Soil Remediation

Applications and New Technologies
Since the nineteenth century, the development of societies led to the exponential growth of industrial and other economic activities that have originated thousands of cases of land- and groundwater contamination. During the last century these occurrences became more frequent and problematic because of the increase of the world’s population as well as the fast development of science that promoted the use of new technologies, some of them more polluting than their antecessors. More recently, the valorization by modern societies of environmental aspects and its preservation implied the inversion of this tendency and led to the reduction of the rate of new contamination cases. Nevertheless, the contamination heritage still requires the urgent implementation of remediation actions. Another aspect that should not be ignored is the appearance of new contaminants that started to be considered only recently because of the advances in several scientific areas such as analytical methods and toxicology. These new contaminants are called Emerging Contaminants and pose a new challenge to industry, service providers, regulators and the scientific community.

A recent report from the European Environment Agency (2014) indicates that there are near 2.5 million potentially contaminated sites in Europe and that the waste disposal & treatment and the industrial & commercial activities are responsible for 72% of these sites. However, these numbers only correspond to the data of some European countries, so the real numbers should be much higher. A similar situation occurs in the United States of America; neither the U.S. Department of Agriculture nor the Department of Interior have a complete inventory.

In this light a more extensive evaluation of contaminated sites is essential and extremely urgent. Where necessary, the most appropriate remediation technology should subsequently be implemented. It is therefore useful to collect the knowledge about the most recent advances on the existent remediation technologies as well as the development of new remediation options that use innovative technologies and new materials to face new contamination challenges namely with emergent contaminants that require specific, and in several cases expensive treatments.

The objective of this book is to gather valuable information on soil remediation and related issues such as case studies, decision making tools
(e.g., Life Cycle Assessment) and new and innovative remediation technologies (e.g., nanoremediation), that could aid stakeholder activities.

We are thankful to all the contributors for their collaboration that made the present book possible. We also extend our appreciation to Science Publishers for their extraordinary support.
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Electrokinetic Remediation and Hybrid Technologies for the Treatment of Organic Pollutants

María Ángeles Sanromán, Olalla Iglesias, Emilio Rosales and Marta Pazos

ABSTRACT

Electrokinetic remediation is an in situ technology that has been successfully applied for the removal of inorganic pollutants since the past 20 years. In this technique, an electric field is applied to promote the movement of contaminants toward the electrode chambers, located in the polluted soil, from where the pollutants can be extracted. However, in the remediation of soils polluted with organic compounds, the main limitation is that the pollutants should be soluble in the interstitial soil fluid to be transported by the action of the electric field. Therefore, the application to low solubility pollutants such as, for example, hydrophobic organic pollutants is limited. Nowadays some technique improvements can be applied in order to solve this problem and the application of this technique alone or combined with other processes like Fenton or bioremediation is giving satisfactory results in organic pollutant removal. This chapter describes the foremost principles to carry out the electrokinetic remediation of soils contaminated with organic pollutants, as well as the different alternatives to improve the process and new methodologies for organic pollutants removal by using hybrid technologies.
Introduction

**Fundamentals**

Electrokinetic remediation process arises as an effective technique for the *in situ* treatment of soils with organic and inorganic pollution. It is based on a flushing process generated from the action of an electric current that allows the transport of pollutants even when the soil is characterized with low permeability. This technique can be found in the literature with several terms such as electrokinetic remediation, electrokinetics, electroremediation, or electrochemical remediation, among others (Acar and Alshawabkeh 1993).

The principle of electrokinetic remediation consists of the controlled application of low intensity direct current through the soil between appropriately distributed electrodes (Fig. 1). One of the most important advantages of this technique is its efficiency for the treatment of low hydraulic permeability soils, where other techniques such as pump-treat are not adequate (Acar and Alshawabkeh 1993).

![Fig. 1. Schematic diagram of an electrokinetic process application.](image)

The applied electric current induces the transport of species in the interstitial soil fluid, depending on their electrical charge, towards the anode or cathode chambers (mainly due to electro-osmosis and ion migration) that is coupled with electrolysis and geochemical reactions.
**Transport Mechanisms**

The application of the direct current in the soil induces the generation of fluid transport and the mobilization of species due to reactions that take place in the soil and the electrode chambers. The main electrokinetic transport mechanisms include electrophoresis, electro-osmosis, and ion migration (electromigration) (Fernandez et al. 2009). These three phenomena can be summarized as follows:

- **Electrophoresis** is the migration of charged colloids under an electrical potential gradient towards the electrode with opposite charge. In a saturated system such as a soil, the electrophoresis process has less importance because the solid phase is in stationary status (Yu and Neretnieks 1996).

