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Electrode Materials a Key Factor to Improve Soil Electroremediation

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1. Introduction

Pollution of top and subsurface soil, as well as underneath groundwater has been one of the consequences of industrial activities; actually environmental professionals are facing a time consuming issue when they look for potential solutions for heavy metals and organic compounds removal. Although many soil remediation technologies are available, electrokinetic processing has been an emerging technology offering advantages for a wide variety of pollutants being either organic or inorganic; as well as its versatility of being applied in soil wetting conditions ranging from unsaturated to saturated; one of the main advantages of this technology is the fact that this process can be applied to low permeability soils, like clays.

Initially electrokinetics was applied for soil consolidation, in this process water flux is forced by an electrical field action, an approach to explain how it works is based on setting up a soil structural change analysis based on modification of soil matrix, plasticity index and crystalline state (Gray, 1970). For clayey soils it has been accepted that they behave like an osmotic membrane, therefore it is important to understand how physicochemical factors affect its response in regulating osmotic pressure into the soil matrix (Fritz, 1986). Another report (Darmawan, 2002) reinforce the necessity of knowing how the solid matrix response to the electric field, since obtained electrical current is function of electrolyte concentration, buffering capacity, and chemical form of involved metals, these can be in either soluble, electrostatically adsorbed, or surface complexed forms; also, metal migration is favored when soil is dominated by clay minerals, otherwise migration is lowered when soil has a high buffering capacity and/or high humic content, the last one acts like an additional resistance to the current transference throughout the soil.

Electrokinetics as a remediation experimental procedure requires having a wetted soil in which electrodes are inserted and terminals are connected to a power source. As soon as an electric field is generated, electrode reactions take place producing protons (H^+) at the anode

and hydroxide (OH^-) at the cathode; concentration of these ions increases exponentially creating an acid front which moves from anode to cathode, and a basic front moving from cathode to anode; during its passage through the soil protons and hydroxides interact with sorbed pollutants releasing them into solution. Soluble ion transport occurs by three mechanisms: 1) Diffusion due to concentration gradients, 2) Convection due to fluid movement and 3) Migration due to the electric field.

A sample of initial published results (Acar et al, 1994; Hamed et al, 1991; Khan & Alam, 1994; Kim et al, 2002; Pamucku et al 1990; Pamucku & White, 1992; Reddy et al, 1999) is enough to claim that this method is highly efficient on restoration actions for clayey soils having very low heavy metal concentrations, for which regular mining procedures would result very expensive; although, for this method one of the minuses is the time required to get metal removals above 90%. Most of these studies report soil characterization providing information about: sand, clay, silt content; organic matter as well as hydraulic permeability. Although, few reports have covered soil electrical resistance, which according to Vázquez et al (2004), it could be used as a method for analyzing soil behavior in presence or absence of an electrical field.

In order to improve the process and get shortening of experimental times, applied efforts have covered a wide set of conditions. Some examples of reported research have addressed for modifying pH and current density (Hamed & Bhadra, 1997), chemical conditioning of electrode wells (Reed et al, 1995; Murillo-Rivera et al, 2009), cation inclusion (Colleta et al, 1997), as well as addition of complexing (Yeung et al, 1996) and lixiviant agents (Cox et al 1996); another approach has been the inclusion of reactive barriers into the soil matrix (Cundy & Hopkinson, 2005; Ruiz et al, 2011).

When treating PAHs (Polyaromatic Hydrocarbons) soil pollution it is important to care about lateral effects like lowering the electroosmotic flow rate (EOF), which can be consequence of controlling pH at the electrode wells, by doing this an affectation of soil and/or solution chemistry can be induced producing an accumulation at the neutral or alkaline soil regions (Saichek & Reddy, 2003). Another factor affecting EOF derives from surfactant inclusion, then it becomes necessary to evaluate if it is worthy lowering EOF for increasing PAHs removal (Kolosov et al, 2001). Also, pollutant mobilization should be evaluated as a function of pH control and surfactant addition, since flow can occur in anodic direction (Ribeiro et al, 2005), or be enhanced in the cathodic direction.

Finally, organics and metal removal can be affected by geometry cell and flow direction, in this sense a report about an upward electrokinetic soil remediation (Wang et al, 2007) points out that removal efficiency is increased for organics when electroremediation cell is smaller in diameter, or larger in height; otherwise for metals, removal is improved when the cell is smaller in diameter or shorter in height.

Electrode materials are a key parameter to assure that electron transference takes place at fast rates. Selection of materials should be based on thermodynamic and kinetic response, so interface molecular interactions are fast enough to release the oxidant species. Also, it must be considered aspects like mechanical, thermic and corrosion resistance; as well as the procedures and solutions used in surface cleaning, pretreatment, and surface activation. In this sense, materials which satisfy these requirements are: vitreous carbon, titanium, stainless steel, platinum, gold and silver; but it must not be discarded that all materials can

reduce its activity as experimental conditions favor metal deposition and so far electrode passivation. Then, in order to increase active sites number, reduce passivation and increase useful lifetime; some efforts had addressed electrode modification using oxide materials such as Carbon | TiO_2 , Ti | SnO_2 -Sb, Ti | IrO_2 - Ta_2O_5 , Ti | RuO_2 . Electrodes prepared in this way have been named Dimensionally Stable Anodes (DSA) and they have proven be effective in organic degradation (Comminellis, 1994), because in addition to their high capacity to generate hydroxyl radicals, they also are mechanically resistant to abrupt pH changes.

Titanium dioxide exists in three crystalline forms namely anatase, rutile, and brookite, from which the first is the one exhibiting higher catalytic activity; which is highly dependent on the surface specific area of the particulate form, a phenomena which is exemplified by Baiju et al (2009), in their work they used anatase- TiO_2 in dye removal; these authors provide evidence on how switching from a particulate form to nanotubes it results in a concurrent change in the mechanism of dye removal from an aqueous solution. Although, other authors (Yigit & Inan, 2009) have provided evidence on how a mixture anatase-rutile provides a higher efficiency in humic acid mineralization.

In wastewater treatment use of Dimensionally Stable Anodes (DSA) made of a Ti mesh covered with a film of iridium or tin has proved being an effective tool for organics degradation while keeping its mechanical resistance (León et al, 2009); also, there is a theory proposed by Comminellis (1991) in which it is shown that the iridium DSA posses a highly reactive surface which directly oxidizes the substrate, at this respect an improvement in oxidant activity is obtained when titanium mesh is covered with a film including a mixture of oxides like Ir-Ta (Hu et al, 2002). Use of modified electrodes favors electrocatalytic processes by supporting higher current densities and so far reducing the corresponding oxidation potentials, because inner sphere mechanisms allow for hydroxyl radicals generation at an interfacial level, by which there it is possible to increase organic molecules decomposition reaching total mineralization levels. About the electrode matrix it can be affirmed that DSA usually exhibit higher mechanical resistance because they are prepared onto a rigid matrix, while the ones based on Reticulated Vitreous Carbon (RVC) have higher reactive surface but a lower mechanical resistance.

Considering that few attention have been dedicated to the role that electrode material plays on soil electroremediation, since a higher electrode activity would allow developing conditions which could enhance pollutant removal, specially when the pollutant is an hydrocarbon product. In this sense, this contribution presents results from two research approaches in which it is tested how inclusion of a catalytic specie, like anatase (TiO_2) in a reticulated vitreous carbon (RVC) or a titanium anode covered with IrO_2 - Ta_2O_5 film will help to improve occurrence of water electrolysis reactions; also, each experimental approach allowed to elucidate the role played by materials used as anode and cathode, as well as the influence exerted by additional resistance factors like electrode position in respect to the soil interphase. Finally, it is an opportunity to test the theory by which it is expected an enhancement of electrokinetic hydrocarbon removal as consequence of the higher electrode activity.

Experimental work is organized as follows: 1) Electrodes made of Reticulated Vitreous Carbon (RVC), in which anode was modified by inclusion of an anatase deposit (TiO_2), and keeping constant a RVC cathode, this provides two combinations bare RVC electrodes and RVC- TiO_2 anode with bare RVC cathode; 2) Anode made of a titanium plate covered with

$\text{IrO}_2\text{-Ta}_2\text{O}_5$, and two cathode materials carbon felt (CF) and titanium plate (Ti), plus a variation of its position respect to the soil matrix. These experiments are described in the following paragraphs.

