January 2010

Application Of Electrochemical Techniques For The Remediation Of Soils Contaminated With Organic Pollutants

Elisa Ferrarese  
Università degli Studi di Trento

Gianni Andreottola  
Università degli Studi di Trento

Follow this and additional works at: https://scholarworks.umass.edu/soilsproceedings

Recommended Citation  
Available at: https://scholarworks.umass.edu/soilsproceedings/vol13/iss1/26

This Conference Proceeding is brought to you for free and open access by ScholarWorks@UMass Amherst. It has been accepted for inclusion in Proceedings of the Annual International Conference on Soils, Sediments, Water and Energy by an authorized editor of ScholarWorks@UMass Amherst. For more information, please contact scholarworks@library.umass.edu.
Chapter 25

APPLICATION OF ELECTROCHEMICAL TECHNIQUES FOR THE REMEDIATION OF SOILS CONTAMINATED WITH ORGANIC POLLUTANTS

Elisa Ferrarese§, Gianni Andreottola
Università degli Studi di Trento, Dipartimento di Ingegneria Civile e Ambientale, Via Mesiano 77, I-38050 Trento (TN), Italy

ABSTRACT

Direct Current Technologies (DCTs) are remediation techniques for contaminated soil, in which an electrical field is created in the polluted medium by applying a low-voltage direct current across electrodes placed in the ground. This study aimed at evaluating the feasibility of using DCTs for the remediation of different organic contaminants from various types of fine grain soils and sediments. For this purpose, a one-dimensional experimental setup for bench scale testing was assembled and several laboratory tests were performed. The experimental setup included an electrochemical cell, two stainless steel plate electrodes, a stabilized DC generator and tanks for the pore fluid collection. Two types of soils contaminated by diesel fuel and river sediments polluted by polycyclic aromatic hydrocarbons (PAHs) were considered in the investigation. In the experiments, the contaminant removal was evaluated under the influence of the electric current generated by a constant potential difference (0.5-6 V/cm) for a fixed period of time. The results showed that a high efficiency of organic pollutant removal could be achieved via electrochemical methods. About 90% contaminant removal was achieved for PAH-contaminated sediments after a one month treatment, while the diesel fuel contaminated soils resulted in about 45-55% TOC removal and in 70-85% TPH removal. The main factors influencing the process seem to be the process duration and the soil mineralogy, especially the iron content of the treated medium. On the opposite, the applied voltage seems to have a limited influence on the contaminant removal efficiency, good results being achieved with specific voltages as low as 1 V/cm. The results suggest that DCTs can be effectively used for the mineralization of many organics with low energy expenditure, especially in very fine soils, like clays, which are often more difficult to treat with conventional chemical methods, because of their low permeability and high sorption capacity.

Keywords: Electrochemical remediation, electrooxidation, polycyclic aromatic hydrocarbons, diesel fuel

§ Corresponding Author: Elisa Ferrarese, Università degli Studi di Trento, Dipartimento di Ingegneria Civile e Ambientale, Via Mesiano 77, I-38050 Trento (TN), Italy, Tel: +39 0461 88263, Email: elisa.ferrarese@ing.unitn.it
1. INTRODUCTION

The remediation of fine grain soils contaminated with sorbed organic pollutants is as far as today a challenging task. Despite the fact that many techniques have been developed to remediate contaminated soils, sediments and groundwater, it is still difficult to remove hydrophobic organic compounds (HOCs), which are often strongly sorbed onto soil particles. These pollutants are in fact difficult to remove by biological methods, while the low permeability of clayed soils limits the applicability of flushing and chemical oxidation. On the other hand, conventional ex situ methods, as the disposal in sanitary landfill or incineration are discouraged because they are very expensive and may represent a source of air pollution. Electrochemical treatments are emerging technologies for the in situ or ex situ remediation of fine grain soils: they seem amenably applicable especially for silts and clays, in which the low permeability constrains the applicability of conventional remediation techniques.

1.1 Electrochemical Oxidation

The base method for the current research, the electrochemical oxidation, is a branch of Direct Current Technologies (DCTs), which are remediation techniques for contaminated soils, in which an electrical field is created in the polluted medium by applying a low-voltage direct current (DC) to electrodes placed in the ground. Usually, for real scale in situ DCT applications, the applied electric current density is of the order of milliamperes per square centimeter (1 mA/cm²) and the electric potential difference is on the order of a few volts per centimeter across the electrodes (1 V/cm) (Van Cauwenberghe, 1997; USAEC, 2000; Chung and Kamon, 2005; Reddy et al., 2006).

At first, DCTs were used mainly for the remediation of metals, radionuclides and polar inorganic pollutants from soil and groundwater, the method being named electrokinetic remediation. Many researchers demonstrated the feasibility of electrokinetic remediation for many hazardous inorganic pollutants, as lead, chromium, copper, zinc and cadmium (Acar et al., 1995; Puppala et al., 1997; Chung and Kamon, 2005; Zhou et al., 2005; Reddy et al., 2006; Lynch et al., 2007). In recent years, research has been developed about DCTs and their effectiveness in the removal of organic pollutants, such as polycyclic aromatic hydrocarbons (PAHs) and chlorinated solvents, from soils and sediments (Röhrs et al., 2002; ECP, 2003; Chung and Kamon, 2005; Reddy et al., 2006; Isosaari et al., 2007; Szpyrkowicz et al., 2007; Zheng et al., 2007). These studies seem to suggest that DCTs can be effectively used for the mineralization of many organics, with lower energy expenditure than traditional electrokinetic methods (Acar et al., 1995). Empirical evidences indicate that the reaction rates are inversely proportional to grain size (Acar et al., 1995), such that this remediation technique is particularly effective in saturated low permeability soils (like clays and silts), which are often more difficult to treat with conventional remediation methods, such as chemical oxidation or soil flushing, because of their low permeability and their high sorption capacity.

The application of an electrical field to a soil environment has several complex physical and chemical effects that involve soil particles, water and contaminants. The most important electrochemical phenomena are electrolysis, electroosmosis, electromigration, electrophoresis, changes in soil pH and geochemical reactions (Acar et al., 1995; Puppala et al., 1997; USAEC,
2000; Rahner et al., 2002; Alshawabkeh et al., 2004; Chung and Kamon, 2005; Reddy et al., 2006). On the whole, the processes induced by electric field can be distinguished into two categories: electrokinetic transport (including electroosmosis, electromigration and electrophoresis), and electrochemically induced chemical reactions within the soil matrix (Rahner et al., 2002), responsible of the destruction of immobile organic contaminants.

Under the influence of the electrical field, water electrolysis reactions take place at the electrodes, also resulting in pH changes: oxidation of water occurs at the anode and generates hydrogen ions (H\(^+\)). On the opposite, reduction of water occurs at the cathode and generates hydroxyls ions (OH\(^-\)). The hydrogen ions H\(^+\) generated at the anode create an acid front which moves towards the cathode, while hydroxyls ions OH\(^-\) generated at the cathode create a base front which moves towards the anode (Acar et al., 1995; USEPA, 2004; Chung and Kamon, 2005; Reddy et al., 2006). Since the transport of H\(^+\) is faster than the transport of OH\(^-\) the acid front moves faster (approximately two times faster) than the base front; unless the H\(^+\) transport is not retarded by the soil buffering capacity, this difference in the fronts’ moving rates leads to an acidification of the soil between the electrodes (Acar et al., 1995; Puppala et al., 1997; USAEC, 2000). The migration of the acid and basic front also depends on the buffering capacity of the soil, which may neutralize H\(^+\) or OH\(^-\) ions (Reddy et al., 2006).

Electroosmosis is a bulk transport of water, which flows through the soil as a result of the applied electrical field (Acar et al., 1995; USAEC, 2000; Chung and Kamon, 2005, Reddy et al., 2006; Lynch et al., 2007). The electric field causes fluids to flow from the anode compartment to the cathode compartment, producing a flow, called electroosmotic flow, and forcing the water table to arise in the cathode compartment (Acar et al., 1995). Electrophoresis consists in a movement of charged particles under the influence of an electrical field, as a result of Lorentz force: cations, like most of metals, tend to migrate towards the cathode and anions tend to migrate towards the anode. Electromigration is the transport of particles induced by the gradual movement of the ions (electrophoresis) due to the momentum transfer between charged particles and nearby particles. Because of electrophoresis and electromigration (the whole process being often named as electroosmotic transport), ions tend to concentrate near the opposite charged electrode (Acar et al., 1995; Alshawabkeh et al., 2004; USAEC, 2000; Chung and Kamon, 2005; Reddy et al., 2006); this process is the principle of electrokinetic remediation. The electroosmotic transport depends on many parameters, including the soil pH, the zeta potential, the soil activity coefficient and the ionic concentration (Lynch et al., 2007). In particular the pH changes, regulated by water electrolysis, play an important role in contaminant migration, since they can influence metal solubility and mobility in the soil (Acar et al., 1995). Since neutral or acid pH may favor the metal migration and prevent metal precipitation (Lynch et al., 2007), the electrokinetic remediation is commonly enhanced by the addition of conditioning agents to adjust the soil pH. Various reactions involving ions can occur nearby the electrodes; for example, metals ions can be plated onto the electrodes (electrodeposition), or can precipitate or co-precipitate, while gaseous compounds can be liberated (USAEC, 2000).

