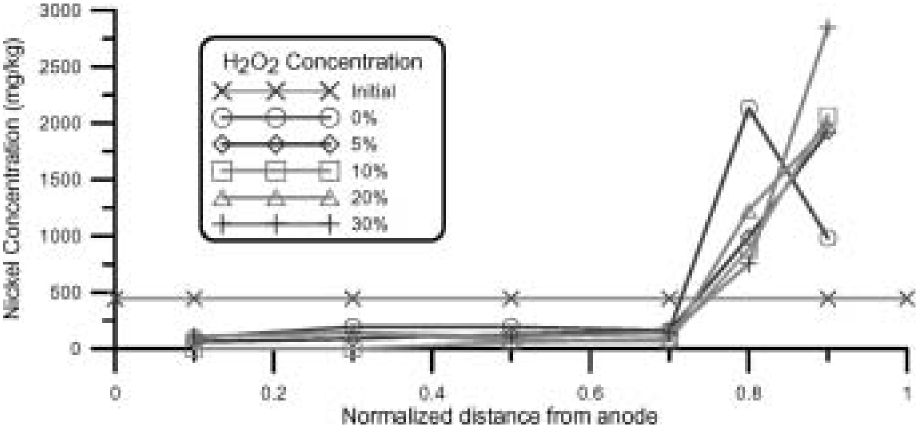

Figure 3. Effect of hydrogen peroxide concentration on nickel concentration

In all the experiments with H_2O_2, phenanthrene concentrations decreased throughout the soil when compared to the initial concentration (Figure 4). Phenanthrene removal into the electrode reservoirs was insignificant in all the experiments. The insignificant removal of phenanthrene from the soil was comparable to that in the batch experiments. The supernatant solutions of the batch experiments also did not show any removal of phenanthrene from the soil mass. This could be due to the hydrophobic nature of phenanthrene, which is limiting the dissolution of phenanthrene into the pore solution.

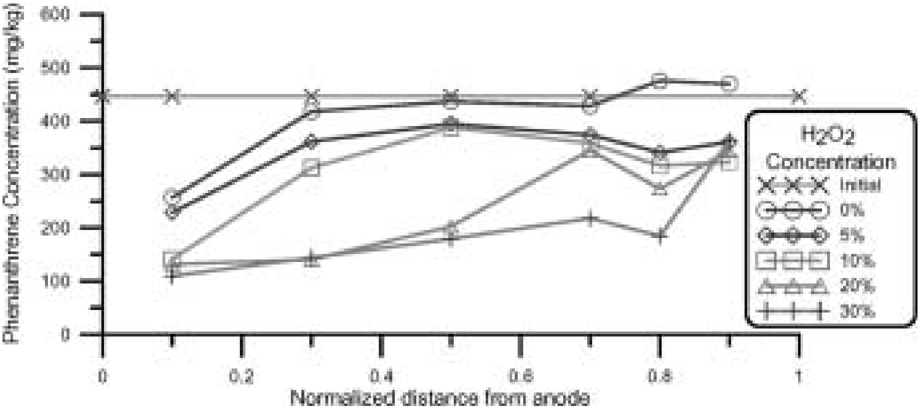

Figure 4. Effect of hydrogen peroxide concentration on phenanthrene concentration

These results show that as the concentration of oxidant was increased, the remedial efficiency of phenanthrene also increased. As shown in Figure 5, higher oxidation of phenanthrene was observed with higher concentration of H_2O_2. However, the amount of phenanthrene oxidation in electrokinetic experiments was significantly lower than that observed in the batch experiments. This may be due to relatively low amount of H_2O_2 delivery as a result of less than two pore volumes of electroosmotic flow. Phenanthrene concentration increased gradually from anode to cathode in all the experiments.

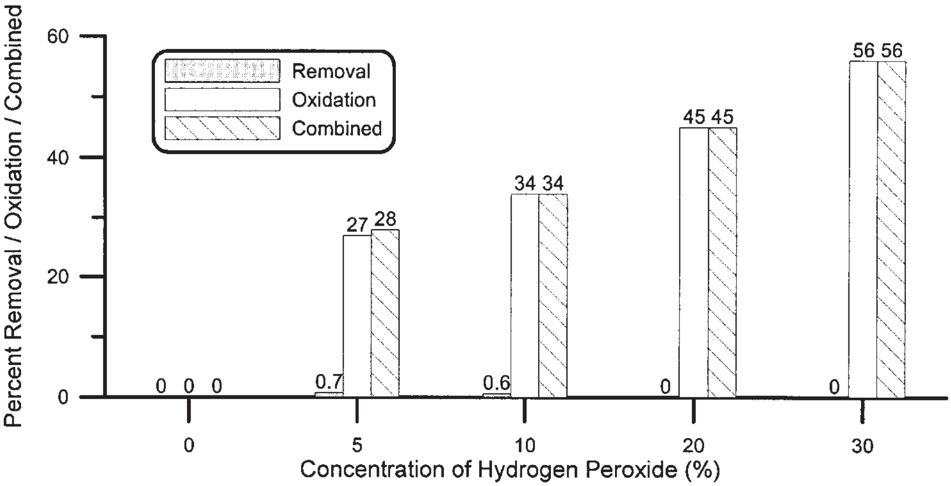

Figure 5. Effect of hydrogen peroxide concentration on phenanthrene remedial efficiency

In general, high concentrations of iron were observed throughout the soil in all the experiments. Low amount of easily soluble iron was still present in the soil in the baseline deionized water and H_2O_2 experiments. Leachable iron concentration increased gradually from anode to cathode in all the experiments. This shows that very low amount of iron was getting leached into the solution form, and high amounts of iron were still left in the soil at the end of electrokinetic testing. This result implies that native iron is sufficiently available to act as a catalyst in the reaction with the H_2O_2 for the Fenton-like reaction.

Conclusions

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

1. Batch experiments showed that significant oxidation of phenanthrene can occur using H_2O_2 as an oxidizer. Using 5% H_2O_2, 76% of phenanthrene was oxidized. With increasing concentration of oxidant, the phenanthrene oxidation increased. About 87% oxidation of phenanthrene was observed in case of 30% H_2O_2. This indicates that an optimum low level of oxidant concentration should be selected to minimize the costs.
2. Electrokinetic experiments showed that higher concentration of H_2O_2 increased phenanthrene oxidation. With 5% H_2O_2, about 27% oxidation of phenanthrene was achieved, whereas with 30% H_2O_2, almost 56% oxidation of phenanthrene was achieved.
3. Significant migration of nickel towards the cathode occurred. Comparison of baseline and H_2O_2 experiment results shows that nickel mobility was slightly increased in the presence of H_2O_2. However, removal of nickel from the soil was insignificant in all the experiments. This could be because of reduced electroosmotic flow and the precipitation of nickel as nickel hydroxide near the cathode due to high pH conditions. Increasing the electroosmotic flow and lowering soil pH near the cathode could enhance removal of nickel from the soil.

4. The presence of leachable native iron in the soil indicates that iron was not a limiting factor for the catalytic reaction of H_2O_2 to oxidize phenanthrene.

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