Application of Electrochemical Technologies to Treat Polluted Soil by Diesel

Elisama Vieira dos Santos, Mariana Oliveira Medeiros, Aecia S. Dantas dos Anjos, Carlos A. Martínez-Huitle*, Djalma Ribeiro da Silva

Federal University of Rio Grande do Norte, Institute of Chemistry, Lagoa Nova CEP 59078-970 - Natal, RN, Brazil
carlosmh@quimica.ufrn.br

This study reports on the effects of electrokinetic remediation to remove organic contaminants and heavy metals from contaminated soil by using different electrolytes. $Ti/Ru_{0.3}Ti_{0.7}O_2$ electrode with an area of 50 cm^2 was used as anode, while as cathode a grid of Ti. Different electrokinetic total petroleum hydrocarbon (TPH) removal efficiencies were achieved, depending on the supporting electrolyte used, as follows: Na_2SO_4 (96.46%), citric acid (81.36 %) and NaOH (68.03 %) during the first 15 days of electrochemical treatment. The results described here suggest that the application of electrokinetics can be a promising soil remediation technology; if the soil parameters (electric current and electrolyte) are appropriately controlled based on the understanding of interaction between organic pollutants and soil. The main removal mechanism of diesel from soil was electroosmosis. On the other hand, wastewater collected from the electrokinetic remediation process, which was polluted with TPH, it was successfully oxidized by using electrochemical oxidation treatment. The level of degradation achieved was considerably high (>70%) in all cases, after 10 h of electrolysis.

1. Introduction

The Electrokinetic (EK) process is promising for organic and metals removal from soil. Several research groups have studied on organic movement to and retention near the anode by the EK technique (Reddy, and Saichek, 2004; Chil-Sung et al., 2010; Alcántara et al., 2010; Reddy, 2010; Byung-Gon et al., 2011; Méndez et al., 2012; Cameselle and Reddy, 2012; Pazos et al., 2013). Recently, the application of electrokinetic technology to organic is attracting interest from the scientific community to removal pyreno, total petroleum hidrocarbon (TPH), heavy metals, naphthalene (Reddy, 2010; Ferri et al., 2009). The remediation can be conducted in situ to treat contaminants in low-permeability zones by applying a direct current between electrodes placed in the remediation site, achieving high efficiency on removal. The transport phenomena of contaminants in the soil can be briefly described as follows: electromigration, electroosmosis and electrophoresis. Electromigration is the transport of ions and ion complexes toward the electrode of opposite charge; Electroosmosis is defined as the movement of soil moisture or groundwater, which generally takes place from the anode to the cathode and is due to the existence of a space-charge on the solution side of the particle/solution interface. Its migration toward the cathode causes solution displacement too, thus generating a cathode-directed electroosmotic flow. Electrophoresis, as the movement of charged particles under an electric gradient, contaminants bound to mobile particulate matter can be transported in this manner as well (Ferri et al., 2009; Pazos et al., 2012; Bustos, 2012). These mechanisms facilitate decontamination by initiating physical, chemical or hydrological changes such as desorption, adsorption, oxidation, gas generation, dissolution, precipitation, reduction, ion exchange, pH gradient formation, destruction of soil particle active sites (Pazos et al., 2012; Bustos, 2012).

Several studies have also been assessed the effect electrolytes such as NaCl, KCl, NH_4, CH_3COONa, Na_2SO_4, Na_3PO_4, MnO_4^-, H_2O_2, $CaCl_2$ and citric acid on the electrokinetic and rheological behaviours of soil obtaining different removal organic matter efficiencies (Ferri et al., 2009; Pazos et al., 2012; Bustos,

2012). It has been demonstrated to be successful and cost-effective in removing wide variety of pollutants such as heavy metals and organic contaminants in many bench- and field-scale studies.

EK remediation has also been proposed as an innovative technology for remediation of saturated or unsaturated soils, Few studies have investigated the removal of diesel from contaminated soil by electrokinetically enhanced oxidation with the presence of both H_2O_2 and Fe_3O_4 (iron electrode corrosion), achieving higher TPH-D removal efficiency (97%) compared to the efficiencies observed from EK (55%) or Fenton oxidation (27%) alone. To improve of individual remediation techniques and to achieve better organic compounds removal efficiencies have been proposed; various combinations of physical, chemical and biological, as a   physical-chemical treatment, physical-biological treatment, biological-chemical, physical-chemical-biological treatments to treat diesel contaminants in soil (Ferri et al., 2009; Reddy, 2010; Pazos et al., 2012; Bustos, 2012).

