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Chapter 9

Advances in Electrokinetic Remediation for the Removal of Organic Contaminants in Soils

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1. Introduction

Soil contamination is associated to industrial activities, mining exploitations and waste dumping. It is considered a serious problem since it affects not only the environment, living organisms and human health, but also the economic activities associated with the use of soil [1]. The risks associated with soil contamination and soil remediation are important points in the agenda of politicians, technicians and scientific community. The present legislation establishes a legal frame to protect the soil from potentially contaminant activities; however, the present situation of soil contamination is the result of bad practices in the past, especially related to bad waste management [2-3].

Soil contamination affects living organisms in the subsurface but also affects the plants that accumulate contaminants as they grow. Thus, contaminants enter the food chain with a potential impact in public health [4]. On the other hand, contaminants can be washed out the soil by rain and groundwater, resulting in the dissemination of the contamination. This process is not desirable because the area affected by the contaminants is bigger and bigger and the possible remediation is more difficult and costly as the affected area grows [5]. Therefore, soil contamination is a serious problem that requires a rapid solution in order to prevent more environmental damages. Prevention is the best “technology” to save our soils from the contamination. A strict management of the wastes and good environmental practices associated to industrial activities, mining, transportation and dumping management are required to prevent the contamination of the environment. However, many sites have been identified as contaminated sites. The European Union, USA, Canada, Japan and South Korea made a lot of efforts in recent years to identify the contaminated sites in each country. The new legislation, especially in the European Union, forces the administration to identify the
contaminated sites and evaluate the risks associated to the environment and public health. Then, the remediation of those sites must be carried out, starting with the riskier sites for humans and living organisms [6]. This is the aim of the present legislation in Spain about the management of wastes and soil contamination [7, 8] which is the transposition of the European Directive 2008/98/CE [9].

Soil remediation implies the application of a technology able to remove or eliminate the contaminants following by the restoration of the site to the original state. So far, it sounds easy to do. However, there is not a technology able to remove any kind of contaminants in any kind of soil. Moreover, the restoration of the site to the original state is not always possible due to the characteristics of the soil and/or the remediation technology. Thus, the common objective in soil remediation is to remove the contaminants to a safe level for humans and the environment, and restore the properties of the soil to a state appropriate for the common soil uses [10-12]. So, the final target concentration to consider the soil non-contaminated will be different depending on the future use of the soil: urban, agriculture or industrial.

During the last 20 years, scientists and technicians spent a lot of efforts in the developing of innovative technologies for soil remediation [13]. Those technologies use the physical, chemical and biological principles to remove and/or eliminate the contaminants from soil. Thus, for instance, bioremediation uses the capacity of soil microorganisms to degrade organic contaminants into the soil [14]. Thermal desorption was designed to remove volatile and semi-volatile organics. Gasoline, BETX, chlorinated organics can be removed by thermal desorption, but also PAHs or PCBs [15]. Soil washing uses a solution in water to dissolve the contaminants from soil. Once the soil is clean, it can be stored in the same place and the contaminants will undergo a stabilization process [16]. Soil remediation technologies can be applied in situ, i.e. in the contaminated site without excavation, or ex-situ: the soil is excavated and it is treated in a facility specifically designed for the remediation process. In situ technologies are preferred because they result in lower costs, less exposition to the contaminants and less disruption of the environment. However, the control of the operation is more difficult and depending on the permeability of the soil and soil stratification, the operation may result in very poor results. On the other hand, ex-situ technologies permit a better control of the operation, and the remediation results are not very affected by some soil characteristics as permeability and stratification [17-19].

2. Electrokinetic remediation: Basis and applications

Electrokinetic remediation is an environmental technique especially developed for the removal of contaminants in soil, sediments and sludge, although it can be applied to any solid porous material [20]. Electrokinetic remediation is based in the application of a direct electric current of low intensity to the porous matrix to be decontaminated [21]. The effect of the electric field induces the mobilization and transportation of contaminants through the porous matrix towards the electrodes, where they are collected, pumped out and treated. Main electrodes, anode and cathode, are inserted into the soil matrix, normally inside a chamber.
which is filled with water or the appropriate solution to enhance the removal of contaminants (Figure 1). Typically, a voltage drop of 1 VDC/cm is applied to the main electrodes.

Contaminants are transported out of the soil due to several transportation mechanisms induced by the electric field [22, 23]:

- **Electromigration** is defined as the transportation of ions in solution in the interstitial fluid in the soil matrix towards the electrode of the opposite charge (Figure 2). Cations move toward the cathode (negative electrode), and anions move toward the anode (positive electrode). The ionic migration or electromigration depends on the size and charge of the ion and the strength of the electric field.