2. Methodology

Results correspond to two independent experimental sets, so far methodology for each one will be discussed in an independent section.

2.1 Anode modification

For this set of experiments soil was collected at 50 cm depth in an undisturbed site of Guanajuato, México. Applying the ASTM D4318-10 methodology soil was characterized for liquid (LL) and plastic (PL) limits, the water content difference between LL and PL provides the plasticity index (PI), which is an indicator of soil response, because greater PI values correspond to a soil which is more plastic and compressible and so far it exhibits greater volume changes using LL and PI values on the plasticity chart (Helwany, 2007), can be obtained a fast classification of soil type, providing an insight on the possible soil response, before any electrical perturbation is applied. Also, textural classification was done following the USCS-P13-B-2 procedure. This soil was artificially polluted by mixing it with a phenanthrene solution, let stand overnight, and room temperature dried. Later on, it was characterized for sorbed phenanthrene, which resulted in 12 mg Kg^{-1} . For experiments polluted soil was rewetted with deionized water.

This set of experiments considered electrodes made from 100 ppi (pores per inch) reticulated vitreous carbon (RVC), impregnated with TiO_2 by a sol-gel method. Impregnating solution was prepared dissolving metallic Ti in concentrated HCl; later on it was precipitated with NH_4OH , obtained product was filtered and washed before dispersing it into a 10% ethanol solution; in this solution RVC pieces were immersed for 24 hours; after that, they were dried and subjected to a 3 hours calcination, this procedure pursues formation of the anatase phase in the deposit; confirmation of anatase presence was done by Raman spectroscopy and some micrographs were obtained with a Leica S8APO stereomicroscope. The electrochemical cell was a rectangular one (14 cm length, 10 cm width, 9 cm high).

Electrokinetic experiments were run for 24 hours, a 25 mA cm^{-2} electrical current density was imposed with an electrophoresis power supply FR500-125 BIOELEC. Electrode arrangement considered keeping constant a bare RVC cathode, and switching the anode from bare RVC to RVC- TiO_2 , recorded parameters correspond to: pH and electric conductivity measured with a Multipurpose Lab Interphase Vernier Software; electroosmotic flow was registered with an illuminated multitester MUL-270 Steren.

In order to quantify residual phenanthrene concentrations, at the end of each experiment, soil sample was cut in slices, room temperature dried, and phenanthrene was Soxhlet extracted with ethylic ether. After that, the solvent was evaporated and phenanthrene was solubilized in 5 mL of HPLC grade acetonitrile, this sample was centrifuged and injected into an inverse phase Hypersil chromatographic column C-18 ODS (100 $\text{mm} \times 4.6 \text{ mm}$, and 3 mm particle size); detection was done using a mobile phase made of a mixture $\text{CH}_3\text{CN}/\text{H}_2\text{O}/\text{CH}_3\text{OH}$ in proportions 30:15:55 % v/v; using a flow rate of 0.4 mL min^{-1} and 254 nm detection wavelength.

2.2 Cathode modification

Soil sample corresponds to a hydrocarbon polluted weathered soil, for which a physical characterization is done by using the ASTM D4318 as well as the USCS-P13-B-2 procedure, by which it was established soil type and textural composition. Since this soil has hydrocarbon pollutants, its concentration was determined as oil and grease by the Soxhlet technique. According to published results (Murillo-Rivera et al, 2009), 0.1M NaOH solution is an electrolyte that works fine for hydrocarbon polluted soils, so this one was chosen as the electrolyte for soil wetting, and wells replenishment.

Experimental cell was a rectangular one (10 cm length, 2 cm width, 4 cm high), a current density of 20 mA cm⁻² was imposed with a PDC-GP 4303DU Power Source, in a galvanostatic mode during 4 hours.

Considering that a DSA anode provides oxidant species at higher rates, then for this hydrocarbon polluted soil electroremediation it was chosen an electrode arrangement, considering a modified DSA made of a titanium plate covered with an iridium-tantalum film (Ti|IrO₂-Ta₂O₅), and two types of cathode: carbon felt (CF) and a titanium plate (Ti). Also, in these set of experiments it was considered two electrode positions: in the first one, a physical barrier of filter paper was included between soil and electrode, while in the second one the electrode was set in direct contact with soil sample.

Registered experimental parameters were: applied electrical current, developed electrical potential, with these it was possible to calculate cell resistance and energy consumption. At the end of each experiment soil was cut in 3 sections (anode, middle, cathode), hydrocarbon removal was estimated from soil residual concentrations, which were extracted by the Soxhlet technique, and later analyzed by UV-Vis (XLS, Perkin-Elmer) gas chromatography coupled to mass spectroscopy (CG-EM, Agilent GC 19091-413).

3. Results

3.1 Anode modification

Soil characterization results are reported in Table 1. As it can be observed this soil is classified as a Low plasticity Clay (CL), then it will no exhibit a great volume change during experimentation; also, clay and silt content indicate that this is a low permeability soil.

Parameter	Value	Methodology
Liquid Limit (LL) %	36	ASTM D4318-10
Plastic Limit (PL) %	24	ASTM D4318-10
Plasticity Index (PI) %	12	ASTM D4318-10
Classification	Low plasticity clay (CL)	Plasticity Chart (Helwany, 2007, page 13)
Sand %	34	USCS-P13-B-2
Silt %	53	USCS-P13-B-2
Clay %	13	USCS-P13-B-2

Table 1. Physical and textural properties of Guanajuato soil.

Based on the above described soil characteristics, it was considered important to determine how this type of soil responds to the action of an electric field. To accomplish this step, clean soil was wetted with deionized water, and later on tested with the bare RVC electrodes. Measurements of pH were done at the electrode interface (anode, cathode) and two middle points (4 and 7 cm). Experimental pH profiles are presented in Figure 1. As it can be observed, natural pH is slightly alkaline ($\text{pH}=8$); also, even though protons are generated at the anode, its penetration is slow, and their amount is not enough to get a high pH depletion at this position; otherwise intermediate points (4 and 7 cm) show an alkalization since its values are increased by up to 2 units; also, at the cathodic position, pH response satisfies expectations of high alkaline values, since final pH is closer to 13. Considering that alkaline pH favors organic pollutants removal (Murillo-Rivera et al, 2009), then this soil is considered adequate to evaluate hydrocarbon removal.

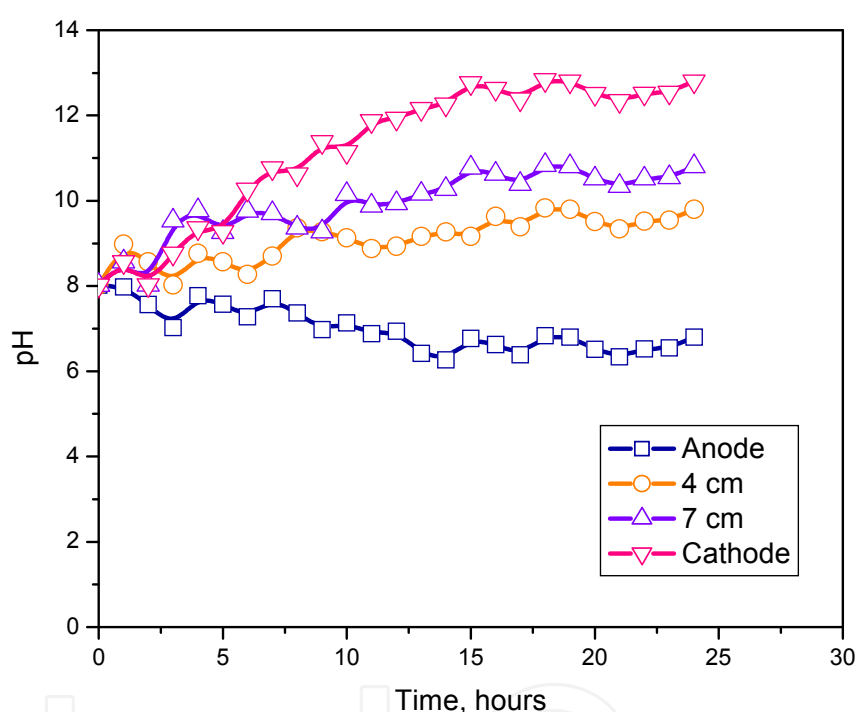


Fig. 1. Graph of pH evolution at anodic and cathodic wells during the electrokinetic experiments for clean soil, applying a current density of 25 mA cm^{-2} , and using bare RVC anode and cathode electrodes.

