Electrokinetic Delivery and Activation of Persulfate for Oxidation of PCBs in Clayey Soils

Yeliz Yukselen-Aksoy and Krishna R. Reddy, F.ASCE

Abstract: Contamination of soils by polychlorobiphenyls (PCBs) is of environmental concern because of their toxicity, persistence, hydrophobic nature, and slow biodegradation potential. Among the PCB remedial technologies, direct oxidation by persulfate is considered to have great potential to be both simple and rapid. However, to produce faster reaction rates, persulfate is often activated using heat, metal chelates, hydrogen peroxide, or high pH. Furthermore, delivery of persulfate in low permeability clayey soils is difficult. Integrating electrokinetic remediation with persulfate has the potential to overcome such difficulties because the applied electric potential can facilitate the delivery of persulfate in low permeability soils as well as activate oxidizing radicals and simultaneously induce oxidative/reductive reactions directly in the soil. This study investigates the potential for in situ oxidation of PCBs in low permeability soils using persulfate as an oxidant and also evaluates the benefits of integrating oxidation with electrokinetic remediation. Several series of laboratory batch and bench-scale electrokinetic experiments were conducted using kaolin, a representative clayey soil, spiked with 50 mg/kg of 2,2',3,3',4,4',5,5'-octachlorobiphenyl (PCB 126), a representative PCB. Persulfate oxidation activators [elevated temperature (45°C) and high pH (at the cathode)] were investigated to maximize the PCB degradation. In addition, the effect of oxidant dosage on PCB degradation was investigated. The electrokinetically enhanced temperature-only activated persulfate oxidation test resulted in better PCB remediation (77.9%) than the temperature and high-pH activated persulfate oxidation (76.2%) in a 7-day period. The optimal dosage for effective remediation was 30% Na-persulfate (76.2%) because a 20% concentration of the oxidant yielded a lower rate of degradation (55.2%) of PCB 44. The results are encouraging for the use of electrokinetically enhanced persulfate oxidation for the effective remediation of PCBs in soils. DOI: 10.1061/(ASCE)GT.1943-5606.0000744, © 2013 American Society of Civil Engineers.

CE Database subject headings: Remediation; Soil treatment; Oxidation; Clays; PCB.

Author keywords: Electrokinetic remediation; Soil remediation; Persulfate oxidation; Advanced oxidation process; Polychlorobiphenyls.

Introduction

Polychlorobiphenyls (PCBs) are a group of chlorinated compounds that include up to 209 variations or congeners [U.S. Environmental Protection Agency (USEPA) 1987] with various physiochemical properties. They were first synthesized in the 1920s and since then global production has been estimated to have reached 10^6 Mg (Yao et al. 2003). Since the 1930s, PCBs have been synthesized massively for their use in many industrial applications because of their high chemical stability, noninflammability, and apparent harmlessness. However, since the 1960s and 1970s, PCB use and production has dramatically decreased because PCBs were identified as a dioxin precursor. It was demonstrated that one of its most appreciated properties, chemical stability, was also its main problem; once PCBs are released into the environment they are practically indestructible. The USEPA has determined that PCBs may cause adverse reproductive effects, developmental toxicity, and cancer; thus, they are dangerous to human health and wildlife. Because of their hydrophobic nature and low water solubility PCBs tend to persist in the environment and remain in natural media, such as soil, sediments, and water. Soils with various concentrations of PCBs have been detected at sites around the world and are shown to pose danger to public health and the environment.

Current methods of remediation of PCB-contaminated soils, such as incineration and bioremediation, are expensive or ineffective. The aim of this study is to evaluate the combination of persulfate oxidation and electrokinetic (EK) treatment as an in situ technology to effectively deliver persulfate into subsurface soils, including low permeability clayey soils, as well as achieve its activation within the soils to oxidize the PCBs. A comprehensive experimental program consisting of batch and bench-scale EK experiments was conducted to investigate various system variables (e.g., dosage, pH, temperature) and assess the feasibility of such technology.

Background

PCBs were used as dielectric fluids in electrical transformers and capacitors and were often mixed with organic solvents such as chlorinated benzenes. PCBs were also commonly used in hydraulics, in lubricating and heat transfer fluids, as plasticizers in paint, and as dye carriers in carbonless copy paper. As a result of its widespread use, large amounts of PCBs have been released into the environment. Furthermore, PCB exposure still occurs because of its presence in old transformers and capacitors even though the commercialization of PCBs has been banned in the United States since
1979 and those installations could only be used legally until 1997. The European Union regulations also prohibit manufacturing and commercialization, and imposed a control of all the installations with PCB, which must be dismantled. Effective PCB remediation technologies are greatly needed around the world.

