

Scale-up on Electrokinetic Treatment of Polluted Soil with Petroleum: Effect of Operating Conditions

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This study investigates the influence of the scale-up of electrokinetic remediation (EKR) approach in carbonaceous soils. The scale-up study was performed in an electrokinetic lab scale (2.55 dm^3) by using two graphite electrodes placed in the cathodic and anodic compartments. The solution used was to humidify the soil were Na_2SO_4 0.1 M and water. A soil polluted (1.5 Kg) with petroleum (ranging from 500 to 2500 ppm) was treated by applying different currents (ranging from 0.5 A to 0.2 A). The effects such as current, pH, conductivity, z-potential and solution were evaluated to understand the better conditions to remove the organic matter from polluted soil. An increase in scale directly influenced the amount of energy supplied to the soil being treated. As a result, electroosmotic and electromigration flows and electric heating are more intense than in previous study performed where a smaller-scale cell was used.

Keywords: electrokinetic treatment, petroleum, scale-up, soil remediation, z-potential.

1. INTRODUCTION

Electrokinetics (EK) or electrochemical soil remediation (ESR), is a depollution technology where direct current is applied within subsurface porous media to induce specific transport phenomena (Fig. 1) [1]: electroosmosis, electromigration and electrophoresis. In the first case, the bulk movement of fluid through pores is attained, while the movement of ions in solution is achieved in the second phenomenon. Meanwhile, the movement of charged, dissolved or suspended particles in pore fluid is achieved by electrophoresis.

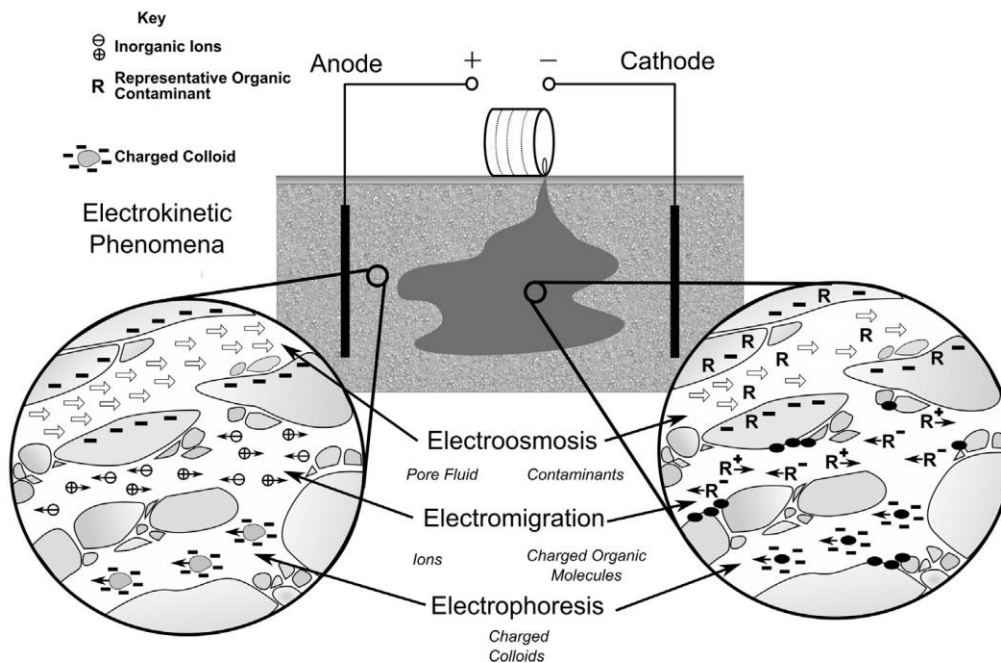


Figure 1. Phenomena achieved during EK processes to eliminate dissolved-phase organic substances in the saturated zone. Adapted from [1].

The electrolysis of water at the electrodes [2] is also a characteristic of the EK:



while water reduction at the cathode produces an alkaline front, which will move toward the anode:



The reaction products, hydrogen (H^+) and hydroxyl (OH^-) ions migrate towards their oppositely charged electrode, generating acid and base fronts [3]. Electromigration and electroosmosis are independent of hydraulic conductivity and EK can be used to generate mass flux in zones impervious to advective transport [4]. At the same time, secondary reactions are feasible at the cathode, as the elimination of metals:



The elimination of the organic and inorganic contaminants can be also accomplished by electrodeposition, precipitation, or ion exchange, either at the electrodes or in an external extraction system. These principles about the EK approach have been reviewed by Acar and Alshwabkeh [3], Virkutyte et al. [4], Yeung and Gu [5].

EK treatment promotes the release of organic contaminants bound to clay particles and organic matter in soils and sediments [6-8] favoring an efficient decontamination. This effect is due to disruption of the surface charge that binds molecules to soil particle surfaces by the advective flux resulting from electroosmosis. However, no complete elimination of pollutants is achieved due to the heterogeneity that take place naturally in electroosmotic flow from changes in pH, voltage gradient and electrical conductivity [9-16]. Therefore, the present work concerns a laboratory investigation on the

use of an EK treatment for removing of petroleum from a carbonaceous soil, investigating the effects of current, contamination concentration, pH, energy consumption and effluents produced.

2. MATERIALS AND METHODS

2.1. Reagents

Petroleum (American Petroleum Institute (API) gravity > 30, it consists basically of alkanes, and approximately 15 to 25% of cycloalkanes) and hexane were obtained from Sigma-Aldrich (Spain). Chemicals were of the highest quality commercially available, and were used without further purification: FeSO₄, K₂CrO₇, H₂SO₄ and Na₂SO₄ were purchased from Fluka. Deionized water (Millipore Milli-Q system) was used to prepare all solutions.