As far as the geochemical reactions are concerned, during the electrochemical treatment of a contaminated soil, the soil-pore water system can be considered as an electrochemical cell, in which oxidation and reduction reactions occur. Water electrolysis provides the partners for redox reactions. In an electrochemical cell, hydrogen peroxide (H\(_2\)O\(_2\)) can be produced as a result of redox reactions, and in particular by the reduction of O\(_2\) from air at the cathode (Da Pozzo et al.,
2005; Meinero and Zerbinati, 2006; Laine and Cheng, 2007), according to the following reaction:

\[ O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \]  

(1)

In soils, redox reactions are supposed to occur not only nearby the electrodes as in a traditional electrochemical cell, but also simultaneously at any and all interfaces between soil and pore water, thus leading to a contaminant removal within the treated medium. In fact, according to the “microconductor principle” (Rahner et al., 2002), electrochemical reactions can be induced within the soil matrix if the soil contains particles of films with electronic conducting properties (microconductors). In the presence of microconductors, the electric current can induce the wet soil to act as a diluted electrochemical solid bed reactor and allow the occurrence of the redox processes.

The microconductors that can be found in soils are mainly weathering products of rocks and minerals, such as fine particles or films of iron, manganese or titanium compounds, carbonaceous particles and humic substances (Rahner et al., 2002). Their occurrence, abundance and distribution depend on the soil type and origin. When an electric filed is applied to a soil, the microconductors are polarized and may act as microelectrodes (both monopolar or bipolar microelectrodes), able to induce redox reactions in their vicinity (Rahner et al., 2002). The composition, size, electronic conductivity and electrochemical activity of microconductors may vary from type to type. For example, among iron compounds, graphite was found to be able to enhance redox reactions, as well as iron ions, while magnetite seems inactive (Rahner et al., 2002). The reactions that are induced by the microconductors depend on the nature of the contaminant, on the nature of the microconductor itself, and on the characteristics of the electrolyte solution (such as the solution pH), which may enhance or constrain the redox reactions. Therefore, the degradation of organic contaminants depends on the occurrence of the suitable microconductors in combination with a proper redox system (Rahner et al., 2002). Also, the prediction of the degradation products is difficult since they can include a large number of by-products and reaction intermediates, some of which may be mobile and be influenced by the electrokinetic processes, besides the geochemical reactions.

Since soils commonly contain significant amounts of iron, once hydrogen peroxide has been created (reaction (1)), hydroxyl radical (\(^{1}OH\)) can be produced, according to the Fenton’s reaction:

\[ Fe^{2+} + H_2O_2 + H^+ \rightarrow Fe^{3+} + H_2O + ^{1}OH \]  

(2)

This catalytic reaction is propagated by the \(Fe^{3+}\) reduction, which leads to the \(Fe^{2+}\) regeneration, which is enhanced by the electrochemical process itself (Meinero and Zerbinati, 2006). Hydroxyl radicals are strong non-selective oxidant agents (standard oxidation potential about 2.8 V) that are able to react with most organic pollutants (Watts et al., 2002; ITRC, 2005; Rivas, 2006), and they are considered the main entities responsible for the organic matter mineralization. In fact, this radical-based redox process (also addressed as indirect oxidation) seem the most probable mineralization mechanism for electrooxidation, as the alternative pathway (i.e. the direct oxidation or reduction at the soil microconductor surface) may be
effective on mobile contaminants, but seems unlikely for immobile organic pollutants due to its very high activation energies of the reactions involved (Rahner et al., 2002).

It must be pointed out that since the pore fluid plays a very important role in all electrochemical processes, the presence of a pore fluid in soil pores is required in order for the electrochemical remediation to be effective, both to conduct the electric field and to transport target species across the soil mass (Acar et al., 1995). Moreover, the soil must be wet to keep the resistance low and provide significant currents flowing (Röhrs et al., 2002). Theoretically, it may be possible to saturate a partially saturated soil by electroosmotic flux of the pore fluid, but this process must be carefully engineered and controlled (Acar et al., 1995).

Different configurations can be used for real scale outdoor applications of DCTs. The electrodes can be made of different materials such as stainless steel or carbon, and they can be placed in the soil either in a vertical or horizontal array. A significant interest in the effectiveness of different electrode materials has recently arisen for the application of electrochemical remediation techniques, especially in aqueous systems, as groundwater and wastewater treatment, with the use of platinum, PbO₂, titanium compounds, boron doped diamond, graphite and ceramics (Röhrs et al., 2002; Meniero and Zerbinati, 2006; Laine and Cheng, 2007). Nevertheless, since all electrodes in soil remediation applications undergo corrosion, fouling and passivation, the use of low cost materials, as stainless steel or graphite, is commonly preferred for real scale applications.

For in situ electrokinetic applications, the electrodes are usually placed in wells with permeable walls and filled with processing fluid to promote the pollutant extraction (Röhrs et al., 2002), while when electrooxidation is used, the contaminant recovery is not necessary. Usually, a spacing of a few meters between cathodes and anodes is used (Alshawabkeh, 2001). Because of their rather simple setup, electrochemical systems are often considered less environmentally intrusive than traditional chemical remediation methods, such as chemical oxidation or soil flushing (Laine and Cheng, 2007).

When the remediation of heavy metals and radionuclides is performed, the electrokinetic transport is commonly enhanced by flushing the soil with chelating agents, complexing agents or conditioning fluids, i.e. acid solutions which adjust soil pH to promote metal solubilization and transport (Puppala et al., 1997; Alshawabkeh, 2001; Zhou et al., 2005). Solvents, surfactants or cyclodextrins can be used to enhance the mobilization and flushing of apolar organic pollutants (Reddy et al., 2006; Isosaari et al., 2007). Moreover, recent research has shown that direct currents can lead to better contaminant removal than alternate or pulsing currents, probably because alternate currents cause continuous changes in the soil polarization and consume a relatively high energy to discharge or recharge the double layer of soil particles (Röhrs et al., 2002).

In some recent studies traditional chemical oxidation was used in combination with electrochemical methods. Different reactants were tested, including hydrogen peroxide, Fenton’s reagent (the method being named electro-Fenton or EK-Fenton), chlorine species or persulfate (Yang and Liu, 2001; Kim et al., 2005; Park et al., 2005; Kim et al., 2006; Isosaari et al., 2007; Szpyrkwicz et al., 2007, Zheng et al., 2007), with good results on different organic contaminants, as chlorinated solvents and PAHs. Significant benefits seems to be possible by
integrating electrokinetic remediation with in situ chemical oxidation, because the electrokinetic treatment is supposed to facilitate oxidant delivery and promote the production of radicals (Isosaari et al., 2007).

To date, there are several examples of application of DCTs to real cases of contamination in Europe and North America (USAEC, 2000; USEPA, 2002; ECP, 2003; USEPA, 2004), but a deep knowledge of the phenomena ruling the remediation process has not been reached yet. In particular, it is not clear what processes play the most important roles in organic mineralization, and what factors can affect the results of this technique. Therefore, at the moment the calibration of the remediation action is mainly based on empirical data and on the results of field preliminary tests. Further investigation is needed to better understand the mechanisms of electrooxidation.

### 1.2 Research Objectives

This experimental investigation aimed at evaluating the effectiveness of electrochemical oxidation for the remediation of different organic pollutants from fine grain soils and sediments, in case of unenhanced electroremediation, i.e. when the application of the electric field is not supported by the addition of conditioning fluid to adjust soil pH, help contaminant transport or promote soil conductivity.

Other objectives of the study were to assess the most important design parameters that can affect the system’s efficiency (as applied voltage, treatment duration or soil mineralogy) and to understand any link between removal efficiency and macroscopic electrochemical phenomena, as electroosmotic flux and changes in soil pH. A better knowledge of these processes will help to design more efficient and more effective remediation actions.

During the first phase of this experimental investigation, a systematic study was conducted to assess the effects of electrooxidation on fine grain soils contaminated with diesel fuel. Two types of soil were considered in the study: a silty clay (Speshite kaolin) and a clay, mainly composed of montmorillonite, to evaluate the influence of soil type and mineralogy on the effectiveness of the electrochemical processes. During the second phase of the research, a feasibility study was carried out to assess the applicability of electrochemical oxidation to degrade sorbed PAHs in river sediments, in case of old date contamination. In all the tests performed, the contaminant removal was evaluated under a constant voltage gradient of 0.5-6 V/cm in unenhanced conditions.

