Int. J. Electrochem. Sci., 12 **(2017)** 1247 – 1262, doi: 10.20964/2017.02.18

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Electrokinetic Treatment of Polluted Soil with Petroleum Coupled to an Advanced Oxidation Process for Remediation of Its Effluent

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Received: 11 September 2016 / *Accepted:* 29 November 2016 / *Published:* 30 December 2016

In this work, the treatment of soil polluted with petroleum in laboratory scale was studied using electrokinetic soil remediation (ESR) technology followed by boron doped diamond electrolysis (BDD-electrolysis) for washing liquid treatment. Results evidently show that ESR is an efficient treatment removing the petrochemical compounds from soil. Depollution of the effluents by BDD-electrolysis is related to the pre-treatment of liquid as well as the higher removal of petroleum from soil. BDD-electrolysis favors the complete elimination of organic matter from liquid produced after ESR. However, the ions in the effluent play an important role during the BDD-electrolysis because strong oxidants are electrochemically produced at diamond surface, improving the efficiency of the process.

Keywords: petroleum, electrokinetic, coupled treatments, electrolysis, and diamond electrode.

1. INTRODUCTION

Recently, an increasing interest in the remediation of soil and water polluted with petroleum has been attained [1-3]. The petrochemical activities by industries have generated serious environmental problems in water and soil ecosystems. In the former, the petrochemical wastewaters generated contain many chemicals (volatile phenol, suspended solids, sulfides, cyanides, benzene, nitrogen compounds, ammonia, and heavy metals) [4]; while hydrophobic organic compounds (HOCs) (e.g.: petroleum hydrocarbons, polychlorobiphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAH)) are extremely difficult to remove from the later [5]. In this context, the persistence of HOCs in soils has been a matter of significant importance, regarding the accumulation of them in the soil or the environmental problems provoked by their potential toxicity, mutagenicity and carcinogenicity [5,6]. Due to their slow degradation in the aquatic and soil ecosystems, these compounds are very persistent in the environment [5,7,8].

The HOCs interactions with the soil and their physical-chemical properties influence on the accumulation and mobility of them in the soil [8,9] as well as the efficacy of the treatment used for removing these pollutants from soil. Therefore, several soil treatments have been developed in the last years; however, these processes have different disadvantages such as high perturbation of the soil texture, high costs, long treatment time requirements, low efficiency, or selectivity toward target pollutants [5]. In this frame, more efficient, less expensive and ecofriendly approaches were technologically advanced in the last years [5,10].

Recently, electrokinetic method, so called electrokinetic soil remediation (ESR), can be considered as a promising alternative for soil treatment. This technique involves several steps, but it minimally disturbs the soil surface during the treatment of subsurface contaminants [11-17]. This technology is investigated in some parts of the world, aiming to understand the potential application from laboratory scale to a viable in-situ soil remediation method [11-17]. By applying a low direct current or a low potential gradient to electrodes inserted in the low permeable soils, several complex mechanisms are promoted (electrolysis, electro-osmosis, electro-migration and electrophoresis) in order to favor the transportation of pollutants (inorganic and organic species) across the soil. Also, desirable non-toxic compounds can be introduced during the treatment for enhancing the removal efficiency of the pollutants from soil [18]. For these reasons, the main objectives of the present research are to evaluate the efficacy of ESR to depollute soil and BDD-electrolysis for treating the effluent obtained after the soil treatment.

2. MATERIALS AND METHODS

2.1. Chemicals

Petroleum (American Petroleum Institute (API) gravidity > 30, it consists basically of alkanes, and approximately 15 to 25% of cycloalkanes) and hexane were obtained from Sigma-Aldrich (Brazil). Chemicals were of the highest quality commercially available, and were used without further purification: $FeSO_4$, K_2CrO_7, H_2SO_4 and Na_2SO_4 were purchased from Fluka. Deionized water (Millipore Milli-Q system) was used to prepare all solutions.

2.2. Preparation of simulated soil

Spiking soil samples with organic compounds is proposed as contamination method in the lab-scale studies [5,19]. In this context, carbonaceous soil was chosen as a model soil and it was polluted with petroleum. Petroleum-contaminated samples were prepared by mixing raw soil and crude oil by dissolving a known amount of petroleum (1.5 g and 2.5 g) in 50 mL of hexane, after that, this petroleum/hexane solution was mixed with soil. The spiked soil was aerated for 24 h to evaporate the hexane, favoring a homogeneous distribution of petroleum on the soil.

2.3. Physicochemical Characteristics

Measurements of conductivity, pH, zeta-potential (particle-size distribution), dry weight and humidity were performed in order to evaluate the soil conditions, before and after, electrochemical treatment.

2.4. Electrokinetic cell

The cell employed for the ESR experiments is illustrated in Fig. 1 with dimensions of approximately 250 × 80 × 80 mm, consisting of a closed system with two electrode compartments (a and c), a soil compartment (b) and electrical contacts. Graphite electrodes were used as anode and cathode with working areas of 50 cm^2.

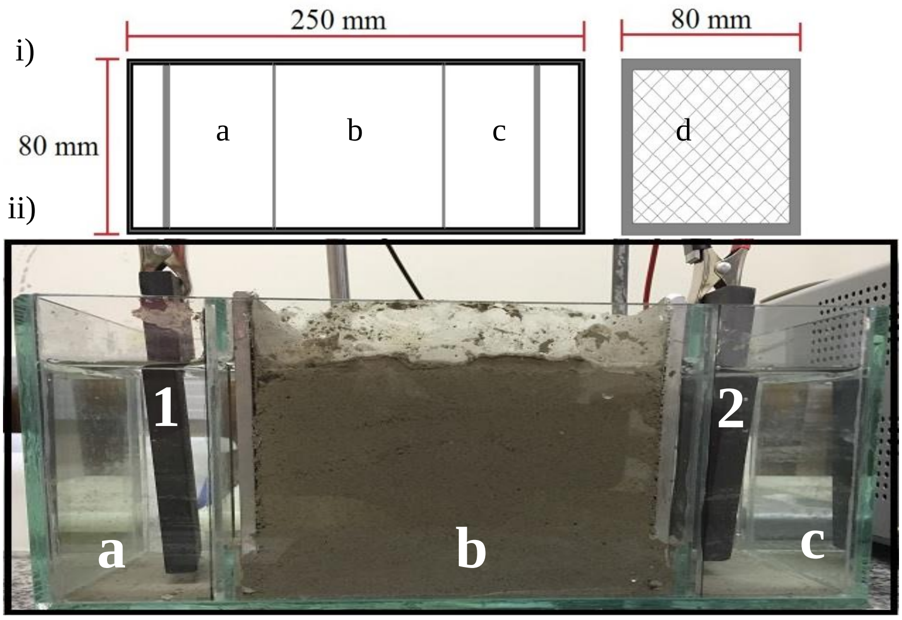


Figure 1. i) Diagram of the cell for electrokinetic soil remediation with dimensions of each one of the compartments in millimeters and ii) Parts of the electrokinetic cell illustrated by photography. (a) anodic compartment, (b) soil sample compartment, (c) cathodic compartment, (d) lateral section of cell and graphite electrodes: (1) anode and (2) cathode.