2.2. Soil

Spiking soil samples with organic compounds is a common pollution method used in the laboratory studies [11,12], for this reason, carbonaceous soil was chosen as model soil and polluted with petroleum. Petroleum-contaminated samples were prepared by mixing raw soil and crude oil. Samples of polluted soil were prepared by dissolving a known amount of petroleum (0.5 g and 2.5 g) in 50 mL of hexane and then mixing this petroleum/hexane solution with soil (1.5 Kg). The spiked soil was aerated for 24 h to evaporate the hexane and, in this way; the petroleum was homogeneously distributed on the soil.

2.3. Physicochemical Characteristics

Soil sample was analyzed for sludge conductivity, particle-size distribution and pH, based on the standard method; humidity and dry weight were also determined according to the UNI EN 12880:2002, UNI-EN 13346:2002 and EPA-SW 846-3051 official European methods, as reported in [13, 16].

2.4. EK cell description

A closed system, similar to the previous work [13], with a sludge bed, two electrode compartments and electrical contacts was used for EK tests; however, dimensions of current cell were increased in order to scale-up the technology (25 × 10 × 10 cm). Graphite electrodes were used as anode and cathode with about 50 cm². Filter-paper separations were used to separate the soil sample from electrode compartments. Supporting electrolyte (Na₂SO₄ 0.1 M) was manually added in the electrodes compartments, when necessary. EK studies were performed by using the same

electrochemical cell for testing different experimental conditions: applied current (ranging from 0.05 A to 0.2 A), treatment time and petroleum contamination (0.5 g and 2.5 g).

2.5. Electrokinetic experiment conditions

Graphite electrodes were employed, and then different operating conditions were investigated during 360 h. To gain information about the process, cell potential, pH, temperature and conductivity were measured before and after each treatment, in the soil and in cathodic and anodic compartments. In the case of soil, a sample was drawn and mixed with water by using a bortex for 5 min to favor the determination of pH and conductivity via the complex composition of soil in the water. For temperature, it was directly measured in the soil sample with a thermometer. For pH, temperature and conductivity in the cathodic and anodic compartments, these parameters were directly measured in the solutions after or before of ESR treatment. A sample of 1.5 Kg of homogenized soil was placed in the EK cell. 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 reservoir solutions and zeta potential (z-potential) was also measured using a Zeta Meter System 3.0+[®].

2.6. Energy consumption and costs

The energy consumption for the removal of one m³ of soil was estimated in order to determine the viability of the EK approach (Equation 4). Also, the electrical energy cost of about 0.4 real per kWh (Brazil) was considered to estimate the cost of the remediation process by Equation 5.

$$\text{Energy consumption (kWh/m}^3\text{)} = \frac{[\text{Test energy (Wh)/1000}]}{\text{Volume (m}^3\text{)}} \quad (4)$$

$$\text{Cost (Real/m}^3\text{)} = \text{Energy consumption (kWh/m}^3\text{)} \times 0.4 \text{ (real/kWh)} \quad (5)$$

3. RESULTS AND DISCUSSION

3.1. Physicochemical characterization of the Sludge

Carbonaceous soil samples were dried at two temperatures, 60 and 105 °C, for 12 h or more (until a constant weight was obtained). Two specimens were initially considered: the corresponding dry weight values were 21.3% and 21.0% at 60°C, whereas 20.5% and 20.1% at 105 °C. Accordingly, the soil humidity was relatively constant, for the two samples and at both temperatures, ranging from 79% to 80%. For pH measurement, soil specimens (50 g) were centrifuged at 20 °C and 9000 rpm for 30 min; by using the small amount of extracted liquid, a pH evaluation was performed, obtaining a pH, equal to 6.12.

3.2. Preliminary EK test: Current-potential behavior

1.5 Kg of polluted soil were homogeneously mixed and used for ESR tests by applying different currents (ranging from 0.05 A to 0.2 A) using 0.1 M of Na_2SO_4 as electrolyte at both electrode compartments (see Table 1). Na_2SO_4 was the supporting electrolyte used [14,15] because it does not affect significantly the nutrients present in the soil. Potential cell variations and final soil resistance were determined.

Table 1. ESR operating conditions for removing petroleum from carbonaceous soil samples: (1) amount of petroleum (in g) added to 1.5 Kg of soil; (2) treatment time (h); (3) current (A); (4) temperature ($^{\circ}\text{C}$) and (5) potable water, this medium was only considered with its actual conductivity. Na_2SO_4 concentration: 0.1M.

Test	Soil pollution ⁽¹⁾	t ⁽²⁾	i ⁽³⁾	Anode reservoir			Cathode reservoir		
				Anode	Solution	T ⁽⁴⁾	Cathode	Solution	T
1	1.5	360	0.05	graphite	Na_2SO_4	26.5	graphite	Na_2SO_4	25.8
2	1.5	360	0.1	graphite	Na_2SO_4	27.5	graphite	Na_2SO_4	30.6
3	1.5	360	0.2	graphite	Na_2SO_4	27.2	graphite	Na_2SO_4	28.6
4	2.5	360	0.1	graphite	Na_2SO_4	26.9	graphite	Na_2SO_4	27.6
5	0.5	360	0.1	graphite	Na_2SO_4	26.9	graphite	Na_2SO_4	27.6
6	2.5	360	0.1	graphite	potable water ⁽⁵⁾	26.9	graphite	potable water ⁽⁵⁾	27.6
7	0.5	360	0.1	graphite	potable water ⁽⁵⁾	26.9	graphite	potable water ⁽⁵⁾	27.6

According to the potential measurements, it increases with an increase on the current applied (Fig. 2). Also, this parameter is directly related to the resistance of soil, then, it also increases when an increase on the current is attained. At 0.2 A, higher potential was achieved in short times, evidencing that the resistance of soil rapidly increased. Conversely, 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 [1,15,16]. 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. As commented in the introduction, porous media to induce specific transport phenomena, electroosmosis (the bulk movement of fluid through pores); electromigration (the movement of ions in solution); and electrophoresis (the movement of charged, dissolved or suspended particles in pore fluid), and all of them are related to the acidic and alkaline fronts and conductivity [1].