The contaminants considered in this study are typical pollutants that derive from petroleum product spills. Diesel fuel is a mixture of hydrocarbon produced from crude oil. It is composed of about 75% saturated hydrocarbons (mainly paraffins) and 25% aromatic hydrocarbons. In this study diesel fuel was chosen as soil contaminant to represent the environmental pollution due to spills of oil and various petroleum products. Oil spills are a frequent source of contamination that may derive from underground fuel leaks, industrial activities or oil refinery. Due to the high occurrence of these events, petroleum spills have contaminated many large areas and are widely recognized as posing a strong environmental threat (Saner et al., 1996; Watts and Dilly, 1996; Curtis and Lammey, 1998; Iturbe et al., 2005; Powell et al., 2007).
PAHs are a group of organic molecules composed of fused benzene rings, classified among HOCs. PAHs are released during the incomplete combustion of coal, petroleum products and wood. Their presence in environmental matrices is of great concern due to their high toxicity, carcinogenic effects and environmental persistence (IARC, 1983; IARC 1984; Wild and Jones, 1995; Harvey, 1997; Henner et al., 1997; Cupyers et al., 1998; Haapea and Tuhkanen, 2006; O’Mahony et al., 2006). A summary of the main physico-chemical properties of the 16 PAH species considered in this study is reported in Table 1.

### Table 1. Summary of the main physico-chemical properties of the PAHs considered in this study (Wild and Jones, 1995; Muller, 2002).

<table>
<thead>
<tr>
<th>PAH specie</th>
<th>Chemical formula</th>
<th>Molecular weight</th>
<th>Partition coefficient Log(Kow)</th>
<th>Number of aromatic rings</th>
</tr>
</thead>
<tbody>
<tr>
<td>naphthalene</td>
<td>C_{10}H_{8}</td>
<td>128.2</td>
<td>3.28</td>
<td>2</td>
</tr>
<tr>
<td>acenaphthylene</td>
<td>C_{12}H_{8}</td>
<td>152.2</td>
<td>4.07</td>
<td>2</td>
</tr>
<tr>
<td>acenaphthene</td>
<td>C_{12}H_{10}</td>
<td>154.2</td>
<td>3.98</td>
<td>3</td>
</tr>
<tr>
<td>fluorene</td>
<td>C_{12}H_{11}</td>
<td>166.2</td>
<td>4.18</td>
<td>3</td>
</tr>
<tr>
<td>phenantrrene</td>
<td>C_{14}H_{10}</td>
<td>178.2</td>
<td>4.45</td>
<td>3</td>
</tr>
<tr>
<td>anthracene</td>
<td>C_{14}H_{11}</td>
<td>178.2</td>
<td>4.45</td>
<td>3</td>
</tr>
<tr>
<td>fluoranthene</td>
<td>C_{16}H_{10}</td>
<td>202.3</td>
<td>4.90</td>
<td>4</td>
</tr>
<tr>
<td>pyrene</td>
<td>C_{16}H_{10}</td>
<td>202.3</td>
<td>4.88</td>
<td>4</td>
</tr>
<tr>
<td>chrysene</td>
<td>C_{18}H_{12}</td>
<td>228.2</td>
<td>5.16</td>
<td>4</td>
</tr>
<tr>
<td>benzo(a)anthracene</td>
<td>C_{18}H_{12}</td>
<td>228.2</td>
<td>5.61</td>
<td>4</td>
</tr>
<tr>
<td>benzo(b)fluoranthene</td>
<td>C_{20}H_{12}</td>
<td>252.3</td>
<td>6.01</td>
<td>5</td>
</tr>
<tr>
<td>benzo(k)fluoranthene</td>
<td>C_{20}H_{12}</td>
<td>252.3</td>
<td>6.06</td>
<td>5</td>
</tr>
<tr>
<td>benzo(a)pyrene</td>
<td>C_{20}H_{12}</td>
<td>252.3</td>
<td>6.06</td>
<td>5</td>
</tr>
<tr>
<td>dibenzo(a,h)anthracene</td>
<td>C_{22}H_{14}</td>
<td>278.4</td>
<td>6.84</td>
<td>6</td>
</tr>
<tr>
<td>benzo(g,h,i)perylene</td>
<td>C_{22}H_{12}</td>
<td>276.3</td>
<td>6.50</td>
<td>6</td>
</tr>
<tr>
<td>indeno(1,2,3-cd)pyrene</td>
<td>C_{27}H_{13}</td>
<td>276.3</td>
<td>6.58</td>
<td>6</td>
</tr>
</tbody>
</table>

Several remediation techniques can be applied for the remediation of petroleum products and PAHs from contaminated sites. The bioremediation of many types of hydrocarbons has been well documented by several authors (Luthy et al., 1994; Saner et al., 1996; Curtis and Lammey, 1998; Höhener et al., 1998; Hunkeler et al., 1998; Taylor and Jones, 2001; Namkoong et al., 2002; Rivera-Espinoza and Dendooven, 2004; Sarkar et al., 2006), but the strong hydrophobicity of many hydrocarbons constrains their bioavailability, so that their biologic degradation rates are often too slow for bioremediation to be amenable applied to real scale remediation actions (Luthy et al., 1994; Saner et al., 1996; Taylor Jones, 2001). Moreover, many high-molecular weight hydrocarbons have proven to be recalcitrant to biological degradation (Luthy et al., 1994; Henner et al., 1997; Antizar-Ladislao et al., 2005; Haapea and Tuhkanen; 2006). Among physical and chemical remediation techniques, soil venting is usually ineffective for the remediation of the low volatility hydrocarbons. Chemical oxidation seems to be effective on a wide range of organic pollutants (Watts and Dilly, 1996; Masten and Davies, 1997; Kong et al.,...
1998; Watts et al., 2002; Flotron et al., 2005; ITRC, 2005; Haapea and Tuhkanen; 2006; O’Mahony et al., 2006; Rivas, 2006; Bissey et al., 2006), but in saturated fine grain soils its application is constrained by the soil low permeability and by the limited mass transfer of hydrophobic compounds.

A few Authors (Chung and Kamon, 2005; Kim et al., 2005; Park et al., 2005; Kim et al., 2006; Reddy et al., 2006; Isosaari et al., 2007) have studied the removal of PAHs from soils by electrochemical methods, while the application of electrooxidation to nonhalogenated aliphatic contaminants is still limited. The results of these studies are encouraging, and suggest that PAHs can be effectively removed from clay soils (ECP, 2003; Isosaari et al., 2007), with a removal efficiency dependent on the soil type (Isosaari et al., 2007). Most of these studies investigated the combined effect of electrooxidation and electrokinetic removal, i.e. aimed at removing PAHs by flushing them or by decomposing them by electrochemical oxidation. Despite the fact that PAHs are apolar molecules and do not carry an electric charge, they can in fact be transported with the electroosmotic flux (Reddy et al., 2006; Isosaari et al., 2007). However, the low recovery of organic compounds in the catholyte solution during combined electrokinetic-electrochemical tests suggests that the main part of the pollutant removal was achieved via electrooxidation rather than via electromigration (Röhrs et al., 2002; Reddy et al., 2006; Isosaari et al., 2007).

2. MATERIALS AND METHODS

2.1 Materials

Two types of fine grain soils were used to carry out the experimental investigation on diesel fuel remediation.

The first soil (Speswhite kaolin) could be classified as a silty clay (BSI, 1999), being mainly composed of particles having dimensions ranging between 2 µm and 75 µm (40%) or lower than 2 µm (60%). From a chemical point of view, it was mainly composed by SiO₂ (47%) and Al₂O₃ (38%), its Cation Exchange Capacity (CEC) was 8.3 mₑq/100g and its pH was about 6.

The second soil was essentially composed by montmorillonite (65%), the remaining part being quartz (12), mica (12%) and kaolin (11%). The granulometric analysis led to the following results: 2-10 µm 33%, 0.5-2 µm 16%, <0.5 µm 42%, thus the soil could be classified as clay. Also this soil was mainly composed of SiO₂ (58%) and Al₂O₃ (38%); its CEC was 34.2 mₑq/100g and its pH was about 10.

In order to assess any influence of the metal content on the system efficiency, the iron and manganese concentrations of the addressed soils were determined. The kaolin proved to be characterized by a iron content about 2794 mg/kgₜs, and a manganese content about 34 mg/kgₜs. The montmorillonite clay showed a much higher metal content, with an iron concentration of 10180 mg/kgₜs and a manganese concentration of 44 mg/kgₜs. Before being mixed with diesel fuel, the TOC of the two soils was negligible (about 0.01 mg/kgₜs for kaolin and 0.12 mg/kgₜs for montmorillonite).
The diesel fuel used in this study was commercially available and was purchased from a gasoline pump at a typical refuel station. To prepare the diesel contaminated soil samples, the soil was at first dried and then spiked with diesel fuel. One kilogram of dry soil was mixed with about 100 mL of diesel fuel. Then the sample was stirred with stainless steel spoons in a glass beaker, to ensure that the contaminants were evenly distributed through the soil. After mixing, the sample was allowed to evaporate for about two weeks. Before the tests, the spiked samples were saturated with demineralized water and allowed to evaporate overnight at room temperature before being inserted in the experimental setup.

Two parameters were used to consider the contaminant content in the soil samples: TPH (total petroleum hydrocarbons), which refers to a family of many petroleum-based hydrocarbons, and TOC (total organic carbon), which represents the whole content of organic substances in the soil samples.

