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Abstract

Soil contaminated with hydrocarbons (HC) in all over the world is a recurring problem arising from distribution, storage and illegal connections. A wide range of methods are used in all the world like remediation with biological and physicochemical treatments, however, for the purpose of reducing time and increasing the scope of new technologies that have proven its viability in experimental laboratory tests later tested implemented on field are necessary. One of the main advantages of electroremediation processes (ER) is the relatively short implementation time as well as its ease of removing contaminants in highly heterogeneous soils with low permeability. In this chapter, the ER process is described starting from the laboratory scale, determining the supporting electrolyte used, through the choice of material of the electrodes as well as its configuration; finally pilot-scale implementation and fieldwork.

Keywords: electrokinetic, polluted soil, hydrocarbons, resistivity

1. Introduction

Oil is the main source of energy in developed countries, its derivatives such as diesel, paraffin and liquefied gas are used for transport, heating and electricity production; in contrast, the pollution generated by the production processes required for the production, processing, transportation and distribution has generated a serious environmental problem affecting bodies of water, soil and air.
Polluted soil by hydrocarbons (HC) is important in the environment, because the soil could be affected changing its physicochemical characteristics and losing its ability to regenerate itself, or this regeneration takes a long time.

Because of this it is necessary to implement new techniques that allow the rehabilitation of soils in a shorter time and facilitate the process of restoration to the affected area.

There are plenty of available technologies to remediate soils contaminated with hydrocarbons, which are divided under three main headings: biological, physical, chemical and thermal treatments; however in the world most of the companies are dedicated to remediate soil using biological methods (bioremediation). Another important part of the mostly used technologies are soil washing, chemical oxidation and physical separation.

However, over the years a technique called physical chemistry electro-remediation has been developed, which has proved its viability on the laboratory level and has been successfully applied in the field in some countries of Europe and the USA.

The electro-remediation (ER) process, also called electrokinetic electrochemical treatment and/or electro-claim among others [1], is a technique within physicochemical treatments. ER has been considered to be a promising process addressing problems such as heterogeneous soils and low permeability, also can be applied in situ or ex situ, and is especially useful for remediation of inaccessible sites with minimal disruption to the surface, where other technologies fail. Besides it is also sensitive to a wide variety of contaminants.

The ER process is relatively safe, effective, easy to implement, economic and flexible from the points of applying on various types of soils and contaminants. Moreover, most of the in situ conventional methods present difficulties in treatment time in the case of fine-grained soils with high water content and high organic or clay content; in contrast, the ER method is suitable for these types of soils too [2].

ER is a technology to restore contaminated soil based on the generation of an electric field from imposing direct current. For the application of potential difference or direct current, the use of electrodes (anode and cathode) placed in wells previously dug into the ground is required, usually the soil is wetted with an electrolyte to improve conditions driving the electric field. The action of the electrolyte makes the pollutant transport to the wells where it will be extracted. Unlike the fluid drag, this technique allows for a directed migration preventing contaminant dispersion outside the treatment zone [3].

The main mechanisms of the electric field leading the contaminants to the electrodes are electro-migration, electro-osmosis and electrophoresis. The first two processes have the greatest influence on contamination transport. These processes are described below [1]:

**Electro-migration** is a phenomenon in which ions in solution and colloids having electric charge move through the electric field with a velocity that is proportional to the product of the strength of the electric field and mobility of the ion or particle.

The negatively charged ions (anions) will move toward the positively charged electrode and the positively charged ions (cations) will gravitate toward the negatively charged electrodes.
This process is favored when the contaminations to be removed are metals with different oxidation states.

*Electro-osmosis* is the transport process describing the movement of mass of fluid through the pores of the soil under the influence of a potential gradient. When a potential gradient is generated in presence of moist soil, a movement of ions appears toward the electrode polarized in order of their electric charge, generating a migration of them by movement of the water due to the hydration of these ions, and causing movement of fluid through the soil pores. The electro-migration of species and the establishment of a double layer at the solid-liquid interface generate an electro-osmotic flow through the soil pores [4].

Electro-osmosis is the most important transport mechanism for removal of compounds uncharged or weakly charged as organic pollutants. The electro-osmotic component almost disappears in the cases of coarse sands and plastic clays wherein the electro-migration is the most important contaminant removal mechanism. It becomes as important as the electro-migration in the cases of fine sand and silt with high amounts of water and low conductivity [4].

*Electrophoresis* is a mechanism observed when particles, colloids or micro-surface electric charges that the contaminants bound to this material can be transported by the electric field [3].