- **Electro-osmosis** involves interstitial water pore transport at the solid/liquid interface. Most of the particles on the surface of the soil grains are negatively charged due to isomorphic substitutions and the presence of broken links. These negative charges attract the positive charges present in the interstitial fluid (cations) in order to reach electroneutrality. Therefore, there is an inert layer of cations on the surface of the soil pore named fixed layer. These cations do not have enough density to compensate all the negative charges; thus, a second layer of cations, which are further away from the negative groups, is not very strongly linked and constitutes a mobile layer. The combination of both layers is known as the double diffuse layer of cations. When an electrical gradient is applied to a soil-water system, the particles are fixed, but the mobile diffuse layer moves and the solution is carried with it towards the cathode. In most cases, the soil is negatively charged and the electro-osmotic transport generates a hydraulic flux towards the cathode chamber.

- **The ion migration** is a diffusive transport generated by electrical forces on ions. Anions are transported towards the anode (positive electrode) and cations are transported towards the cathode (negative electrode).

In addition to these mechanisms, common mass-transport mechanisms, such as diffusion or convection, and the physical and chemical interactions of the species with the medium also take place; however, their relative importance is almost negligible (Fernandez et al. 2009). Therefore, Fig. 2 shows the main phenomena that have a clear influence on the net pollutant transport in electrokinetic treatments of soils.

**Advantages and Disadvantages**

Electrokinetic remediation has attracted interest among scientists and governmental officials in the last decade, due to several promising laboratory and pilot-scale studies and experiments. However, regardless of promising results, this method has its own advantages and drawbacks.
Advantages

Electrokinetic remediation has become a technology with great prospects (Huang et al. 2012; Niroumand et al. 2012). The main advantages of this process are described below:

Remediation of low permeability soils

Electrokinetic remediation is the most effective treatment for low permeability soils because it can operate even at a low hydraulic gradient, when the application of traditional technologies is restricted. In clayey sediments, hydraulic flow through pores can be extremely limited. This technology has been an effective method of inducing movement of water, ions, and colloids through fine-grained sediment (Murillo-Rivera et al. 2009; Reddy et al. 2009). Whereas values of hydraulic conductivity can vary among many orders of magnitude for different soil types, the electroosmotic conductivity lies in a narrow range of $1 \cdot 10^{-9}$ to $1 \cdot 10^{-8} \text{ m}^2 \cdot \text{s}^{-1} \cdot \text{V}^{-1}$. Thus, an electric field is a much more effective force driving the fluid through fine grained soils of low hydraulic conductivity than a hydraulic gradient (Niroumand et al. 2012).
In situ remediation

In situ remediation technologies for contaminated soils include isolation and containment, soil flushing, biochemical treatment, phytoremediation, and electrokinetic remediation. The advantages of electrokinetic remediation techniques rest with possible applications under sealed surfaces and in fine-grained soils. In the in situ treatment of polluted soil, the main considerations are the spatial arrangement and spacing between the electrodes that significantly influences the distribution of the potential isolines (Alshawabkeh et al. 1999), the electrode chambers construction and the electrolyte which should be formulated depending on the type of soil and its pollution (Wieczorek et al. 2005).

Disadvantages

pH

The electrokinetic remediation process is highly dependent on pH conditions during the application, which influences the release of pollutants into the interstitial soil fluid and modifies the transport mechanisms. During the remediation process, the application of the direct current induces chemical reactions upon the electrode surfaces. The dominant and most important electron transfer reactions that occur during the electrokinetic process are the electrolysis of water:

\[
\text{Anode: } \text{H}_2\text{O} \rightarrow 2\text{H}^+ + (1/2)\text{O}_2(g) + 2e^- \quad (1)
\]

\[
\text{Cathode: } 2\text{H}_2\text{O} + 2e^- \rightarrow 2\text{OH}^- + \text{H}_2(g) \quad (2)
\]

As it is represented in reaction (1), the protons are generated in the anode chamber and as consequence of the applied direct current an acid front is carried towards the cathode by electrical migration. Therefore, generated protons travel through the soil decreasing the pH. At the same time, hydroxyl anions are produced in the cathode chamber (2) and they travel through the soil towards the positive electrode. This fact produces an increase in the pH near the cathode. These changes in the pH of the interstitial fluid drastically affect the characteristics of the soil and the evolution of the electrokinetic remediation process.