- **Electro-osmosis** is the net flux of water or interstitial fluid induced by the electric field (Figure 2). Electro-osmosis is a complex transport mechanism that depends on the electric characteristics of the solid surface, the properties of the interstitial fluid and the interaction between the solid surface and the components in solution. The electro-osmotic flow transports out of the porous matrix any chemical species in solution. Soils and sediments are usually electronegative (solid particles are negatively charged), so the electro-osmotic flow moves toward the cathode. In the case of electropositive solid matrixes, the electro-osmotic flow moves toward the anode. Detailed information about electro-osmosis can be found in literature [24].
Electrophoresis is the transport of charged particles of colloidal size and bound contaminants due to the application of a low direct current or voltage gradient relative to the stationary pore fluid. Compared to ionic migration and electro-osmosis, mass transport by electrophoresis is negligible in low permeability soil systems. However, mass transport by electrophoresis may become significant in soil suspension systems and it is the mechanism for the transportation of colloids (including bacteria) and micelles.

Diffusion refers to the mass transport due to a concentration gradient, not to a voltage gradient as the previous transport mechanisms. During the electrokinetic treatment of contaminated soils, diffusion will appear as a result of the concentration gradients generated by the electromigration and electro-osmosis of contaminants. Diffusive transport is often neglected considering its lower velocity compared to electromigration and electro-osmosis.

The two main transport mechanisms in electrokinetic remediation are electromigration and electro-osmosis [25]. The extent of electromigration of a given ion depends on the conductivity of the soil, soil porosity, pH gradient, applied electric potential, initial concentration of the specific ion and the presence of competitive ions. Electromigration is the major transport processes for ionic metals, polar organic molecules, ionic micelles and colloidal electrolytes. The electro-osmotic flow depends on the dielectric constant and viscosity of pore fluid as well as the surface charge of the solid matrix represented by zeta potential. The zeta potential is a function of many parameters including the types of clay minerals and ionic species that are present as well as the pH, ionic strength, and temperature. Electro-osmosis is considered the dominant transport process for both organic and inorganic contaminants that are in dissolved, suspended, emulsified or such similar forms. Besides, electro-osmotic flow though low permeability regions is significantly greater than the flow achieved by an ordinary hydraulic gradient, so the electro-osmotic flow is much more efficient in low permeability soils [26].

The application of an electric field to a moisten porous matrix also induces chemical reactions into the soil and upon the electrodes that decisively influences the chemical transportation and speciation of the contaminants and other constituents of the soil. Chemical reactions include acid-alkaline reactions, redox reaction, adsorption-desorption and dissolution-precipitation reactions. Such reactions dramatically affect the speciation of the contami-
nants and therefore affect the transportation and contaminant removal efficiency [27]. The main reaction in the electrochemical/electrokinetic systems is the decomposition of water that occurs at the electrodes. The electrolytic decomposition of water reactions generates oxygen gas and hydrogen ions (H\(^+\)) due to oxidation at the anode and hydrogen gas and hydroxyl (OH\(^-\)) ions due to reduction at the cathode as shown in equations 1 and 2.

At Anode (Oxidation):

\[
2 \text{H}_2\text{O} \rightarrow 4 \text{e}^- + 4\text{H}^+ + \text{O}_2(\text{gas}) \quad E^\circ = -1.229 \text{ V}
\]

At Cathode (Reduction):

\[
4 \text{H}_2\text{O} + 4 \text{e}^- \rightarrow 2 \text{H}_2(\text{gas}) + 4\text{OH}^- (\text{aq}) \quad E^\circ = -0.828 \text{ V}
\]

Essentially, acid is produced at the anode and alkaline solution is produced at the cathode, therefore, pH in the cathode is increased, while pH at the anode is decreased. The migration of H\(^+\) ions from the anode and OH\(^-\) from the cathode into the soil leads to dynamic changes in soil pH. H\(^+\) is about twice as mobile as OH\(^-\), so the protons dominate the system and an acid front moves across the soil until it meets the hydroxyl front in a zone near the cathode where the ions may recombine to generate water. Thus, the soil is divided in tow zones with a sharp pH jump in between: a high pH zone close to the cathode, and a low pH zone on the anode side. The actual soil pH values will depend on the extent of transport of H\(^+\) and OH\(^-\) ions and the geochemical characteristics of the soil. The implications of these electrolysis reactions are enormous in the electrokinetic treatment since they impact the absorption/desorption of the contaminants, the dissolution/precipitation reactions, chemical speciation and the degradation of the contaminants. Moreover, pH changes into the soil affects the contaminant migration, and the evolution of the electro-osmotic flow which is decisive in the removal of non-charged organic contaminants [20]. In electrokinetic remediation, it is also common the use of chemical to enhance the dissolution and the transportation of the contaminants. The enhancing chemical are going to interact with the soil and the contaminants, therefore it is necessary to evaluate the geochemistry of the soil and the possible reactions with the enhancing chemicals, considering at the same time the effect of the pH, in order to design a satisfactory technique that removes or eliminates the contaminants keeping the natural properties of the soil for its use after the remediation process.