During the second part of the research, the effectiveness of the electrochemical remediation was evaluated for old date PAH-contaminated sediments. The contaminated sediments of concern were collected in a canal in Trento, Italy, which for several decades had experienced industrial wastewater pollution by organic and inorganic compounds, deriving from a coal tar production site (Ferrarese et al., 2007). Several samples (total weight about 10 kg) of fine-grain silty sediments were collected from the first 30-40 cm layer at the bottom of the canal; these samples were then mixed together and mechanically stirred to produce an homogeneous sample.

At first, the collected sediments were characterized and analyzed for BTEX (i.e. aromatic hydrocarbons: benzene, toluene, ethylbenzene, xilene), PAHs, pH, and total organic matter, represented by the value of TOC. Both organic pollutants and natural organic matter occurred in the sediment samples, which proved to be contaminated by PAHs, but not by BTEX, whose presence was detected just in traces. The initial total PAH concentration in sediment samples was about 1090 mg/kgSS (light PAHs about 731 mg/kgSS, heavy PAHs about 359 mg/kgSS) and a 90% degradation was required to meet the remediation goals. The initial PAH concentrations in the samples may vary because the pollutant content of the sediments was not homogeneous. The TOC content was about 99 g/kgSS and the sediment pH was about 7.8. The sediments also showed a significant metal content, with a total iron concentration about 30621 mg/KgSS and a manganese content about 614 mg/kgSS.

### 2.2 Experimental Apparatus and Procedure

In order to conduct the experimental investigation, a one-dimensional experimental setup for bench scale testing was developed and several laboratory tests were performed.

The setup (Figure 1) consisted in a rectangular reactor (10 cm wide, 10 cm high and 50 cm long, made up of 10 mm thick transparent PVC), a pair of electrodes, a stabilized DC power supply (Mitek MICP 3005S-2, providing up to 60 V and up to 5 A), and tanks for the pore fluid collection at both electrode compartments. In this system, the soil specimen was 10 cm wide, 10 cm high and its length could be varied from 2 cm to 50 cm by changing the position of the electrodes. The electrodes were rectangular plates (10 cm by 10 cm) made up of stainless steel with holes to allow the pore fluid to flow across them. After positioning the electrodes in the
setup, the space between them was filled with the contaminated soil. The soil was compacted to achieve the same density of natural soils (about 2 kg/L) and trying to avoid leaving cavities in the specimen. Filter papers were inserted between the electrodes and the soil. The setup was also equipped with a digital multimeter (ISO-Tech IDM 207, with the data logging software ISO-Tech 300 Virtual DMM) for continuous current monitoring, a scale (Sartorius GW6206 Gold Scale) which allowed the monitoring of the electroosmotic flux and a pc for data logging.

A list of the tests performed during the experimental investigation is given in Table 2. During each experiment, a soil sample was placed in the experimental setup, and a constant electric potential was applied across it for a fixed period of time. At the end of the trial, the soil specimen was removed from the test setup and transversally sliced into five segments. Each segment was analyzed for soil moisture content, pH and contaminant concentrations, in order to assess the extent of electrochemical reactions at different distances from the electrodes and the eventual contribution of electromigration. Equal parts of these segments were mixed together to produce a final homogeneous sample, representing the whole specimen. The setup also allowed us to open the reaction cell to measure soil pH and to collect samples while the tests were in progress: during all tests except for test 5, samples were collected once a week from the upper part of the soil specimen, to assess the extent of the oxidation process. During each test, other physical parameters were recorded, including the electroosmotic flux, voltage, and current.

![Scheme of the test setup used in the experimental investigation.](image)

*Figure 1. Scheme of the test setup used in the experimental investigation.*
Table 2. List of the laboratory tests performed.

<table>
<thead>
<tr>
<th>Test</th>
<th>Matrix</th>
<th>Contaminant</th>
<th>Sample length [cm]</th>
<th>Applied voltage [V]</th>
<th>Specific voltage [V/cm]</th>
<th>Duration [d]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>kaolin</td>
<td>diesel fuel</td>
<td>10</td>
<td>5</td>
<td>0.5</td>
<td>28</td>
</tr>
<tr>
<td>2</td>
<td>kaolin</td>
<td>diesel fuel</td>
<td>10</td>
<td>10</td>
<td>1</td>
<td>28</td>
</tr>
<tr>
<td>3</td>
<td>kaolin</td>
<td>diesel fuel</td>
<td>10</td>
<td>30</td>
<td>3</td>
<td>28</td>
</tr>
<tr>
<td>4</td>
<td>kaolin</td>
<td>diesel fuel</td>
<td>10</td>
<td>60</td>
<td>6</td>
<td>28</td>
</tr>
<tr>
<td>5</td>
<td>kaolin</td>
<td>diesel fuel</td>
<td>50</td>
<td>50</td>
<td>1</td>
<td>28</td>
</tr>
<tr>
<td>6</td>
<td>montmorillonite</td>
<td>diesel fuel</td>
<td>10</td>
<td>5</td>
<td>0.5</td>
<td>28</td>
</tr>
<tr>
<td>7</td>
<td>montmorillonite</td>
<td>diesel fuel</td>
<td>10</td>
<td>10</td>
<td>1</td>
<td>28</td>
</tr>
<tr>
<td>8</td>
<td>sediments</td>
<td>PAHs</td>
<td>10</td>
<td>15</td>
<td>1.5</td>
<td>14</td>
</tr>
<tr>
<td>9</td>
<td>sediments</td>
<td>PAHs</td>
<td>10</td>
<td>10</td>
<td>1</td>
<td>28</td>
</tr>
<tr>
<td>10</td>
<td>sediments</td>
<td>PAHs</td>
<td>10</td>
<td>20</td>
<td>2</td>
<td>28</td>
</tr>
</tbody>
</table>

All the tests were performed at room temperature and were unenhanced, i.e. no conditioning fluid was dosed at the electrode compartments to improve the soil conductivity, to adjust the soil pH or to promote contaminant migration. Moreover, no hydraulic gradient was applied across the electrodes.

Four trials (tests 1, 2, 3 and 4) were performed on contaminated kaolin samples (the specimens being 2 kg, 10 cm long, 10 cm high and 10 cm wide), with test duration of 4 weeks (28 days), and constant voltages of 5, 10, 30 and 60 V respectively (specific voltages 0.5, 1, 3 and 6 V/cm). The recorded initial current densities were about 0.1-1 mA/cm² and the flowing current tended to decrease with time after an initial increase. Another test (test 5) was performed on contaminated kaolin to assess the treatment efficiency in case of larger soil specimen. In this test, the soil specimen had a length of 50 cm, with a cross section of 100 cm² (10 cm by 10 cm), and it was tested under a constant voltage gradient of 50 V (1 V/cm) for 4 weeks.

Two tests were performed on diesel contaminated montmorillonite (tests 6 and 7), each one on a soil specimen having dimensions of 10 cm x 10 cm x 10 cm. Both tests lasted for 4 weeks and the voltages applied were 5 and 10 V respectively (0.5 and 1 V/cm).

During tests 1, 2, 3, 6 and 7, samples were also collected from the soil specimen at different times (7, 14 and 21 days after the beginning of the trial) during the test, so as to assess the extent of the electrochemical reactions with time.

The tests on PAH-contaminated sediments (tests 8, 9 and 10) were performed on specimens having dimensions of 10 cm in length, 10 cm in height and 10 cm in width, with a mass of about 2 kg. The sediment samples were saturated with demineralized water and carefully stirred before being inserted in the electrochemical cell. During test 8, a sample of sediments was tested under a constant voltage of 15 V (specific voltage 1.5 V/cm) for 14 days. In tests 9 (1 V/cm) and 10 (2 V/cm) samples were tested for 4 weeks. The PAH volatilization was evaluated during test 8, while ecotoxicity tests were carried out on the sediment samples before and after tests 9 and 10.
3. ANALYSIS

The TOC content was determined by IR analysis of thermal induced carbon dioxide with a TOC Analyzer Shimadzu TOC-V CSH, after heating the sample at 900°C with a Shimadzu Solid Sample Module.

The TPH content was determined by gravimetric method after pollutant extraction by sonication and solvent addition. To perform the analysis, a soil sample (mass about 5 g) was carefully weighted and mixed with anhydrous sodium sulfate to eliminate soil humidity. The sample was extracted by sonication for 15 min, then 10 mL of solvent (HPLC grade n-esane) were added to it. About 5 mL of the obtained solvent were collected and cleaned-up on a Florisil tube. The solvent sample was transferred into a pre-weighted vial, it was allowed to evaporate and the vial was weighted. The TPH content was determined from the difference between the initial and final weight of the vial.

As for PAH detection in sediment samples, in order to achieve a good resolution both for light and for heavy PAH species, light PAH concentrations in sediments samples were determined with analysis by gas chromatography (GC) and heavy PAH concentrations were detected by high performance liquid chromatography (HPLC).