The basic front increases the precipitation of cationic pollutants, which may inhibit their removal by the proposed technology. On the other hand, the low pH environment promotes the solubilization of inorganic compounds, facilitating their transport by electro-osmosis and electromigration. However, the low pH in the interstitial fluid of soil modifies the zeta potential (the electric potential at the junction between the fixed and mobile parts of the double layer) of soil particle surfaces, reverting the electro-osmotic flow from the cathode towards the anode (Probstein and Hicks 1993). These effects may diminish each other depending on the chemical state and polarity of charges.
Soil Remediation: Applications and New Technologies

of the inorganic compounds of soil. As a result, there are many complexities of the electrochemical processes for researchers to untangle. Moreover, due to the low pH at the anode compartment, the anode is easily corroded. This becomes a serious concern when the process scale is enlarged. Anode material should, therefore, be resistant to corrosion in order to supply stable electricity for long-term operations (Kim et al. 2011). Nonetheless, many enhancement techniques on electrokinetic remediation of soils were developed on the basis of pH control (Alcántara et al. 2008; Cang et al. 2013; Lee and Yang 2000; Saichek and Reddy 2003); although achieving these acidic conditions might be difficult when the soil buffering capacity is high (Pazos et al. 2009). One plausible solution is the inversion of polarity, a technique that consists in inverting the electric field for a short period in order to control pH in the electrode chamber (Alcántara et al. 2008; Pazos et al. 2006). In these conditions, the electrical resistance is reduced and the transport of pollutants is improved.

Remediation of liquid collected from soil

Additionally, to obtain the total degradation of mobilized pollutants from the contaminated soil, the liquid collected by electrokinetic remediation must be treated. To overcome this problem, innovative processes that combine soil electrokinetic remediation and liquid electrochemical oxidation, for the degradation of organic compounds present in a polluted soil, were developed and evaluated (Sanromán et al. 2005; Gómez et al. 2009).

Electrokinetic Treatment for Organic Pollutants Removal

Considering the different physical and chemical properties of the organic contaminants compared to the properties of inorganic pollutants, the operating conditions of the electrokinetic treatment should be modified in order to increase the removal efficiency. Therefore, some enhancements should be performed during the electrokinetic treatment in order to favor the remediation of organic pollutants by the electric field action (Table 1).

The simplest case is the electromigration of soluble organic pollutants, such as dyes, from the solid matrix. In this field, Pazos et al. (2007) determined that in the treatment of clay polluted with Reactive Black 5 dye, a complete removal was achieved using K₂SO₄ as processing fluid and pH control in the anode chamber. The used electrolyte enhanced the desorption of Reactive Black 5 from the kaolin matrix and the pH control favored the alkalization of the system and, at high pH values, Reactive Black 5 was ionized and migrated towards the anode chamber (Fig. 3 right).

There, the dye was degraded by the electro-oxidation on the anode surface. The previous process can be simplified when the electrolyte used in the electrode chambers contributes to the basic pH in the soil.
Table 1. Working conditions and removal efficiency of several electrokinetic remediation processes applied at different polluted soils.