### 3. Removal of organic contaminants by electrokinetics: Limitations and enhancements

Electrokinetic remediation was first proposed and tested for the removal of heavy metals and other charged inorganic contaminants in soils, sediments and sludges. However, the electroki-
netic remediation is also useful for the removal or elimination of organic contaminants [28]. Considering the different physico-chemical properties of the organic contaminants compared to the properties of heavy metals, the operating conditions of the electrokinetic treatment and the enhancing chemicals will be rather different than those used for heavy metal polluted soils. The main transportation mechanisms in electrokinetic remediation are: electromigration and electro-osmosis. In general, the more dangerous and persistent organic contaminants are not soluble in water (which is the interstitial fluid in natural soils) and are neither ionic nor ionizable molecules. Therefore, electromigration cannot be considered as the transport mechanisms for organic contaminants. Electro-osmosis is the net flux of water in the soil matrix that flows through the soil from one electrode to the other due to the effect of the electric field. Electro-osmotic flow moves towards the cathode in electronegatively charged soils, which is the most common case. Again, organic contaminants are not soluble in water and therefore their elimination from soils cannot be achieved in an unenhanced electrokinetic treatment. In order to achieve an effective removal or elimination of organic contaminants from soils, their solubility in has to be enhanced with the use of co-solvents, surfactants or any other chemical agent. Alternatively, the removal or elimination of organic contaminants can be achieved by the combination of electrokinetics and other remediation techniques such as chemical oxidation/reduction, electrolytic reactive barriers, or thermal treatment. For the removal of organic contaminants, both solubilization of the contaminants and adequate electro-osmotic flow are required, which appear to be quite challenging to accomplish simultaneously. The electro-osmotic flow is found to be dependent on the magnitude and mode of electric potential application. The electro-osmotic flow is higher initially under higher electric potential, but it reduces rapidly in a short period of time. Interestingly, the use of effective solubilizing agent (surfactant) and periodic voltage application was found to achieve the dual objectives of generating high and sustained electro-osmotic flow and at the same time induce adequate mass transfer into aqueous phase and subsequent removal. Periodic voltage application consists of a cycle of continuous voltage application followed by a period of “down time” where the voltage was not applied was found to allow time for the mass transfer, or the diffusion of the contaminant from the soil matrix, to occur and also polarize the soil particles. Several laboratory studies have demonstrated such desirable electro-osmotic flow behavior in a consistent manner, but field demonstration projects are needed to validate these results under scale-up field conditions [29, 30].

Figure 3. Chemical structure of reactive black 5
3.1. Electrokinetic removal of soluble organics

Although most dangerous organic contaminants in soils, sediments and sludges are persistent hydrophobic organics, several works in literature focused on the treatment of soils with soluble organics. Thus, reactive black 5 is a common dye used in the industry. Reactive black 5 is a complex organic molecule difficult to biodegrade in the environment and shows a significant toxicity for living organisms in soils and water. Reactive black 5 is soluble in water, but it can be retained in soils and sediments adsorbed upon the surface of mineral particles and organic matter. Considering the chemical structure of the reactive black 5 (figure 3), the molecule can be ionized at alkaline pH when the sulfonic groups are neutralized forming an anion with 4 negative charges. In this conditions, reactive black 5 can be transported by electrokinetics toward the anode, but only if the molecule is in solution. The desorption of the molecule can be achieved using potassium sulfate as flushing solution in the anode and cathode chambers. Figure 4 shows the advance of the Reactive Black 5 toward the anode by electromigration. The advance of the day is evident in the 4th day of treatment, and it is completely removed from the soil in 5 days. The removal of Reactive black 5 is only possible when the molecule is desorbed from the soil particles but the electromigration was only possible when the pH into the soil was alkaline [31]. The pH was controlled in the anode (the left hand side in figure 4) at a value below 7 and the alkaline front electrogenerated at the cathode (the right hand side in figure 4) advanced through the soil favoring the dissolution and electromigration of reactive black 5. Negligible Reactive Black 5 was observed if the pH into the soil was not alkaline.