Other mass transport phenomena occurring during ER are:

- **Diffusion:** the movement of the species due to concentration gradients and advection generated hydraulic gradients [4].

- The electrolysis of water: this occurs on the surface of the electrodes when applying electrical current, which creates an acidic border (with a pH value near 2) at the anode and a basic border (pH value about 12) at the cathode due to the generation of H⁺ and OH⁻, respectively. The reactions are:

  - At the anode: \( 2H_2O - 4e^- \rightarrow O_2(gas) + 4H^+ (ac) \quad E^\circ = +1.229 \text{ V} \)
  
  - At the cathode: \( 2H_2O + 2e^- \rightarrow H_2(gas) + 2OH^- \quad E^\circ = -0.828 \text{ V} \)

  It is noteworthy that electrolysis reactions depend on the type and arrangement of the electrodes [5] as well as the chemical species and electric potential applied during electro-remediation. Thus, protons generated at the anode move through the soil to the cathode by:

  - Migration of ions due to electrical gradient.
  
  - Advection of fluid through the pores due to electro-osmotic flow.
  
  - Fluid flow through the soil pores due to a difference in hydraulic potential internally generated or externally applied.
  
  - A diffusion caused by chemical gradients.

The alkaline medium developed at the cathode moves toward the anode by ion migration and diffusion of OH⁻, which is transport overshadowed by the electro-osmotic flow and neutralization of H⁺, ranging to the cathode where the ions can recombine to form water [4].
In the last three decades, there have been several investigations at laboratory and pilot even applying electrokinetic basis to remove a variety of contaminants. The electro-remediation has been successfully tested in the USA [1–7]. There are even companies offering it as an alternative remediation method within the portfolios of their services a large scale in soils with high clay content.

The ER method has demonstrated its ability to remove some organic contaminants in studies at laboratory, pilot or field [6], but its main application was on sites contaminated with metals in order to remove elements such as chromium, cadmium, mercury, lead, zinc, etc. [7].

In several studies, the application of the ER process has helped to achieve efficiencies close to 100% removal, particularly if the pollution is caused by a single metal (Pb). In on-site applications, the results depended on soil-type variables and the type of pollutant [3].

One example is the consortium formed by Monsanto, DuPont and General Electric, where the applied technology was called Lasagna™ ER in situ to remove trichloroethylene, achieving removal of 98% [8].

Another practical example was developed by Sandia National Laboratories, for electrochemical in situ remediation of soil contaminated with chromium, where electrodes of Iridium/Titanium were used with applying a power of 1572 kW/h; after 5 months of continuous treatment 64% efficiency was obtained [9].

Also, the ER was made at the Centro de Investigación y Desarrollo Tecnológico en Electroquímica, S. C. (CIDETEQ) at laboratory level in order to be able to apply it at pilot and on field level. For that reason, several investigations were developed that led to get familiar with different aspects of field application helping implementation of the technique in a petroleum industrial area. Meanwhile the Geological and Geophysical Institute of Hungary developed an analytical method for investigating the physical and chemical characteristics of soil.

2. Methodology

2.1. Selecting the type of electrodes

The activity was carried out with testing cyclic voltammetry using a potentiostat BAS Epsilon and a glass cell with three electrodes as a reference electrode Ag/AgCl saturated with KCl, wire Ti as auxiliary electrode and plaques of different materials to evaluate as working electrodes. The supporting electrolyte used in these tests was phosphate buffer solution at pH 12 \((i = 0.1)\), because it has been reported that hydrocarbons are best removed in alkaline medium [10].

2.2. Choosing the supporting electrolyte

Solutions of KOH, NaOH, K₂HPO₄, Na₂HPO₄, KH₂PO₄ and Na₂HPO₃ were all prepared at 0.1M in water, which was used to wet soil for an electrolysis. UV-Vis spectrophotometry was used to verify the removal of HC after electrochemical treatment in the different solutions used [11].
2.3. Choosing the best treatment

The technologies described below were compared in order to find the best treatment for decontaminating soils; in all the three cases the removal of oil by Soxhlet extraction at the end of treatment was evaluated. The initial content of fats and oils of the contaminated soil was 4000 mg HC/kg of dry soil [12].

**Soil washing surfactant Triton X-114**: Triton X-114 (4% V/V) was passed at a flow rate of 1.5 mL/min into a tubular reactor containing 30 g soil, for a period of 5 h.

**Biological treatment with solid culture**: 30 g of soil was added to agro-industrial waste bagasse and filter cake with a-residue soil agro-industrial 100:2:2, together they were placed in glass containers while maintaining a temperature of 28°C, for a period of 15 days with aeration every 3 days for 20 min.