<table>
<thead>
<tr>
<th>Pollutant</th>
<th>Conc. (mg/kg)</th>
<th>Voltage/Intensity</th>
<th>Soil</th>
<th>Electrolyte</th>
<th>Removal (%)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diesel</td>
<td>10,000</td>
<td>40 V</td>
<td>Natural soil</td>
<td>Sodium chloride</td>
<td>55</td>
<td>(Tsai et al. 2010)</td>
</tr>
<tr>
<td>Dinitrotoluene</td>
<td>500</td>
<td>1 V/cm</td>
<td>Kaolin</td>
<td>Sodium bicarbonate, calcium chloride, magnesium chloride</td>
<td>45</td>
<td>(Reddy et al. 2011a)</td>
</tr>
<tr>
<td>Hexachlorobenzene</td>
<td>100</td>
<td>1.5 V/cm</td>
<td>Kaolin</td>
<td>Sodium hydroxide</td>
<td>63</td>
<td>(Pham et al. 2009)</td>
</tr>
<tr>
<td>Lindane</td>
<td>1,000</td>
<td>1 V/cm</td>
<td>Kaolin</td>
<td>Sodium bicarbonate, calcium chloride, magnesium chloride</td>
<td>57</td>
<td>(Reddy et al. 2011a)</td>
</tr>
<tr>
<td>Lissamine Green B</td>
<td>300</td>
<td>30 V</td>
<td>Kaolin</td>
<td>Disodium hydrogen phosphate</td>
<td>94</td>
<td>(Pazos et al. 2008)</td>
</tr>
<tr>
<td>Pentachlorophenol</td>
<td>100</td>
<td>1 V/cm</td>
<td>Kaolin</td>
<td>Sodium bicarbonate, calcium chloride, magnesium chloride</td>
<td>75</td>
<td>(Reddy et al. 2011a)</td>
</tr>
<tr>
<td>Pentachlorophenol</td>
<td>100</td>
<td>2 V/cm</td>
<td>Kaolin</td>
<td>Sodium bicarbonate, calcium chloride, magnesium chloride</td>
<td>78</td>
<td>(Reddy et al. 2011b)</td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>1.9</td>
<td>14 V</td>
<td>Kaolin</td>
<td>Sodium chloride</td>
<td>25</td>
<td>(Ko et al. 2000)</td>
</tr>
<tr>
<td>Phenanthrene Fluoranthene</td>
<td>100</td>
<td>1.5 V/cm</td>
<td>Kaolin</td>
<td>Sodium hydroxide</td>
<td>84 90</td>
<td>(Pham et al. 2009)</td>
</tr>
<tr>
<td>Reactive Black 5</td>
<td>390</td>
<td>30 V</td>
<td>Kaolin</td>
<td>Potassium sulphate</td>
<td>94</td>
<td>(Pazos et al. 2007)</td>
</tr>
</tbody>
</table>
**Electrokinetic remediation**

<table>
<thead>
<tr>
<th>Pollutant</th>
<th>Conc. (mg/kg)</th>
<th>Voltage/Intensity</th>
<th>Soil</th>
<th>Electrolyte</th>
<th>Removal (%)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Indigo</td>
<td>1,132</td>
<td>30 V</td>
<td>Sand</td>
<td>-</td>
<td>76</td>
<td>(Sanromán et al. 2005)</td>
</tr>
<tr>
<td>Total Petroleum Hydrocarbons</td>
<td>12,500</td>
<td>2 V/cm</td>
<td>Oil contaminated soil</td>
<td>Potassium phosphate dibasic, potassium phosphate monobasic, magnesium sulfate, ammonium nitrate</td>
<td>28.6</td>
<td>(Dong et al. 2013)</td>
</tr>
</tbody>
</table>

**Electrokinetic-Fenton**

<table>
<thead>
<tr>
<th>Pollutant</th>
<th>Conc. (mg/kg)</th>
<th>Voltage/Intensity</th>
<th>Soil</th>
<th>$\text{H}_2\text{O}_2$ concentration</th>
<th>Removal (%)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diesel</td>
<td>10,000</td>
<td>40 V</td>
<td>Natural soil</td>
<td>8%</td>
<td>97</td>
<td>(Tsai et al. 2010)</td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>200</td>
<td>30 V</td>
<td>Kaolin</td>
<td>7%</td>
<td>80</td>
<td>(Kim et al. 2005b)</td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>200</td>
<td>140 V</td>
<td>Sandy soil</td>
<td>5%</td>
<td>81.6</td>
<td>(Park et al. 2005)</td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>200</td>
<td>30 V</td>
<td>Commercial soil</td>
<td>7% and sodium dodecyl sulfate</td>
<td>70</td>
<td>(Park and Kim 2011)</td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>200</td>
<td>30 V</td>
<td>Hadong clay</td>
<td>7% and sodium dodecyl sulfate</td>
<td>75–80</td>
<td>(Kim et al. 2007)</td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>500</td>
<td>3 V/cm</td>
<td>Kaolin</td>
<td>10%</td>
<td>99</td>
<td>(Alcántara et al. 2008)</td>
</tr>
<tr>
<td>Total Petroleum Hydrocarbons</td>
<td>11,680</td>
<td>3 V/cm</td>
<td>Marine sediments</td>
<td>10% and sodium ethylenediamine tetra acetic</td>
<td>90</td>
<td>(Pazos et al. 2013)</td>
</tr>
<tr>
<td>Trichloroethylene</td>
<td>233</td>
<td>1 V/cm</td>
<td>Loamy sand</td>
<td>4000 mg/L</td>
<td>39.5–88</td>
<td>(Yang and Liu 2001)</td>
</tr>
</tbody>
</table>
### Electro-bioremediation