3.2. Co-solvents

Most of organic contaminants of environmental concern are practically insoluble in water but they can be dissolved in other organic solvents. Thus, the use of other processing fluid than water may help in the desorption and dissolution of the organic contaminants in soils, sediments and sludges. Electrokinetic remediation is an in situ technique, and water is always present in soils. So, the organic solvent will not be used alone but in combination with water as a co-solvent. Thus, the possible organic solvents to be used are now reduced to those miscible with water. But this is not the unique condition a co-solvent has to meet. Organic co-solvents have to be safe for the environment or with a minor environmental impact, and it has to be easy to recover from soil after the treatment. Apart from the environmental limitations in the selection of the co-solvents, there are also some technical aspects to take into account. The use of co-solvents mixed with water decreases the conductivity of the processing fluid due to the decrease of salts solubility in the organic co-solvent. It decreases the current intensity through the soil. The presence of an organic co-solvent will also affects the viscosity of the processing fluid and change the interaction between the processing fluid and the soil particles. Those alterations will impact directly the evolution of the electro-osmotic flow which is the main transportation mechanism for the removal of organic contaminants. Any rate, the increase in the contaminant solubility due to the use of the co-solvent may largely compensate the decrease in the electroosmotic flow, being the result positive for the removal of the organic contaminants. Some of the co-solvents used in literature are: ethanol, n-butanol, n-butyamine, tetrahydrofuran, or ace-
Phenanthrene was the target contaminant in the studies with co-solvents. The removal of phenanthrene was negligible when water was used as flushing solution but the removed fraction of phenanthrene clearly increased with the use of co-solvents, especially n-butylamine which resulted in a removal of 43% in 127 days in a lab test with a soil specimen of 20 cm long. The removal can be enhanced controlling other variables such as the pH into the soil and improving the electro-osmotic flow operating at higher voltage gradient or with periodic voltage application [34].

Figure 4. Removal of Reactive Black 5 from a kaolin specimen by electrokinetic remediation

3.3. Surfactants

The name surfactant is the short version of “surface-active agent”. It means that the so-called surfactants are a group of substances that has in common a special capacity to change the sur-
face properties of the solution when they are present. In environmental applications, the interest of surfactants is their ability to lower the surface and interfacial tension of water improving the solubility of hydrophobic organics. There is a wide variety of chemical structures and families that fits in the definition of surfactant. Basically a surfactant is a chemical compound whose molecule includes a hydrophilic group in one side of the molecule and in the opposite side a hydrophobic group or chain. The interaction of the hydrophilic group with water assures its solubility whereas the interaction of the hydrophobic group with the organic contaminants assures the solubilization of hydrophobic organics. The hydrophobic group or chain in the surfactant molecule is repelled by water, so the surfactant molecules tend to form spherical structures with the hydrophilic group outside and the hydrophobic chains inside. These spherical structures are called micelles. Thus, the surfactant creates a hydrophobic environment very appropriate for the solubilization of organic compounds. The formation of micelles depends on the surfactant concentration and the micelle formation reach a maximum for a surfactant concentration called CMC “critical micelle concentration” [26].

There is a wide variety of chemical structures in the surfactants, but usually they are classified by the electric charge in the molecule in 4 groups: cationic, anionic, neutral and zwitter-ionic (includes positive and negative charges in the same molecule). In environmental applications, neutral or anionic surfactants are preferred because cationic surfactants tend to interact with the soil particles, retarding their advance and reducing their effectiveness [26]. The toxicity of surfactants to the soil microorganisms it is also very important for the remediation and restoration of soils. That is why in recent years the research was redirected to the use of natural surfactants or biosurfactants [35].