Remediation techniques for soils contaminated with PCBs include incineration, thermal desorption, chemical dehalogenation, solidification/vitrification, bioremediation, and air sparging. Selection of PCB remedial technologies is dependent on many factors, such as the structures and properties of PCBs, site conditions, and cost, among other factors. Although incineration at high temperature is a widely used technology for treating soils and sediments contaminated with PCBs, there is a potential danger of the release of dioxin via the flue gas stream (Dávila et al. 1993). In addition, incineration often arouses negative public opinion. Some of these methods are sensitive to soil grain size, clay content, soil pH, etc., and are unsuccessful treatments for the complete remediation of heavily contaminated soils (Ferrarese et al. 2008). Some of these methods also produce other residuals that must also be treated and/or disposed of. Therefore, a new technology that has the potential to overcome these shortcomings is greatly needed. Recently, chemical oxidation (CO) has gained interest as a result because it is a rapid, aggressive process that can be applied in situ, avoiding the need to disturb ground structures or undertake expensive excavation procedures.

In situ CO (ISCO) is an emerging technology based on the injection of chemical oxidants into contaminated soil and groundwater to oxidize the contaminants. The USEPA identified ISCO as one of the innovative remediation technologies for the Brownfield sites (USEPA 2001). The effectiveness of the reaction depends on the hydraulic conductivity of the soil as well as the distribution of the contaminants. ISCO can be applied to the remediation of sites contaminated with unsaturated halogenated volatile organic compounds (VOCs), pesticides, and polycyclic aromatic hydrocarbons (PAHs), as well as PCBs (USEPA 1998).

When compared with other treatment methods, CO is a quicker, simple to use process. Common oxidants, such as permanganate or peroxy, are readily available and economical. Because most of the contaminants are degraded completely within the soil, it eliminates the collection of contaminants in the effluents, thereby reducing the cost and efforts of treatment. Also, this is an in situ technique; therefore, it could avoid the need for disturbing ground structures and expensive excavation procedures. The CO remediation processes have gained much importance during the last decade. They are applicable to a wide range of organics, and contaminant destruction is rapid and effective even with complex and recalcitrant molecules. In addition to hydrogen peroxide and permanganate, other widely used oxidants include Fenton’s reagent and ozone. However, reagent chemical stability and fast reaction also have drawbacks. For example, hydrogen peroxide and ozone have relatively short lifetimes in the subsurface and Fenton’s reagent has some limitations such as a fast reaction between the oxidant and catalyst, ineffective utilization of quickly generated hydroxyl radicals, and the inherent instability of hydrogen peroxide (Watts et al. 2007). Persulfate is an alternate oxidant that overcomes those drawbacks because it requires activation. Although persulfate was frequently used in diverse industrial processes, it has been recently identified as an oxidant for treating many types of contaminants, including trichloroethylene (Liang and Bruell 2008; Waldemer et al. 2007), tetrachloroethylene (Dahmani et al. 2006), PAHs (Rivas 2006; Cuypers et al. 2000; Ferrarese et al. 2008), trichlorobenzene (Barbash et al. 2006), lindane (Cao et al. 2008), methyl tert-butyl ether (MTBE) (Huang et al. 2002), and benzene/toluene/ethyl benzene/xylene (BTEX) (Crimi and Taylor 2007).

Huang et al. (2002) used the heat-assisted persulfate oxidation for remediation of MTBE in contaminated groundwater. They reported some advantages of using persulfate instead of Fenton’s chemistry and ozonation. Persulfate is more stable and highly soluble under normal subsurface conditions and it can be transported to contaminated zones more effectively with reactants. There are studies that show that persulfate oxidation is a very effective remediation method for the removal of PAHs. Issaani et al. (2007) studied remediation of creosote contaminated clay by the integration of EKs and CO. According to their results, electrokinetically enhanced oxidation using sodium persulfate resulted in better PAH removal (35%) than either EKs (24%) or persulfate oxidation (12%) alone. Ferrarese et al. (2008) used activated sodium persulfate to degrade PAHs in old sediment contamination. The remediation efficiency was around 90% with activated persulfate; however, when the activated persulfate and hydrogen peroxide were combined the removal of total PAHs was more successful (92%). Huang et al. (2005) used thermally activated persulfate oxidation for degradation of 50 VOCs. They observed that compounds with carbon-carbon double bonds and benzene rings bonded to reactive functional groups are easy to degrade in VOCs. Rastogi et al. (2009) used Fe(II)-mediated activation of persulfate for remediation of PCBs in aqueous and sediment systems and found 54% removal for 2-chlorobiphenyl in the sediment-sluurry phase.