**Electro-remediation of contaminated soil**: a tubular reactor was used with 30 g soil and 0.1 M NaOH as supporting electrolyte with a flow rate of 1.5 mL/min, by applying a current of 2 mA for a period of 3.5 h; the working electrodes were titanium mesh (cathode) and Ti|IrO$_2$-Ta$_2$O$_5$ (anode).

2.4. Choosing the best configuration of electrodes

Three-electrode configurations were evaluated: (a) face to face consisting of four cathodes and eight anodes (all rectangular) placed opposite the cathodes; (b) the arrangement of alternating electrodes consisted of six cathodes and six anodes alternating rows of three; and (c) the circular configuration resided in a central cathode and six anodes around this one [13]. The sample amount was 1.9 kg for the three cases and hydrated for a period of 18 h with 800 mL of 0.1M NaOH; the current applied was 0.23 A for a period of 6 h. The used working electrodes were made of Titanium plates and IrO$_2$-Ta$_2$O$_5$|Ti as cathodes and anodes respectively, all at a distance of 6 cm.

The removal process was followed by Soxhlet extraction on the ground and in the solution for determination of chemical oxygen demand (COD), samples for fats and oils were obtained near the anodes and cathodes, as well as in the half-cell.

2.5. ER pilot scale in situ and ex situ

The arrangement of circular electrodes was used during ER pilot scale in situ and ex situ. The cathode was used in the center of the electrochemical cell, and the IrO$_2$-Ta$_2$O$_5$|Ti anodes were used around this one. All the electrodes were used during ER pilot system with dimensions of 60 cm length × 24 cm diameter, which were placed 117 cm between them. In these experiments the amount of soil type Vertisol pellic treated was 3.3 m$^3$ [13, 14].

**Ex situ**: The soil was contaminated with 1126 mg/kg by gasoline. To ER a constant current of 9 A during 4.5 h by day was applied, adding every day 60 L of 0.7 μM NaOH as supporting electrolyte.
In situ: Soil contamination by hydrocarbon was up to 58,000 mg/kg, a current of 11 A was applied for a period of 7.5 h; in this case hydrate first with water and then 135 L of the supporting electrolyte is added (0.1M NaOH) to the cathode hole.

The removal of fats and oils (F&O) were measured by Soxhlet extraction.

2.6. Application of ER in the field

Antrosol-type soil (275 m³) contaminated with hydrocarbons was treated, a constant current of 9 A was applied for 4 h for each cell in a six-cell system mounted in series, the soil removed to insert the electrodes was treated ex situ and then returned to its place. The volume necessary for moisturizing the soil was 120 L of 0.1M NaOH per cell, and the solution extracted at the end of the process of ER was treated by an advanced oxidation process.

The treatment consisted of applying the electric field for 4 h to the first block of six cells; once it is completed the first block of the treatment is continued with the second block and so on until the end of treatment with a total of 14 blocks for complete 84 cells mounted on a three-week period, the ex situ process is followed on par with the same operating conditions.

DC resistivity measurements were carried out using a Digital Ground Resistance Tester Model 4500 AEMC® INSTRUMENTS applying a current of 2 mA, using four copper electrodes, placed at a distance of 1 m, before and after treatment.

Determination of hydrocarbon medium (NMX-AA-145-SCFI-2008) and heavy (NMX-AA-134-SCFI-2006) fractions was performed, as well as polycyclic aromatic hydrocarbons (NMX-AA-146-SCFI-2008) before and after electrochemical treatment.

3. Results and discussion

3.1. Selecting the type of electrodes

The argument for selecting the electrode material was based on selecting the material with the greatest electro-active area. Table 1 shows the electrode materials evaluated with the corresponding electro-active areas, having been calculated using the equation Randles-Sevcik with cyclic voltammetry at different sweep speeds of 20–150 mV/s in the presence of 1 mM Cl₃Ru(NH₃)₃. It showed a reversible behavior only with the reticulated vitreous carbon (RVC) and quasi-reversible for all other electrodes in 0.1 M KCl [15].

The electrode showing the highest electro-active area was the RVC; however, its use was discarded because it has a great capacity to adsorb organic compounds from its surface. Therefore, IrO₂-Ta₂O₅/Ti anode was used during the different ER treatment, because they have an effective life of 5–10 years [16] and as a cathode of Ti.
Material Electro-active area (cm²)
Ti | RuO₂-SnO₂ 14.362
RVC 1000ppp 30.328
Ti | IrO₂-Ta₂O₅ 13.333
Ti | RuO₂-IrO₂ 5.741
Ti | RuO₂ 2.724
Stainless steel 316 1.414

Table 1. Electro-active area for different materials.