A wide variety of surfactants have been used in electrokinetic remediation for the removal of organic contaminants: Sodium dodecyl sulfate (SDS), Brij 35, Tween 80, Igepal CA-720, Tergitol and other. Target contaminant in these studies includes hydrophobic and persistent organics such as: phenanthrene, DDT, diesel, dinitrotoluene, hexachlorobenzene and others. In general, it can be conclude that the reported results in literature are quite good reaching removal efficiencies over 80% in many studies, at least in bench scale laboratory test with both model and real contaminated soils [36, 37]. Reddy et al. demonstrated the removal of phenanthrene by electrokinetics using surfactants as an enhanced flushing solution in the electrode chambers. Different types of soils, commonly kaolin and glacial till, were used in this study. In general, there is no elimination of phenanthrene when water was used as flushing solution despite the large electro-osmotic flow registered in these experiments. The use of surfactants such as Igepal CA-720, Tween 80 or Witconol tend to decrease the electro-osmotic flow due to the changes in the interaction of the flushing solution with the soil particle surface, the decreasing in the electric conductivity of the system, and the increase of the viscosity of the flushing solution. Despite the decreasing of the electro-osmotic flow, the increase of phenanthrene solubility in the surfactant flushing solution resulted in a very important transportation and removal of phenanthrene in the fluid collected on the cathode side. The specific removal results did not only depend on the type and concentration of surfactant but also in the pH evolution into the soil, the type of soil and the ionic strength in the processing fluid. Those variables affect the solubilization of the organic contaminants by the
surfactant, but the main influence is in the development and evolution of the electro-osmotic flow. Thus, the limitation of very acidic environments into the soil avoids a sharp reduction of the electro-osmotic flow. This can be achieved controlling the pH on the anode or using a buffering solution with the flushing surfactant solution. The buffering capacity of the soil also contributes to avoid the acidification of the interstitial fluid [26, 33, 38, 39]. However, the only use of surfactants seems to be not enough to get a complete removal of phenanthrene from polluted soils, and it is necessary to enhance the electro-osmotic flow using high voltage gradients (2 V/cm or higher) and even the use of periodic voltage applications operating with a constant voltage drop intermittently. The periodic voltage application resulted in about 90% of the phenanthrene removed on the cathode solution [40].

3.4. Cyclodextrins

Glucose may form cyclic structures with 6, 7 or 8 molecules called cyclodextrins. The resulting molecule has the structure of a truncated cone. The internal cavity has different size depending on the number of glucose units. The inner diameter of the molecule ranged from 0.45-0.53 nm for α-cyclodextrin (ring of 6 glucose molecules); 0.60-0.65 nm for β-cyclodextrin (ring of 7 glucose molecules); and 0.75-0.85 nm for γ-cyclodextrin (ring of 8 glucose molecules). Cyclodextrin shows an amphiphilic behavior due to the rings of –OH groups present at the both ends of the molecule. The hydroxyl groups are polar and confer to the cyclodextrin the solubility in water. However, the inner surface of the molecule is hydrophobic and cyclodextrins can accommodate different non-polar, hydrophobic molecules such as aliphatic, aromatic or lipophilic compounds. Moreover, the different size of the inner cavity of the cyclodextrin molecules can be used as a select the molecules to be trapped inside, and therefore, transported and removed.

Cyclodextrins have been used to enhance the removal of hydrophobic organics such as phenanthrene [41], dinitrotoluene [42], the herbicide atrazine [43], and other contaminants [44] in real and model soils. In general, cyclodextrins are facilitating agents that improve the removal of organic contaminants from soil compared to other experiments with unenhanced electrokinetics, but results from cyclodextrin tests are usually less effective than test with surfactants, iron nanoparticles or with chemical oxidants. The efficiency of the removal can be enhanced combining more than one facilitating agent. Thus, Pham et al. [45] and Oonnit-tan et al. [46] used the electrokinetic treatment with a cyclodextring flushing solution, combined with ultrasounds or chemical oxidation with hydrogen peroxide. Anyway, the use of cyclodextrins may enhance the removal of the hydrophobic contaminants but the results are usually lower than that found with surfactants.

4. Combined technologies

4.1. Electrokinetics and chemical oxidation/reduction

Electrokinetic remediation is a technique that removes the contaminants from the contaminated soil by transportation (electro-osmosis and electromigration). However, organic con-
Contaminants are difficult to remove from soils, mainly due to the low solubility in water, and their strong adsorption to organic matter and soil particles. There are some other ways to look at the problem of organic contaminants in soil. One possibility is to degrade the contaminants in situ. To achieve such degradation, it is necessary to create the adequate conditions into the soil supplying strong oxidizing chemicals to the soil pores to perform the degradation in situ. Oxidants such as ozone, hydrogen peroxide or persulfate can be transported into the soil by electromigration and/or electro-osmosis. As the oxidants advance through the soil, they react with the organic contaminants resulting in smaller molecules usually less toxic that the original ones. The objective is to be able to completely oxidize the organic contaminants to carbon dioxide and water. If such complete degradation is not possible under the operating conditions into the soil, the formation of simpler molecules are considered enough, because small and simpler molecules can be degraded easily by the microorganisms into the soil. Thus, this technology can be a very attractive solution for the degradation of complex organic contaminants into soil. This technology does not generate waste effluents with harmful compounds because they are destroyed into the soil. Moreover, the contact of the workers with the contaminants and contaminated soil particles are reduced to a minimum, which is a very important point in the field operation.