Filter-paper separations were positioned between the soil sample and electrode reservoirs. Supporting electrolyte (Na_2SO_4 0. 1 M) was manually added in the electrodes compartments, when necessary. ESR remediation studies were performed by using the same electrochemical cell for testing different experimental conditions: applied current (ranging from 0.03 to 1 A), treatment time and petroleum contamination (1.5 g and 2.5 g).

2.5. ESR experiments

Graphite electrodes were employed, and then different operating conditions were investigated during 360 h. To gain information about the process; pH, variation in electrolyte volume (electroosmotic flow), cell potential, temperature and conductivity were measured before and after each treatment, in the soil and in both electrolyte compartments (anodic and cathodic). Soil compartment in the ESR cell was filled with 0.80 Kg of homogenized soil. A power supply (MINIPA 3035) was used to provide constant currents. During the ESR process, total organic carbon (TOC) was determined by using a Multi N/C 3100 Analytik Jena analyzer in the soil. Also, some samples in the cathodic and anodic compartments were analyzed by TOC for determining organic matter content and zeta potential (z-potential) was also measured using a Zeta Meter System 3.0+®. The effluents produced at anodic and cathodic compartments (a complex aqueous mixture of petroleum, sodium sulfate and soluble species) were subsequently treated by BDD-electrolysis.

2.5. Bulk treatment of the soil effluents by BDD-electrolysis

BDD-electrolysis (application of electric current in the liquid waste) was employed as alternative approach for treating the effluents produced after ESR. These experiments were performed in a single-compartment electrochemical flow cell with BDD and steel electrodes as anode and cathode, respectively [20]. Characteristic of BDD are as follows: sp^3/sp^2 ratio: 225; boron content: 500 ppm; width of the diamond layer: 2.68 µm [20,21]. The electrical current was applied using a MINIPA 3035 DC power supply. Temperature was kept constant by means of a water bath. The applied current density used (20 and 60 mA cm^{-2}) in this work was chosen according the existing literature about the treatment of other pollutants [20,22,23]. The organic removal was monitored through the COD content during the treatment. Measurements of pH were carried out with an mPA-210 pH-meter, while the conductivity data were collected with a Tec-4MP analyzer.

2.6. Energy consumption and costs

The energetic and economic aspects play a key role for the development of clean methodologies, for this reason, the energy consumption for the removal of one m^3 of soil was calculated by Equation 1; subsequently, taking into consideration an electrical energy cost of about 0.4 reals per kWh (Brazilian cost), the process expenditure was estimated by Equation 2.

$$\text{Energy consumption (kWh/m}^3\text{)} = \frac{[\text{Test energy (Wh)}/1000]}{\text{Volume (m}^3\text{)}} \quad (1)$$

$$\text{Cost (Real/m}^3\text{)} = \text{Energy consumption (kWh/m}^3\text{)} \times 0.4 \text{ (real/kWh)} \quad (2)$$

3. RESULTS AND DISCUSSION

3.1. Physicochemical characterization of the soil

Dry weight, humidity and pH were measured for the soil sample. For this, it was dried at 60°C for 12 h until a constant weight was obtained. The corresponding dry weight value was about 21.3%. Accordingly, the soil humidity was relatively constant, ranging from 79% to 80%. For pH measurement, carbonaceous soil (50 g) was centrifuged at 25 °C and 9000 rpm for 30 min; by using the small amount of extracted liquid, a pH evaluation was performed: achieving a value about 7.9. Also, as-received soil samples were dried at 105 °C and subsequently ground in an Agate mortar; a weighted amount of powder (1-2 g) was then treated according to Walkley titrimetric method, obtaining a mean value of 0.02 mg of carbon.

3.2. Electrokinetic experiments

Table 1. ESR for the removal of petroleum from carbonaceous soil samples: (1) amount of petroleum (in g) added to 800 g of soil; (2) treatment time (h); (3) current (A); (4) potential cell values (V) at 160 min of treatment; (5) pH conditions at the final of ESR; (6) conductivity (mS/cm); (7) temperature (°C). Electrolyte concentration: 0.1 M.

Test	**Soil pollution (1)**	$t^{(2)}$	$i^{(3)}$	**E** $^{(4)}$	**Anodic compartment**					**Cathodic compartment**				
					Anode	**Electrolyte**	**pH (5)**	**C** $^{(6)}$	**T** $^{(7)}$	**Cathode**	**Electrolyte**	**pH**	**C**	**T**
1	1.5	360	0.03	4.7	graphite	Na_2SO_4	1.71	229.3	26.5	graphite	Na_2SO_4	12.04	229.7	25.8
2	1.5	360	0.05	5.0	graphite	Na_2SO_4	1.14	230.1	27.5	graphite	Na_2SO_4	11.54	230.1	30.6
3	1.5	360	0.1	33.1	graphite	Na_2SO_4	2.04	230.5	27.2	graphite	Na_2SO_4	10.44	230.1	28.6
4	2.5	360	1	31.2	graphite	Na_2SO_4	1.21	230.9	26.9	graphite	Na_2SO_4	12.19	230.7	27.6

800 g of polluted soil were homogeneously mixed and used for ESR tests (see Table 1). Potential cell variations and final soil resistance were determined by applying constant currents ranging from 0.01 A to 1 A using 0.1 M of Na_2SO_4 as electrolyte at both electrode compartments. The supporting electrolyte has a significant influence on the organic pollutants removal, but Na_2SO_4 has already used by other authors [24] and it is considered a good chose because it does not affect significantly the nutrients present in the soil.