As for light PAH detection by GC, the pollutants were at first extracted by sonication and solvent addition (HPLC grade acetonitrile), then a sample of solvent was injected into the gas-chromatograph and analyzed using a Varian 4000 GC/MS. As for heavy PAH detection, the samples were at first extracted by solvent addition (HPLC grade dichloromethane) and filtered on a 0.45 µm filter. The solvent was allowed to evaporate; then an acetonitrile solution (70% HPLC grade acetonitrile and 30% water) was added to the sample. A sample of the obtained solution was injected into the HPLC and analyzed. The HPLC included: auto-sampler Gilson ASPEC XL (solid base extraction), Dionex P680 HPLC Pump, Dionex STH 585 Column Oven, HPLC detector Dionex UVD 340U (diode array). A Supelco-SIL LC-PAH column (520 mm × 4.6 mm i.d., 5 µm particle size) was used for PAH detection. The setups were tested before analyzing the samples; external standards were used for HPLC calibration, while internal standards were used for GC calibration. The extraction efficiencies were about 85% both for HPLC and for GC.

BTEX concentrations were determined through purge and trap extraction followed by gas chromatographic analysis with VARIAN 4000 GC/MS.

To detect the contaminant content in the samples, the solid and liquid phases were extracted together, so as to take into account all pollutants in the samples.

Metal (iron and manganese) contents were determined by inductively coupled plasma (ICP): the samples were at first mineralized according to method EPA 3051: a sample of soil having a mass about 1 g (carefully weighted) was mixed with 10 mL of demineralized water and 8 mL of nitric acid in a closed teflon bottle. The sample was then mineralized in a microwave oven at 180°C for 20 minutes and allowed to cool. A certain volume of demineralized water was added so as the final sample volume was exactly 100 mL and the sample was passed thought a 0.45 µm filter. Then the sample was analyzed according to the method APAT IRSA-CNR 3020 using a
VARIAN ICP-OES VISTA. Before the analysis, the setup was calibrated using five external standards and one internal standard.

The ecotoxicity tests on PAH-contaminated sediment samples were performed according to the international standard methods ISO 113348-3:1998(E) “Water quality – determination of the inhibitory effect of water samples on the light emission of Vibrio fischeri (Luminescent bacteria test)”, using a Microbics Mictrotox 500. Each test was conducted on a soil sample having a mass of 7 g diluted with 35 mL of demineralized water; after stirring the sample for 10 minutes, sub-samples were collected to evaluate the sediment toxicity at different dilution rates.

The pH was taken in a soil/water suspension using a pH-meter, the HI 99121 by Hanna Instruments, with HI 1292D electrode for soil pH measurement. The same instrument was also used to measure soil and water temperature.

4. RESULTS AND DISCUSSION

The results of the tests performed are presented as follows. For the diesel contaminated soils (kaolin and montmorillonite), the influence of electric current, electroosmotic flow, soil pH and moisture content are also discussed.

4.1 Electric Current Densities

The electric current was monitored at regular time intervals during the tests. As shown in Figure 2, in all tests the current started to decrease rapidly after the application of the voltage gradient and reached a steady state value a few days after the beginning of the tests. In the experiments performed with diesel contaminated kaolin (tests 1-4), the initial values of the electric current ranged from 16 mA to 150 mA, while at the steady state the current was about 1-9 mA. During test 5, which was performed on a 50 cm-long kaolin specimen, the maximum current value, about 17 mA, was achieved after a one-day test, then the current gradually decreased and at the steady state it was lower than 0.01 mA. When the montmorillonite was tested (trails 6 and 7), the values of the electric current were much lower than those registered with kaolin, the initial values ranging from 3 mA to 6 mA, with steady state values about 0.05-0.6 mA.

Commonly in electrochemical and electrokinetic tests the current is found to be decreasing with time. In fact, the capacitive current decreases to zero at the steady state. Moreover, the metal oxide and hydroxide precipitation reduces the number of ions and of microconductors available to carry the charge and increases the soil electric resistance (Rahner et al., 2002; Röhrs et al., 2002; Lynch et al., 2007). Current densities can also be affected by changes in soil pH, which influence chemical precipitations and dissolutions, so that unless conditioning agents are used to adjust soil pH to low values and to provide new ions as charge carriers, the soil resistivity increases and the current decreases with time (Reddy et al., 2006). In the tests performed the measured electric currents are thought to be so low because the tests were unenhanced, i.e. no
buffer solution was added to increase the ion concentration. It is expected that if a ion solution had been added to the system, the current would have increased (Isosaari et al., 2007).

Figure 2. Current densities measured during the first hours in the tests with diesel contaminated kaolin (a) and montmorillonite (b).

From the values of voltage and current, it was possible to make an approximate estimation of the energy consumption required for a remediation action. To calculate the energy expenditure, the current was modeled as an exponential function of time with a constant component at the steady state. The following function was used to model the current:

$$i = (i_0 - i_{ss}) \cdot \exp\left(-\frac{t}{\tau}\right) + i_{ss}$$  \hspace{1cm} (3)

where $i_0$ is the initial current, $i_{ss}$ is the current at the steady state, $t$ is time and $\tau$ is a time constant. For kaolin tests (the soil samples having a volume of about 1 L and a mass about 2 kg) the estimated energy expenditure increased with the applied voltage, ranging from 17 kJ (test 1)
to 1933 kJ (test 4), while the maximum applied power (corresponding to the maximum current) was about 0.08-9.0 W.

For montmorillonite, the energy expenses were lower since the applied currents were lower than for kaolin: in these cases the energy expenditure was about 3.5-7.6 kJ, with maximum required powers of 0.015-0.6 W.

Thus, according to the results achieved, the process seems to require a low energy expenditure, being the current densities applied very low (< 0.01-1 mA/cm²).

### 4.2 Electroosmotic Flux

During the experiments performed with kaolin, an electroosmotic flux occurred when the intensity of the electric current was appreciable (e.g. for current of the order of magnitude of 10 mA or above). As during the tests the electric current showed to start to decrease a few hours after the beginning of the tests, the electroosmotic flux, when occurring, was appreciable only in the first days of treatment, and became negligible afterwards. The electroosmotic flow has already been reported to decrease rapidly with time, especially when no ionic solution is added to the soil and the resulting current is weak (Reddy et al., 2006; Isosaari et al., 2007).

When kaolin was tested, the volume of the pore fluid collected at cathode compartment was limited, about 7 mL, 42 mL, 22 mL, 13 mL and 11 mL for tests 1, 2, 3, 4 and 5 respectively, with no clear dependence on the applied voltage. In both the tests performed with montmorillonite, the electroosmotic flux was negligible, as the current densities were lower than for kaolin, being about 3-6 mA at the beginning of the trials and lower than 2 mA after a one-day treatment. However, since a good contaminant removal was achieved during the tests (see section 3.4), the occurrence of the electroosmotic flux does not seem to be necessary to achieve a significant mineralization of the organic pollutants, although the electroosmotic flux was previously considered necessary to provide fresh water for electrolysis and for further redox reactions (Röhrs et al., 2002).

### 4.3 Soil pH Profiles and Soil Moisture

During the tests performed, the soil pH tended to increase at the cathode and to decrease at the anode (Figure 3) as a result of water hydrolysis, which leads to the production of an acid front moving from the anode toward the cathode and a base front moving from the cathode toward the anode. This effect was particularly evident in the tests performed with kaolin, for which the initial pH (about 6) gradually changed to about 3-4 nearby the anode and to about 8-10 near the cathode a few days after the beginning of the tests. For longer test duration (e.g. 2-4 weeks), all the soil volume tended to be acidified, because of the acid front moving across the soil form the anode towards the cathode. This evidence was stronger for high specific voltages (i.e. 3-6 V/cm) rather than lower voltages (0.5-1 V/cm). When the electroosmotic flow occurred, the fluid collected at cathode compartment was slightly acidic, with pH ranging from 6.2 to 6.7.
As for montmorillonite (initial pH about 10), the pH variations were very limited, because of the high buffer capacity of this type of soil.

Figure 3. Results of the tests performed on diesel-contaminated soils: pH and TPH concentration at different distances from the electrodes at the beginning and at the end (4 weeks) of the tests performed on kaolin (a, b, c and d) and montmorillonite (e and f).

The soil humidity at the beginning of the tests was about 37% for kaolin and 38% for montmorillonite. Despite the fact that no fluid was provided at the electrodes, the soil did not dry out. The final water content near the anode ranged from 33% to 34% for kaolin, from 37% to
38%, and for montmorillonite, with even slightly higher moisture contents in other sections. On the whole, the soil moisture content remained fairly constant and comparable to the initial water content.

Occasional monitoring of soil temperature did not show any changes, which were however not expected, since an increase in soil temperature have been reported to occur as a consequence of electric processes only when higher currents are flowing (Isosaari et al., 2007).

The soil slightly compacted near the anode at the end of the tests. This effect has already been observed in previous studies (Isosaari et al., 2007). Moreover, a change in the oxidation state of iron and probably other metals was observed near the anode, so that after a few weeks from the beginning of the test, some clogging proved to occur near this electrode. The soil also changed to a yellow-orange color, probably because of the formation of iron hydroxides from the soil natural iron content; a further iron supply deriving form the anode corrosion is also possible (Röhrs et al., 2002). The formation of iron oxides or oxohydrates has already been reported to occur and to be able to block the electrode surface, resulting in a decrease of the flowing current (Rahner et al., 2002). Sometimes complexing or conditioning agents are used to retard the electrode fouling and to increase the current flow.