The objective of this work is to test a combined process of electrokinetic remediation for diesel remediation from soil contaminated followed by electrochemical oxidation to remove organic pollutants from wastewater produced. The influence of operating parameters that play an important role in the electrokinetic process, such as effect of the electrolyte and applied current density were investigated

2. Materials and Methods

2.1 Preparation of soil samples

Sample of soil was collected from Northeast Brazilian gas & oil station. The soil was spiked with commercial diesel fuel by introducing a pollutant solution of diesel fuel (10 mL) in n-hexane (20 mL) into soil samples (1 Kg) to obtain a representative contaminant concentration for soil. About 950 g of soil material were treated in each test. The mixture was easily stirred and blended homogeneously. The mixture was kept at room temperature (25°). All physical parameters of soil were determined according to the ASTM standard methods and are listed in Table 1. The soil pH and electrical conductivity were determined by a pH meter and a conductivity-meter respectively, with a ratio of 1:2.5 soil to water. The organic carbon and cation exchange capacity (CEC) were analysed by dichromate oxidation method and ammonium acetate extraction method, respectively. Afterwards, a representative sample (approx. 50 g) of the mixture was taken for initial analysis of diesel concentration. X-ray diffraction analysis was performed. Table 1 shows the characteristic of the soil used.

2.2 Analysis of organic matter removal from soil and Diesel removal

During EK process, organic matter removal from soil was monitored in terms of TOC removal in three soil sections (near to cathodic, central and near to anodic section). Also, Diesel concentration was measured as total petroleum hydrocarbons (TPH) using 10 g of sample treated in order to evaluate the elimination of TPH in the treated soil. The sample was mixed with n-hexane in a Soxhlet extractor for 6 h and 10 g of soil were mixed with 100 mL of n-hexane in a separate funnel. The superior phase was mixed with internal standard and analysed by gas chromatography. The HP-5 capillary column was used with helium carrier gas at a flow rate of 1 mL min^{-1} and air at 400 mL min^{-1}. The temperature program used was of 50 °C min^{-1}, after 8 °C min^{-1}, and 320 °C for 10 min^{-1}. The removal efficiency was calculated according to Eq.(1):

$$Removal \ (\%) = \frac{C_i - C_f}{C_i} \times 100 \qquad (1)$$

where C_i is the initial concentration of TPH in the soil and C_f is the final concentration of TPH in the treated soil.

2.3 Electrokinetic cell

The experiments were performed in a rectangular acrylic cell showed in Fig.1. The sample soil was introduced in the central compartment, in a rectangular system of 30 cm of length × 10 cm of width × 10 cm of height. Two electrode chambers, with a working volume of 0.5 L, were placed at the lateral positions of the electrokinetic cell and it was isolated from the test soil by means of filter paper. Ti/Ru$_{0.3}$Ti$_{0.7}$O$_2$ electrodes were used as cathode and anode, with an area of 50 cm^2, each one of them. The electrode chambers were filled with a solution of Na$_2$SO$_4$ 0.1 M, NaOH 0.1 M and citric acid 0.1 M for each one of the experiments. A current density of 2 mA cm^{-2} was applied for 15 days in all experiments. Electrical potential and pH (in the electrode compartments) were periodically monitored, during the experimental tests. Table 2 shows a summary of the experiments carried out.

2.4 Electrochemical oxidation experiments

Bulk oxidations were performed in undivided electrochemical cell, the reaction compartment having a capacity of 1 L, and the solution was stirred by a magnetic stirrer. The electrolytic solution (effluent formed after electrokinetic treatment of soil) was stored in the electrochemical batch cell for treating 0.5 L. The oxidation experiments of solution were performed under galvanostatic conditions using a power supply MINIPA-3305M at 25 °C. The cell contained a $Ti/Ru_{0.3}Ti_{0.7}O_2$ electrode as anode with 50 cm^2 of area. A current density of 20 mA cm^{-2} was applied during 10 h in all experiments.