According to the potential measurements and current applied, a soil resistance increased as a function of ESR treatment. In fact, the potential increases as a function of time, in all cases and it is directly related to the resistance of soil (Fig. 2). However, when currents about 1 A and 0.1 A were applied, higher potential was achieved in short times, evidencing that the resistance of soil rapidly increased. Meanwhile, at lower currents, the potential was gradually increased. This behavior may be related to the transport of charged particles (e.g.: ions, molecules, colloids, etc.), limiting the pass of the current through the solid waste [25]. Then, the study of the pH and conductivity could give important information about the permeability of the polluted soil during the application of different currents, explaining the potential trends.

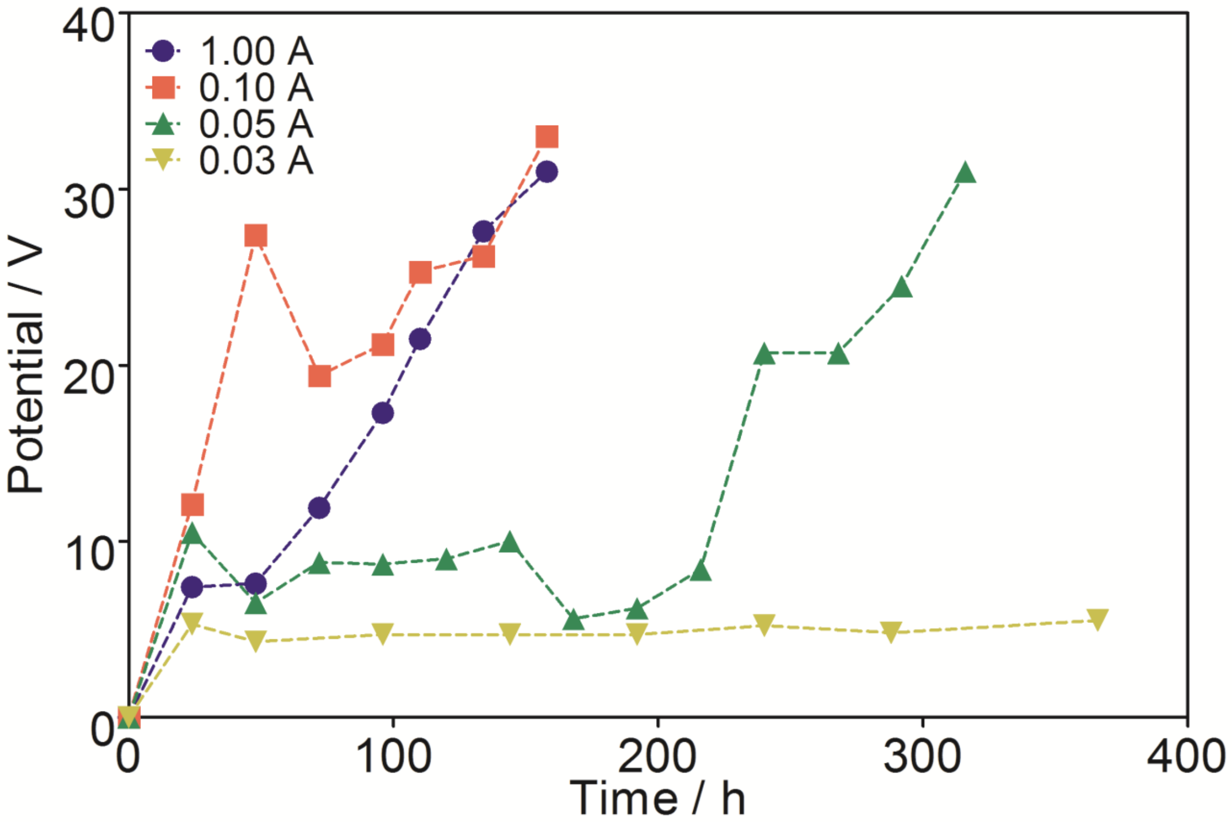


Figure 2. Influence of the current, as a function of time, during ESR for 800 g of carbonaceous soil polluted with petroleum at 25°C with 0.1M Na_2SO_4 as supporting electrolyte in anodic and cathodic compartments by using graphite electrodes.

In fact, important variations in pH (acidic and alkaline values in the anode and cathode reservoirs, respectively) and conductivity values were observed, as a result of water electrolysis (see Table 1) at graphite electrodes. Fig. 3 illustrates the changes on the pH conditions at anodic and cathodic compartments after 150 h of treatment by applying 1.0 A. Similar behavior was observed when 0.1 A; 0.05 A and 0.03 A were used for treating electrochemically the soil contaminated with petroleum.

The electrolysis of water favors the production of specific species at anode and cathode surfaces, respectively. In the former, oxygen gas and H^+ is produced in the anodic compartment (equation 3), while hydrogen gas and hydroxyl anions are formed at the cathode (equation 4). Then, both H^+ and OH^- are able to move across the soil, causing acidic and alkaline fronts to migrate through the porous media [25]. The former behavior causes contaminant desorption and/or dissociation, and results in an initiation of electromigration; while the alkaline front tends to precipitate the heavy-metals, in the latter.