The reactions of persulfate ions with various organic and inorganic compounds have been studied (Huang et al. 2002; Waldemer et al. 2007; Liang and Bruell 2008). As a result of its relatively high stability under normal subsurface conditions, persulfate can travel through the subsurface into the contaminated zone effectively. The major advantages of persulfate when compared with other oxidant systems are greater chemical stability, lesser affinity for natural soil organics (less than permanganate ion), it can be transported longer distances in subsurface, and its fast reaction when activated. Persulfate is able to oxidize many organic substances into carbon dioxide. The strong oxidant will break up the biphenyl ring and cleave the aromatic ring, resulting in smaller, nontoxic organic fragments after oxidation. Complete oxidation will result in the formation of CO₂, H₂O, and Cl⁻ (usually referred to as mineralization).

Persulfate may destroy the contaminants by direct oxidation; however, after activation persulfate is decomposed in sulfate radicals (SO₄²⁻), which are very powerful and kinetically fast oxidants. There are four primary methods to activate the persulfate: heat, metal chelates, hydrogen peroxide, and high pH. Selecting the right activator depends on the site conditions, such as lithology (clay, sand, etc.), hydrogeology, and the application method. The sulfate radical is the strongest aqueous oxidizer with redox potential estimated to be 2.6 V.

The integration of CO with EK remediation may benefit the treatment of contaminated soils with organics and mixed contaminants (Reddy and Cameselle 2009). Thus, EK treatment can facilitate oxidant delivery and activation of oxidizing radicals and simultaneously induce oxidative/reductive reactions directly within soils. The organic contaminants do not require solubilization and removal from the soils but they are oxidized in situ by the persulfate delivered and activated with the electric field. Also, this technique can be used in low permeability soils and heterogeneous soils.

Materials and Methods

Soil

Kaolinite clay (kaolin) was used in this study to represent low permeability soils. Kaolin is often used in EK research because it has been studied extensively; has a low organic content, consistent, and
uniform mineralogy; is fairly nonreactive; and has a low cation exchange capacity (Eykholt 1992). Thus, kaolin is a good control soil for laboratory EK testing because the amount of experimental variation as a result of soil heterogeneity is minimized and the influence of variables such as oxidant dosage in the EK treatment can be drawn easily. Furthermore, the white color of kaolin helps in the visual monitoring of any changes through the kaolin specimen. The properties of the kaolin used in this study are shown in Table 1.

**Chemicals**

The 2,2',3,5'-tetrachlorobiphenyl (PCB 44) was obtained from Ultra Scientific (North Kingston, Rhode Island) with a purity higher than 97% and a chemical formula of C12H6Cl4. Sodium persulfate with a chemical formula of Na2S2O8 and purity > 99% was obtained from FMC (Philadelphia, Pennsylvania). Reagent grade acetone was obtained from Fisher Scientific (Fair Lawn, New Jersey).

**Experimental Setup**

Fig. 1 shows the schematic of the EK test setup developed and used in this study. The setup consisted of a cell, two electrode compartments; anode, cathode, and Na-persulfate reservoirs; thermocouples; power supply; multimeter; pH controller; and data acquisition system. The EK cell was made of Plexiglas with 3.7-cm inside diameter and 13.2-cm length. Each electrode compartment contained filter paper, a porous stone, and a perforated graphite electrode. Three thermocouples were placed along the soil specimen, one in the middle, and the other two near the anode and cathode, respectively. The temperature in the soil sample was recorded by an ACR SmartReader plus six thermocouple data loggers at specific time intervals. A constant direct current (DC) electric field was applied by a Protek 3006B DC power supply. The current was measured using an Agilent 34405A digital multimeter. The multimeter was connected to the computer and current intensity readings were recorded at varied time intervals. At the beginning of the tests, the current was recorded every 2 min. Gas vents were provided in the electrode compartments to allow gases resulting from electrolysis reactions to escape.