Artificial polluted sample was prepared as it is described in the methodology section. Next step is to use this sample with different anode materials, and establish if these are useful on improving electrokinetic process performance for removal of phenanthrene from polluted soil. In Figure 2 it is shown the pH evolution at the anodic and cathodic wells, for a 24 hours soil electroremediation experiment. It can be observed that using bare RVC electrodes (Anode I and Cathode I) makes pH at the anode be slightly depleted during the first hours, but later on occurs an increase of its value, which keeps it around 8 (the initial value) during the rest of the experiment; otherwise, at the cathodic well a fast alkalization is observed, this remains around 10.5 during the whole experiment, but this value is lower than the one obtained with clean soil.

Otherwise, anode replacement by the RVC-TiO₂ option (Anode II, Cathode II), it enhances proton production, so in short time pH goes to acidic values, and after 5 hours it stabilizes around 5. Keeping the cathode as bare RVC makes that the cathodic well pH go to slightly higher alkaline values, than those registered when the anode was bare RVC; but still pH values are lower than the ones obtained with the clean soil. It seems that pollutant inclusion makes a more resistive system by which hydroxyl production is lowered respect of the rates achieved with clean soil.

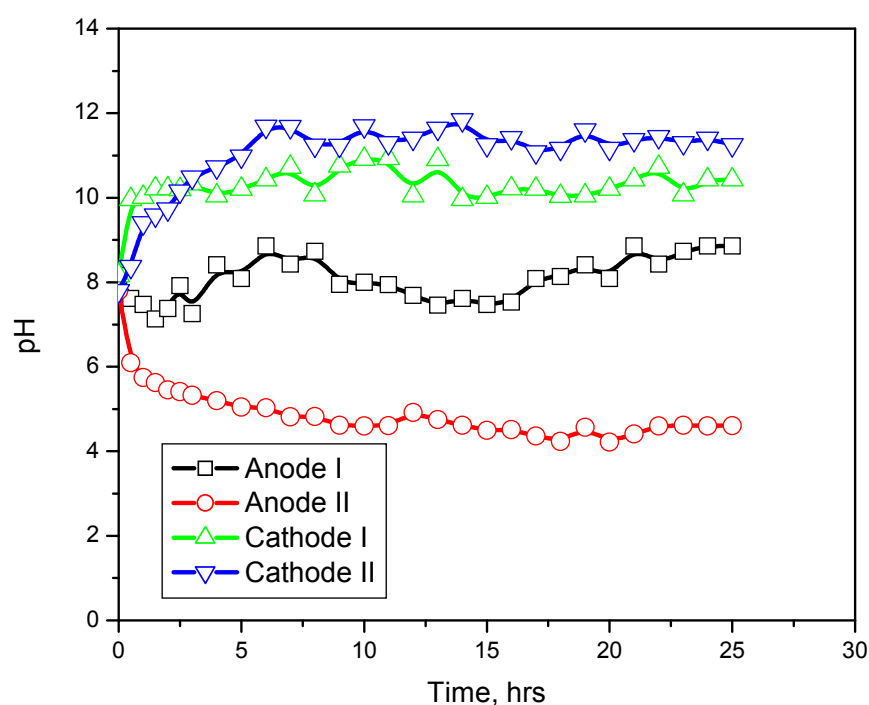


Fig. 2. Graph of pH evolution at anodic and cathodic wells during the electrokinetic experiments for clay soil contaminated with 12 mg Kg⁻¹ of phenanthrene, applying a current density of 25 mA cm⁻², and using different electrode materials: (I) Bare RVC anode and cathode; and (II) RVC-TiO₂ anode with RVC cathode.

For these experiments drained volume was collected, results are presented in Figure 3. As it can be observed keeping a bare RVC cathode, and switching from (I) bare RVC to (II) RVC-TiO₂ anodes, exhibit similar water transport during the first 3 hours; but after that water transport is increased for the RVC-TiO₂ anode; therefore this modification it allows enhancing the amount of water being displaced from anode to cathode. After 10 hours, water transport reach and steady rate of transport, corresponding regression lines are described as follows: for the RVC (system I) $y = 72.31x - 54.995$, $R^2 = 0.995$, while the RVC-TiO₂ (system II) is described by $y = 88.15x - 2.0373$, $R^2 = 0.999$.

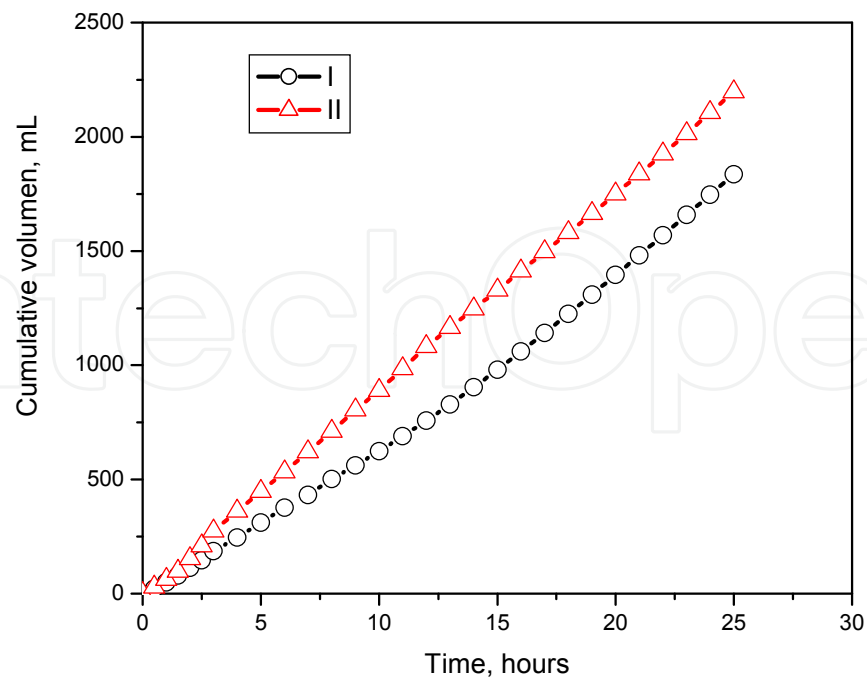


Fig. 3. Graph of collected cumulative volume at the cathodic well during electrokinetic experiments for clay soil contaminated with 12 mg Kg⁻¹ of phenanthrene, applying a current density of 25 mA cm⁻², having a bare RVC cathode and using different anode materials: (I) Bare RVC anode; and (II) RVC-TiO₂ anode.

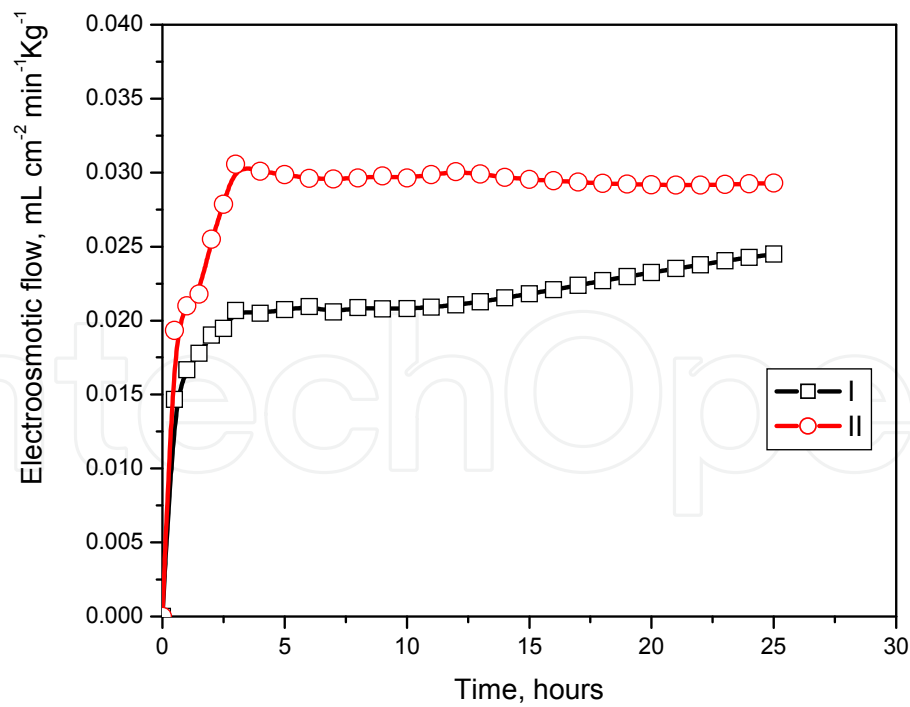


Fig. 4. Comparison of cumulative electroosmotic flow registered at the cathodic well during the electrokinetic experiments for clay soil contaminated with phenanthrene using different anode materials: (I) Bare RVC anode and cathode; and (II) RVC-TiO₂ anode with RVC cathode.