4.4 Diesel Fuel Remediation

The main results of the tests performed on diesel-contaminated kaolin are reported in Table 3 and in Figure 4. As can be seen from the data shown, the TPH removal after 28 days of treatment increased significantly as the applied voltage increased form 0.5 V/cm to 1 V/cm, ranging from 66% in test 1 to 80% in test 2. As the voltage increased to 3 V/cm (test 3), the TPH removal slightly increased to 85%. During test 4 (6 V/cm) the removal efficiency was even lower than for tests 2 and 3: this is thought to be due to sample heterogeneity, and the result achieved in test 4 with 6 V/cm can be considered of the same order of magnitude of the results of tests 2 and 3. During these tests, the TOC removal also increased from 46% to 54% as the specific voltage increase form 0.5 V/cm to 1 V/cm, but it remained almost constant afterwards.

The fact that the removal efficiency of TOC was always lower than the TPH removal is due to the fact that TOC represents all the organic matter in a soil sample; therefore, it accounts also for the presence of by-products that derive from the degradation of petroleum hydrocarbons, which on the opposite do not appear in the TPH content.

During tests 1, 2 and 3, the increase of the contaminant removal efficiency with time was monitored. As seen in Figure 4, both the TOC and the TPH removal significantly increased with time during the first weeks of treatment. The time dependency was, however, different for different voltages. In fact, when the lowest voltage was applied (i.e. 0.5 V/cm), the contaminant removal gradually increased, so that more than 20 days of treatment were required to achieve a good contaminant removal efficiency (e.g. more than 40% TOC removal and 60% TPH removal). When higher voltages were applied, these remediation performances could be achieved in shorter times, i.e. about 15 days for 1 V/cm and less than 10 days for 3 V/cm. An increase in the applied voltage therefore allowed to achieve a good contaminant removal in shorter times than lower voltages, but this advantage is counterbalanced by the fact that higher
specific voltages (e.g. 3 V/cm or more) result in higher energy expenditure and require more complicated setups for real scale applications.

One additional test (test 5) was performed on diesel-contaminated kaolin to assess treatment efficiencies in case of larger soil specimen. In this test, the soil specimen had a length of 50 cm, with the usual cross section of 100 cm² (10 cm by 10 cm). As in test 2, a specific voltage gradient of 1 V/cm was applied for 4 weeks. This test resulted in 49% TOC removal and 89% TPH removal, thus confirming, despite some variability due to sample heterogeneity, the results achieved with the same specific voltage on a smaller soil specimen during test 2.

One test was performed on diesel contaminated kaolin without the applications of electric current, as a reference test to assess any loss of contaminants due to volatilization or other chemical, physical or biological phenomena not linked with the electrochemical processes. The test was performed with the same setup used for the other experiments and lasted for four weeks. At the end of the trial, the soil sample showed a TOC content about 209.7 g/kgSS and a TPH content about 144.5 g/kgSS. The test was conducted in parallel with test 3; therefore, the loss of contaminants during the trail was about 5% for TOC and 22% for TPH, significantly lower than the removal achieved with the electrochemical method (about 54% and 85% respectively).

<table>
<thead>
<tr>
<th>Test</th>
<th>Elapsed time</th>
<th>TOC [g/kgSS]</th>
<th>TPH [g/kgSS]</th>
<th>TOC Removal</th>
<th>TPH Removal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Test 1 -</td>
<td>0</td>
<td>208,1</td>
<td>131,0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>189,9</td>
<td>93,8</td>
<td>9%</td>
<td>28%</td>
</tr>
<tr>
<td>0.5 V/cm</td>
<td>14</td>
<td>183,1</td>
<td>83,7</td>
<td>12%</td>
<td>36%</td>
</tr>
<tr>
<td></td>
<td>21</td>
<td>126,0</td>
<td>70,3</td>
<td>39%</td>
<td>46%</td>
</tr>
<tr>
<td></td>
<td>28</td>
<td>112,3</td>
<td>45,2</td>
<td>46%</td>
<td>66%</td>
</tr>
<tr>
<td>Test 2 -</td>
<td>0</td>
<td>208,1</td>
<td>131,0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1 V/cm</td>
<td>7</td>
<td>113,6</td>
<td>65,0</td>
<td>45%</td>
<td>50%</td>
</tr>
<tr>
<td></td>
<td>14</td>
<td>109,2</td>
<td>60,3</td>
<td>48%</td>
<td>54%</td>
</tr>
<tr>
<td></td>
<td>21</td>
<td>107,8</td>
<td>30,9</td>
<td>48%</td>
<td>76%</td>
</tr>
<tr>
<td></td>
<td>28</td>
<td>95,5</td>
<td>26,6</td>
<td>54%</td>
<td>80%</td>
</tr>
<tr>
<td>Test 3 -</td>
<td>0</td>
<td>221,1</td>
<td>185,3</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>3 V/cm</td>
<td>7</td>
<td>128,9</td>
<td>49,9</td>
<td>42%</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>14</td>
<td>121,7</td>
<td>43,6</td>
<td>45%</td>
<td>76%</td>
</tr>
<tr>
<td></td>
<td>21</td>
<td>112,1</td>
<td>33,8</td>
<td>49%</td>
<td>82%</td>
</tr>
<tr>
<td></td>
<td>28</td>
<td>101,3</td>
<td>27,4</td>
<td>54%</td>
<td>85%</td>
</tr>
<tr>
<td>Test 4 -</td>
<td>0</td>
<td>185,0</td>
<td>179,8</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>6 V/cm</td>
<td>28</td>
<td>84,0</td>
<td>40,3</td>
<td>55%</td>
<td>78%</td>
</tr>
<tr>
<td>Test 5 -</td>
<td>0</td>
<td>133,6</td>
<td>37,4</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1 V/cm</td>
<td>28</td>
<td>94,4</td>
<td>19,2</td>
<td>49%</td>
<td>89%</td>
</tr>
</tbody>
</table>

Two tests were performed on diesel-contaminated montmorillonite (tests 6 and 7): the results achieved are shown in Table 4 and Figure 5.
Since the results obtained with kaolin had showed that good results could be achieved with specific voltages as low as 1 V/cm, only two voltages (5 and 10 V, i.e. 0.5 and 1 V/cm) were tested with diesel-contaminated montmorillonite. The results proved the electrochemical method to be very effective for the remediation of this type of soil. In fact test 6, characterized by a specific voltage of 0.5 V/cm, resulted in 60% TOC removal and 73% TPH removal after a 4 week treatment, while test 7 (1 V/cm) showed even higher performances, with 69% TOC removal and 87% TPH removal after 4 weeks. Similarly to kaolin, the contaminant removal proved to increase significantly with time, and more than two weeks were required to achieve a TOC and TPH removal higher than 50%.

As can be seen from the data shown in Table 3 and Table 4, the removal efficiencies achieved with montmorillonite were much higher than for kaolin. This difference is not due to a higher conductivity of montmorillonite, which on the opposite showed lower current densities (i.e. a higher electric resistivity) than kaolin. Therefore, these results are thought to be due to the different mineralogy of the two soils considered in this study, and in particular by the higher iron content of montmorillonite than kaolin, which is supposed to have enhanced both the production of H2O2 (microconductor effect) and the Fenton-like reactions that lead to the production of hydroxyl radicals, responsible of the oxidation processes.

<table>
<thead>
<tr>
<th>Test</th>
<th>Elapsed time [d]</th>
<th>TOC [g/kg ss]</th>
<th>TPH [g/kg ss]</th>
<th>TOC Removal</th>
<th>TPH Removal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Test 6 - 0.5 V/cm</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>264.8</td>
<td>176.0</td>
<td></td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>14</td>
<td>131.6</td>
<td>102.2</td>
<td>50%</td>
<td>42%</td>
<td></td>
</tr>
<tr>
<td>21</td>
<td>113.4</td>
<td>72.8</td>
<td>57%</td>
<td>59%</td>
<td></td>
</tr>
<tr>
<td>28</td>
<td>107.0</td>
<td>47.0</td>
<td>60%</td>
<td>73%</td>
<td></td>
</tr>
<tr>
<td>Test 7 - 1 V/cm</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>264.8</td>
<td>176.0</td>
<td></td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>7</td>
<td>184.2</td>
<td>77.0</td>
<td>30%</td>
<td>56%</td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>127.4</td>
<td>71.4</td>
<td>52%</td>
<td>59%</td>
<td></td>
</tr>
<tr>
<td>21</td>
<td>95.5</td>
<td>55.0</td>
<td>64%</td>
<td>69%</td>
<td></td>
</tr>
<tr>
<td>28</td>
<td>81.6</td>
<td>23.0</td>
<td>69%</td>
<td>87%</td>
<td></td>
</tr>
</tbody>
</table>

*Figure 4. Results of the tests performed on diesel-contaminated kaolin: comparison of the TOC and TPH removal efficiencies achieved during tests 1, 2 and 3.*

*Table 4. Results of the tests performed on diesel contaminated montmorillonite: TOC and TOH removals.*
On the whole, the results of the tests performed indicated that a significant oxidation of organic pollutants can be achieved with electrochemical methods. For example, after a 28 day treatment about 50% TOC removal and 60% TPH removal were encountered for kaolin (Table 3), and about 70% TOC removal and 85% TPH removal were reached for montmorillonite (Table 4).