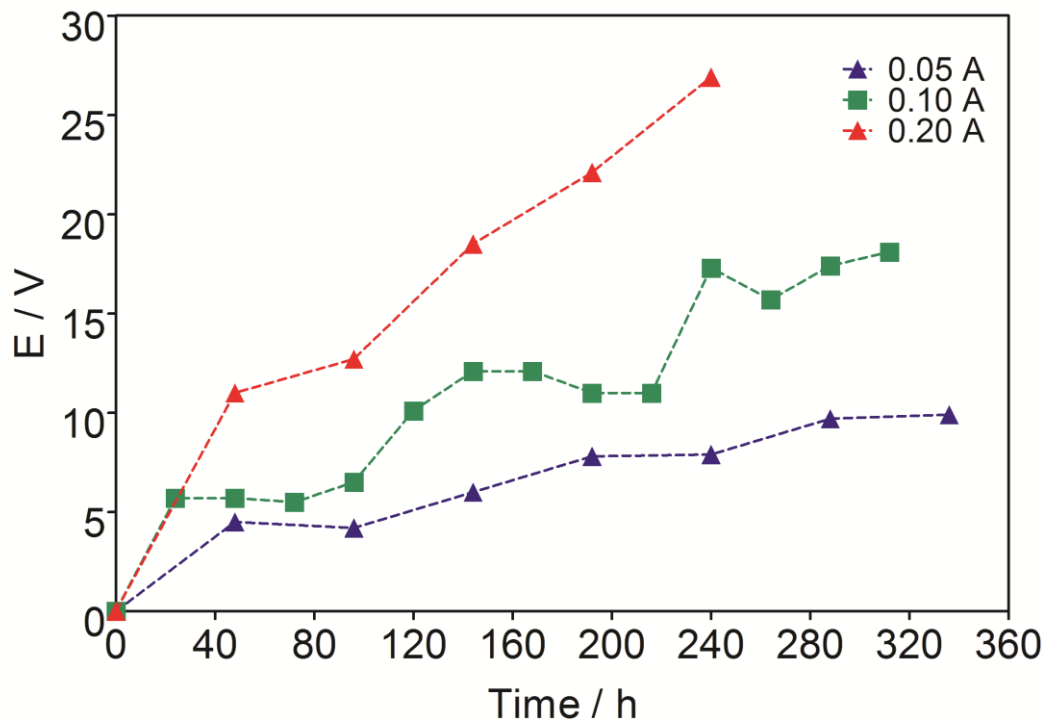


Figure 2. Dependence of E on time at different applied, as a function of time, during ESR for 1.5 Kg of carbonaceous soil polluted with petroleum at 25°C using 0.1 M Na₂SO₄ as supporting electrolyte in anodic and cathodic compartments with graphite electrodes (see Table 1).

In fact, variations on the pH conditions at the anode and cathode compartments as well as the conductivity were observed, as a consequence of water electrolysis at graphite electrodes [13]. Fig. 3 illustrates the changes on the pH conditions at anodic and cathodic compartments after 360 h of treatment at different currents. By applying 0.05 A and 0.2 A; acidic (~1.5) and alkaline (~12) conditions were registered, at the anodic and cathodic solutions, respectively. This behavior is in accordance with the electrode reactions (equations 1 and 2). Conversely, different pH conditions were achieved when 0.1 A was applied (acidic (~4.0) and alkaline (~10.5) conditions were attained, for anodic and cathodic reservoir solutions). This indicates that, buffer solution-potential conditions were attained because O_{2(g)} and H⁺ in the anode compartment were produced while H_{2(g)} and hydroxyl anions are formed at the cathode due to the water electrolysis reaction; then, both H⁺ and OH⁻ are able to move across the soil, causing an acidic and an alkaline front to migrate through the porous media [15,16]. 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 [1,13,15,16].

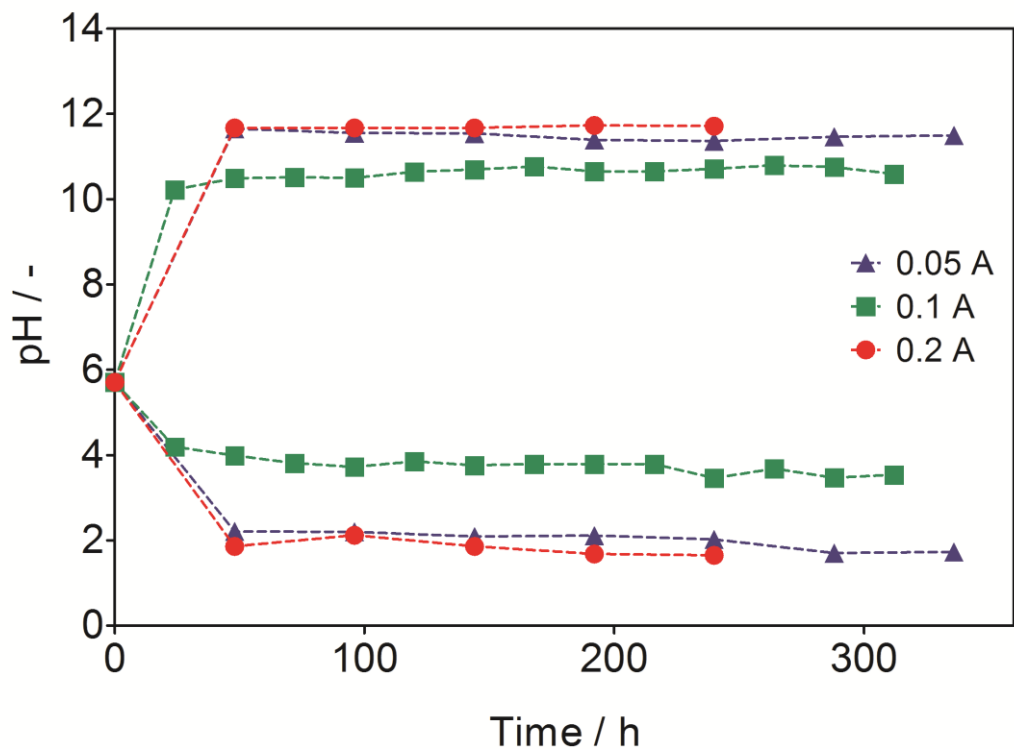


Figure 3. Effect of the pH conditions at cathodic (alkaline) and anodic (acidic) reservoirs during the ESR of 1.5 Kg of carbonaceous soil polluted with petroleum by applying different currents at 25°C using 0.1 M Na₂SO₄ as supporting electrolyte.