$$2H_2O \rightarrow O_2(g) + 4H^+ + 4e^- \quad (3)$$

$$2H_2O + 2e^- \rightarrow 2OH^- + H_2(g) \quad (4)$$

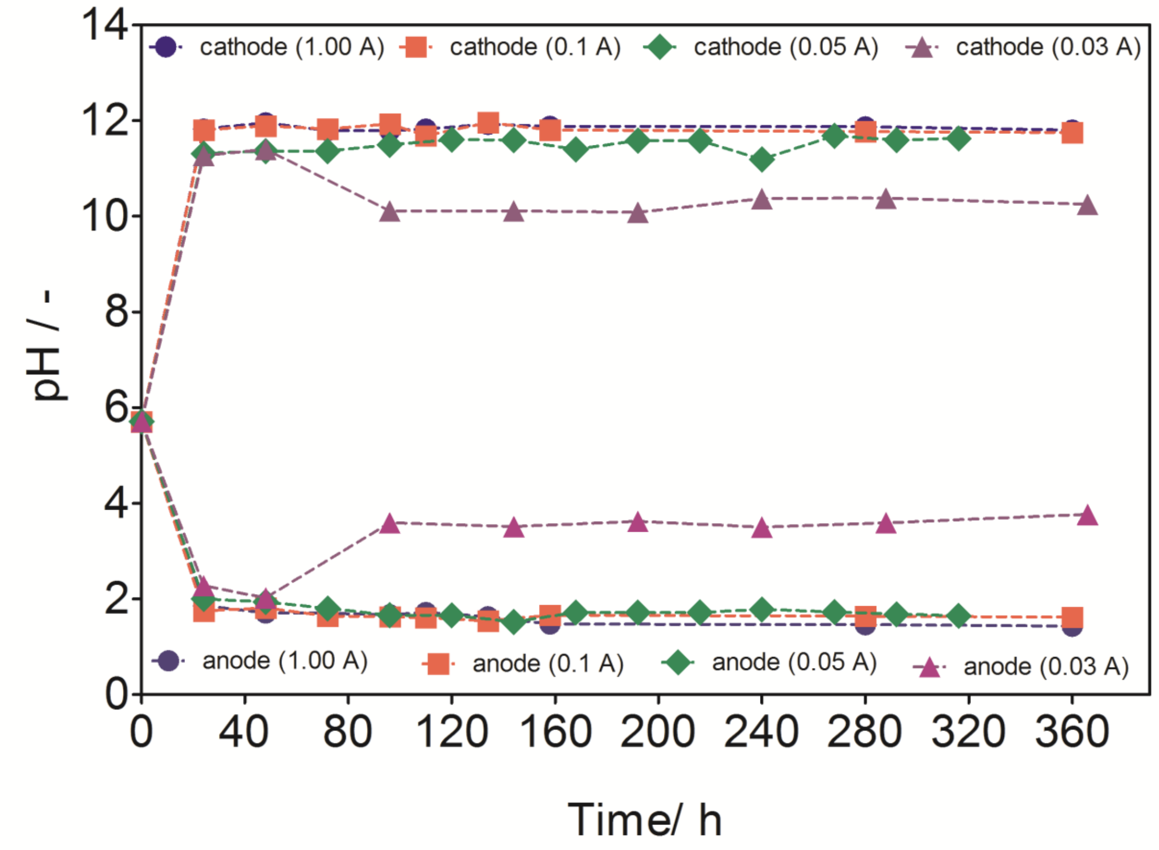


Figure 3. Effect of the pH conditions, as a function of time, at cathodic and anodic compartments during the ESR for removing petroleum from soil by applying different current values (0.03, 0.05, 0.1 and 1 A) at 25°C with 0.1 M Na_2SO_4 as supporting electrolyte by using graphite electrodes (see Table 1).

Secondary reactions may exist at the electrode compartments, which removal of the organic and inorganic pollutants can be accomplished by precipitation, ion exchange, or electrodeposition [25,26]. These behaviors are in agreement with the data in Fig. 2 because the pH conditions are an indicative of the rapid transport of the pollutants (inorganic or organic) through the soil (porosity) due to the effect of acidic or alkaline fronts. For currents of about 1.0 A and 0.1 A; pH about 2 and 12.1 are rapidly achieved at anodic and cathodic compartments and consequently, higher potentials are obtained after 100 min of treatment [25]. Conversely, at lower currents, a buffer pH effect is observed at the same time, mainly when 0.03 A are applied. This behavior could explain the lower rate increase of the potential values under these conditions (see Fig. 2). Also, problems of homogeneity in the soil samples results in some discrepancies in the potential obtained. Another interesting feature in the soil was that two differently colored areas were created during the electrokinetic treatment (the influence of petroleum migration). This behavior is related to the change in pH values at both soil bed sides (discussed below), forming a barrier. It consequently increased the resistance of the soil.

Meanwhile, the conductivity in the anodic and cathodic compartments had a similar behavior for all ESR experiments; a slight increase was achieved from 225.2 mS/cm to more than 229.5 mS/cm (Fig. 4). It is related to the concentration of supporting electrolyte that provides enough conductivity to the solution and the material into the soil is transported to the solutions, increasing slightly the conductivity [25, 26].

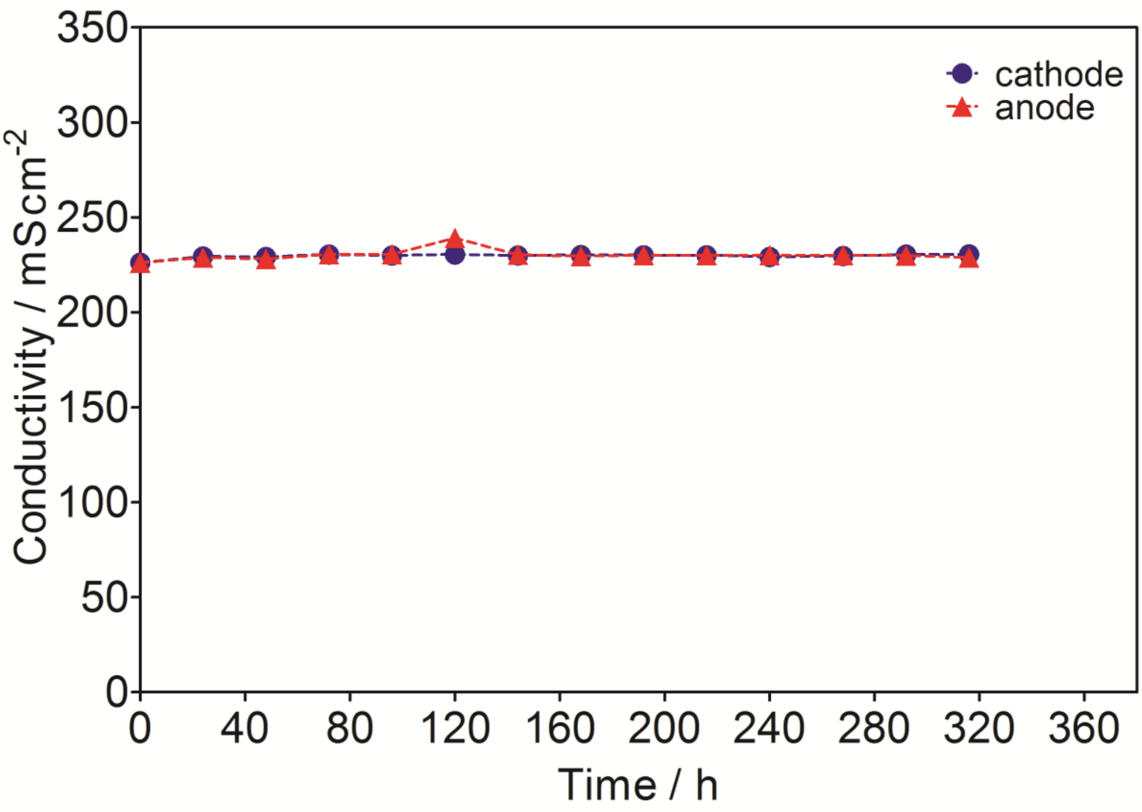


Figure 4. Effect of the conductivity, as a function of time, at cathodic and anodic compartments during the ESR for removing petroleum from soil by applying 1.0 A at 25°C with 0.1 M Na_2SO_4 as supporting electrolyte by using graphite electrodes.