**Table 1. Properties of Kaolinite Clay**

<table>
<thead>
<tr>
<th>Property</th>
<th>Kaolin</th>
<th>Particle-size distribution (ASTM D422; ASTM 2007b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gravel</td>
<td>0%</td>
<td></td>
</tr>
<tr>
<td>Sand</td>
<td>4%</td>
<td></td>
</tr>
<tr>
<td>Silt</td>
<td>18%</td>
<td></td>
</tr>
<tr>
<td>Clay</td>
<td>78%</td>
<td></td>
</tr>
</tbody>
</table>

Atterberg limits (ASTM D2487; ASTM 2007a)

- Liquid limit: 50%
- Plastic limit: 27.4%
- Plasticity index: 22.6%
- Specific gravity (ASTM D854; ASTM 2007b): 2.6
- Hydraulic conductivity (cm/s) (ASTM D5084; ASTM 2007c): $1.0 \times 10^{-8}$
- pH (ASTM D4972; ASTM 2007i): 4.9
- Cation exchange capacity (meq/100 g) (ASTM D7503; ASTM 2007e): 1–1.6
- Organic content (ASTM D2974; ASTM 2007d): 0
- USCS classification (ASTM D2487; ASTM 2007a): CL

Note: Mineralogy consists of kaolinite (100%), muscovite (trace), and illite (trace).

Experimental Procedure

Several series of batch and bench-scale EK experiments were conducted to determine the ability of persulfate to oxidize PCBs in the contaminated soil and to compare the effectiveness of the various activators. All of the batch and EK experiments used kaolin spiked with PCB at an initial target concentration of 50 mg/kg. For spiking the soil, the mass of PCB required to yield the target concentration was measured and completely dissolved in hexane. The PCB-hexane mixture was subsequently combined with the measured amount of soil and with additional hexane so that the soil-PCB-hexane mixture could easily be blended homogeneously. The mixtures were stirred for 20 min with stainless steel spoons in glass beakers to ensure uniform distribution of PCB in the soil. The soil-PCB-hexane mixture was then placed in a ventilation hood for nearly 10 days until the hexane evaporated completely and the contaminated soil was dry. The initial concentration in the samples was routinely analyzed before each test to assess the initial PCB contaminant concentration in the soil specimen.

For each batch test, 1 g of dry contaminated soil was placed in a 50-mL centrifuge tube. About 10 mL of Na-persulfate solution was added to the tube to obtain a soil-liquid mixing ratio of 1:10 (g:ml). Sodium persulfate (Na2S2O8) was used in various concentrations of 10, 20, 30, and 40%. Sulfuric acid was used for the pH adjustment. Once the soil sample and persulfate solution were mixed together, the mixture was placed in a mechanical shaker for various reaction times (1, 2, 4, and 7 days). At the end of the reaction time, the soil and supernatant solution were separated by centrifugation at 6,400 rpm for about 10 min. The soil was then treated with acetone for 24 h to determine the residual PCB concentration in the soil after treatment with persulfate. The experimental details of the batch tests are summarized in Table 2.

Based on the batch testing results, bench-scale EK experiments were conducted to investigate the influence of the persulfate concentration and activation method. The initial dry mass of soil that was placed into the cell varied slightly from test to test; however, it was approximately 130 g for each test in the EK cell. After the spiking process, when the soil was again dry, it was homogenously mixed with a measured amount of deionized (DI) water in a glass pan. The moist soil was then placed into the EK cell in layers and each layer was tamped into the cell using an aluminum tamper to minimize the amount of void space. The compacted soil samples had dry densities of 1.26–1.36 g/cm3 and moisture contents of 33–35%. Once the soil was fully packed into the cell, the cell assembly was completed and the anode, cathode, and Na-persulfate reservoirs were filled with the corresponding solution for each test. The cathode compartment and reservoir were filled with DI water and the Na-persulfate reservoirs were filled with the selected flushing solutions. A constant 1 VDC/cm voltage gradient was applied through the cell. The voltage gradient may affect the remediation efficiency; however, to determine the remediation efficiency of electrokinetically enhanced Na-persulfate oxidation, a constant voltage gradient was selected for these tests.

During testing, the electrical current, temperature, and pH were measured, controlled, and recorded. The electrical current and temperature were recorded automatically at every specified time interval by the computer data acquisition system. The effluent samples were collected in glass vials in order to measure the pH and persulfate concentrations. The tests were run until the current was greatly decreased and, correspondingly, the effluent volume was significantly reduced. At the completion of the test, the soil specimen was extruded and sectioned into three equal parts. Each part was weighed and the specimen was placed into glass bottles for further analysis. Representative samples were taken from each soil sample for determination of its moisture content, soil pH, and soil PCB 44 concentration.