3. Results and Discussion

3.1 Efficiency carbon organic total removal and electrical power consumption

EK experiments were performed using $Ti/Ru_{0.3}Ti_{0.7}O_2$ and Ti as anode and cathode, respectively, by applying 2 mA cm^{-2}. During EK process, pH, conductivity and TOC removal were monitored in three soil sections (near to cathodic, central and near to anodic section). After EKR process, hydrocarbon content was also evaluated in the same three soil sections. Results in Fig. 1a clearly show that the initial TOC decreases as a function of time, obtaining different efficiencies depending on the electrokinetic cell sections: 48.11%; 48.51% and 73.14% on anodic, central and cathodic section for NaOH 0.1 M. The organic matter was easily transported via electroosmoic flow. This behaviour confirms the migration of organic pollutants (Ferri et al., 2009; Reddy, 2010; Pazos et al., 2012; Bustos, 2012) from different sections of soil to solutions reservoirs (anodic and cathodic solutions). In the case of Na_2SO_4, TOC decreases as a function of time in all electrokinetic cell sections removing 83.35%, 71.49% and 80.83%, at cathodic, central and anodic section, respectively (Fig. 1b). On the other hand, when citric acid was employed, TOC decay was around 43.35%, 73.49% and 42.83%, at cathodic, central and anodic section, respectively (Fig. 1c). These figures indicate that the Na_2SO_4 favours the elimination of organic matter from all sections in the polluted soil.
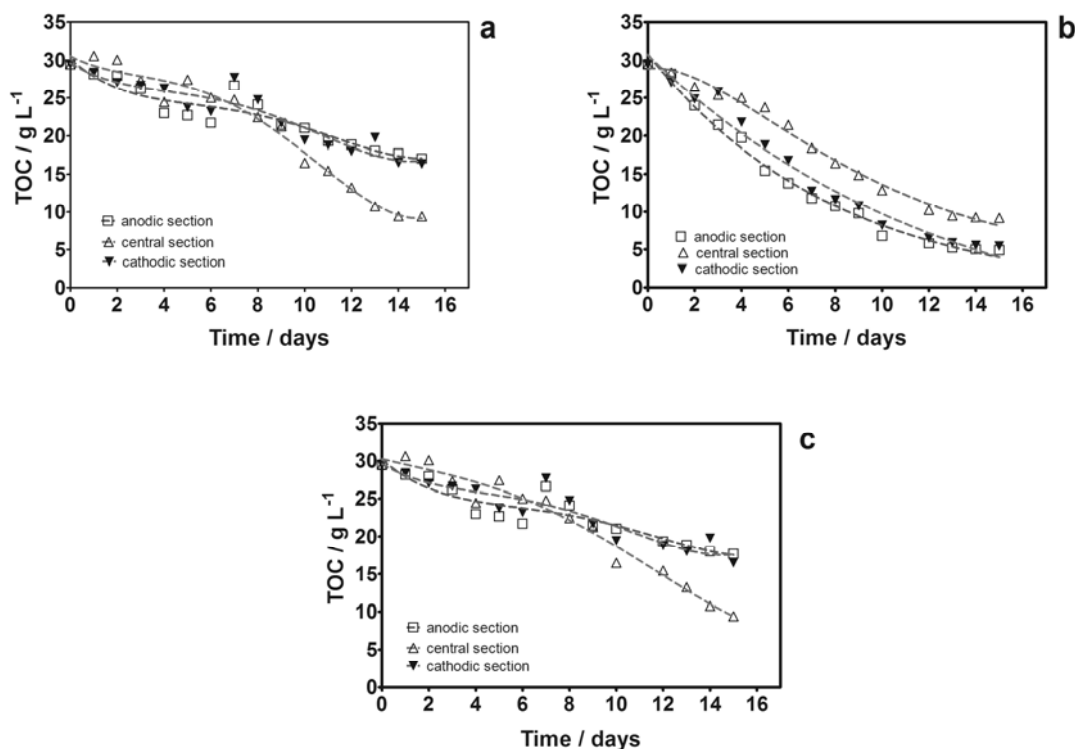

Figure 1. TOC removal during EK process in three soil sections using as supporting electrolyte (a) NaOH, Na_2SO_4 and (c) citric acid by applying 2.0 mA cm^{-2} for 15 days. Anode was $Ti/Ru_{0.3}Ti_{0.7}O_2$ and as cathode, titanium (Ti).

On the other hand, considering the electrical potential measured during the EK experiments, energy consumption was estimated. A total consumption of 121.21 kWh m^{-3} was spent after 15 days of EK treatment when NaOH was used as supporting electrolyte. Whereas, 111.16 kWh m^{-3} was necessary to obtain modest TOC decays when citric acid was employed. Conversely, lower energy consumption was employed when Na$_2$SO$_4$ was employed about 44.83 kWh m^{-3}.