Collected drained volume values, cell characteristics and soil mass were used to mathematically obtain cumulative electroosmotic flow ($\text{mL cm}^{-2} \text{ min}^{-1} \text{ Kg}^{-1}$), results are shown in Figure 4. From the plot can be established that effectively catalytic activity of TiO_2 allows for getting higher electroosmotic flow. As it can be observed in three hours the RVC- TiO_2 anode (II) reached steady response, while the bare RVC anode (I) provides a much lower electroosmotic flow which seems to smoothly reach steady response at similar times, but after 10 hours, a new perturbation takes place and it goes to a transient response, the last taking place at a slower rate in respect to the initial one.

As it was mentioned in the methodology section, electroremediated soil sample was cut in slices and recovered residual phenanthrene was injected in an inverse phase Hypersil chromatographic column. Elution time for phenanthrene was 5.8 min, while humic and fulvic acids appear at about 2 min of elution time (Chongsan et al, 2006; Xing & Kang, 2005; Yanzheng et al, 2007). In Figure 5 it is shown a chromatogram for the soil extracted phenanthrene before any electrokinetic experiment, this reference signal is about 1 arbitrary unit (A.U.).

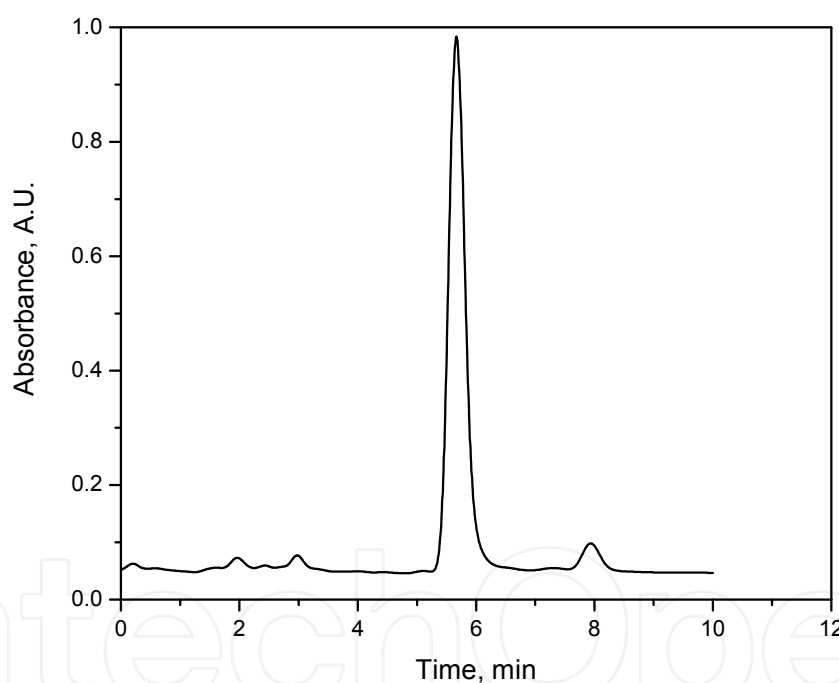


Fig. 5. Chromatogram of the Phenanthrene standard, reference signal obtained from the artificially polluted soil.

Obtained chromatograms for each soil section, after the electrokinetic experiment with bare RVC anode and cathode are shown in Figure 6, and those for the RVC- TiO_2 anode with bare RVC cathode are shown in Figure 7.

As it can be observed in Figure 6, none of the positions amount concentrations higher than 0.25 A. U., also there are several peaks between the humic and fulvic acids (2 min) and the phenanthrene (5.8 min), these peaks are smaller than other signals, and they can be

associated to a phenanthrene decomposition by products from lateral reactions, which take place as electrolyte moves through the soil during the electrokinetic experiment; the higher residual phenanthrene concentration for bare RVC electrodes was about 0.25 A.U. and it occurs at the 0.7 dimensionless position, that is the section before to the one closer to the cathode.

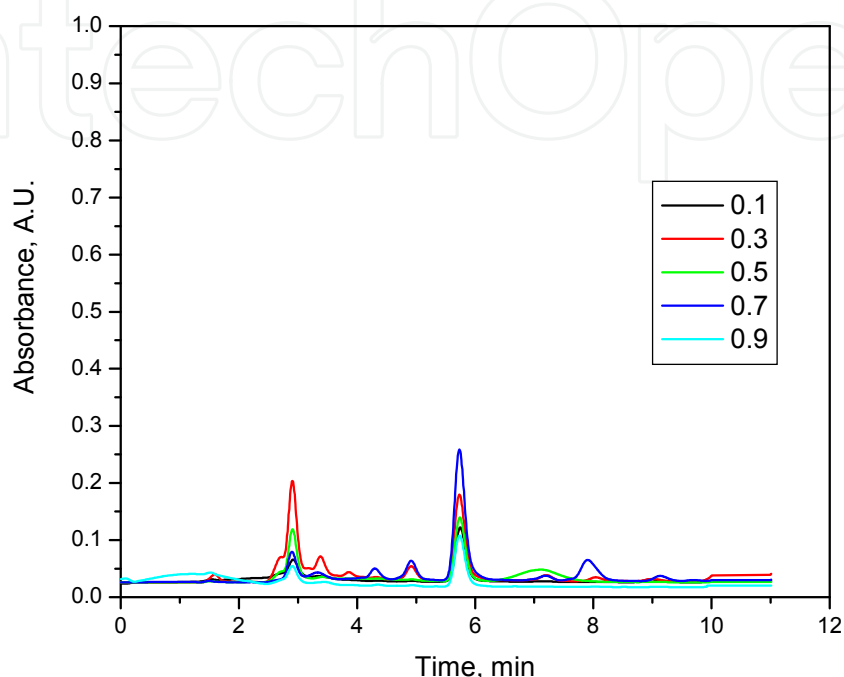


Fig. 6. Chromatograms of residual phenanthrene concentrations in each soil slice for the system of bare RVC electrodes.

Otherwise, when the experiment was run with the RVC-TiO₂ anode (Figure 7) the presence of smaller peaks it is practically null; also, an opposite phenomena is observed since in this case the higher residual concentration was about 0.9 A.U., while the lower one is not less than 0.6 A. U., this last takes place at the 0.3 cm position (near the anode). In general, with this option phenanthrene removal was lower than the one attained with the bare RVC electrodes.

In order to make more explicit the above expressed, concentration was calculated from each soil slice chromatogram, this was done by an integration of the area under phenanthrene peak; in this way, its residual concentration was estimated. Results are reported in Figure 8 as percentage of the original concentration in soil (12 mg Kg⁻¹=100%), it can be observed that effectively higher removal was obtained with the bare RVC electrodes, an average of 80%; and even though replacing the anode by the RVC-TiO₂ provides higher oxidation conditions and a faster water transport; this fact does not allowed for getting a right residence time for solubilizing and transporting phenanthrene, since removal amounts an average of 20%. It is noticeable that for the bare RVC electrodes, higher residual phenanthrene concentration took place at the same position where it is the lower one when the anode was RVC-TiO₂.