The EK testing program conducted is shown in Table 3. During testing, Na-persulfate solution was added to the system using a
separate compartment closer to the cathode (Fig. 1). Test 1 was a baseline test carried out using distilled water in the electrode compartment and without persulfate or an activation process. Test 2 was performed with 30% Na-persulfate without any activation. Test 3 was performed with temperature activation only. The temperature was controlled at 45°C inside the cell using a silicone heat band wrapped around the EK cell and was measured and controlled by three thermocouples installed in the EK cell. Test 4 was performed with combined temperature and high pH activation. In Test 5, temperature and high pH activators similar to Test 4 were used but with a lower concentration of Na-persulfate (20%).

**Analytical Methods**

The PCB in the soil was extracted and analyzed according to USEPA Method 8082 using a gas chromatograph (Agilent Model 6890; Wilmington, Delaware) equipped with a microelectron capture detector. The extracting procedure was as follows: 1 g of dry soil sample was extracted with acetone using a soil-to-solvent extraction ratio of 1:25 (g/mL). The soil-acetone mixture was shaken in a reciprocal shaker for 24 h. Then, the soil-acetone mixture was centrifuged at 640 rpm for 1 min. The supernatant liquid was collected and diluted in ethanol. Liquid-liquid extraction was performed to transfer the PCBs from the diluted water-ethanol phase into a hexane phase, which was used for gas chromatography analyses. Soil pH and moisture content measurements were determined as described in ASTM Methods D4972 (ASTM 2007f) and D2216 (ASTM 2007g), respectively. Replicate samples were tested for each analysis to ensure accuracy.

**Results and Discussion**

**Batch Test Results**

A series of batch experiments were conducted to investigate the effectiveness of various control variables to maximize PCB degradation and to determine the optimal conditions to adopt in EK experiments. As persulfate oxidation activators, high pH and elevated temperatures were investigated. In addition, the effects of

![Fig. 1. Schematic of EK test setup](image-url)
oxidant dose and reaction time combined with other parameters (pH, temperature) were evaluated to maximize the destruction of the PCBs.

The effect of temperature on the activation of persulfate in PCB oxidation was evaluated by performing batch tests at room temperature (23°C) and two elevated temperatures (35 and 45°C). The PCB degradation increased as the temperature increased and the temperature was a strong activator of the persulfate with 30% sodium persulfate and natural pH (7.2). As the temperature increased from 23 to 45°C, the PCB degradation increased from 22.5 to 92.6% [Fig. 2(a)]. Furthermore, increasing the temperature from 35 to 45°C caused an increase of PCB degradation by 28.4%. Temperatures greater than 45°C were not considered because the relatively short lifetime of the persulfate at elevated temperatures (e.g., > 50°C) will limit the delivery time to contaminated soils in the field (Johnson et al. 2008).

To determine the pH effect on persulfate oxidation, the batch tests were performed for pH levels of 2, 4, natural, 9, and 12 at 30% persulfate for 24 h at room temperature. The results are shown in Fig. 2(b). The highest PCB degradation was 45.5% at pH 12. In addition, the PCB degradation was greater for pH 2 than for pH 4, 7, and 9 because persulfate is active at pH values less than 3 (Block et al. 2004). PCB degradation for pH-activated persulfate oxidation was significantly lower compared with PCB degradation with temperature-activated persulfate oxidation.

The PCB degradation increased with the increasing concentration of persulfate in the solution, with the highest PCB degradation obtained for 30% persulfate dosage at pH 12 and room temperature.