ESR experiments were carried out during 360 h in order to evaluate the efficiency removal with similar petroleum pollution for test 1, 2 and 3; while an increase on the amount of petroleum spiked was achieved at test 4 (see Table 1). The transport of the organic matter from the soil to electrode compartments was effectively achieved, as showed in the photographs (Fig. 5).

In fact, in the beginning of the ESR treatment, uncolored solutions are present (Fig. 5a). After that, when a current is applied, the cathodic and anodic solutions acquire a characteristic coloration (Fig. 5b and c). In the case of cathodic compartment, a modest yellow color is assessed, while an intense black color is observed at the anodic reservoir. This indicates that the electrokinetic phenomena are promoted, allowing that the organic matter migrate to the electrodes compartments. Another interesting feature is that, a significant accumulation of petroleum, in the soil, is observed in the proximity to the anodic compartment (see Fig. 5c); it is probably the barrier formed during the transport of organic matter from center of soil to solutions, increasing the resistance of the sample and consequently, increasing the potential values (see Fig. 2).

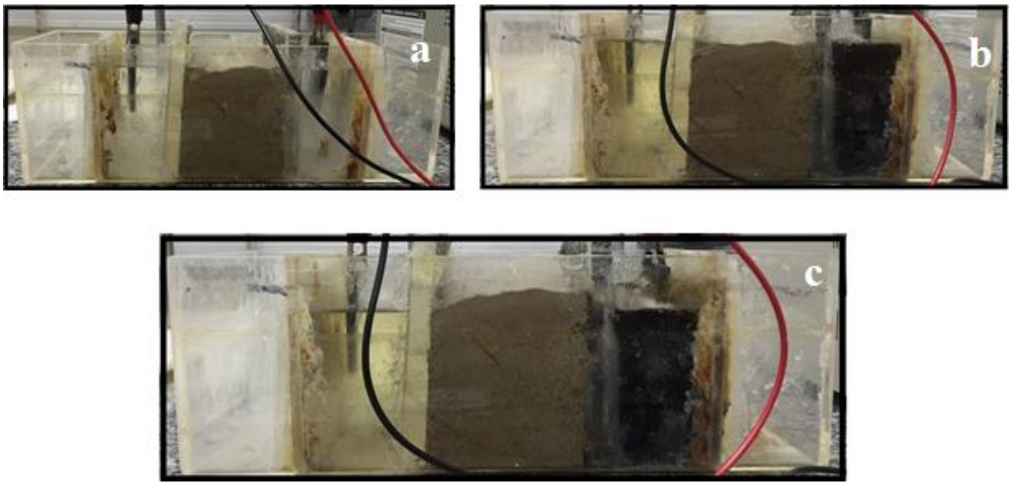


Figure 5. Transport of organic matter from soil to anodic compartment during the ESR treatment for 360 h of 800 g of soil sample polluted with petroleum (2.5 g) by applying 1.0 A at 25°C with 0.1 M Na_2SO_4 as supporting electrolyte by using graphite electrodes.

Regarding the solutions, spectrophotometric analyses were performed in order to confirm the color increase in the liquids during the ESR treatment. As can be observed in Fig. 6, the absorbance increases during the ESR process up to 100 min, after that, the color is relatively constant. This behavior confirms the migration of the pollutants from soil to the solutions. The result showed in the Fig. 6 was the general tendency observed under all experimental conditions studied. However, no quantitative information was obtained from these results because the determination was performed fixing a wavelength and measuring the absorbance changes attained, but the UV-vis spectra of solutions suffer different variations in a range between 190 nm and 800 nm, depending on the ESR conditions used. For this reason, the TOC measurements were carried out in the anodic and cathodic compartments during ESR treatment.

From the results of TOC monitored directly in the solutions during electrokinetic experiments, Fig. 7, the accumulation of organic matter was gradually achieved. This indicates that the pollutants (organic and inorganic) were induced to migrate from the soil to the anodic and cathodic compartments. Nevertheless, the elimination of petroleum from soil to solutions was significantly achieved in the anodic compartments when 0.05 A, 0.1 A and 1.0 A were applied. Conversely, at lower current (0.03 A), a gradual elimination was attained, limiting the induce transport of pollutants. This indicates that the electrokinetic phenomena (electromigration, electrophoreses and electroosmose) was efficiently favored [25-28]. But, secondary reactions in the anodic and cathodic compartments, such as gas evolution (oxygen, hydrogen and chlorine) can occur.