Fig. 2 shows the variation of pH, as a function of time, in the proximity of anode compartment, cathode reservoir and middle section using NaOH, Na$_2$SO$_4$ and citric acid as supporting electrolytes, for removing organics. When the electric potential is applied, the electrolysis reactions occur in the electrodes, producing H$^+$ and OH$^-$ ions at the anode and cathode reservoirs, respectively. The initial pH of the soil-Na$_2$SO$_4$ (middle section) was around 6.1 and it decreases to 4.1 during EKR tests, at anodic and middle sections; while at cathodic reservoir, pH increased considerably to around 10.5. Using NaOH 0.1 M, initial pH was around 8.90, after that, it decreases up to 6.1, at anodic and middle sections; while pH around 12 was attained after 15 days of treatment at cathodic section. Similar behaviour was observed at all sections when citric acid was used (Fig. 2c). A key feature of electrokinetic experiments is the electrolysis of water at the electrodes, resulting in the generation of acid and base at the anode and cathode respectively (Ferri et al., 2009; Reddy, 2010; Pazos et al., 2012; Bustos, 2012). The electrolytic reduction of water at the cathode causes H$_2$ evolution and oxidation at the anode causes O$_2$ evolution. An alkaline zone surrounds the cathode and an acidic zone is created at the anode:

At the cathode: $4H_2O + 4e^- \rightarrow 2H_2(g) + 4OH^-$

At the anode: $2H_2O \rightarrow O_2(g) + 4H_+ + 4e_-$

The pH is reduced not only the high concentration of H$^+$, but also in a secondary manner by the release of Al^{3+} due to kaolinite dissolution (composition of soil) (Ferri et al., 2009; Reddy, 2010; Pazos et al., 2012; Bustos, 2012). The reduction of water molecules at the cathode leads H^2 generation and increasing pH. Therefore, these reactions cause an acidic solution to be generated at the anode and an alkaline solution to be generated at the cathode. The electrolysis of water affects the remediation process because the ionic products may electromigrate and be transported by electro-osmosis towards the opposite charged electrode location.
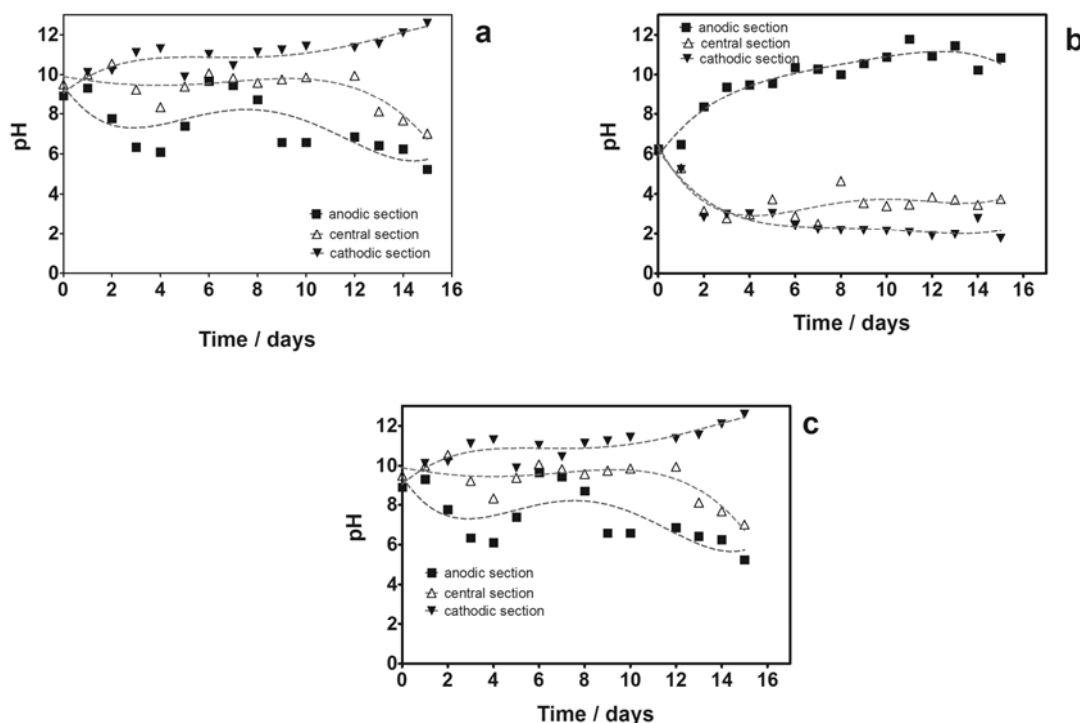

Figure 2. pH variation, as a function of time, during electrokinetic tests at different supporting electrolytes: (a) NaOH (b) Na$_2$SO$_4$ and (c) citric acid.