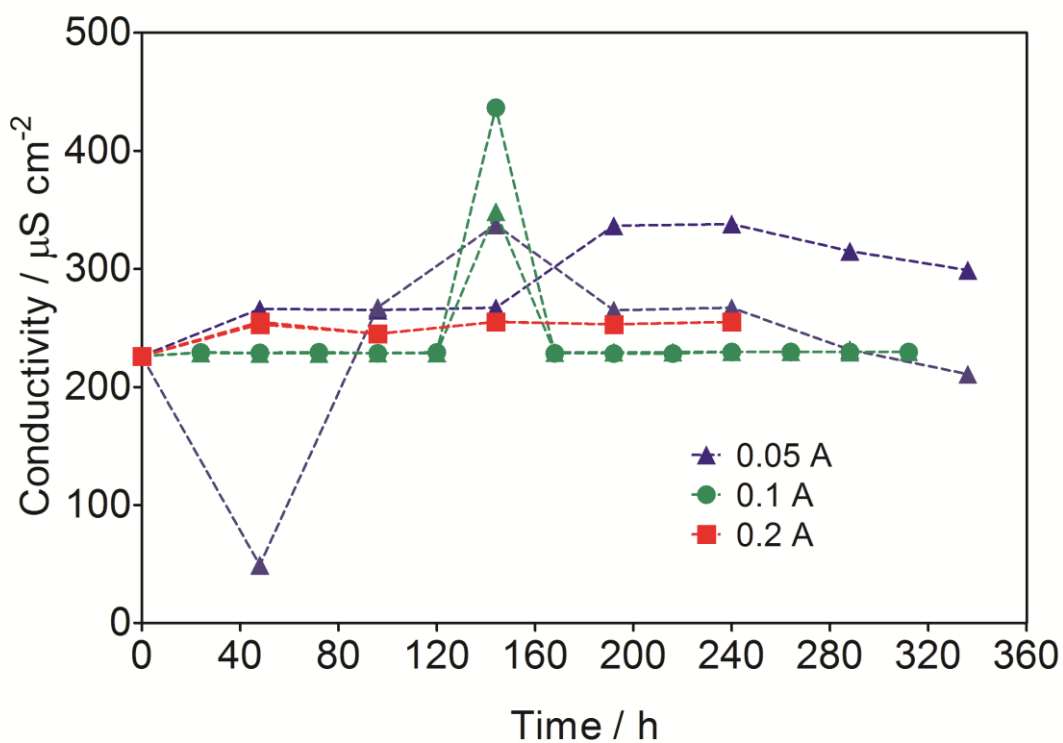


Figure 4. Effect of the conductivity at cathodic and anodic reservoirs during the ESR of 1.5 Kg of carbonaceous soil polluted with petroleum by applying different currents at 25°C using 0.1 M Na₂SO₄ as supporting electrolyte (see Table 1).

On the other hand, the conductivity in the electrode reservoirs had a comparable behavior for all ESR experiments; a slight increase was achieved (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 [15-18].

Another interesting feature is that, potential-time behavior demonstrates to be constant (Fig. 2), and consequently, favoring the electroosmotic conditions to remove organic matter in the soil. For this reason, an increase in petroleum concentration in electrode reservoirs can be expected because the organic pollutants can migrate from the soil to reservoirs. This behavior is demonstrated by the TOC evolution during ESR treatment, as reported in Fig 5. In fact, in the beginning of the ESR treatment, the absence of organic matter confirms the non-migration of species. After that, when a current is applied, the cathodic and anodic solutions acquire a characteristic coloration (Fig. 6). In the case of cathodic compartment, a modest yellow color is assessed, while an intense black color is registered at the anodic reservoir. This indicates that the electrokinetic phenomena are promoted, allowing that the organic matter migrate to the electrodes compartments [15-17].

Another interesting feature is that, a significant accumulation of petroleum, in the soil, is observed in the proximity to the anodic reservoir (see Fig. 6); 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).