### Table 3. Testing Program for the Coupled EK-CO Experiments

<table>
<thead>
<tr>
<th>Test</th>
<th>Soil matrix</th>
<th>Anode solution</th>
<th>Cathode solution</th>
<th>Na-persulfate concentrationa (%)</th>
<th>Persulfate activation method</th>
<th>Voltage gradient (VDC/cm)</th>
<th>Duration (days)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Kaolin</td>
<td>Distilled water</td>
<td>Distilled water</td>
<td>—</td>
<td>—</td>
<td>1</td>
<td>7</td>
</tr>
<tr>
<td>2</td>
<td>Kaolin</td>
<td>Distilled water</td>
<td>Distilled water</td>
<td>30</td>
<td>Temperature (45°C)</td>
<td>1</td>
<td>10</td>
</tr>
<tr>
<td>3</td>
<td>Kaolin</td>
<td>Distilled water</td>
<td>Distilled water</td>
<td>30</td>
<td>Temperature (45°C) + high pH (pH 12 at anode)</td>
<td>1</td>
<td>7</td>
</tr>
<tr>
<td>4</td>
<td>Kaolin</td>
<td>Distilled water + 2 M NaOH</td>
<td>Distilled water</td>
<td>30</td>
<td>Temperature (45°C) + high pH (pH 12 at anode)</td>
<td>1</td>
<td>7</td>
</tr>
<tr>
<td>5</td>
<td>Kaolin</td>
<td>Distilled water + 2 M NaOH</td>
<td>Distilled water</td>
<td>20</td>
<td>Temperature (45°C) + high pH (pH 12 at anode)</td>
<td>1</td>
<td>7</td>
</tr>
</tbody>
</table>

*a *Introduced at the oxidant compartment located between the cathode and the soil.

**Fig. 2.** Batch test results: (a) temperature and time effect; (b) pH effect; (c) Na-persulfate concentration effect
(23°C). When the persulfate dosage increased from 30 to 40%, the PCB degradation decreased from 42 to 38% [Fig. 2(e)]. Therefore, the 30% persulfate dosage was selected as the optimum persulfate dosage for the other tests in this study.

The effect of the reaction time on the degradation of PCB 44 were tested with 30% persulfate at pH 12 and at temperatures of 23 and 45°C for 1, 2, 4, and 7 days. The PCB degradation increased with the reaction time; the PCB degradation at room temperature (23°C) after 7 days was 65.7%. The greatest PCB degradation was obtained after 7 days of oxidation for both soils, where degradation increased to 97.4% when the temperature was increased to 45°C at the end of the 7 days.

To improve the removal efficiency, elevated temperature and high pH activators were investigated in batch tests. These tests were done at 45°C and pH 12 with 30% Na-persulfate dosage and the reaction time was 1 day. When these results were compared with the temperature-only activation results, kaolin had a slightly lower level of degradation (92.6%) with the elevated temperature activation of persulfate. According to these results, the oxidation of PCB can be enhanced effectively by using temperature-only activation. A detailed discussion on the batch experiments is presented in Yukselen-Aksoy et al. (2010).

**Electrokinetic Test Results**

The results of the EK experiments were analyzed to assess the influence of electric current, temperature, and electroosmotic flow on contaminant removal during the EK tests, as well as the moisture content, pH, and residual PCB distribution in the soil at the conclusion of the tests.

**Electrical Current**

The electric current in every EK test was measured and recorded using a multimeter and a data logger connected to a computer. Fig. 3 shows the electric current profile along the treatment time for all the EK tests. The current values followed the same trend during Tests 2–5. Initially, or within a few hours after applying the voltage gradient, the current increased, reached peak values, and then began to decrease. High current was measured as a result of the partial solubilization of salt precipitates and mobilization of Na-persulfate ions resulting in a higher ionic concentration in the pore-water (Mitchell 1993; Saichek and Reddy 2005). The current values decreased over time as the ions in the pore solution electromigrated toward the electrodes. However, each Na-persulfate addition event significantly increased the electric current intensity as a result of the increase in the ion concentration in the interstitial fluid. The electric current began to decrease and, finally, the electric current attained relatively stable values for all tests. In Test 1, only distilled water was added to the anode, cathode, and persulfate reservoirs. For that reason, there were not enough ions in the solution to reach values that were similar to other tests in electric current. The electric current values were higher in the 30% Na-persulfate tests than in those with 20% Na-persulfate. The higher current in the 30% Na-persulfate was a result of the presence of a greater number of mobile ions in the pore fluid when compared with the 20% Na-persulfate.

**Temperature**

Persulfate is a strong oxidant; however, it shows a very slow reaction rate for complex and recalcitrant organics unless persulfate is activated. Activation of persulfate anions (S\(_2\)O\(_8\)^{2−}\)) produces sulfate free radicals (SO\(_4\)^{2−}\), which are very powerful oxidants. There are four primary methods for activation of persulfate; i.e., heat, metal chelates, hydrogen peroxide, and high pH. Thermal activation was investigated in this study. Heating the EK cell was achieved with a thermostatic heat band wrapped around the cell. The change in temperature was controlled and recorded by thermocouples and a data acquisition system. The change in temperature during Test 4 is shown in Fig. 4. The effect of temperature on activation of persulfate on PCB oxidation was evaluated by performing tests at room temperature (23°C) and an elevated temperature of 45°C. The results show that the test with the elevated temperature (45°C) resulted in a sharp increase of PCB degradation from 22.5 to 92.6%.