Major conclusions can be drawn from the results achieved. An increase in the applied voltage proved to cause a limited contaminant removal increase, a good removal being encountered for specific voltages as low as 1 V/cm. On the opposite, the contaminant removal seems to increase significantly with process duration. For example, the application of a constant voltage of 1 V/cm to a montmorillonite sample led to 30% TOC decrease after 7 days, but the TOC removal increased to about 70% after 28 days of treatment (Table 4).

The final contaminant concentrations were found to be evenly distributed across the treated sample, as shown in Figure 3. This suggests that the oxidation reactions take place within all the treated volume and not only nearby the electrodes. Moreover the results indicate that the pollutants electromigration during the test performed, which were unenhanced, can be considered negligible.

The pH changes were expected to influence the system efficiency, since a low pH can enhance the Fenton-like reactions, which lead to the production of hydroxyl radicals. However, the mineralization process did not seem to be influenced by pH changes, the contaminant removal being of the same order of magnitude both in areas with low and high pH (Figure 5). On the opposite, the soil mineralogy, and in particular the iron content, seems to affect significantly the treatment results. In fact, the removal efficiency achieved for montmorillonite (iron content about 2794 mg/kg_{SS} and manganese content about 34 mg/kg_{SS}) were much higher than for
kaolin, which was characterized by a lower metal content (iron content about 10180 mg/kgSS, manganese content about 44 mg/kgSS), despite the fact that the two soils showed similar current densities, which were even lower for the montmorillonite than for the kaolin. Even if the addition of ferrous ions has been reported not to have any influence on the electric conductivity of the soil, the large reservoir of iron that is present in natural occurring iron-containing minerals is supposed to act as a microconductor source, promoting redox reactions and the formation of $\text{H}_2\text{O}_2$ and to enhance the Fenton-like reactions that promote the oxidation processes (Rahner et al., 2002; Isosaari et al., 2007).

4.5 PAH Remediation

This part of the study aimed at investigating the feasibility of using electrochemical oxidation for the remediation of river sediments contaminated by PAHs, in case of old date pollution.

Three tests (tests 8, 9 and 10) were performed to assess the applicability of the electrochemical methods to the contamination of concern and the results achieved are presented in Table 5. To assess the efficiency of the tested treatments, the removal percentages were calculated for single PAH species and of PAH summation, as well as for TOC, which stands for the total amount of the organic matter in the sample, both from natural and anthropogenic origin. The results were also correlated with PAH octanol-water partition coefficient $K_{ow}$, which represents the lipophilicity of a certain chemical and indicates the tendency of that compound to be sorbed onto organic matter or to dissolve in water.

The first laboratory test performed on PAH-contaminated sediments (test 8) was conducted to assess the effectiveness of electrooxidation in removing the addressed contaminants. During the trial a constant specific voltage of 1.5 V/cm was applied for 14 days. An initial current of 50 mA and a final current of 4 mA were recorded. At the end of the test an 85% total PAH removal was encountered (light PAH removal 90%, heavy PAHs removal 75%), with a final total PAH concentration in the treated sample about 162.8 mg/kgSS. The TOC removal was about 14%. In this case the low values of TOC removal can be considered due to the very high natural organic matter content in the sediment samples. At the end of the test, a part of the soil specimen was transversally sliced into five segments and each segment was analyzed for pH and contaminant concentrations, in order to assess the extent of electrochemical reactions at different distances from the electrodes and the eventual contribution of electromigration.

The values of soil pH and contaminant concentration across the specimen are presented in Figure 6. Despite some variability due to sample heterogeneity, which can be considered a typical feature of PAH contamination, final pollutant concentrations were found to be evenly distributed across the treated sample, both for PAHs and for TOC, without any trend towards the electrodes. The same result had been found for diesel fuel contamination. Other Authors who studied the PAH removal via electrochemical processes reported that PAHs can be transported towards the cathode zone and also be partially removed from soil with the catholyte solution if the occurrence of a sufficient electroosmotic flow is enhanced by the application of sufficient voltages and hydraulic gradients (Chung and Kamon, 2005; Isosaari et al., 2007); however, in this case this effect was not expected because the electroosmotic flux was very limited. In fact, at the end of the trial, 103 mL of pore fluid were found to be accumulated in the tank at the cathode.
compartment as a result of the electroosmotic flux. The water collected showed a strongly basic pH (about 9.3), while the TOC content was 525 mg/L. All PAH species were below the detection limit (<0.1 mg/L), showing that no significant transport effect occurred as a result of the electroosmotic flux for the addresses contaminants, which are, indeed, very hydrophobic organic species, with very little water solubilities (Table 1).

As already observed for diesel fuel contaminated soils, during the tests the soil pH tended to increase at the cathode and to decrease at the anode (Figure 6). However, the mineralization process did not seem to be influenced by pH changes, the contaminant removal being evenly distributed both in areas with low and high pH.

During tests 8 the PAH volatilization was estimated. The reactor was kept closed while the test was in progress to avoid vapors diffusing into external air. At the end of the trial, before opening the reactor, the air was sampled onto an ORBO Tube for collecting airborne PAHs. An ORBO-43 (Supelco, Bellefonte, PA) was used for the air sampling and a vacuum pump was used to induce the air flow across the tube (200 mL/min). The ORBO tube was then analyzed by GC to determine the PAH content. The analysis showed that the PAH content in the tube was less than 0.1 mg, so it can be concluded that no significant contaminant loss due to volatilization occurred during the test.

Other two laboratory tests (tests 9 and 10) were performed to assess the influence of the applied voltage (1-2 V/cm) and treatment duration (7, 14, 21, 28 days) on PAH removal efficiency, in order to optimize the remediation conditions. During these tests the initial current values were about 6.5 mA (test 9) and 50 mA (test 10), while at the end of both trials the electric current was below 1 mA. The results achieved are presented in Figure 7.

During test 9, a 72% total PAH removal was encountered 7 days after the beginning of the trial; as the treatment proceeded, the total PAH removal gradually increased to 74% (14 days), 81% (21 days) and 91% at the end of the test, after a 28-day treatment. In the meanwhile, the TOC removal increased from about 2% (7 days) to 8% (14 days), 17% (21 days) and 25% (28 days).

Higher removal efficiencies were encountered during test 10, when a higher specific voltage (2 V/cm) was applied. In this case the total PAH removal efficiency was about 33% after 7 days after the beginning of the treatment, but it rapidly increased to 85% after 14 days, 93% after 21 days and 96% after 28 days. The results achieved in these two latter tests are consistent with the removal efficiencies measured at the end of test 8, with a total PAH removal efficiency about 74-85% after a two-week treatment.

In all the tests performed with PAH-contaminated sediments, the removal efficiency for light PAHs was found to be higher than for the heavy PAHs. This can be considered as a typical behavior of PAHs, whose lighter species are generally more available to reactants than heavy species, which are more hydrophobic and more sorbed onto sediments (Ferrarese et al., 2007; Zheng et al., 2007). For traditional chemical oxidation, the PAH contaminant availability has been well reported to influence the treatment efficiency, the less sorbed pollutants (i.e. the species that are less hydrophobic) being more available for mineralization, while the more hydrophobic and more sorbed molecules proved to be more resistant to oxidation than
Table 5. Results of the tests performed on PAH-contaminated river sediments.