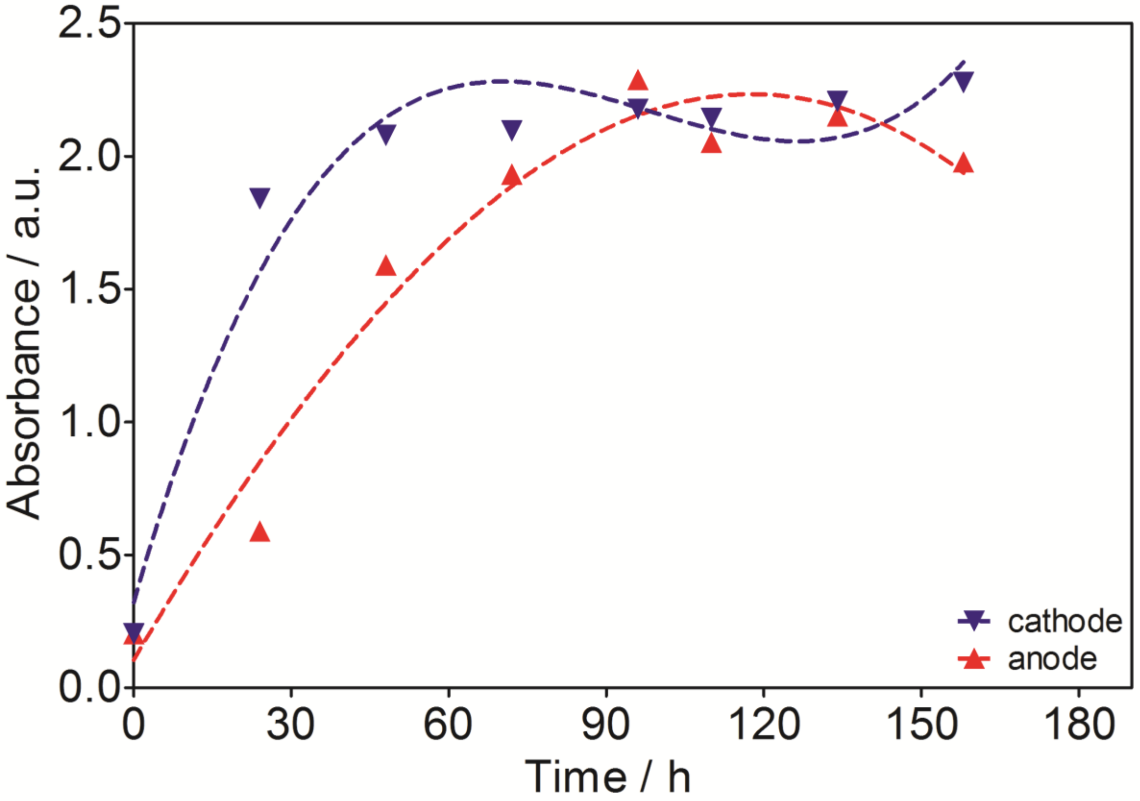
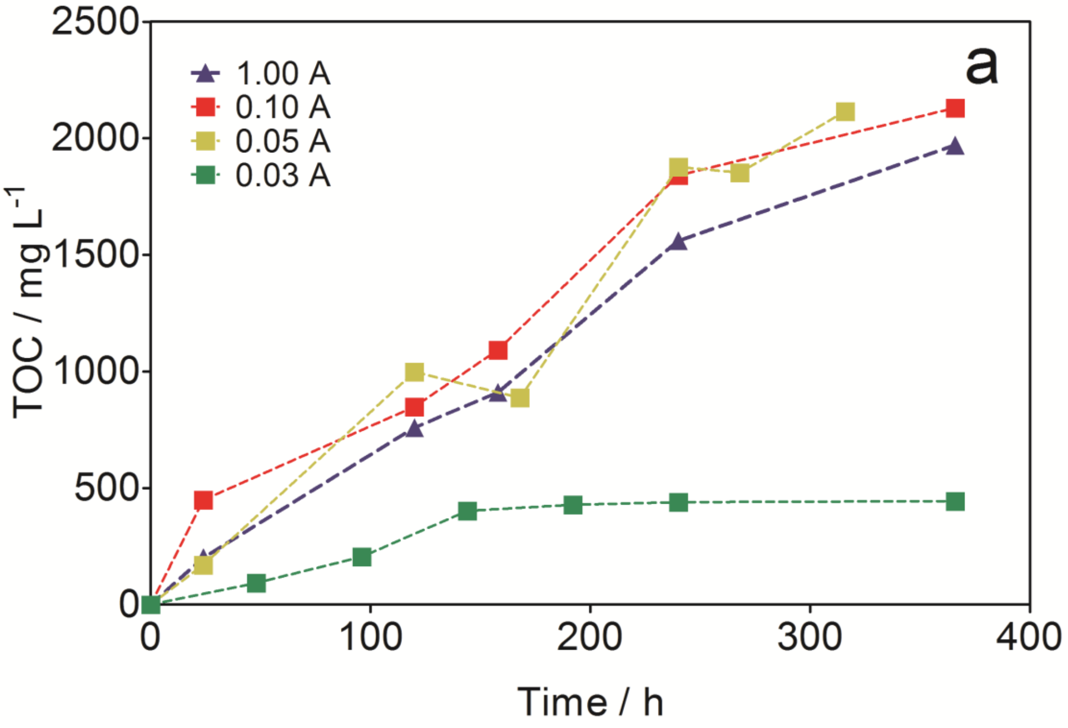


Figure 6. Absorbance increase in cathodic and anodic solutions, as a function of time, during the ESR treatment for removing petroleum from soil by applying 1.0 A at 25°C with 0.1 M Na_2SO_4 as supporting electrolyte by using graphite electrodes.