On the other hand, the chemical destruction of organic contaminants can be carried out by chemical reduction, when a reductive chemical process results in less toxic compounds. Thus, organochlorine pesticides can be degraded by reductive dechlorination. The result is the organic molecule without chlorine atoms in its structure. Thus, the resulted organic compounds are much less toxic than the original compound and they can be easily degraded by the microorganisms into the soil.

There are several applications of chemical oxidation combined with electrokinetics in literature. Yukselen-Aksoy and Reddy [47] have tested the degradation of PCB in contaminated soils by persulfate. Sodium persulfate is a strong oxidizing agent with a standard reduction potential of 2.7 V which assures the effective oxidation of most of the organic contaminants. Persulfate is firstly transported into the soil by electromigration and/or electro-osmosis, and then it is activated by pH or temperature. To active the persulfate, it is necessary to achieve over 45ºC or acidify the soil below 4. Both conditions can be reached with the electric field. High voltage gradient results in the heating of soil; and the acid front electrogenerated at the anode can acidify the soil. So, in this case the application of the electric field not only was used as a transportation mechanism but as a tool to control the key variables of the process. In this work [47], the highest degradation of PCBs was achieved in a kaolin specimen with a 77.9% of removal when temperature was used as activator of the persulfate.

The combination of electrokinetics and chemical oxidation was tested in a contaminated soil with hexachlorobenzene [46, 48]. Hydrogen peroxide was supplied to the soil from the anode in a Fenton-like process where the iron content in the soil was sufficient to activate the decomposition of H₂O₂ for the generation of hydroxyl radicals (OH). 60% of HCB was eliminated from the soil in 10 days of treatment avoiding the deactivation of the Fenton reagent at high pH values. Higher removal can be achieved at longer treatment time, control-
ling the pH in the optimum range for Fenton reagent which is slightly acid environments. At alkaline pH, H$_2$O$_2$ decomposes in water and oxygen and do not form OH radicals.

The use of Fe$^0$ for the remediation of soils has been used recently for the ability of the native iron to catalyze the reductive dechlorination of organic compounds such as pentachlorophenol, trichloroethylene, hexachlorobenzene and others. In this technology, the electric field can be used as a driving force to transport the nanoparticles into the soil. Reddy and Karri [49] found that the combination of electrokinetic remediation and Fe0 nanoparticles can be applied for the removal of pentachlorophenol from soil. The transportation of Fe$^0$ nanoparticles was determined by the iron concentration into the soil at the end of the experiments. Iron concentration at the end of the experiments increased with the initial Fe$^0$ concentration used in the anode and with the voltage gradient. However, the transport of nanoparticles was limited by their aggregation, settlement and partial oxidation within the anode. Pentachlorophenol was partially reduced (40-50%) into the soil, but a complete PCP elimination was found near the cathode due to the combination of Fe$^0$ and the reductive dechlorination within the cathode. In order to favor the transportation of nanoparticles into the soil, new strategies are needed to prevent aggregation, settlement and oxidation of iron nanoparticles for enhanced remediation of soils. Cameselle et al. [50] studied the surface characteristics of the iron nanoparticles and proposed several dispersant to favor the transportation and avoid aggregation and settlement. Among the dispersants proposed aluminum lactate presents good characteristics to be used in large scale application. Other metallic catalysts such as Cu/Fe or Pd/Fe bimetal microscale particles were satisfactorily used for the remediation of soils with organochlorines. Dechlorination of hexachlorobenzene up to 98% was achieved with Cu/Fe [51] and only 60% with Pd/Fe [52].

4.2. Electrokinetics and permeable reactive barriers

Permeable reactive barriers (PRB) are passive remediation systems especially designed for the remediation of contaminated ground water. PRBs consist of digging a trench in the path of flowing groundwater and then filling it with a selected permeable reactive material. As the contaminated groundwater passes through the PRB, contaminants react with the active material in the PRB being absorbed, precipitated or degraded. Clean groundwater exits the PRB. In the design of a PRB several factors have to be taking into account. First, the nature and the chemical properties of the contaminants have to be considered for the selection of the reactive material. For organic contaminants, materials such as active carbon or Fe$^0$ were used. Organic contaminants can be retained in in the porous structure of the active carbon. Native iron has been used for the reductive dechlorination of pesticides and other organochlorines. The flow rate of groundwater and the reaction rate of the contaminants with the active material in the PRB are used to define the width of the barrier. The resident time of the groundwater in the barrier has to be enough to reach a complete removal or degradation of the contaminants. Finally, the porous structure of the barrier has to confer the barrier itself a permeability value higher than the surrounding soil, to assure that all the groundwater pass through the barrier and there will not be bypass. The main advantages of the PRB are the stable operation for long treatment time, even several years, with very low invest-
ment and maintenance costs. Anyway, the limited results found in several application impulse the research in several directions in order to improve the removal of the contaminants [53]. One possibility is the combination of the PRB with electrokinetic remediation.