<table>
<thead>
<tr>
<th>Pollutant</th>
<th>Conc. (mg/kg)</th>
<th>Voltage/Intensity</th>
<th>Soil</th>
<th>Microorganism</th>
<th>Removal (%)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>2,4-Dichlorophenol</td>
<td>800–1,200</td>
<td>0.89 A/m²</td>
<td>Silt soil</td>
<td>Burkholderia spp. RASC c2</td>
<td>87.1</td>
<td>(Jackman et al. 2001)</td>
</tr>
<tr>
<td>Crude oil</td>
<td>50,000</td>
<td>1 V/cm</td>
<td>Natural soil</td>
<td>Bacterial consortium</td>
<td>45</td>
<td>(Li et al. 2010)</td>
</tr>
<tr>
<td>Diesel</td>
<td>20,000</td>
<td>1–2 V/cm</td>
<td>Loamy-sand soil</td>
<td>Indigenous microorganisms</td>
<td>64</td>
<td>(Pazos et al. 2012)</td>
</tr>
<tr>
<td>Mixture of PAHs</td>
<td>-</td>
<td>1 V/cm</td>
<td>Industrial</td>
<td>Isolated bacteria</td>
<td>26</td>
<td>(Li et al. 2012)</td>
</tr>
<tr>
<td>Pentadecane</td>
<td>5,000</td>
<td>0.63 mA/cm²</td>
<td>Kaolin</td>
<td>Pseudomonas sp.</td>
<td>77.6</td>
<td>(Kim et al. 2005a)</td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>200</td>
<td>20 V</td>
<td>Natural soil</td>
<td>Bacillus subtilis</td>
<td>80</td>
<td>(Xu et al. 2010)</td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>4,501</td>
<td>0.5–0.6 V/cm</td>
<td>Historical</td>
<td>Novosphingobium sp. LH128</td>
<td>-</td>
<td>(Niqui-Arroyo et al. 2006)</td>
</tr>
<tr>
<td>Total Petroleum Hydrocarbons</td>
<td>2,777</td>
<td>0.5–0.6 V/cm</td>
<td>Historical</td>
<td>Novosphingobium sp. LH128</td>
<td>-</td>
<td>(Niqui-Arroyo et al. 2006)</td>
</tr>
<tr>
<td>Total Petroleum Hydrocarbons</td>
<td>12,500</td>
<td>2 V/cm</td>
<td>Oil contaminated soil</td>
<td>Bacterial consortium</td>
<td>72.8</td>
<td>(Dong et al. 2013)</td>
</tr>
</tbody>
</table>

### Electrokinetic treatment with surfactants

<table>
<thead>
<tr>
<th>Pollutant</th>
<th>Conc. (mg/kg)</th>
<th>Voltage/Intensity</th>
<th>Soil</th>
<th>Surfactant</th>
<th>Removal (%)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzo[a]pyrene</td>
<td>300–400</td>
<td>3 V/cm</td>
<td>Kaolin</td>
<td>Brij 35</td>
<td>76</td>
<td>(Gómez et al. 2009)</td>
</tr>
<tr>
<td>Gasoil</td>
<td>20,000</td>
<td>30 V</td>
<td>Natural soil</td>
<td>Rhamnolipid</td>
<td>86.7</td>
<td>(Gonzini et al. 2010)</td>
</tr>
</tbody>
</table>