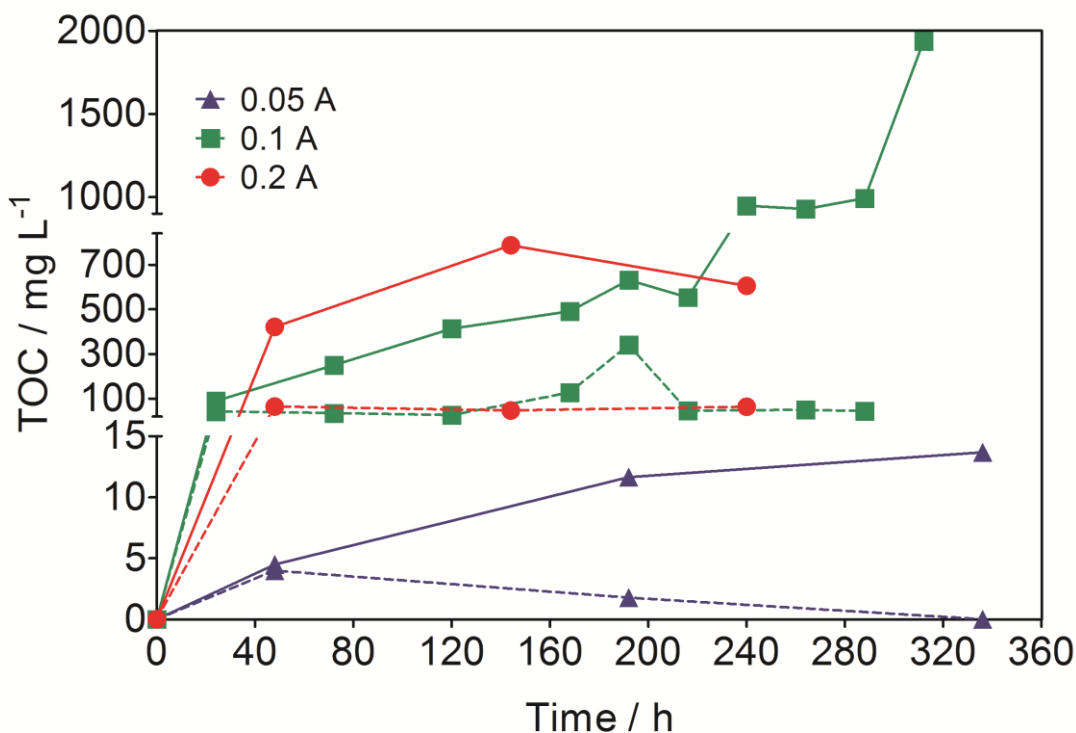


Figure 5. TOC evolution in the solutions of anodic (—) and cathodic (-----) reservoirs, as a function of time, for different applied currents during the ESR of 1.5 Kg of carbonaceous soil polluted with petroleum at 25°C using 0.1 M Na₂SO₄ as supporting electrolyte (see Table 1).

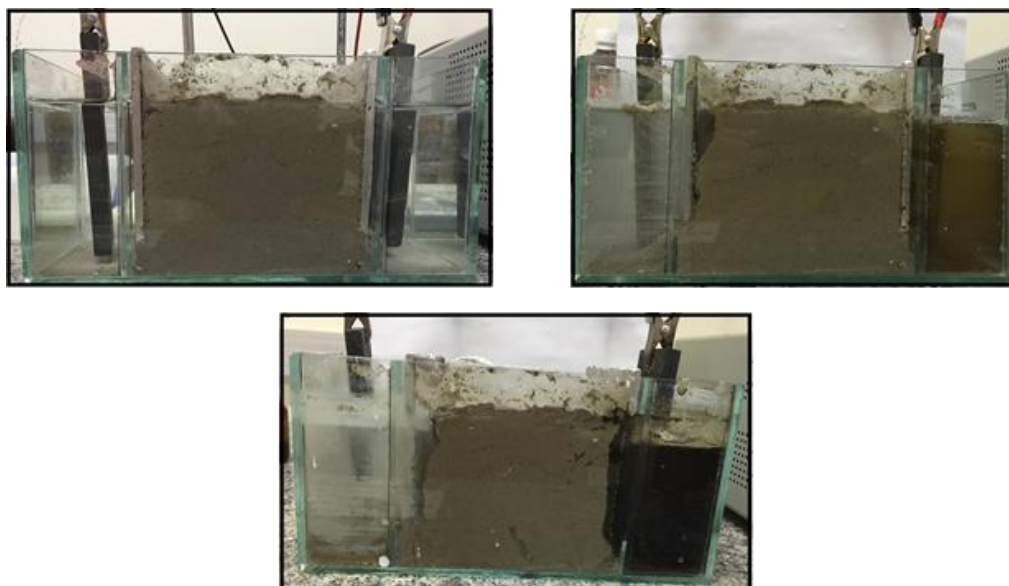


Figure 6. Electrochemical cell used during ESR experiments under experimental conditions reported in Table 1.

From the results of TOC monitored directly in the solutions during electrokinetic experiments, Fig. 5, the accumulation of organic matter was gradually achieved. However, the elimination of petroleum from soil to solutions was significantly achieved in the anodic reservoir when 0.1 A was applied. Conversely, at lower (0.05 A) and higher (0.2 A) currents, a gradual accumulation of petroleum in the electrode compartments was attained, limiting the induced transport of pollutants by electrokinetic phenomena (electromigration, electrophoresis and electroosmosis). Assuming that the water electrolysis favors the acidic and alkaline fronts that promote the mass transport phenomena through the soil, then, favorable pH conditions were achieved at 0.1 A, favoring the organic matter removal from soil, mainly at the anodic compartment, by the induced charge (negative species). In this way, the ESR approach induces the formation of micelles or microdrops of petroleum with negative or positive charge [15]. Then, the surface charge of pollutants is related to the z-potential, and its study could reveal information about the treatment. As can be observed in Fig. 7, no specific charge was detected when lower (0.05 A) and higher (0.2 A) currents were applied, achieving approximately a z-potential value of zero. Meanwhile, at 0.1 A, a superficial charge of -60.58 mV at the cathodic compartment was attained while the value of the effluent at the anodic reservoir was about -20.2 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 particles less negative than those contained in the soil [18]. 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 due to the acidic front observed [13,15-18]. Meanwhile, at the cathodic reservoir, more positive species are present, in fact, a minor 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. 2).