3.2. Choosing the supporting electrolyte

Of the solutions prepared from KOH, NaOH, K₂HPO₄, Na₂HPO₄, KH₂PO₄ and Na₂HPO₄ were chosen for the process of ER KOH and NaOH because they have the highest ionic molar conductivity, in this case for K⁺ and Na⁺ 7.35×10⁻⁴ and 5.01×10⁻⁴ sm²/mol respectively [11].

NaOH was used as electrolyte for the higher removal of HC than KOH, because of its higher molar ionic conductivity.

This behavior can be attributed to the ability of adsorption of K⁺ in the ground which is higher than that of Na⁺ (17). Concentration of K⁺ in solution decreased, causing an increase in electrical resistance in soil, and decreasing the removal efficiency of HC [17–20].

3.3. Choosing the best treatment

Table 2 shows the comparison of the three evaluated treatments. It can be observed that the electrochemical treatment shows the best removal rate with 81.9% with a period of 3.5 h [12, 21].

According to these tests, the process of ER proved to be the most efficient treatment and with 3.5 h of application time, besides being a technology that can remove both organic and inorganic contaminants in soils with high clay content and low permeability. These characteristics make the electrokinetic treatment a viable process to be applied on large scale in HC-contaminated soils.

3.4. Choosing the best arrangement of electrodes

Table 3 summarizes the three proposed arrangements where the circular one shows the best results in removal of HC (47.81%) in soil and the highest amount of COD in solution (8880
mg/L) associated with the presence of organic pollutants transported into the solution. In the results reported in Table 3 and Figure 1, the lowest and highest amounts of HC removed from all the sampled points were chosen at each of the arrangements [13, 22, 23].

<table>
<thead>
<tr>
<th>Configuration</th>
<th>Removal F&amp;O (%)</th>
<th>COD (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Minimum</td>
<td>Maximum</td>
</tr>
<tr>
<td>Face to face</td>
<td>0.51</td>
<td>21.35</td>
</tr>
<tr>
<td>Alternating</td>
<td>3.65</td>
<td>29.29</td>
</tr>
<tr>
<td>Circular</td>
<td>14.97</td>
<td>47.81</td>
</tr>
</tbody>
</table>

Table 3. Results of F&O in soil and COD in solution of three-electrode configurations.

Figure 1. Representation of the different configuration of electrodes (1): face to face (A), alternating (B) and circular (C) where the red alligators are the anodes, and black alligators are the cathodes, with their corresponding removal of HC in mg HC/kg of dry soil (2).
Based on these results, one can be convinced that the circular is the best choice for electrode configuration to be used in fieldwork, because this arrangement allows the concentration of all pollutants to the cathode hollowed by the influence of the electric field where the power lines all converge anode to the cathode.

3.5. ER pilot scale ex situ and in situ

Ex situ: Samples of fats and oils have been collected for analysis as taken from different sections of the soil cell, because the soil heterogeneity represents different behaviors throughout the cell. After three weeks of electrochemical treatment, a decrease of about 84–88% was observed in the concentration of gasoline in the different sampled points (Figure 2A) which is due to electro-migration, electro-osmosis and electrophoresis, aided by water electrolysis. The contribution of the use of modified anodes IrO$_2$-Ta$_2$O$_5$|Ti is also considered, provided the chemical conditions are adequate to desorption and/or destruction of hydrocarbons present in the soil particles [14, 24].

![Figure 2. ER pilot scale ex situ (A) and in situ (B). Middle fraction HC content in the polluted soil before (A) and after (B) its electrochemical treatment in mg HC/kg of dry soil.](image)

In situ: The amount of F&O was registered in the sampling sections (Figure 2B) near the six anodes and cathodes at the beginning (Figure 2C) and the end of treatment (Figure 2D). Table 4 shows the removal percentages obtained after a treatment of 7.5 h. In general, a decrease
appreciated of pollutant in all sampled points is close to 90%; however, this is not the same in all areas, attributed to soil heterogeneity behavior.

Like in the case of ER ex situ treatment efficiency is attributed to transport phenomena occurring during the application of electric field, the use of IrO₂-Ta₂O₅|Ti anodes, the electrolysis of water, adequate wetting and high clay content in the soil.