<table>
<thead>
<tr>
<th>Elapsed time [d]</th>
<th>Test 8 - 1.5 V/cm</th>
<th>Test 9 - 1 V/cm</th>
<th>Test 10 - 2 V/cm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0</td>
<td>14</td>
<td>0</td>
</tr>
<tr>
<td>1 naphthalene</td>
<td>[mg/kgSS]</td>
<td>54.1</td>
<td>1.6</td>
</tr>
<tr>
<td>2 acenaphthylene</td>
<td>[mg/kgSS]</td>
<td>1.5</td>
<td>0.2</td>
</tr>
<tr>
<td>3 acenaphtene</td>
<td>[mg/kgSS]</td>
<td>101.7</td>
<td>7.2</td>
</tr>
<tr>
<td>4 fluorene</td>
<td>[mg/kgSS]</td>
<td>65.4</td>
<td>3.9</td>
</tr>
<tr>
<td>5 phenanthrene</td>
<td>[mg/kgSS]</td>
<td>278.9</td>
<td>21.5</td>
</tr>
<tr>
<td>6 anthracene</td>
<td>[mg/kgSS]</td>
<td>55.7</td>
<td>3.6</td>
</tr>
<tr>
<td>7 fluoranthene</td>
<td>[mg/kgSS]</td>
<td>173.4</td>
<td>34.9</td>
</tr>
<tr>
<td>8 pyrene</td>
<td>[mg/kgSS]</td>
<td>116.2</td>
<td>21.3</td>
</tr>
<tr>
<td>9 chrysene</td>
<td>[mg/kgSS]</td>
<td>45.9</td>
<td>9.9</td>
</tr>
<tr>
<td>10 benzo(a)anthracene</td>
<td>[mg/kgSS]</td>
<td>30.0</td>
<td>7.6</td>
</tr>
<tr>
<td>11 benzo(b)fluoranthene</td>
<td>[mg/kgSS]</td>
<td>56.8</td>
<td>16.0</td>
</tr>
<tr>
<td>12 benzo(k)fluoranthene</td>
<td>[mg/kgSS]</td>
<td>21.2</td>
<td>5.5</td>
</tr>
<tr>
<td>13 benzo(a)pyrene</td>
<td>[mg/kgSS]</td>
<td>41.5</td>
<td>11.3</td>
</tr>
<tr>
<td>14 dibenzo(a,h)anthracene</td>
<td>[mg/kgSS]</td>
<td>3.4</td>
<td>1.0</td>
</tr>
<tr>
<td>15 benzo(g,h,i)perylene</td>
<td>[mg/kgSS]</td>
<td>20.7</td>
<td>7.7</td>
</tr>
<tr>
<td>16 indeno(1,2,3cd)pyrene</td>
<td>[mg/kgSS]</td>
<td>22.9</td>
<td>9.6</td>
</tr>
<tr>
<td>Total light PAHs (1-7)</td>
<td>[mg/kgSS]</td>
<td>730.7</td>
<td>72.8</td>
</tr>
<tr>
<td>Total heavy PAHs (8-16)</td>
<td>[mg/kgSS]</td>
<td>358.6</td>
<td>89.9</td>
</tr>
<tr>
<td>Total PAHs</td>
<td>[mg/kgSS]</td>
<td>1089.3</td>
<td>162.8</td>
</tr>
<tr>
<td>TOC</td>
<td>[g/kgSS]</td>
<td>99.0</td>
<td>85.6</td>
</tr>
<tr>
<td>Total light PAH removal [%]</td>
<td>-</td>
<td>90%</td>
<td>-</td>
</tr>
<tr>
<td>Total heavy PAH removal [%]</td>
<td>-</td>
<td>75%</td>
<td>-</td>
</tr>
<tr>
<td>Total PAH removal [%]</td>
<td>-</td>
<td>85%</td>
<td>-</td>
</tr>
<tr>
<td>TOC removal [%]</td>
<td>-</td>
<td>14%</td>
<td>-</td>
</tr>
</tbody>
</table>
Contaminants in solution; this difference in the removal efficiency can be overcome by using vigorous oxidation conditions, such as high oxidant dosages (Kakarla et al., 2002; Watts et al., 2002; Bogan and Trbovic, 2003; ITRC, 2005; Watts et al., 2005; Ferrarese et al., 2007).

To highlight this effect, the removal efficiency of different PAH species achieved in tests 9 and 10 was compared to the octanol-water partition coefficient ($K_{ow}$) (Figure 8). As the $K_{ow}$ coefficient represents the lipophilicity of a certain chemical, it indicates the tendency of that compound to be sorbed onto organic matter or to dissolve in water. The higher the $K_{ow}$ coefficient is, the more the PAHs tend to be sorbed onto organic matter. As shown in Figure 8, the PAH removal efficiency tended to decrease as the value of Log($K_{ow}$) increases, thus indicating that the removal efficiencies are always higher for light PAH species than for heavy PAHs. This effect has already been observed in previous studies for the electrochemical treatment of PAH-contaminated soils (Isosaari et al., 2007; Zheng et al., 2007). Figure 8 also indicates that as the treatment duration increases, the pollutant removal increases, both for light and heavy PAH species, rising up to 90-99% for light PAHs and about 70-80% for heavy PAHs after a four week treatment.

![Graph of contaminant concentrations and pH](https://scholarworks.umass.edu/soilsproceedings/vol13/iss1/26)

**Figure 6.** Results of test 8: contaminant concentrations (a) and pH (b) at different distances from the electrodes.
Figure 7. Results of tests 9 and 10 performed on PAH-contaminated sediments: comparison of the removal efficiencies achieved for total PAHs, light PAHs, heavy PAHs and TOC.
Figure 8. Results of tests 8 and 9: removal efficiencies achieved as a function of PAH octanol-water partition coefficient (Kow). Since benzo(a)pyrene and benzo(k)fluoranthene are characterized by the same value of Kow, as well as phenentrene and anthracene, in the plots only the results for benzo(a)pyrene and for phenanthrene are presented.

A problem that may arise during the oxidation of PAH contaminated soils is the risk of incomplete mineralization and the consequent production of degradation by-products, which may be of concern because of the high toxicity of certain species. PAHs are known to create a certain number of degradation intermediates, which commonly include aldehydes, ketones, and quinones as main oxidation by-products (oxy-PAHs) (Watts et al., 2002; Brown et al., 2003; Flotron et al., 2005; Lundstedt et al., 2006; Perraudin et al., 2007). Despite the fact that many compounds are known as single PAH derivatives, a complete identification of all PAH by-products has not been achieved yet.

Most of PAH derivatives are known to have polar functional groups, which are likely to enhance not only higher aqueous solubility but also availability for natural biodegradation more than the parental compounds (Brown et al., 2003; Kulik et al., 2006). On the other hand, the fact that in natural soils PAHs are commonly strongly sorbed and incorporated into organic matter is also thought to act as a sort of detoxification process, by reducing their bioavailability and their mass transfer, thus decreasing their toxic effect towards natural microbial community (Richnow et al., 1995; Sun and Yan, 2007). On the other hand this effect is absent in desorbed PAH and PAH derivatives, which may be therefore characterized by a stronger toxic effect than the parental compounds. As a consequence, a remediation action that results in the desorption of PAH molecules without achieving a complete mineralization can even lead to an increase in the toxic effect towards the natural biota, rather than reducing it.

In this study, the identity of the oxidation reaction by-products has not been determined, but the ecotoxicity of the original and final samples has been evaluated in the last experiments (tests 9 and 10), to assess any change in the toxic effect of the sediments toward the local biota. The original untreated sample showed a toxic effect of 0.23 TU50, while the toxic effect in both the treated samples was below the detection limit. These results indicate that the toxic effect of the original sediments was not very high; this is attributed to the fact that PAHs are strongly sorbed onto sediments and do not tend to solubilize in water (Ferrarese et al., 2007). This limits their...
mass transfer and their bioavailability, also preventing them to have a strong toxic effect (Luthy et al., 1994; Taylor and Jones, 2001). Since the toxic effect became negligible after the tests, the electrochemical treatment does not seem to enhance the sole desorption of the addressed pollutants, promoting their mineralization in the sorbed form or oxidizing them as soon as they are desorbed. This result was confirmed by the fact that the PAH concentration in the pore fluid collected at cathode compartment during tests 8 was below the detection limit (<0.1 mg/L).

In sum, based on the results of this study, electrochemical oxidation proved to be an effective remediation technology for the sediments of concern, amenably applicable both for in situ or ex situ remediation actions.

5. CONCLUSIONS

The tests performed allowed to evaluate the feasibility of using electrochemical oxidation for the remediation of different organic contaminants (diesel fuel and PAHs from two types of fine grain soils (kaolin and montmorillonite) and freshwater sediments.

According to the results achieved, electrochemical oxidation proved to be effective for the remediation of fine-grain soils contaminated by various types of hydrocarbons. A good removal was achieved both for PAHs and diesel fuel: about 90% contaminant removal was achieved for PAH-contaminated sediments after a four week treatment, while the diesel fuel contaminated soils resulted in about 50% TOC removal and 60% TPH removal for kaolin, and about 70% TOC removal and 85% TPH removal for montmorillonite.

As for the most important design parameters, the applied voltage seems to have a limited influence on the efficiency of the remediation action, good results being achieved with specific voltages as low as 1 V/cm, with low energy expenditures. On the opposite, the remediation efficiency proved to increase significantly with process duration. For example, the application of a constant voltage of 1 V/cm to a montmorillonite sample led to 30% TOC removal after 7 days, but the TOC removal increased to about 70% after 28 days of treatment. The effectiveness of the process seems also to be affected by soil mineralogy, and primarily by the soil iron content, so that significant iron content in the treated soil is thought to be able to improve the applicability of this remediation method. The final contaminant concentrations were found to be evenly distributed across the treated sample. This suggests that the oxidation reactions take place within all the treated volume and not only nearby the electrodes; moreover, the results indicate that the pollutants’ electromigration during the test performed, which was unenhanced, can be considered negligible. The buffer capacity of the soil can affect soil pH changes, by determining the tendency of the treated medium towards acidification or basification, but the remediation efficiency does not seem to be influenced by changes in soil pH, nor by the occurrence of the electroosmotic flux, which does not seem to be necessary to achieve a significant mineralization of the organic pollutants.

On the whole, electrochemical oxidation seems to be effectively and amenably applicable for the mineralization of many organics with low energy expenditure, especially in finest soils like clays, with significant iron content.
6. REFERENCES


https://scholarworks.umass.edu/soilsproceedings/vol13/iss1/26
Electrooxidation of Organic Pollutant Contaminated Soils