*Table 1. contd....*
### Table 1. Electrokinetic treatment with surfactants

<table>
<thead>
<tr>
<th>Pollutant</th>
<th>Conc. (mg/kg)</th>
<th>Voltage/Intensity</th>
<th>Soil</th>
<th>Surfactant</th>
<th>Removal (%)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mixture of BTEX and PAHs</td>
<td>-</td>
<td>7.5 V</td>
<td>Clay soil</td>
<td>Cetyltrimethylammonium bromide</td>
<td>97</td>
<td>(Sri Ranjan et al. 2006)</td>
</tr>
<tr>
<td>Mixture of PAHs</td>
<td>-</td>
<td>2 V/cm</td>
<td>Industrial contaminated soil</td>
<td>Tween 80</td>
<td>43</td>
<td>48</td>
</tr>
<tr>
<td>Mixture of PAHs</td>
<td>10</td>
<td>1-2 V/cm</td>
<td>Surficial sediments</td>
<td>Poloxamer 407, Nonidet P40</td>
<td>40</td>
<td></td>
</tr>
<tr>
<td>Mixture of PAHs</td>
<td>-</td>
<td>1 V/cm</td>
<td>Industrial contaminated soil</td>
<td>Igepal CA-720</td>
<td>40</td>
<td></td>
</tr>
<tr>
<td>Mixture of sixteen priority PAHs</td>
<td>54</td>
<td>30–60 V</td>
<td>Marine sediment</td>
<td>Tween 80</td>
<td>28</td>
<td></td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>500–800</td>
<td>5 mA</td>
<td>Kaolin</td>
<td>Alkyl polyglycoside, Brij 30, Sodium dodecyl sulfate</td>
<td>57.8–75.1</td>
<td>45.8–38</td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>500–800</td>
<td>10 mA</td>
<td>Kaolin</td>
<td>Alkyl polyglycoside, Calfax 16L-35</td>
<td>63.21–98.03</td>
<td>17.43–24.31</td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>100</td>
<td>12 V</td>
<td>Natural soil</td>
<td>Triton X-100, Rhamnolipid</td>
<td>5</td>
<td>20–30</td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>500</td>
<td>3 V/cm</td>
<td>Sandy soil</td>
<td>Tween 80, Tween 20, Brij 35</td>
<td>90</td>
<td></td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>50</td>
<td>3 V/cm</td>
<td>Kaolin</td>
<td>Triton X-100, Tween 20</td>
<td>95</td>
<td></td>
</tr>
<tr>
<td>Total Petroleum Hydrocarbons</td>
<td>11,680</td>
<td>3 V/cm</td>
<td>Marine sediments</td>
<td>Tween 80 and sodium ethylenediamine tetra acetic</td>
<td>31</td>
<td></td>
</tr>
</tbody>
</table>
## Electrokinetic treatment with cyclodextrins

<table>
<thead>
<tr>
<th>Pollutant</th>
<th>Conc. (mg/kg)</th>
<th>Voltage/Intensity</th>
<th>Soil</th>
<th>Cyclodextrine</th>
<th>Removal (%)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mixture of PAHs</td>
<td>-</td>
<td>2 V/cm</td>
<td>Industrial</td>
<td>Hydroxypropyl-β-cyclodextrin</td>
<td>-</td>
<td>(Reddy et al. 2006)</td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>1.9</td>
<td>14 V</td>
<td>Kaolin</td>
<td>Hydroxypropyl-cyclodextrin</td>
<td>75</td>
<td>(Ko et al. 2000)</td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>500</td>
<td>2 V/cm</td>
<td>Kaolin</td>
<td>Hydroxypropyl-cyclodextrin</td>
<td>50</td>
<td>(Maturi and Reddy 2006)</td>
</tr>
</tbody>
</table>

## Electrokinetic treatment with co-solvent

<table>
<thead>
<tr>
<th>Pollutant</th>
<th>Conc. (mg/kg)</th>
<th>Voltage/Intensity</th>
<th>Soil</th>
<th>Co-solvent</th>
<th>Removal (%)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzo[a]pyrene</td>
<td>300–400</td>
<td>3 V/cm</td>
<td>Kaolin</td>
<td>Ethanol</td>
<td>40</td>
<td>(Gómez et al. 2009)</td>
</tr>
<tr>
<td>Mixture of PAHs</td>
<td>-</td>
<td>2 V/cm</td>
<td>Industrial</td>
<td>n-butylamine</td>
<td>-</td>
<td>(Reddy et al. 2006)</td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>-</td>
<td>-</td>
<td>Glacial till soil</td>
<td>n-butylamine Tetrahydrofuran Acetone</td>
<td>43</td>
<td>(Reddy et al. 2006)</td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>500</td>
<td>2 V/cm</td>
<td>Kaolin</td>
<td>n-butylamine</td>
<td>7</td>
<td>(Maturi and Reddy 2008)</td>
</tr>
</tbody>
</table>
Therefore, Pazos et al. (2008) found that the use of Na$_2$HPO$_4$ as processing fluid increased the electro-osmotic flow, improved Lissamine Green B desorption from the surface of kaolin, and prevented the acidification of the medium. In Fig. 3 (left) the fast movement of the dye through the clay by the electro-osmotic flow can be appreciated. After two days, 94% of the dye was transported to the cathode chamber where it was accumulated. From there, it can be extracted and easily treated using, for example, electrochemical treatment (Pazos et al. 2008).