**Electroosmotic Flow**

Fig. 5 shows the profile of the cumulative electroosmotic flow registered in the EK experiments. The electroosmotic flow fluctuated and decreased with elapsed time in all of the tests. PCB 44 is an uncharged compound; however, electroosmosis was required to maintain the Na-persulfate-PCB interaction. The highest electroosmotic flow was recorded in Test 5, while the lowest flow was recorded in Test 3. The lowest current was recorded in Test 1. However, high current does not necessarily equate to a higher electroosmotic flow. The electroosmotic flow is proportional to the dielectric constant of the fluid,
zeta potential, and electric-field strength, and is inversely proportional to the fluid viscosity. Although distilled water has a high dielectric constant, the test with distilled water resulted in a low electroosmotic flow because of its low ionic strength. The high ionic strength in the Na-persulfate test should have promoted electroosmosis; however, the charge-carrying ions may precipitate at the high pH region near the cathode. As the pH decreases, the zeta potential becomes more positive, which may cause low electroosmotic permeability (Yukselen and Kaya 2003).

**pH Evolution**

Fig. 6 shows the change in the pH at the anode, cathode, and middle (Na-persulfate) influent and effluent solutions. When voltage is applied to the system, electrolysis reactions occur in the electrodes and $\text{H}^+$ and $\text{OH}^-$ ions are generated at the anode and cathode, respectively. As a result, there is low pH at the anode and high pH at the cathode. Generally, the pH values decreased at the anode and increased at the cathode. The initial pH of the Na-persulfate (middle compartment) was around 4.0 and decreased to 2.0 during Tests 2–5. The pH of the solution at the cathode was maintained constant at pH 12 during Tests 4 and 5. In the other tests, the initial pH of the Na-persulfate solution was 6.0 and then it increased to 12.0 at the end of the tests.

Table 4 shows the reading for the soil pH at the anode, cathode, and middle section taken at the end of each test. As a result of electrolysis reactions, it is generally expected that there will be a low pH region near the anode and a high pH region near the cathode. However, during the course of testing, the acidic solution generated at the anode gradually moved through the soil toward the cathode by electromigration and electroosmosis, thereby lowering the pH throughout the soil sample (Acar et al. 1995). Generally, significantly low pH values were observed in the soil for both sections. In Test 1, the final pH values were very close to the initial pH value (6.2) of the kaolin.

**Removal and Degradation of PCB**

PCB was not found in any of the effluent samples that were collected, indicating that PCB was retained within the soil because of its hydrophobic characteristics. Table 5 shows the PCB degradation in the three soil sections after the testing and the average degradation value for each experiment. The baseline test using distilled water achieved 22.7% PCB 44 degradation. The addition of 30% Na-persulfate in place of the distilled water (Test 2) clearly increased the PCB 44 degradation from 22.7 to 40.7%. The highest PCB degradation was found in Tests 3 and 4, which corresponded
to the use of temperature and temperature + high pH, respectively, along with the 30% Na-persulfate in the activation processes. However, the combination of the high pH and temperature activation (Test 4) did not increase the degradation compared with temperature activation alone (Test 3). The lower concentration of Na-persulfate (20%) caused lower degradation of PCB 44 in Test 5.

Persulfate is known to be highly reactive at a low pH (< 3) and at a pH higher than 10 (Block et al. 2004). In this study, the soil pH decreased in the anode regions and increased in the cathode regions with and without the addition of a base (NaOH). Under these pH values, persulfate anions (S\(_2\)O\(_8\)^{2-}\) decompose becoming sulfate free radicals (SO\(_4\)^{2-}\)), which are very powerful oxidants. Tests 3–5 provide results that add to the explanation of the influence of