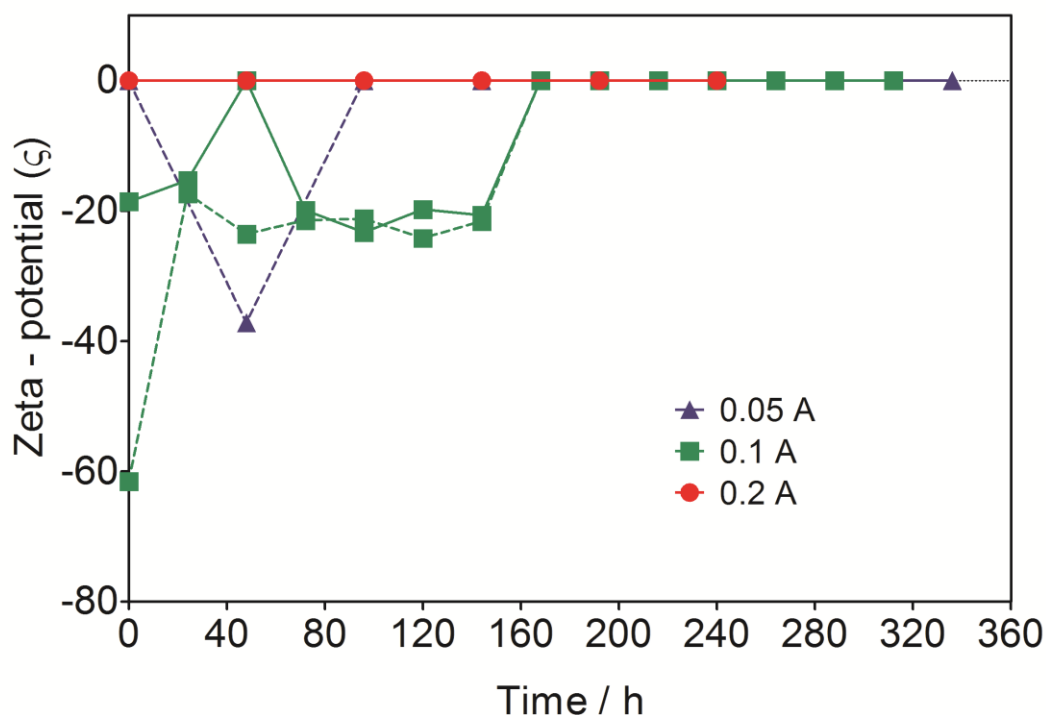


Figure 7. Effect of the z-potential evolution, as a function of time, at the solutions of anodic and cathodic reservoirs during the ESR of 1.5 Kg of carbonaceous soil polluted with petroleum at 25°C using 0.1 M Na₂SO₄ as supporting electrolyte by applying different currents.

3.3. EK experiments: different petroleum contamination

1.5 Kg of soil was homogeneously mixed with an amount of petroleum ranging from 500 to 2500 ppm (see Table 1). The progress of the cell potential was recorded, as a function of time and petroleum contamination, using Na₂SO₄ as supporting solution at both reservoirs (Fig. 8). Results clearly showed a linear dependence, indicating that lower pollution favors a rapid increase on the potential cell. This behavior is related to the pH conditions and the conductivity of the soil, which was evaluated during ESR experiments under different contamination of petroleum. In the case of conductivity, similar behavior was observed with an increment peaks during the ESR tests. However, the pH conditions were significantly affected by the amount of petroleum in the soil (Fig. 8). Species are desorbed from soil particles due to the acidic front during the treatment, and consequently, the pollutants are progressively transported towards the cathode by electroosmotic purging and electromigration [13,15-17]. Later phenomena promoted the migration of different organic species to the electrode compartments increasing their concentration as a function of the treatment time (Fig. 8).

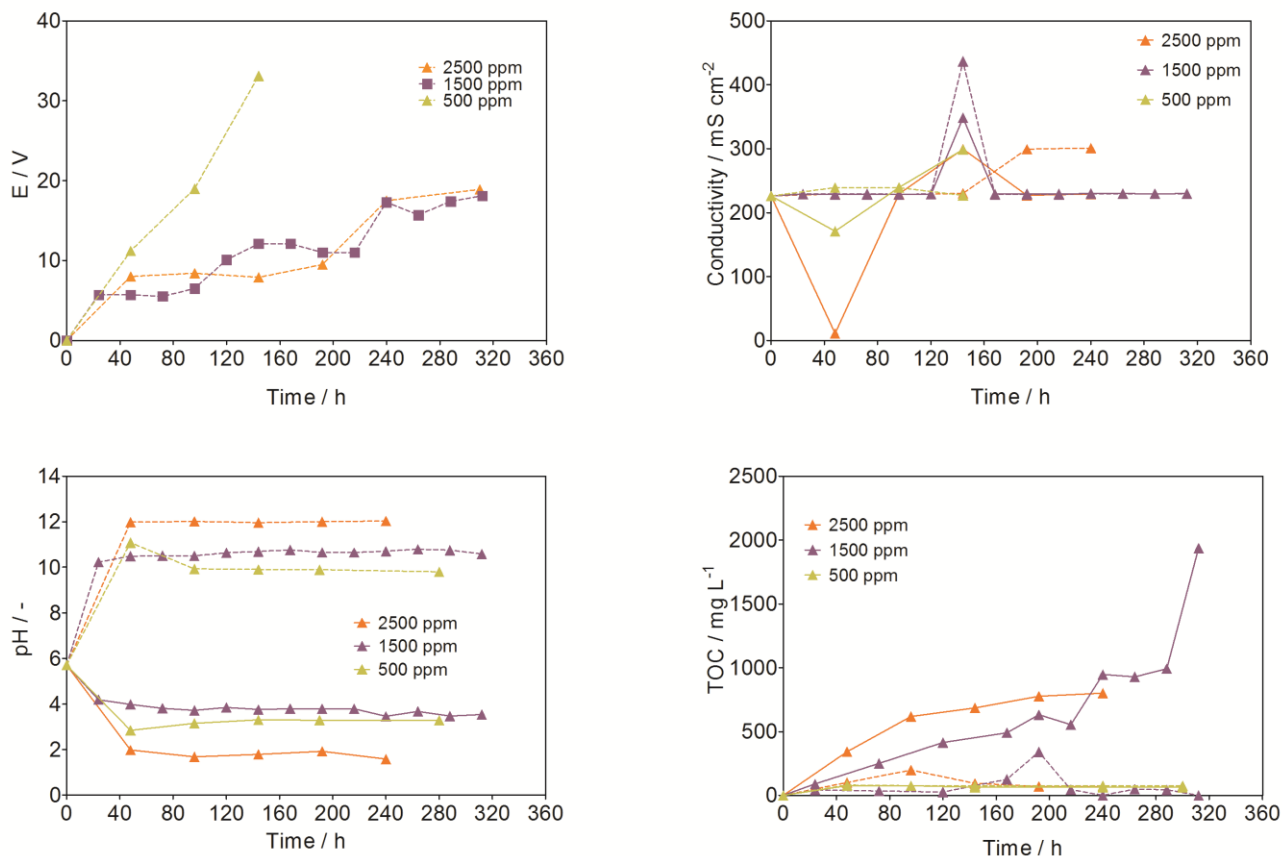


Figure 8. Effect of the amount of contamination of petroleum (500, 1500 and 2500 ppm) in the evolution of potential cell (E) as well as the conductivity (mS cm^{-2}), pH conditions and TOC (mg L^{-1}) in the solution of reservoirs (cathodic (----) and anodic (—)), as a function of time, during the ESR of 1.5 Kg of carbonaceous soil polluted with petroleum at 25°C using 0.1 M Na_2SO_4 as supporting electrolyte by applying 0.1 A.