Thus, an acidic front of solution may move from the anode towards the cathode and an alkaline front of solution may move from the cathode towards the anode. However, the pH will not increase directly to 12 owing to interaction of OH^- with residual H^+ on the cathode surface (Ferri et al., 2009; Reddy, 2010; Pazos et al., 2012; Bustos, 2012).

$H^+ + e^- \rightarrow$ ½ H_2
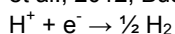
During the electrokinetic remediation, operating acidic and alkaline fronts migrate toward the opposing electrodes and interact approximately with a ¼ of the distance from the cathode to form a zone of abrupt pH change. The movement of these fronts is irregular, and the advection H^+ front depends on electromigration, eletroosmosis, and diffusion mechanisms. Progress is hindered by high soil buffering capacity as a result of substitution with adsorbed cations (Pazos et al., 2012; Bustos, 2012). At the cathode zone OH^- front advection is affected by upstream electromigration and the progress of OH^- ions is hindered by electroosmosis. As shown Fig. 2a, the outlet catholyte pH increased continuously due to the basic front reaching the cathode and neutralizing the high pH. When NaOH was used, the soil pH may reduce the electroosmotic flow rate by causing the soil minerals to process a more positive surface charge and zeta potential, the flow velocity towards the cathode should have decreased over time (Pazos et al., 2012; Bustos, 2012). Fig 2b shown citric acid the soil pH tended to increase near cathode little in the treatments and decreased little anode, this effect can be attributed to the impact of the electro-osmotic flow. This flow has an acidic pH below 4, and can react with the soil to release ions and increase the electrical conductivity (Bustos, 2012).

3.2 Concentration of TPH in soil

The initial concentration of TPH in the soil was found to be 9094.06 mg/Kg. Fig. 3 shows the TPH removal efficiency, in terms of percentage, as a function of supporting eletrolyte used (NaOH, citric acid and Na_2SO_4). There was a pattern of slight increase in the removal efficiency of TPH from cathodic to anodic section, indicating that the oil was removed mainly by electroosmosis flow. Analysing the figures reported, Na_2SO_4 is the most efficient supporting electrolyte because higher TPH elimination was achieved, more than 90%. The order of TPH removal efficiency is Na_2SO_4 (96.46%) > citric acid (81.36 %) and NaOH (68.03 %) during 15 of EK treatment. The registered electro-osmotic flow, approximately 42 mL d^{-1}; 56 mL d^{-1} and 64 mL d^{-1} for NaOH, citric acid and Na_2SO_4 confirm the results obtained for %THP elimination.
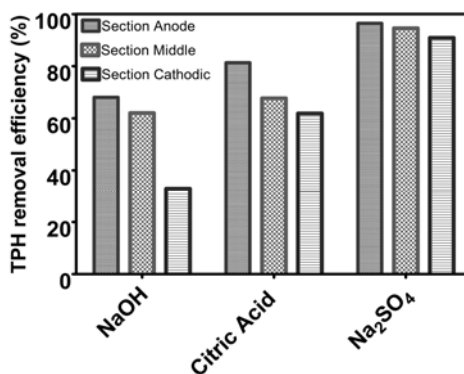

Figure 3. TPH removal efficiency using different supporting electrolytes in EK treatment.