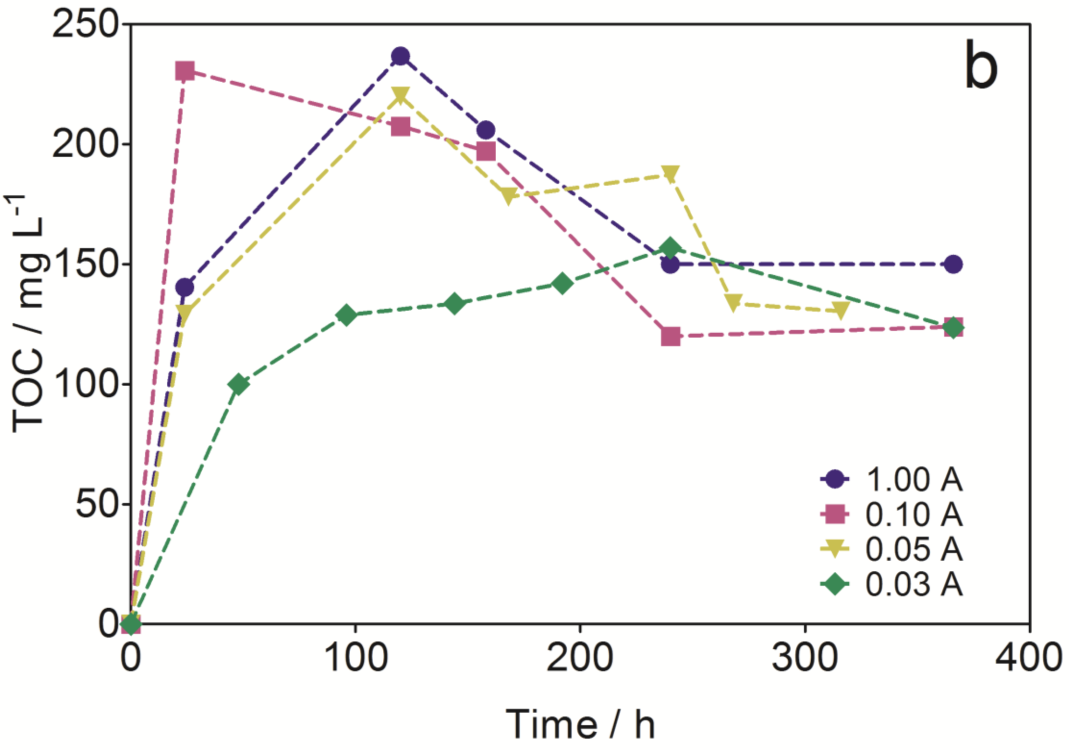


Figure 7. TOC evolution, as a function of time, at anodic (a) and cathodic (b) compartments during the ESR by applying different current values at 25°C with 0.1 M Na_2SO_4 as supporting electrolyte by using graphite electrodes.

Assuming that the water electrolysis favors the acidic and alkaline fronts that promote the mass transport phenomena through the soil, then, favorable pH conditions was achieved (see Fig. 3) at 0.05 A, 0.1 A and 1.0 A, favoring the organic matter removal from soil, mainly at anodic compartment. Instead, at cathodic reservoir, some organic pollutants are accumulated; however, the migration of positive species is favored due to the charge induction [25, 27,28]. Then, it is possible to deduce that pollutants that have a positive charge are transported from soil to cathodic solution. Nevertheless, the TOC decay observed, in all cases, after 100 min of treatment to be due to the secondary chemical processes that occur in the cathode or solution, such as precipitation, sedimentation and so on.

Another feature is that, ESR approach induces to the formation of micelles or microdrops of petroleum with negative or positive charge [28,29]. Then, in consideration of the fact that, the changes in the surface charge of pollutants can give information about the mechanisms of elimination of petroleum form soil, z-potential was monitored during the treatments at both solution compartments. These changes are shown in Fig. 8 during the tests exhibited a superficial charge of –18.58 mV at cathodic compartment while the value of the effluent at anodic reservoir was about –61.51 mV. Then, the increase in the z-potential towards more positive values observed during the ESR treatment in the effluents suggests that the treatment leads to the particles less negative than those contained in the soil. The type of change depends only on the pollutants removed which may indicate a more efficient depletion of the organic and inorganic pollutants from soil, where the negative species, predominantly in the anodic compartment, are stabilized to neutral species may be due to the acidic front observed.

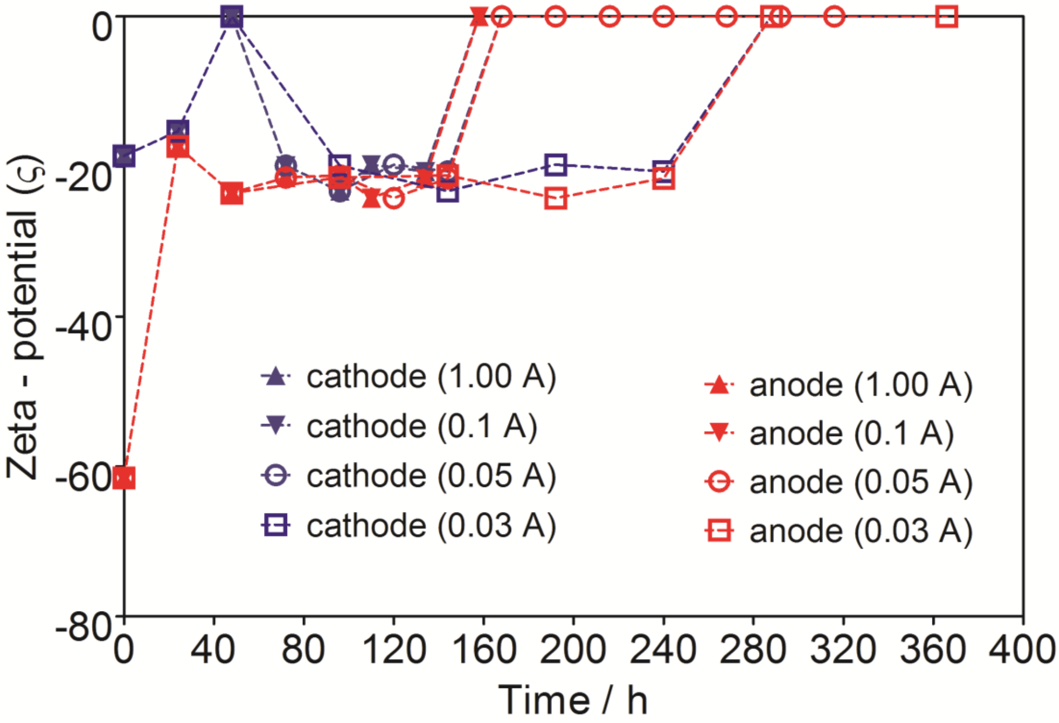


Figure 8. z-potential evolution, as a function of time, at anodic and cathodic compartments during the ESR by applying different currents at 25°C with 0.1 M Na_2SO_4 as supporting electrolyte by using graphite electrodes.

Meanwhile, at cathodic compartment, more positive species are present, in fact, less z-potential was measured, but these pollutants can be precipitated, agglomerated or sedimented due to the secondary reactions attained at the cathode electrode as well as the alkaline front observed (see Fig. 3).

Table 2. Energetic and cost requirements for removing petroleum from carbonaceous soil: (1) amount of petroleum (in g) added to 800 g of soil; (2) treatment time (h); (3) current (A); (4) potential cell values (V); (5) energy consumption in kWh/m^3. Electrolyte concentration: 0.1 M.