In summary, electrokinetic remediation showed to be a feasible methodology to remove petroleum contamination from soil at different concentrations. However, the characteristics of the decontamination strongly depend on the electrokinetic phenomena favored by pH conditions, soil porosity and formation of micelles/microdrops of pollutants, and probably, the elimination of petroleum contamination is more significant when higher concentrations of petroleum are imposed because the organic/inorganic species promote the formation of colloids and micelles that have specific charge inducing two electroosmotic fronts [1,15,18].

3.4. Electrokinetic experiments by using water as liquid in cathodic and anodic compartments

After the main experiments, different solutions were compared in order to obtain good operating conditions for removing pollutants, as reported in Table 1. Figure 9 shows the variations in potential, pH and petroleum concentration in the soil samples during the electrokinetic treatment by using Na_2SO_4 or H_2O as liquids. The use of H_2O (potable water) was proposed due to the elimination of chemical reagent. In this case, the pollutants were transported to electrode compartments in different

levels because of electromigration and electroosmotic phenomena[15]. The removals of petroleum in the soil for each experiment when water is used as supporting electrolyte showed lower efficiencies. It is related to the high potential achieved during ESR treatment, limiting the induction of electrokinetic phenomena.

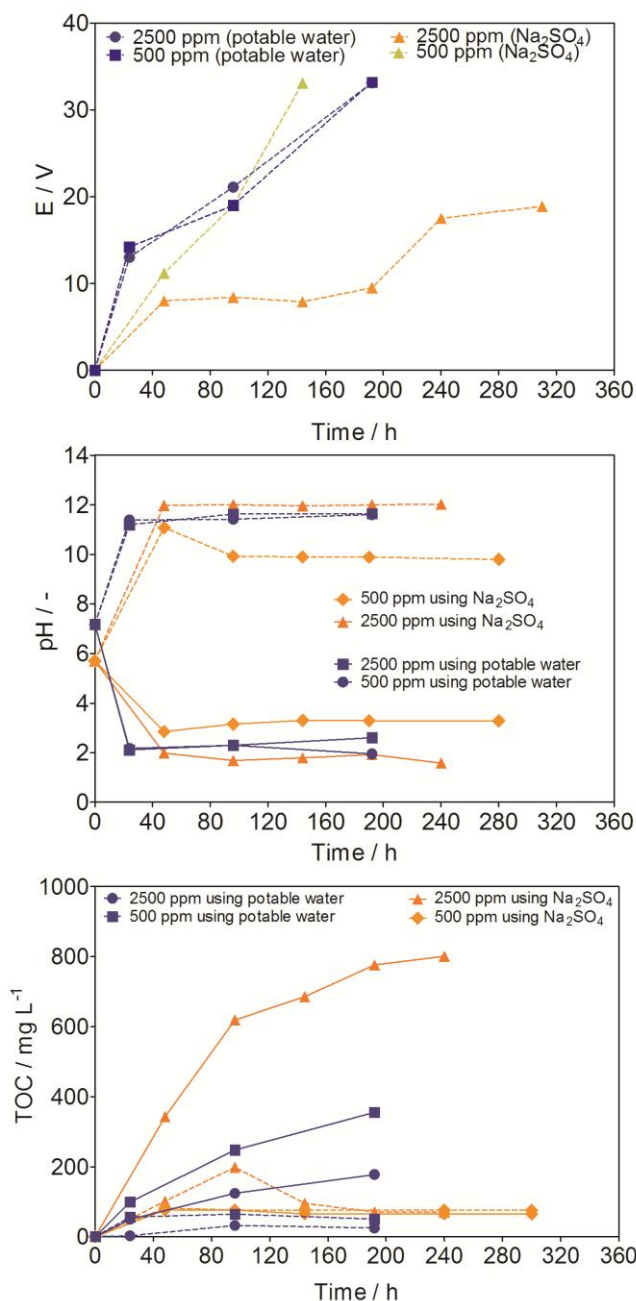


Figure 9. Effect of the supporting electrolyte (sulfate or potable water) and the amount of contamination of petroleum (0.5 g or 2.5 g) in the evolution of potential cell, pH conditions as well as the TOC measurements in the solution of the reservoirs (cathodic (----) and anodic (—)), as a function of time, during the ESR of 1.5 Kg of carbonaceous soil polluted with petroleum by applying 0.1 A.

By applying similar J and t of treatment, results clearly indicated that the movement of charged species from soil to reservoir solutions mainly depends on the solution used because of the porosity of soil, pH conditions and the accumulation of pollutants that can be related to the processing time.

Based on these results, the elimination of organic and inorganic substances from the carbonaceous soil is not feasible when potable water is used because no efficient transport is promoted [1,13,16,18] during EK treatment. Organic matter, in terms of TOC, increases on the reservoir solutions when Na_2SO_4 is used (Fig. 9); however, a notable decrease on the elimination of pollutants was achieved at both reservoirs when water was used as supporting electrolyte. More information about the pollutants that were removed is necessary, for this reason, further experiments are in progress.