The combination of electrokinetic remediation with PRB has been satisfactory used to remediate soils polluted with heavy metals such as chromium. The electric field transports the chromium towards the main electrodes, but in their way, the chromium ions pass through a PRB made of elemental iron. The chemical reduction of chromium takes places reacting with the elemental iron. The electric field also plays a role in the reduction of the chromium [54]. In the case of organic contaminants, Chang and Cheng [55] applied the combination of PRB with electrokinetics to remediate a soil specimen contaminated with perchloroethilene. The experiments were carried out at a constant voltage drop of 1 v/cm and sodium carbonate 0.01 M was used as processing fluid to avoid the formation of an acid front in the anode. It eliminates the acidification of the soil and the possible negative effects on the electro-osmotic flow. The PRB were made of nanoparticles of elemental iron and zinc. The perchloroethy‐lene is dechlorinated upon the nanoparticles of iron and zinc. However, the formation of ferric oxide and ferric hydroxides limits the activity of the PRB and its operational life. The protons electrogenerated at the cathode can contribute in the solubilization and removal of the ferric hydroxides increasing the activity and duration of the PRB. Moreover, the proton also favors the dechlorination reaction. In conclusion, the formation of H+ ions in the anode favors the elimination of perchloroethylene. As the voltage drop applied to the system increases, the formation of H+ upon the anode also increases resulting in more and faster perchloroethylene removal. Thus, the operation at 2 V/cm resulted in the removal of almost 99% of the initial perchloroethylene in only 10 days of operation.

Chung and Lee [56] applied a combination of electrokinetics with PB for the remediation of the tetrachloroethylene contaminated soils and groundwater. The interest of this work is the media used in the PRB. The authors used a mixture of sand with a material they called atomizing slag (material patented) which is basically a mixture of oxides of Si, Fe, Ca and Al. The atomizing slag is mainly used as a construction material but it was selected for the PRB because is much cheaper than other materials reported in literature such as iron nanoparticles. The operation of such system in situ resulted in the removal of 90% of the tetrachloroethylene considering the concentrations measured before and after the system electrokinetic-PRB confirming the suitability of this technology for its application in situ to contaminated soils.

4.3. Bioelectroremediation

The combination of electrokinetic remediation with bioremediation has shown some interesting results that promise this technology a good development in the near future. Basically, the application of an electric field to a polluted site may help in the mobilization of the contaminants. That mobilization makes the contaminants available for the microorganisms. At the same time, soil bacteria are like a colloid with a surface charge. So, they can be moved under the effect of the electric field. The transport of bacteria, even in small distances, may help in the interaction between the bacteria and the contaminants. Finally, the electric field
can be used as a transportation mechanism to introduce into the soil the nutrients and other chemicals that may facilitate the bacterial growth and development, as well as the supply of other chemicals that can contribute to the degradation of the contaminants [57, 58].

Lageman [59] developed a technology called Electrokinetic Biofence (EBF). The aim of the EBF is to enhance biodegradation of the VOCs in the groundwater at the zone of the fence by electrokinetic dispersion of the dissolved nutrients in the groundwater. EBF which consists of a row of alternating cathodes and anodes with a mutual distance of 5 m. Upstream of the line of electrodes, a series of infiltration wells were installed, which have been periodically filled with nutrients. After running the EBF for nearly 2 years, clear results have been observed. The concentration of nutrients in the zone has increased, the chloride index is decreasing, and VOCs are being dechlorinated by bio-activity. The electrical energy for the EBF is being supplied by solar panels.