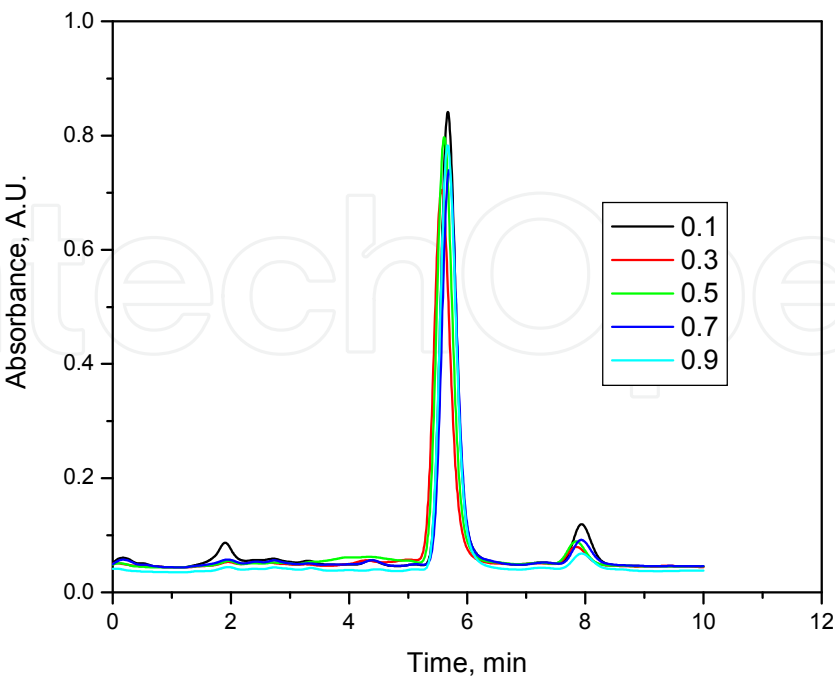


Fig. 7. Chromatograms of residual phenanthrene concentrations in each soil slice for the system of TiO₂-RVC anode and bare RVC cathode.

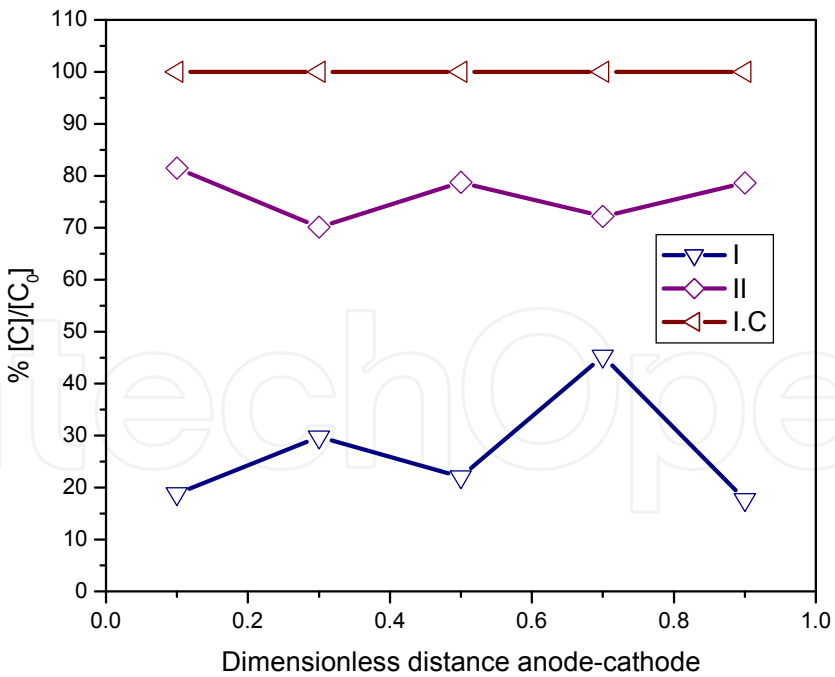


Fig. 8. Comparison of residual phenanthrene concentrations in each soil slice for the system of (I) bare RVC electrodes, and the (II) RVC-TiO₂ anode, RVC cathode, versus initial concentration (IC).

Correlating these results with corresponding pH data it can be affirmed that keeping a shorter difference in pH wells, as it happens with bare RVC electrodes, it favors a soil alkaline condition which, even though produces a slower liquid movement, so far this is good enough for phenanthrene removal since it provides a higher residence time.

Up to here, it was shown that inclusion of one catalytic specie, like anatase, in the anode allowed increasing the oxidant specie production and the electroosmotic flow rate, but obtained phenanthrene removal was lowered. So next step is to analyze what happen if the catalytic activity is maintained at the anode, but cathode is chosen between different materials. Experimental set-up objective was data collection for two different cathode materials, and also to clarify how much the system becomes affected by inclusion of additional physical barriers like a thick filter paper.

3.2 Cathode modification

For this set of experiments soil sample was collected at an industrial area located in Nuevo Teapa, Veracruz, México, this is a highly polluted and weathered area. Physical characterization is reported in Table 2.

Parameter	Value	Methodology
Liquid Limit (LL) %	42	ASTM D4318-10
Plastic Limit (PL) %	28	ASTM D4318-10
Plasticity Index (PI) %	14	ASTM D4318-10
Classification	Medium plasticity clay (CI)	Plasticity Chart (Helwany, 2007, page 13)
Sand %	56	USCS-P13-B-2
Silt %	24	USCS-P13-B-2
Clay %	20	USCS-P13-B-2

Table 2. Physical and textural properties of Nuevo Teapa soil

For this set of experiments it was chosen a dimensionally stable anode (DSA) made of a titanium plate with an iridium-tantalum film ($\text{Ti}|\text{IrO}_2\text{-Ta}_2\text{O}_5$) which was maintained constant; considered cathode materials were: carbon felt (CF) and a titanium plate (Ti). Physical barrier inclusion was evaluated considering two electrode positions: Array I: placing the physical barrier at the soil interphase and the electrode after it; Array II: electrode placed at the soil interphase.

An initial test of soil response was done with the combination DSA-Ti, pH profiles for the option including a physical barrier between electrode and soil (Array I) are presented in Figure 9. As it can be observed soil tends to be acidified, and after 4 hours it is reached a stable pH condition which at the anode is about 2 units lower, and at the cathode is one unit lower, in respect to the initial value. It seems that barrier favors a buffering effect by which the system does not get a drastic pH drop. Although, having a pH variation is evidence of getting a high rate for proton generation and transport throughout soil. It is important to point out that after 3 hours, pH at the middle and cathode sections have similar values, fact which reflects a strong neutralization of transported protons.

Results for Array II are presented in Figure 10, pH profiles for the combination DSA-Ti without barrier clearly show a fast pH drop, and after 1 hour, at the middle section seems to occur an hydroxide accumulation, which could be a factor to accelerate proton penetration, such that at two hours the anode section starts to lowering its pH, and even though it does not reach an acidic condition pH drop is about 5 units at this section, but this pH does not exert a strong impact over the other sections; since it seems that protons penetration displaced hydroxyls to the middle and cathode sections, which suffer a temporary raise in concentration. This behavior corresponds to a pulsed function being displaced from the middle to the cathode section, since when pH starts to decay in the middle, the cathode one start to raise its pH, which it gets a higher value than the initial one. At the final time, the middle section has decreased its pH in 1 unit, while the cathode section has reached stability at pH 12.

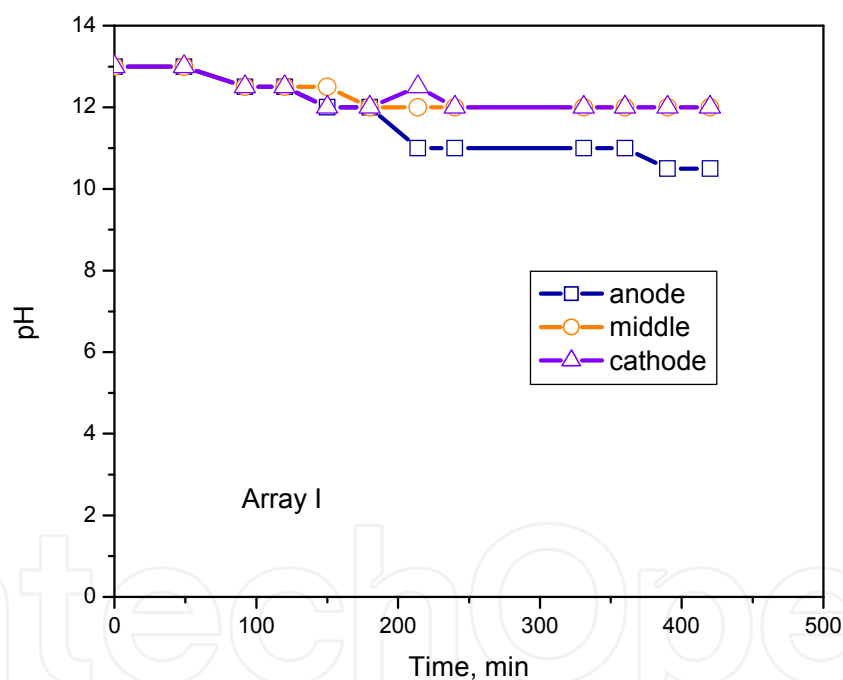


Fig. 9. Graph of pH profiles for array I of the DSA anode and Ti cathode, experimental conditions: 0.1 M NaOH wetting electrolyte, current density 20 mA cm⁻².