3.5. Energy requirements and cost

The viability of the treatment approach was evaluated by determining the energy requirements for removing petroleum from one ton of soil. Table 2 reports the cost regarding to each test, considering the specific values of operating parameters (time and current) as well as the average cell potential value. Costs were estimated between 3 and 134.68 R\$/ton.

Table 2. EK operating conditions for removing petroleum from carbonaceous soil samples: (1) amount of petroleum (in g) added to 1.5 g of soil; (2) treatment time (h); (3) current (A); (4) potential cell values (V); (5) energy consumption in kWh/m^3 . Na_2SO_4 0.1 M or water (test 6 and 7).

Test	Soil pollution (1)	t (2)	i (3)	E (4)	EC (5)	Cost (real/ m^3)
1	1.5	360	0.05	4.7	1.5	0.6
2	1.5	360	0.1	5.0	3.2	1.3
3	1.5	360	0.2	33.1	41.5	16.5
4	2.5	360	0.1	31.2	19.5	7.8
5	0.5	360	0.1	31.2	19.5	7.8
6	2.5	360	0.1	31.2	19.5	7.8
7	0.5	360	0.1	31.2	19.5	7.8

According the electrical expenditure values and cost, the ESR approach can be a feasible alternative for the treatment of sludge containing hazardous materials. Another important feature is that $\text{H}_{2(\text{g})}$ is produced at the cathode during EK treatment. It can be appropriately collected and stored, as an energy resource. However, the amount of $\text{H}_{2(\text{g})}$ produced was modest by using EK cell proposed in this work. Nevertheless, if a plant operating for one year is considered, a significant volume would be produced.

4. CONCLUSIONS

From the results obtained on the ESR of carbonaceous soil, we can conclude that:

i) Level of pollution affects on the potential registered during the ESR treatment due to the mobility of the pollutants in the soil by acidic and alkaline fronts.

ii) Results show that higher removal efficiency is attained when the treatment time is prolonged and an increase on the current density is performed; however, more tests are in progress to understand the dependence of removal efficiencies for organics on their accumulation in the soil matrices.

iii) Efficacy of the ESR was demonstrated by applying 0.1 A with graphite electrodes and Na₂SO₄ as supporting electrolyte during 360 h. A significant removal of petroleum was achieved from soil to reservoirs, and it was confirmed by TOC measurements in the effluents produced.

iv) Comparing the supporting electrolyte, the use of water decreases the cost and reduce the introduction of chemical reagents for treating soil, however, no significant removal efficiencies were achieved for petroleum contamination due to the higher resistance of soil (by lower conductivity) limiting the electromigration and electroosmotic flow of pollutants.

v) Modest costs were estimated from 3 to 37 real/m³, depending on the operating conditions.

The application of ESR approach could be considered an innovative alternative for depolluting soils, obtaining significant removal efficiencies. Finally, further experiments are in progress aiming to the optimization of parameters for increasing the petroleum removal efficiency and the energy consumption as well as to propose alternative use of electrochemical technologies for effluents generated after ESR [19,20].

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References

1. R.T. Gill, M. J. Harbottle, J. W. N. Smith, S. F. Thornton, *Chemosphere* 107 (2014) 31.
2. J. Virkutyte, M. Sillanpää, P. Latostenmaa, *Sci. Total Environ.* 289 (2002) 97.
3. Y.B. Acar, A.N. Alshwabkeh, *Environ Sci Technol.* 27 (1993) 2638.
4. C.J.F.P. Jones, J. Lamont-Black, S. Glendinning, *Geotext. Geomembranes* 29 (2011) 381.
5. A.T. Yeung, Y.-Y. Gu, *J. Hazard. Mater.* 195 (2011) 11.
6. G. Maini, A.K. Sharman, C.J. Knowles, G. Sunderland, S.A. Jackman, *J. Chem. Technol. Biotechnol.* 75 (2000) 657.
7. Q. Luo, H. Wang, X. Zhang, Y. Qian, *Appl. Environ. Microbiol.* 71 (2005) 423.
8. L. Shi, H. Harms, L.Y. Wick, *Environ. Sci. Technol.* 42 (2008) 2105.
9. G.R. Eykholt, *J. Hazard. Mater.* 55 (1997) 171.
10. A.N. Alshwabkeh, T.C. Sheahan, X. Wu, *Mech. Mater.* 36 (2004) 453.
11. C. Trelu, E. Mousseta, Y. Pechaud, D. Huguenot, E. D. van Hullebusch, G. Esposito, M. A. Oturan, *J. Hazard. Mater.* 306 (2016) 149.

12. U. C. Brinch, F. Ekelund, C. S. Jacobsen, *Appl. Environ. Microbiol.* 68 (2002) 1808.
13. E.B. Sabino da Silva, M.D. de Lima, M.M. Oliveira, E.C.T. de A. Costa, D. Ribeiro da Silva, C.A. Martínez-Huitle, *Int. J. Electrochem. Sci.*, 12(2017) 1247-1262.
14. O. Atteia, E.D.C. Estrada, H. Bertin, *Rev. Environ. Sci. Biotechnol.* 12 (2013) 379.
15. M.M. Page, C.L. Page, *J. Environ. Eng.* 128 (2002) 208.
16. V. Ferri, S. Ferro, C.A. Martínez-Huitle, A. De Battisti, *Electrochim. Acta*, 54 (2009) 2108.
17. Y.B. Acar, R.J. Gale, A.N. Alshwabkeh, *J Hazard Mater.* 40 (1995) 117.
18. S. Pamukcu, J.K. Wittle, “Electrokinetically Enhanced In-situ Soil Decontamination”, Marcel Dekker (1994) New York, USA, p. 245-98.
19. C. A. Martínez-Huitle, M. A. Rodrigo, I. Sires, O. Scialdone, *Chem. Rev.* 115 (2015) 13362–13407.
20. E. V. dos Santos, S. F. M. Sena, D. R. da Silva, S. Ferro, A. De Battisti, C. A. Martínez-Huitle, *Environ. Sci. Pollut. Res.* (2014) 21:8466–8475.

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