Besides the dyes, the electrokinetic treatment has been successfully applied to remove other partially water soluble organic compounds such as pentachlorophenol, hexachlorobenzene, lindane, polycyclic aromatic hydrocarbons (PAH), total petroleum hydrocarbons (TPH), among others (Table 1). In these treatments, the uncharged pollutant is transported by the electro-osmotic flow generated under appropriated conditions. In general, these conditions depend on the soil matrix; therefore an alkaline environment is required in most of the treatments in order to increase the electro-osmotic flow. Therefore, the efficiency of this process is severely limited when the compounds have low solubility. Under these conditions, the electrokinetically enhanced *in situ* flushing technique has the potential to improve soil-solution-contaminant interaction and contaminant removal (Gómez et al. 2009).
Electrokinetic Treatment with Solubilizing Agents

In the case of organic pollutants with low water solubility, enhancement agents have been used in the electrokinetic remediation process to keep the contaminants in a mobile phase for an appropriated electrokinetic transport. These agents are commonly used to substantially increase organic pollutant desorption and solubilization through micellization and surface tension reduction. During the remediation process, these agents can be added directly into the soil or to the electrode chamber solutions where they are introduced into the soil by electro-osmosis and/or electromigration (Fig. 4). The most common solubilizing agents, utilized in the electrokinetic technique are co-solvents, surfactants, and cyclodextrins.

Fig. 4. Schematic representation of the PAHs solubilization and migration, by use of surfactants and electric field action, respectively.

Co-solvents

Co-solvents are water-miscible organic compounds as a result of their polar structure. They can promote the removal of organic contaminants in two ways. The first is to increase the apparent solubility of the contaminants in water, which enhances the removal of the mass per unit pore volume. The second way is by reducing the interfacial tension between water and contaminant, which may result in the direct movement of the organic pollutant. Different investigations have shown the high influence of the organic solvent on the adsorption and mobility of organic pollutants (Table 1). Li et al. (2000) performed electrokinetic experiments using different solvents (acetone, tetrahydrofuran, and n-butylamine) to extract phenanthrene from glacial till. They found that after 127 days of treatment the most effective solvent was n-butylamine at a concentration of 20% by removing 43% of the initial phenanthrene. Alcántara et al. (2008) demonstrated that when a solution of 40% ethanol was introduced in the soil by electric field action, the desorption of phenanthrene from kaolin clay was improved and around 95% of initial phenanthrene was removed from the soil and recovered into the cathode chamber.
**Surfactants**

Surface active agents (surfactants) are chemical compounds that consist of a strongly hydrophilic group, typically the head of the molecule, and a strongly hydrophobic group which is the tail. The hydrophilic group causes surfactants to exhibit high solubility in water, while the hydrophobic group prefers a hydrophobic phase, such as several organic pollutants. This fact enables surfactants to enhance the solubility of the contaminant through micellar solubilization. In this process, aggregations of surfactant monomers form a micelle; its interior becomes a hydrophobic region suitable for organic pollutants, which improves their solubilization (Alcántara et al. 2008; Gómez et al. 2009; Pazos et al. 2013). Table 1 summarizes a selection of different researches where surfactants were used in order to enhance the decontamination process by the electric field action. Among the different surfactants (anionics, cationics or non-ionics) non-ionics are often chosen in the remediation process for their high solubilization capacity and biodegradability (Choy and Chu 2001). Several investigations proved that non-ionic surfactants (e.g., Igepal CA-720, Tween 80, Tween 20, Triton X-100, Brij 30, Brij 35, Tyloxapol) efficiently improve the removal of PAHs or TPHs by electrokinetic processes (Table 1).

Gómez et al. (2009) reported that when a solution of surfactant Brij 35 1% was used as processing fluid in the electrokinetic remediation of benzo(a)pyrene, this PAH was successfully transported through kaolin clay towards the cathode chamber. They found that the extent of this recovery depended on the pH profile on the soil. When no pH control was used, around 17% of initial contaminant was detected in the cathode chamber; though, when pH control in the anode chamber was set at 7.0, the recovery of benzo(a)pyrene could be higher than 76%. Similarly, Pazos et al. (2011) used a mixture of Tween 80 and EDTA as processing fluid in the electrokinetic treatment of a soil polluted with diesel fuel. They found that a mixture of both chemical substances increased the removal efficiency reaching around 55% of TPH removal.