<table>
<thead>
<tr>
<th>Position</th>
<th>Removal after ER in soil (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Anodes</td>
</tr>
<tr>
<td>1</td>
<td>55.55</td>
</tr>
<tr>
<td>2</td>
<td>21.70</td>
</tr>
<tr>
<td>3</td>
<td>52.30</td>
</tr>
<tr>
<td>4</td>
<td>44.43</td>
</tr>
<tr>
<td>5</td>
<td>27.65</td>
</tr>
<tr>
<td>6</td>
<td>30.11</td>
</tr>
</tbody>
</table>

Table 4. Percentages of HC removal in soil after ER in situ.

3.6. Field application of ER

In Figure 3, the blue dots ranging from one to five represent the locations of the sampling points located on the orange lines labeled with B, D and F.

Figure 4 shows that for the sampled points, the initial values of the middle fraction HC content (MFHC, Figure 4A) determined from the sampling points were higher than 50,000 mg/kg. The electrochemical treatment decreased these values by 74% with average values of 12,000 mg/kg (Figure 3B).
In the case of heavy fraction HC (HFHC), the results are presented in Figure 5. The contamination content decreased in all points, except 1D and 5D where the slight increase can be possibly due to the sub-products of the electrokinetic process. The removal rates of the remaining 13 variables are ranging from 11% (1F) to 94% (4F) which demonstrated the feasibility of the field application. It was observed that applying the technique the organic compounds can be removed due to the action of the electric field with the effect of the involved transport processes (electro-migration, electro-osmosis, and electrophoresis), to water electrolysis, the applied electrode configuration and the current.
The analysis of section B for 16 kinds of poly aromatic hydrocarbons (PAHs) showed that five of them were present in greater abundance. The behavior of these compounds before (blue bars) and after (pink bars) the treatment are presented in Figure 6. As it is expected the content of PAHs were various throughout the site; the removal percentages are varying according to the type of compound and the site characteristics: for example, pyrene removal varies 29–90%, the Phenanthrene’ removal range is between 18 and 81% and for Benzo (a) pyrene it is 33 and 61%.

Figure 6. Behavior of PAH content in section B before (blue bar) and after (pink bar) the electrochemical treatment.

As an additional tool to follow the distribution of the contaminant in the soil DC resistivity measurements were taken with the aim of appreciating a decrease in HC, a diminution in resistivity values reflects a decrease of HC content [24]. The purpose of applying geoelectric measure in the contaminated site is to find a fast, economic, non-invasive method that could provide a reliable image on the distribution of soil contamination.

The DC resistivity value depends on several geological factors such as the texture class, the minerals present, the moisture content, porosity, these properties change when the soil is exposed to some type of contamination, in this case by organic compounds, which causes an increase in soil resistivity [24–27].

Behavior analysis of apparent resistivity was performed using the Wenner-Alfa array consisting of an array of four electrodes and can be used in moderate depths, and is relatively sensitive to vertical changes under the subsurface to the center of the array, but little sensitive to horizontal changes [28, 29].
In Figure 7, the distribution of the measured apparent resistivity values can be observed at the test site before (left) and after (right) the treatment. It is remarkable that before the remediation process there were two zones where the apparent resistivity was higher than 20 ohmm (marked with white). After the process of ER, the resistivity values decrease to 2–4 ohmm at the same points, which is associated with a decrease in the amount of HC and increase of salts, as the sub-products of ER. This can be validated with the results for middle and heavy fraction HC, in the cases of points 2D (removal rates of 61% HFHC and 71% for MFHC), 2F (removal rates HFHC: 35% and 64% for MFHC) 5F (removal rates: 75% for HFHC and 84% of MFHC).

![Figure 7](image)

Figure 7. Apparent resistivity behavior before (A) and after (B) the electrokinetic treatment.

According to the obtained results, DC resistivity survey method can be used as an effective tool for monitoring the process of HC removal in soils. However the readings taken do not
represent a value of HC concentration, it is an indirect measure of the reduction of these pollutants in the subsurface with respect to an initial value.

4. Conclusions

The success of electrochemical treatment is attributed to several factors: the choice of supporting electrolyte, type of electrodes and their configuration, the distance between them; the cell current, all as a whole allowed the removal of HC from the laboratory scale, pilot and field were appreciable. Removal percentages were ranging from 20 to 90% attributed to soil heterogeneity which does not allow the results to be reproducible in all sampled points, due to geochemical, geophysical and physicochemical factors that occur during the application of electric field such as changes in pH, desorption and/or solubility of the contaminants and redox processes.

The successful field implementation of ER technique makes the ER process an attractive option among the remediation technologies dealing with environmental problems caused by contamination of organic and inorganic compounds. Furthermore due to soil heterogeneity, the ER technique should be used in conjunction with other techniques completing the whole soil rehabilitation process.

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