Table 4. pH Values of Kaolin after EK Testing

<table>
<thead>
<tr>
<th>Test number</th>
<th>Anode</th>
<th>Middle</th>
<th>Cathode</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6.54</td>
<td>5.78</td>
<td>6.60</td>
</tr>
<tr>
<td>2</td>
<td>1.32</td>
<td>1.32</td>
<td>1.25</td>
</tr>
<tr>
<td>3</td>
<td>1.22</td>
<td>1.47</td>
<td>1.57</td>
</tr>
<tr>
<td>4</td>
<td>1.21</td>
<td>1.80</td>
<td>6.09</td>
</tr>
<tr>
<td>5</td>
<td>1.72</td>
<td>2.55</td>
<td>3.10</td>
</tr>
</tbody>
</table>

Table 5. PCB Degradation in Kaolin after EK Testing

<table>
<thead>
<tr>
<th>Test number</th>
<th>Anode</th>
<th>Middle</th>
<th>Cathode</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>30.6</td>
<td>18.8</td>
<td>18.8</td>
<td>22.7</td>
</tr>
<tr>
<td>2</td>
<td>38.9</td>
<td>31.3</td>
<td>51.9</td>
<td>40.7</td>
</tr>
<tr>
<td>3</td>
<td>76.7</td>
<td>79.4</td>
<td>77.6</td>
<td>77.9</td>
</tr>
<tr>
<td>4</td>
<td>85.9</td>
<td>86.7</td>
<td>56.0</td>
<td>76.2</td>
</tr>
<tr>
<td>5</td>
<td>51.8</td>
<td>56.4</td>
<td>57.5</td>
<td>55.2</td>
</tr>
</tbody>
</table>

Fig. 6. pH evolution during EK tests: (a) Test 1; (b) Test 2; (c) Test 3; (d) Test 4; (e) Test 5
the high pH region found at the anode region. The high pH at the anode caused greater PCB degradation (85.9%) in Test 4; however, relatively higher degradation (76.7%) was also obtained in Test 3 even without that increase in the pH at the anode and anode region of the soil. Although Test 5 was conducted with a low concentration of persulfate, the PCB degradation was low (51.8%) in spite of the increased pH in the anode and anode region of the soil. These results show that the activation of persulfate by temperature was significant when compared with the activation caused by the increased pH.

The EK test results were consistent with the batch test results. According to the batch test results, a temperature of 45°C was found to be more effective in causing the activation of persulfate oxidation than a high pH of 12. When both activators (temperature and high pH) were used at the same time in the batch tests, the degradation only increased by 3.3% for the kaolin. When the persulfate dosage alone increased from 30 to 40%, the PCB degradation decreased in the batch tests. Increasing the oxidant dosage not only does not result in higher contaminant removal, it also leads to poorer remediation efficiency (Ferrarese et al. 2008). The EK test results also showed that a 30% persulfate dosage is effective for PCB degradation.

Conclusions

The aim of this experimental investigation was to evaluate the effectiveness of electrokinetically enhanced persulfate oxidation of PCBs in low permeability clayey soils. Kaolin (used as the model for a low permeability clayey soil) was spiked with 2,2',3,3',5'-tetrachlorobiphenyl, or PCB 44 (a model of PCB), and was the basis for several series of batch and bench-scale EK experiments. Various activators, high pH (pH 12), and temperature (45°C) were tested to attain the highest level of degradation.

The batch test results showed that a Na-persulfate concentration higher than 30% does not significantly improve the PCB degradation. In fact, the EK experiments showed that a decrease in Na-persulfate concentration from 30 to 20% led to lower degradation of PCB in the soil. Therefore, the optimal Na-persulfate dosage for effective PCB degradation in the soil was found to be 30%. However, its efficacy also depends on the temperature and pH conditions. The PCB degradation increased as a result of the activation of persulfate with both elevated temperature and pH conditions. The EK experiments showed that the combined activation by elevated temperature (45°C) and pH (>12) did not significantly increase the PCB degradation compared with activation by temperature alone (45°C). The soil pH decreased near the anode and increased near the cathode under applied electric potential, which may help to activate persulfate and enhance PCB degradation. This study showed the most effective EK test used 30% Na-persulfate concentration with thermal activation (45°C), which led to a 77.9% degradation of PCB. Overall, this study demonstrated that persulfate oxidation is a very effective technique for the destruction of PCBs, and the delivery of persulfate into low permeability clayey soils can be achieved through the EK technique.

Acknowledgments

The assistance of Claudio Cameselle and Amid Khodadoust is gratefully acknowledged. The Scientific and Technological Research Council of Turkey (TUBITAK) awarded a fellowship to Yeliz Yukselen-Aksoy, which made it possible to conduct this research at the University of Illinois at Chicago.

References