**Cyclodextrins**

Cyclodextrins are cyclic oligosaccharides of glucopyranose units with a lipophilic cavity in the center. These natural compounds are produced by the action of a group of enzymes known as cyclodextrin glycosyltransferases in starch. Cyclodextrins are capable of forming inclusion complexes with contaminants by taking up a whole contaminant molecule, or some part of it, into the cavity (Gómez et al. 2010). Cyclodextrins appear to be promising agents for improving the solubility of organic compounds because they minimize the environmental impact as a result of their non-toxic nature and biodegradability. The use of these compounds is limited due to their cost and availability; however different researchers have proven their applicability (Table 1). Wang et al. (2013) demonstrated that the electrokinetic remediation combined with
glycine-β-cyclodextrin as processing fluid and pH control may be a good remediation alternative for the treatment of soil polluted with simazine and cadmium. Experimental results reported by Li et al. (2010) showed that migration and removal of hexachlorobenzene in soil was significantly affected by hydroxypropyl-β-cyclodextrin concentrations and cumulative electro-osmotic flow. They found that the electrokinetic remediation combined with hydroxypropyl-β-cyclodextrin flushing and pH buffering was a good alternative for hexachlorobenzene removal from sediments.

**Hybrid Technologies**

Different approaches have been developed by coupling electrokinetic technology with other treatments in order to increase the removal efficiency. Most of these technologies use the electric field action to put reagents into the soil to induce the *in situ* degradation of the organic pollutants. In this sense, new technologies called electrokinetic-Fenton and electro-bioremediation arise.

**Electrokinetic-Fenton (EK-Fenton)**

The use of Fenton’s reagent with electrokinetic treatment has been described as an ecological approach for the *in situ* degradation of organic compounds in soils (Kim et al. 2005b). The electrokinetic treatment can facilitate the inclusion of the oxidant (H$_2$O$_2$) and activates oxidizing radicals, while, at the same time, it may directly cause oxidation or reductive reactions on the soil (Isosaari et al. 2007).

This combined method of oxidation of organic compounds takes place in the soil by means of H$_2$O$_2$ when iron is naturally present in the soil as catalyst. Hydroxyl radicals generated in the Fenton’s reaction are strong oxidants; they oxidize the organic molecule by abstracting hydrogen atoms or by the addition of double bonds and aromatic rings (Iglesias et al. 2013). However, the Fenton reaction is effective only at low pH (about 3), which requires an adjustment of pH during treatment.

The results obtained by several works using this hybrid technology are very encouraging (Table 1). Pazos et al. (2012) demonstrated that using the EK-Fenton process an adequate environment for the Fenton’s reaction can be developed inside the soil because the H$_2$O$_2$ is homogeneously distributed due to the action of the electric field. Their experiences, in the treatment of soil polluted with diesel fuel, reached a removal close to 90%. Furthermore, other chemical substances, as complexing agents, can be introduced in order to increase the removal. Thus, Pazos et al. (2013) treated dredged marine sediments contaminated by petroleum hydrocarbons and metals, by the EK-Fenton treatment. Their research demonstrated that a combination of a Fenton’s reagent and sodium ethylenediamine tetra acetate promoted the *in situ* degradation of petroleum hydrocarbons and solubilized the metals. The
developed EK-Fenton-sodium ethylenediamine tetra acetic process obtained a removal of about 90% for TPH, 57.3% of Zn, 59.8% of Pb, 59.4% of Cu, and 54.5% of Hg.

**Electro-bioremediation**

Electro-bioremediation is a promising hybrid technology for the remediation of organic contaminants. Recently, it has been successfully applied in soil with organic contaminants (Table 1). Electrokinetics can be coupled with bioremediation to enhance the removal of organic contaminants, mainly through the potential to mobilize pollutants and bacteria, as well as the ability to stimulate bacterial activity (Table 1). Therefore the electrokinetic treatment can enhance biodegradation by adding nutrients or spreading indigenous bacteria to polluted soil. Jackman et al. (2001) evaluated the electrokinetic movement and biodegradation of 2,4-dichlorophenoxyacetic acid in silt soil. They inoculated the bacterium *Burkholderia* spp. RASC c2 near of the cathode chamber and used the electric field to promote the movement of the pollutant towards the bacteria. At the end of the experiment, 87.1% of radiolabel had been removed from the soil, 5.8% of which was recovered as $^{14}$CO$_2$. Another way is to transport various additives efficiently to underground polluted area in order to enhance pollutant bioremediation. Accordingly, Pazos et al. (2012) determined that the addition of nutrients via electro-osmotic flow promotes the biostimulation of indigenous bacteria increasing the diesel fuel removal in a loamy soil.
Conclusions

In this chapter the recent approaches to apply the electrokinetic remediation of soil contaminated with organic pollutants are shown. The main drawback for applying this technology is primarily the low solubility of most organic pollutants. However as it was described in this chapter a wide range of technique improvements can be applied in order to increase the removal efficiency. The application of this technique alone or combined with other treatment processes as, for example, Fenton or bioremediation gives satisfactory results in the removal of organic pollutants.

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