Experimental approach considered a follow up through the global electrical resistance (R, Ohms), which was indirectly calculated from experimental values of electrical potential (E, Volts) and applied current (I, Amperes), parameters related by Ohm's law ($R=E I^{-1}$). Results are shown in Figure 11.

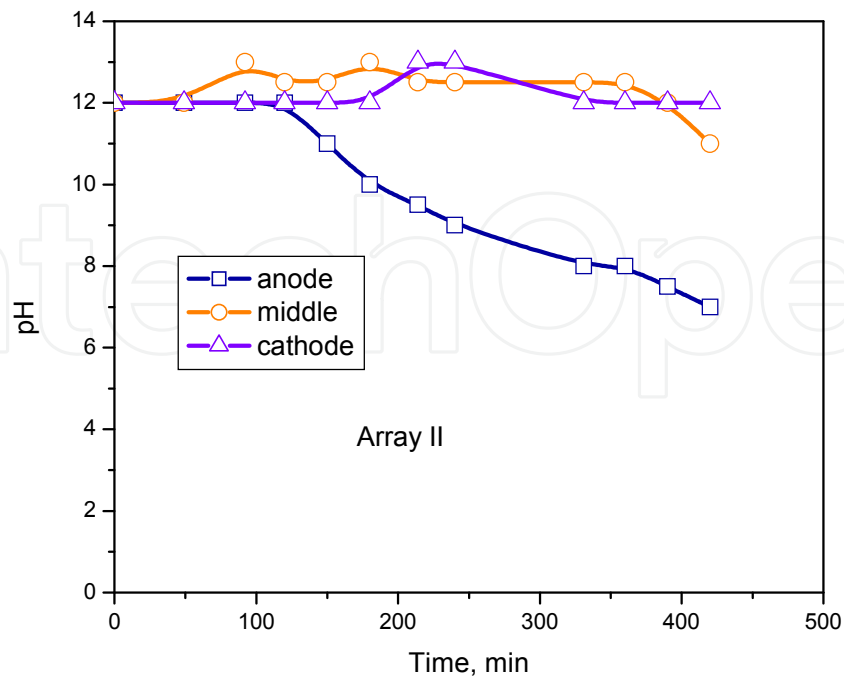


Fig. 10. Graph of pH profiles for array II of the DSA anode and Ti cathode, experimental conditions: 0.1 M NaOH wetting electrolyte, current density 20 mA cm⁻².

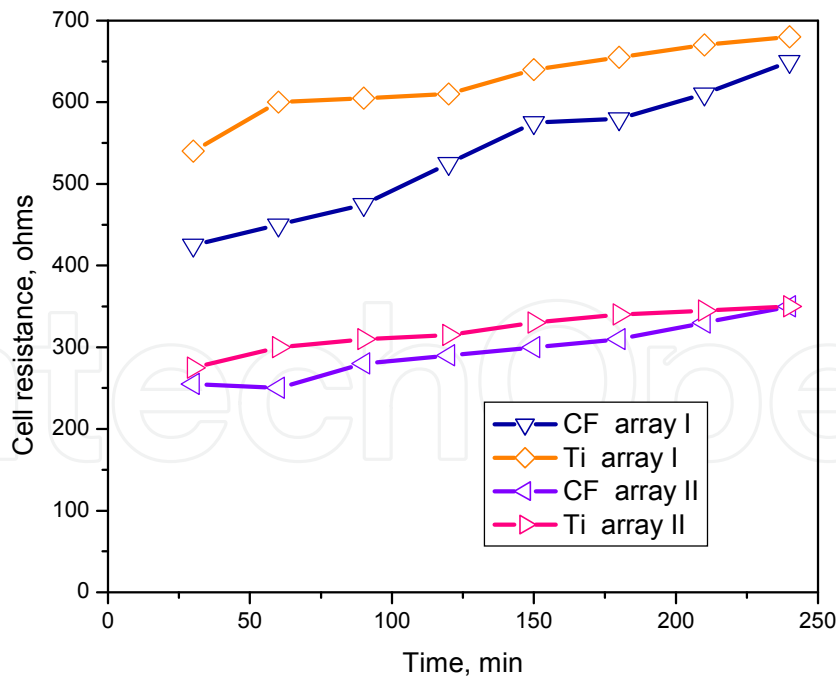


Fig. 11. Calculated resistance for soil electroremediation experiments using a modified IrO₂-Ta₂O₅ anode with either Carbon Felt (CF) or Titanium (Ti) cathode. Array I physical barrier inclusion, Array II soil contact experimental conditions: 0.1 M NaOH wetting electrolyte, current density 20 mA cm⁻².

Observing Figure 11 it is evident that allowing electrodes make contact with the soil (array II) provides a less resistive system; and also there is not a clear advantage between using CF or Ti as cathode, since both systems provide similar initial values at 30 min, $R=255$ ohms for CF, and $R=275$ ohms for Ti; final resistance values are identical for both systems $R=350$ ohms. Although, CF exhibit a slightly higher raise (95 ohms) in respect to Ti (75 ohms). Applying a linear regression analysis to CF data, its slope corresponds to $0.462 \text{ ohm-min}^{-1}$, while the Ti slope is $0.339 \text{ ohm-min}^{-1}$ then, even though initial resistance value is higher for the Ti electrode, this electrode provides a more stable system.

As it can be observed inclusion of the physical barrier makes the experimental system to be more resistive than that where electrodes make contact with the soil, also resistance trends in this system are similar to those of the previous one; since at initial times system with a CF cathode seems to be less resistive at 30 min, $R=425$ ohms, than that with a Ti cathode at 30 min, $R=540$ ohms, but at the end of the experiment (240 minutes), the resistance of the system with CF was increased by about 185 ohms, while the one with Ti by only 140 ohms. Applying a regression analysis the slope for CF is $1.087 \text{ ohm-min}^{-1}$, while the one with Ti has a slope of $0.599 \text{ ohm-min}^{-1}$; these values are higher than the ones observed when the electrode is placed at the soil interphase; but again it is confirmed that using Ti as cathode provides a more stable system. The failure of the CF electrode can be attributed to a poisoning effect since there is a possibility that desorbed hydrocarbons get retained at the cathode.

At the end of each experiment, residual hydrocarbon content in soil was estimated by a Soxhlet technique at 3 points: 0.25, 0.5, 0.75 anode to cathode dimensionless distance; concentration values are normalized respect to the initial concentration condition and presented as percentage. Results are shown in Figure 12 for carbon felt (CF) cathode, and in Figure 13 for titanium (Ti) cathode.

As it can be observed from both Figures (12 and 13) switching the cathode position provides opposite trends in residual hydrocarbon concentrations, since when the physical barrier is between soil and electrode, residual concentration goes from higher to lower in the anode-cathode direction, it seems that transported hydrocarbons are not allowed to accumulate near the cathode; also, CF cathode provides the best conditions for hydrocarbon transport since in the anode-cathode direction hydrocarbon removal goes from 36% to 65% (27% difference), while with the Ti cathode goes from 30 to 42% (12% difference).

In opposite way, when electrodes are at the soil interphase it happens that residual hydrocarbon concentrations increase from anode to cathode, and the higher ones are registered near the cathode; in this case again CF cathode provides the best removal since hydrocarbon removal goes from 60% to 40% (20 % difference), while the Ti cathode removal goes from 40% to 30% (10 % difference).

Based on the cell resistance results, there is an assumption about carbon felt being passivated due to adsorption of those transported hydrocarbon molecules. In order to assess which type of hydrocarbons migrated, and accumulated at the cathode, CF cathodes were washed with a dichloromethane solution, and eluted samples were used for PAHs estimation.