4.4. Electroheating

The removal of volatile and semi-volatile organics from soil can be carried out heating the soil, evaporating the volatile organics and aspirating the vapors, which in turn are trapped in the appropriate absorbent such as active carbon to be finally eliminated by incineration. The heating of soil can be done in several ways. One possibility is the use of an electric current. Soil is not a good electric conductor, so the passing of an electric current generates heat. In electrokinetic remediation, it is used a continuous electric current because the objective is to transport the ionic and nonionic contaminants out of the soil. In the case of electroheating, a transportation of the contaminants using the electric field as a driven force is not necessary. The electric field is only used as a source of energy that is transformed from electric energy into heat. That is why in electroheating the continuous electric field is substituted by an alternate current that supplies the energy but does not induce transportation. Soil is not a good electric conductor. The conductivity of soils is much lower than the typical electric conductor such as metals. The conductivity of soil largely varies with the moisture content and the presence of mobile ions. Anyway, the conductivity of soil is usually low and the heating is easy to achieve with an alternate current. It is recommendable to avoid the use of electroheating in saturated soils. A soil saturated in moisture favors the transportation of current instead of the electric heating.

Electroheating shows several advantages form other technologies designed for the removal of volatile organics from soils. In electroheating, the heating of soil is directly related to the electric field intensity. So, the increase of temperature and the final temperature in the soil can be easily controlled adjusting the intensity of the electric field. Furthermore, the heat is generated into the soil, in the whole volume at the same time, achieving a more uniform temperature in the area to be treated. The uniform temperature permits a uniform removal of the contaminants and a more efficient use of the energy.

Electroheating was used in the remediation of a contaminated site in Zeist, the Netherlands [60]. The site was severely polluted with chlorinated solvents such as perchloroethylene (PCE) and trichloroethylene (TCE) and their degradation products are cis-1,2-dichloroethene (C-DCE) and vinyl chloride (VC). Satisfactory results were obtained in the
application of electrical heating soil and groundwater in the source areas, combined with soil vapor extraction and low-yield groundwater pumping, and enhancing biodegradation in the groundwater plume area. Two years of heating and 2.5 years of biodegradation has been resulted in near-complete removal of the contaminants. A full scale implementation of six phase electrical heating technology was used in Sheffield, UK [61]. Terra Vac Ltd. demonstrated how remediation timescales can be reduced from months/years to weeks, with an electrical heating capable of remediation of soil in difficult geological conditions and in dense populated urban areas. TCE and VC were remediated by electrical heating up to 99.99%. Smith [62] applied the electroheating technology for the remediation of dichloromethane, ethylene dibromide, trichloroethene and tetrachloroethene. Electroheating was an effective technology for the remediation of such organic contaminants, but during the remediation process, the elevation of temperature increases the solubility of the contaminants in the groundwater, the activity of soil microorganisms is enhanced and some reactions, such as hydrolysis of the contaminants and the desorption of gases, takes place. Those factors may affect the removal of the contaminants and it influence has to be considered.

5. Large scale applications

Electrokinetic remediation has been used as a remediation technology in several tests at field scale. In the USA, field projects were carried out or funded by USEPA, DOE, ITRC, US-Army Environmental Centre, as well as companies like Electropetroleum Inc. [63], Terran Corporation, and Monsanto, Dupont, and General Electric which developed the Lasagna™ technology [64, 65]. In Europe, more field projects with electrokinetic remediation have been carried out, specially associated to the commercial activity of the Hak Milieutechniek Company [66, 67]. Recently, some field experiences were reported in Japan and Korea [68]. Some of these tests deal about the remediation of polluted sites with organic contaminants such as organochlorides, PAHs and PCBs. Considering the information available in literature, the cost of field application of electrokinetic remediation is about an average value of 200 $/m³ for both organic and inorganic contaminants, however it must be kept in mind that electrokinetic remediation, like any other remediation technology, is site specific and the costs can be vary from less than 100 to more than 400 $/m³ [69].

6. Future perspectives

The scientific knowledge accumulated in the last 20 years conducted to several lessons learned that must be keep in mind in the design of projects for the remediation of contaminated sites. Thus, the remediation of contaminated soils with organic contaminants is site specific. The results obtained in the remediation of a site cannot be assumed for other contaminated sites. This is due to the large influence of the physicochemical properties of the soil and its possible interactions with the organic contaminants in the results of the electrokinetic remediation treatment. Besides, the chemicals used for enhancing the electrokinetic treat-
ment may complicate the behavior of the system and the removal results may largely vary from one site to another. Recently, it has been considered that the combination of several remediation techniques may improve the remediation results, especially in sites with complex contamination, including recalcitrant organics compounds and inorganic contaminants. The combination of electrokinetics with bioremediation, phytoremediation, chemical oxidation or electrical heating, presents very interesting perspectives for the remediation of difficult sites. It is expected the combination of remediation technologies to improve the remediation results, saving energy and time.

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