3.3 Electrochemical oxidation

Bulk oxidations were performed in undivided electrochemical cell, the reaction compartment having a capacity of 1 L, and the solution was stirred by a magnetic stirrer. The experiments were conducted at 25ºC by applying 20 mA cm^{-2} using $Ti/Ru_{0.3}Ti_{0.7}O_2$ electrode. Fig. 4 shows the TOC decays, as a function of time, for the wastewater generated after EK treatment. TOC measurements confirm the elimination of organic matter accumulated in the reservoirs solutions after EK treatment. As can be observed from Fig. 4, more than 90% of organic materr dissolved was removed after 10 h of electrolysis. This results clearly demonstrated that the wastewater produced after EK treatment could be treated by using electrochemical oxidation process. In this context, two electrochemical technologies could be integrated in order to decrease the time of treatment, and consequently, decreasing the energy costs. The elimination of

dissolved organic pollutants is due to the fact that OH radicals are produced at anode surface, favoring the electrochemical oxidation of them. However, this electrode is considered an active anode, limiting the efficiency on the removal. This limitation could be avoided when a non-active anode is used, for this reason, it is a new objective of our research. Also, the formation of superior metal oxide at this electrode material decreases the efficiency of the electrochemical oxidation process at solution of NaOH.
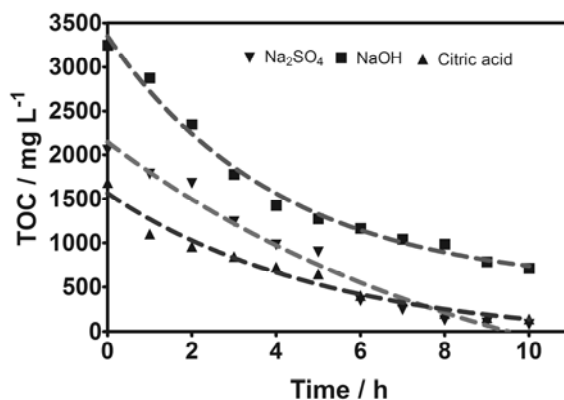

Figure 4. Electrochemical degradation of wastewater produced after EK treatment. Anode was Ti/Ru$_{0.3}$Ti$_{0.7}$O$_2$ by applying 20 mA cm^{-2}.

4. Conclusions

The organic matter was eliminated from polluted soil due to the electromigration and electroosmotic flows, removing more than 80% of organic compounds using Na$_2$SO$_4$ 0.1 M and 68% employing NaOH 0.1 M after 15 days. The soil pH variation is observed due to the buffering capacity of soil as well as the production of H$^+$ and OH$^-$ at the electrocatalytic materials used. On the other hand, the liquid collected from the electrokinetic remediation process; it was successfully oxidized by using the electrochemical treatment (electrooxidation), verifying the applicability of combination of two electrochemical technologies.

References

Alcántara, M.T., Gómez, J., Pazos, M., Sanromán, M.A., 2010, Electrokinetic remediation of PAH mixtures from kaolin. J. Hazard. Mat. 179, 1156–1160.

Byung-Gon, R., Geun-Yong, P., Ji-Won, Y., Kitae B., Electrolyte conditioning for electrokinetic remediation of As, Cu, and Pb-contaminated soil, 2011, Sep. Purif. Technol., 79, 170–176.

Cameselle, C., Reddy, R. K., 2012, Development and enhancement of electro-osmotic flow for the removal of contaminants from soils, Electrochim. Acta, 86, 10– 22.

Chil-Sung, J., Jung-Seok, Y., Kyung-Jo, K., Kitae, B., 2010, Research article electrokinetic removal of petroleum hydrocarbon from residual clayey soil following a washing process, Clean, 38, 189–193.

Ferri, V., Ferro, S., Martínez-Huitle, C.A., De Battisti, A., 2009, Electrokinetic extraction of surfactants and heavy metals from sewage sludge, Electrochim. Acta, 54, 2108–2118.

Méndez, E., Pérez, M., Romero, O., Beltrán, E.D., Castro, S., Corona, J.L., Corona, A., Cuevas, M.C., Bustos, E., Effects of electrode material on the efficiency of hydrocarbon removal by an electrokinetic remediation process, 2012, Electrochim. Acta, 86, 148–156.

Pazos, M., Iglesias, O., Gomez, J., Rosales, E., Sanromán, M.A., 2013, Remediation of contaminated marine sediment using electrokinetic–Fenton Technology, J. Ind. Eng. Chem., 19, 932–937.

Pazos, M., Plaza, A., Martín, M., Lobo, M.C., 2012, The impact of electrokinetic treatment on a loamy-sand soil properties, Chem. Eng. J. 183, 231– 237.

Reddy, R. K., Saichek, E. R., Enhanced electrokinetic removal of phenanthrene from clay soil by periodic electric potential application, 2004, J. Environ. Sci. Health A, A39, 1189–1212.

Reddy, R. K., Technical Challenges to In-situ Remediation of Polluted Sites, 2010, Geotech. Geol. Eng. 28, 211–221.