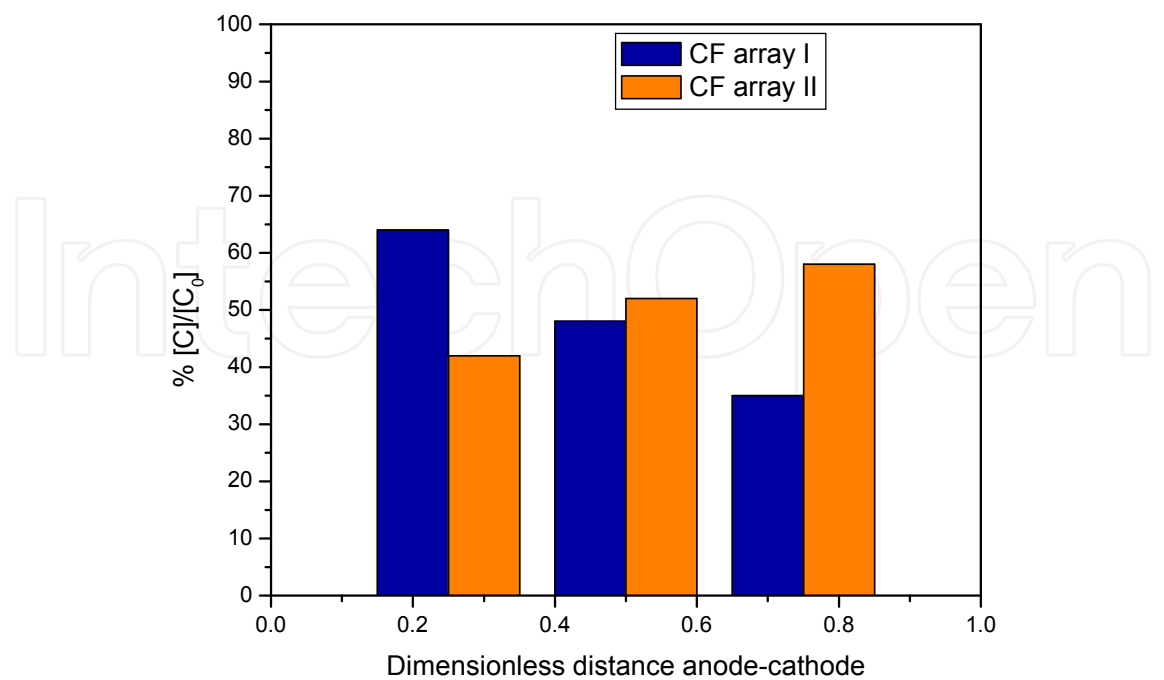


Fig. 12. Graph of normalized residual concentrations for carbon felt (CF) cathode. Array I physical barrier inclusion, Array II soil contact, experimental conditions: 0.1 M NaOH wetting electrolyte, current density 20 mA cm⁻².

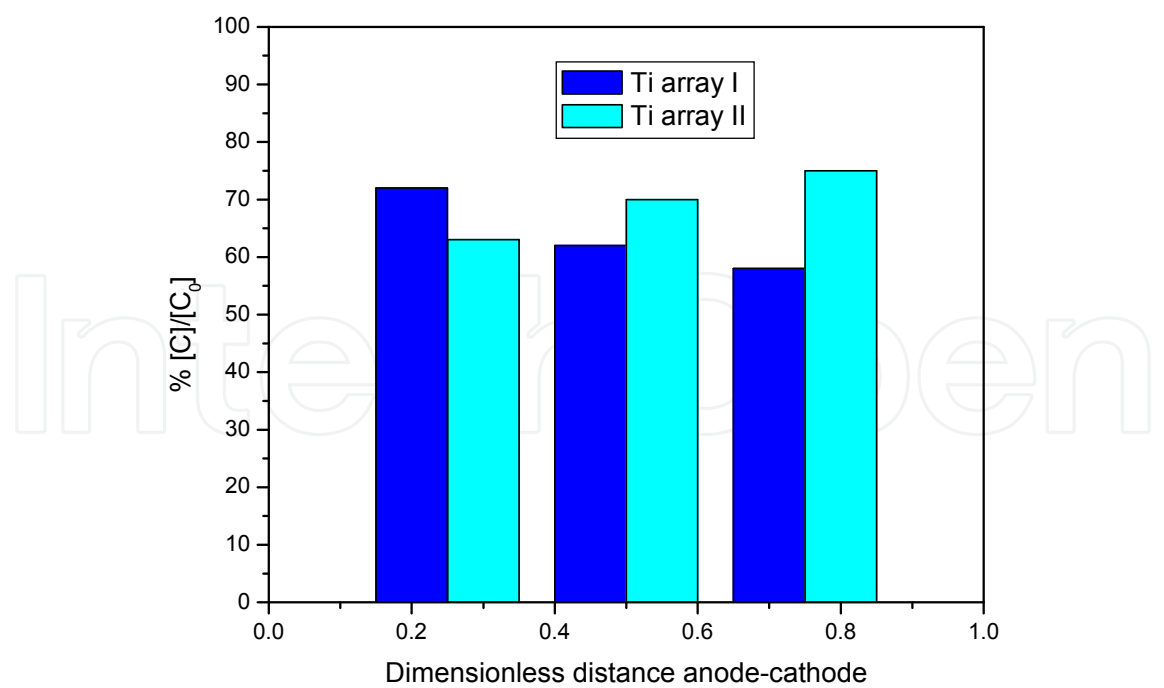


Fig. 13. Graph of normalized residual concentrations for Titanium (Ti) cathode. Array I physical barrier inclusion, Array II soil contact, experimental conditions: 0.1 M NaOH wetting electrolyte, current density 20 mA cm⁻².

In order to assess risk exposition levels for oil exploration and production sites, it takes relevance to detect the EPA's 16 priority Polycyclic Aromatic Hydrocarbons (PAHs) (Bojes & Pope, 2007). Analytical techniques that can be applied to PAHs detection consider HPLC coupled with UV-Vis detection, with this technique the 16 priority PAHs can be detected at wavelengths between 227 and 297 nm (Maureen, 2011); another useful technique is gas chromatography (GC) coupled with mass spectroscopy (MS) (Amzad Hossain & Salehuddin, 2011).

Based on this information, a first approach to PAHs detection was done with UV-Vis, in Figure 14 are shown obtained results for CF cathode in array I (physical barrier included), and array II (soil contact), from these spectra it is obvious that physical barrier presence has enhanced PAHs partition at the interphase soil-water, so keeps hydrocarbon accumulation low in the region nearby; also, the electrode behind the physical barrier has acted like a sink for transported PAHs, so far it is logical to get lower concentrations in the position near the cathode. Otherwise, having the cathode in contact with soil makes PAHs partition to occur at slower rate since PAHs face the hydroxide production at the soil boundary.

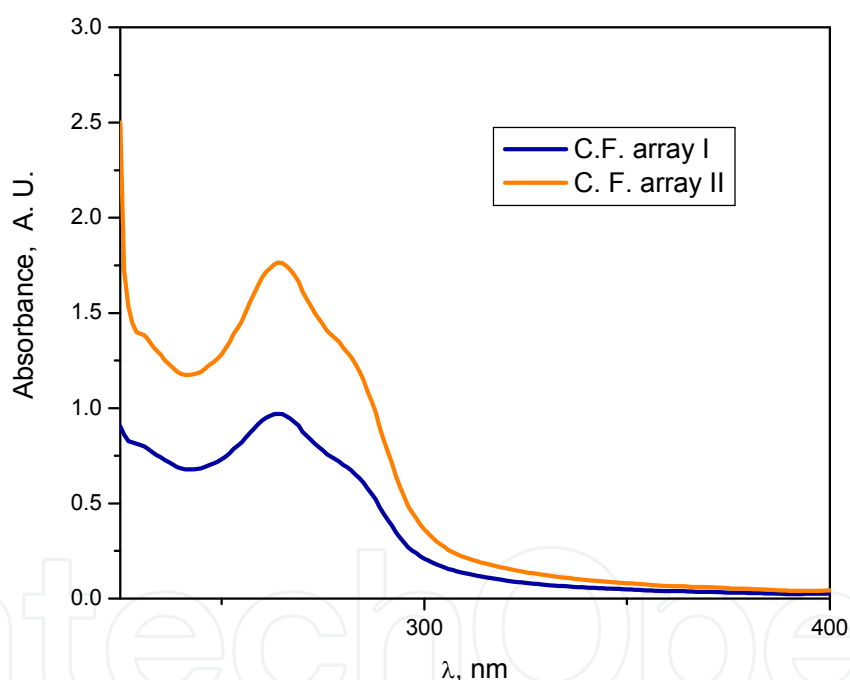


Fig. 14. UV-Vis spectra of sorbed hydrocarbons onto carbon felt cathode in Array I and Array II. Experimental conditions 0.1 M NaOH, current density 20 mA cm⁻², experimental time 4 hours.