Test	**Soil pollution** (1)	***t*** (2)	***i*** (3)	**E** (4)	**EC** (5)	**Cost (real/Kg)**
1	1.5	360	0.03	4.7	52.8	21.15
2	1.5	360	0.05	5.0	93.7	37.5
3	1.5	360	0.1	33.1	1241.2	496.5
4	2.5	360	1	31.2	11700	4680

Likewise, the z-potential of the particles obtained at the final of treatment remains in the same range for all processes, with values ≈ -0.1 mV. Based on the results obtained, for decontamination of soil polluted with petroleum with a low solubility in water, the ESR treatment is an efficient method to extract petrochemical contaminants from soil because high efficiencies were attained. This indicates that, the characteristics of the decontamination strongly depend on the electrokinetic phenomena favored by pH conditions, porosity and formation of micelles/microdrops of pollutants, and probably, the elimination of petroleum contamination is more significant when soft electrical conditions were used (0.03 A and 0.05A) [29-31]. Latter indication is completely related to the energy consumption of the process. In fact, higher currents promoted a higher energy consumption of ESR treatment, as showed in Table 2.

3.3. Bulk electrolysis of waste produced by ESR

The depollution of soil leads to generate contaminated effluents and these must be treated. In this context, the efficacy of BDD-electrolysis was evaluated by treating these effluents with higher TOC contents. Fig. 9 shows COD decay, as a function of time, during the treatment of polluted fluid obtained after ESR via BDD-electrolysis by applying 20 and 60 mA cm^{-2}. As can be observed, partial degradation of the organic matter in the waste was attained at both applied current densities. However, at 20 mA/cm^2, the COD decay was more rapid in the beginning of the process. Conversely, a slower elimination of organic matter from solution was attained at 60 mA/cm^2. These findings indicate that the raw pollutants were not completely degraded but partially oxidized [32-40]. This leads to the formation of reaction intermediates due to the break-up of the molecules or even to the simple attack to any functional group by means of the oxidant agents generated at BDD-electrolysis [32,33, 35]. However, in general, this behavior indicates that, organic pollutants are efficiently removed from washing fluid, and their by-products formed during the application of these oxidative processes [33,36,39].

BDD-electrolysis generates strong oxidant species [32] in solution (e.g.: hydroxyl radicals ($^{\bullet}$OH), active chlorine, peroxophospates, etc.) that are the responsible on the elimination of organic matter. In the case of BDD anode, the degradation reactions mainly occur via the action of $^{\bullet}$OH radicals by water discharge (equation 5) [32,33,35]:

$$H_2O \rightarrow {}^{\bullet}OH + H^+ + e \qquad (5)$$

At this point, it is worth taking into account that, the wastes contain higher concentration of sulfates. Then, the oxidation of sulfate ions can lead to the formation of persulfates during the electrochemical treatments (equation 6), as previously suggested [34]:

$$2\ SO_4^{2-} \rightarrow S_2O_8^{2-} + 2\ e^- \qquad (6)$$

When these oxidants are produced by BDD-electrolysis, these are also considered the responsible species for the electrochemical combustion of organic pollutants in the effluents generated at ESR treatment, as can observed in previous studies [32-40].

In order to evaluate the efficiency of the second depollution system, we estimate the energy consumptions as a function of percentage of COD removal. Table 3 shows the energy consumption required for each one of the treatments by applying 20 and 60 mA cm^{-2}. As can be observed, higher energy consumption was spent when higher applied current density was applied with lower efficacy to remove organic pollutants from washing liquid.

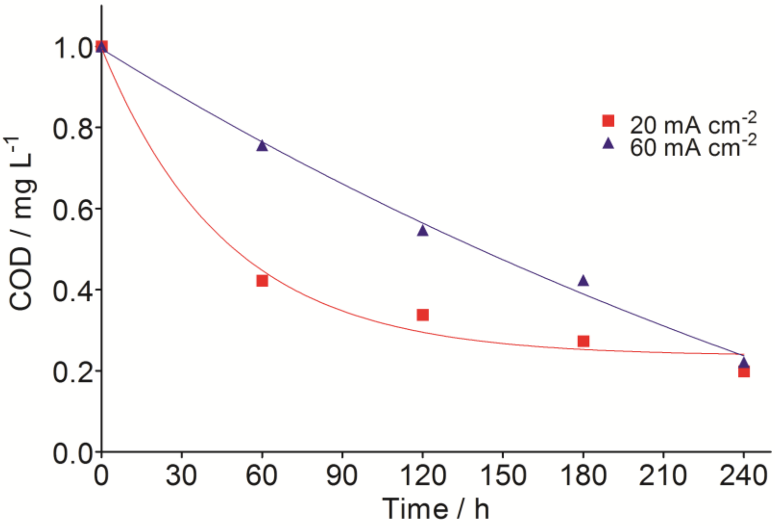


Figure 9. Effect of the COD evolution, as a function of time, during the electrochemical treatment of effluents produced after ESR of soil polluted with petroleum by applying 20 and 60 mA cm^{-2}.

Table 3. BDD-electrolysis conditions for removing organic matter from effluents obtained after ESR treatment: (1) applied current density (mA/cm^2); (2) treatment time (h); (3) percentage of COD removal; (4) energy consumption in kWh/m^3.

j **(1)**	***t*** **(2)**	**COD removal (3)**	**EC (4)**	**Cost (real/m^3)**
20	4	76.1	34.15	19.35
60	4	81.5	157.00	88.96

This indicates that side reaction, such as oxygen evolution, is promoted when 60 mA cm^{-2} was used, and consequently, reducing the efficacy of the treatment process. Conversely, higher elimination of organic matter was achieved (more than 80% of COD removal) by using BDD-electrolysis at 20 mA cm^{-2} with modest energy requirements.

4. CONCLUSIONS

- Electrokinetic remediation showed to be a feasible methodology to remove petroleum contamination from soil. However, the characteristics of the decontamination strongly depend on the electrokinetic phenomena favored by pH conditions, porosity and formation of micelles/microdrops of pollutants, and probably, the elimination of petroleum contamination is more significant when soft electrical conditions were used (0.03 A and 0.05A)

- The combination of two electrochemical technologies was considered an efficient approach for removing petroleum pollutants from soil and effluents.
- BDD-electrolysis is a good chose for treating effluents generated by ESR because the oxidants electrochemically produced (hydroxyl radicals and persulfate) in solution eliminate efficiently the dissolved organic matter.

ACKNOWLEDGEMENTS
The authors are grateful to PRH-22 program for the financial support to this work. Brazilian financial support from National Council for Scientific and Technological Development (CNPq - 446846/2014-7 and CNPq - 401519/2014-7) is gratefully acknowledged. E.B.S. da Silva, M.D. de Lima and M.M. Oliveira acknowledge the PhD and IC grants awarded from PETROBRAS and CNPq.

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