Otherwise, observing the spectra, it can be notice that there is not a clear and unique peak; which means there is a possibility of having more than one PAH in the desorbed material. Therefore, a more refined technique should be used for PAHs detection and quantification, requirements widely covered by GC coupled to MS; analytical detection was limited to three of the 16 PAHs in EPA's priority list, the ones chosen were one having three aromatic rings (phenanthrene) and two with 4 rings (fluoranthene and pyrene).

In order to assess soil electroremediation efficiency in removal of phenanthrene, fluoranthene and pyrene, GC-MS was applied to the soxhlet extracted samples including both original and electroremediated soil. Concentration values were calculated from the area under the curve, and these were converted to percentage taking as reference concentration the one for each PAH registered in the extract from the original weathered soil. Results for the Ti cathode are shown in Figure 15 for the array I (physical barrier inclusion), and Figure 16 for array II (soil contact).

As it can be observed in Figure 15, (array with the physical barrier) there is a higher to lower trend from anode to cathode for the three PAHs which were analyzed, and removals are low; it seems that molecule size exerts an influence on their movement through the soil, since the 3 rings molecule (phenanthrene) has reached removals between 80 and 90%, while those with 4 rings (fluoranthene, pyrene) get similar removals between 60 and 85%. Otherwise, in Figure 16 it can be observed that allowing the electrode to make contact with soil enhances PAHs removal, getting similar residual concentrations for all, in this experiment removals are above 90%.

Correlating these residual concentrations with pH observations (Figures 9 and 10) it seems that the fact of having a physical barrier between soil and electrode, which produces a more resistive system, does not allow for getting a high concentration gradient between electrodes, resulting in lower removals than those obtained when the electrode make contact with the soil; since the last arrangement produces a higher pH gradient between anode and cathode, so far a higher driving force for PAHs transport.

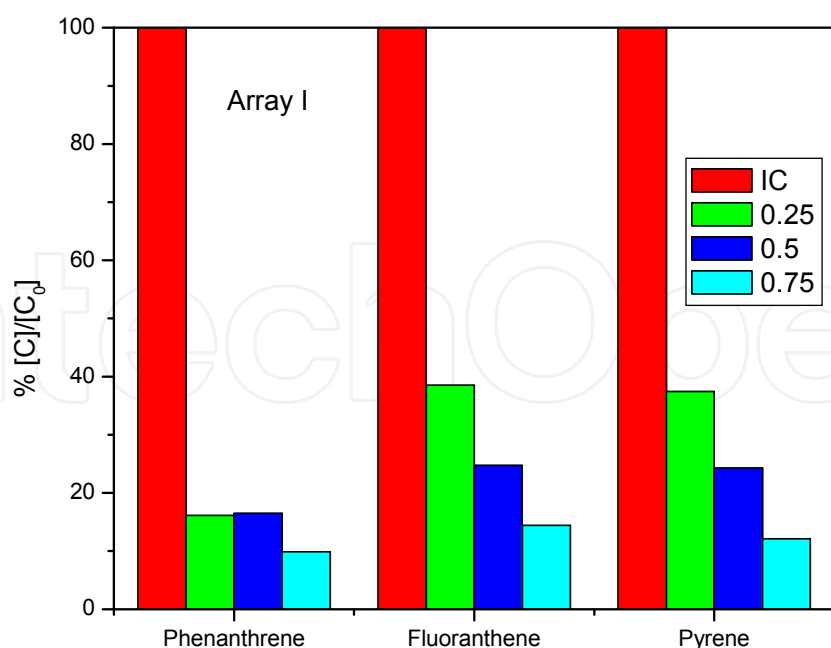


Fig. 15. Residual concentrations of representative PAHs in Array I physical barrier included, experimental conditions 0.1 M NaOH, current density 20 mA cm⁻², experimental time 4 hours.

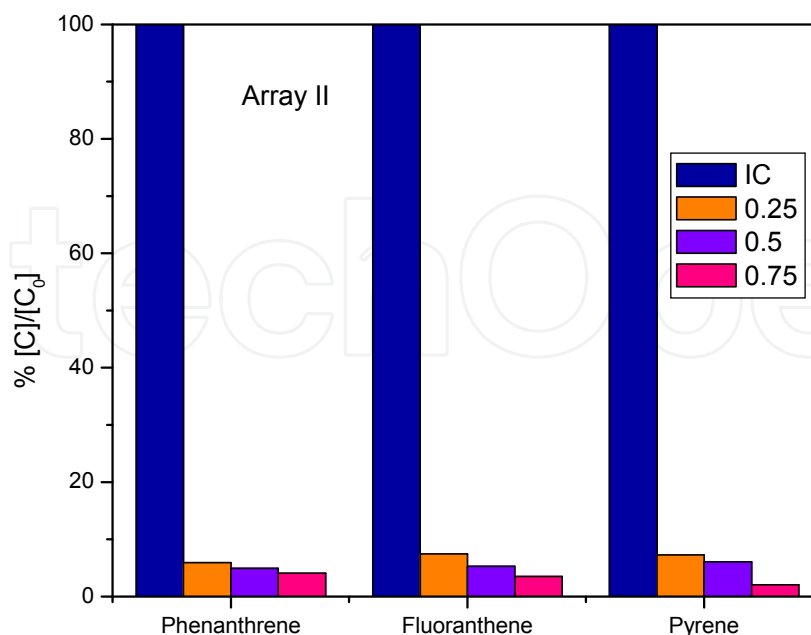


Fig. 16. Residual concentrations of representative PAHs in Array II, experimental conditions 0.1 M NaOH, current density 20 mA cm⁻², experimental time 4 hours.

4. Conclusions

For anode modification obtained results allows to claim that, effectively inclusion of anatase into the RVC matrix makes electrode reaction being more efficient. Also, by using the modified RVC-TiO₂ electrode it is possible to increase the rate at which protons are generated and transported throughout the soil, and so far this influences pH at both electrode wells: anodic and cathodic. Also, it provides a higher electroosmotic flow, but this fast water transport does not allow for an adequate residence time, lowering phenanthrene removal. So far, the bare RVC electrodes provided a lower pH gradient between anode-cathode, as well as a lower electroosmotic flow, both parameters are providing a better environment for phenanthrene removal, since with this option it was obtained up to 80% lowering in soil phenanthrene concentration.

For cathode modification obtained results have shown that cell resistance is lower when electrodes are in contact with soil sample, and this allowed for higher hydrocarbon mobility, so residual concentration profile exhibits an increasing trend from anode to cathode. Otherwise, physical barrier inclusion increased soil resistance and so far, hydrocarbon mobility is lowered, this fact resulted in a decreasing concentration trend from anode to cathode. From oil and grease extractions it was determined that CF provides higher hydrocarbon removal, although this option is not the best because transported hydrocarbons get adsorbed in the electrode, being difficult its recovery.

Even though Ti cathode provided lower hydrocarbon removal as it was estimated from Soxhlet extractions, when extracted samples were tested by GC-MS for quantification of three priority hydrocarbon pollutants, it happens that phenanthrene, fluoranthene and

pyrene concentrations have been lowered in values higher than 60% when the physical barrier was included; and higher removal was obtained more than 95% when cathode was placed at the soil interface.

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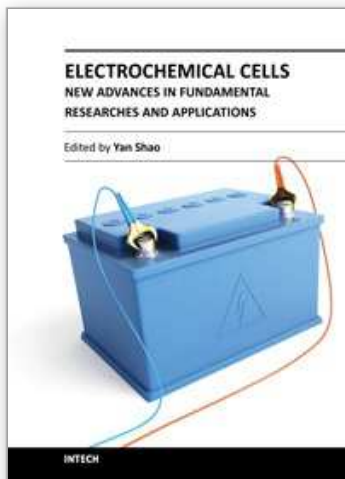
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