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# A promising Electrochemical Test for Evaluating the Hydrocarbon – Type Pollutants Contained in Industrial Waste Soils

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Soil pollution has become one of the most serious problems due to its negative repercussion on ecosystems. For this reason, different analytical techniques have been developed to evaluate the quantity of organic pollutants using electrochemical techniques that are based on the polarity of solvents, and by verifying the change in the resistance of ionic transference originating from the pollutants in the form of hydrocarbons present in soil with the use of electrochemical impedance spectroscopy.The good response of the electrochemical impedance spectroscopy test for evaluating hydrocarbon – type pollutants contained in industrial waste soils was verified across the interaction hydrocarbon – soil, where the clean soil showed increased ionic transference in a logarithmic manner with increasing particle size; in contrast, polluted soil showed decreased ionic transference in an exponential manner with increasing particle size. These results were verified with Soxhlet extraction and quantification of hydrocarbon in polluted soil.

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**Keywords:** Soil, electroremediation, particles, hydrocarbon and impedance.

## 1. INTRODUCTION

The oil industry has had a negative impact on the environment due to flights or spills caused by flaws in its infrastructure, either inside or outside its facilities. However previously, there were not appropriate disposal means for these pollutants, hence, contaminated areas where oil was confined caused soil pollution [1-2].

Due to the above, the petrochemical industry has shown a deep interest in rehabilitating polluted areas, and demonstrated this interest by promoting various technologies to reduce this problem, such as bioremediation (on-site land farming, composting, aerobic remediation, aerobic bioreactor and anaerobic remediation) [2-3], thermal treatment [3], microwave-induced thermal treatment [4], solvent extraction (extraction with water and organic solvents, surfactant-added, cyclodextrins, vegetable oil and supercritical fluid) [3], phytoremediation (with grass, trees and alges) [3], chemical oxidation (as oxidant Fenton's reagent, ozone and hydrogen peroxide) [3], photocatalytic degradation [3] and electrokinetic remediation [3, 5].

Among these, electrokinetic remediation or electroremediation can be applied *in situ* and *ex-situ* to remove organic and inorganic pollutants in low permeability clays and sediment soils. Among species being treated with this technique are inorganic and organic species [6]. The first step is to apply an electric field to the soil being studied, and to take advantage of the properties of the matrix this system creates in order to remove all the pollutants. Therefore, it is necessary to pass a current between electrodes (anode and cathode), that are strategically buried in the soil being studied [6].

The electroremediation movement of pollutants is demonstrated by three important phenomena: (1) electrophoresis –movement of loaded particles; (2) electroosmosis –movement of solvent inside soil pores; and (3) electromigration –ion movement toward oppositely charged electrodes, through an electric field. Other processes that also occur during mass transportation are reactions in anode and cathode (electrolysis), of chemical species in the soil and the water, and the electrolysis of water which defines the pH along the sample of soil being treated [6-8].

Effects of organic pollutants as hydrocarbons in soil affect different physical and chemical characteristics such as permeability, structure, particle size, moisture and organic matter content. Knowing these characteristics for each component will allow the identification of a soil pollutant [9-10].

Diverse analytic techniques have been used to study different properties of soil, such as: FT-IR (Fourier Transform Infrared Spectroscopy) [11], ATR-FTIR (Attenuated Transmittance Reflectance coupled to FT-IR) [7], XRD (X-Ray Diffraction) [11-12], HPLC (High Performance Liquid Chromatography) [13-14], HPLC-MS (HPLC coupled to Mass Spectrometry) [14], HPLC – DAD (HPLC in combination with a Diode Array Detector) [15], GC-MS (Gas Cromatography coupled to Mass Spectroscopy) [13-14], GC-FID (GC with Flame Ionization Detection) [16-17], FAAS (Flame Atomic Absorption Spectrometry) [18], CVAAS (Cold Vapor Atomic Absorption Spectrometry) [18], UV-Vis (Ultraviolet-Visible Spectroscopy) [14, 19], UV-Vis-MAS (UV–Vis Molecular Absorption Spectrometry) [18], LIBS (Laser – Induced Breakdown Spectroscopy) [20], UVIF (Ultraviolet induced Fluorescense) [21], XPS (X-Ray Photoelectron Spectroscopy) [22] and EIS (Electrochemical Impedance Spectroscopy) [23-27].

EIS is a technique across the interfacial phenomenon can be evaluated to obtain resistance of the solution, ionic transference resistance, electrode capacitance and others kinetic and thermodynamic parameters over the electrode. When EIS is developed in a potentiostat manner, a sinusoidal perturbation of potential is applied ($\Delta E = |\Delta E|\sin(\Delta t)$) and the current has a sinusoidal behavior too ($\Delta i = |\Delta i|\sin(\Delta t)$). The relationship between these both variables is defined as the impedance of the system [28-29].

Soil is an ionic conductor because of the salts which are present, and when the composition or structure of soil is modified by the presence of other kinds of compounds, its constitution and properties change. In this manner, EIS can indicate the change of the ionic transfer resistance in the soil by the variation of the particle size and the hydrocarbon presence.

This work propose an electrochemical impedance spectroscopy test for evaluating hydrocarbon – type pollutants contained in industrial waste soils by studying the interaction between hydrocarbon – soil in organic and inorganic solvents. A theoretical model was proposed and fitted to the experimental results of electrodes of soil used to verify the change in the resistance by ionic transference originating in the hydrocarbon present in polluted soil. These theoretical results were verified with the quantification of confined pollutants in greater quantity in particles with smaller size due to the major superficial surface area that they had using Soxhlet extraction.

## 2. EXPERIMENTAL.

In this study two punched samples of soil were obtained: clean soil (CS) and polluted soil (PS) by hydrocarbon. Both of them were taken in a base of NMX2-12/1-1987 and the chapter 9 of SW82-EPA of an industrial zone.

Once two samples were obtained, they were physically and chemically characterized to understand their behavior during the EIS probes. In this sense, the polluted soil was electro-remediated to developpe the electrochemical test to verify the removal of pollutants after the treatment. From this, the parameters and theoretical models were constructing to simulate the different EIS spectra obtained.

### *2.1. Physical and chemical characterization of soil.*

To define the physico-chemical characteristics of soil with and without hydrocarbon, different criteria were established:

### *2.1.1. Particle size.*

It was carried out by granulometry by evaluating samples with and without hydrocarbon using different size sieves (12.5, 1.0, 0.63, 0.315 and 0.1 mm) to get a better idea of the distribution of HC in the soil.

### *2.1.2. Texture determination.*

The percentage of clay, silt and sand was determined with a Bouyoucos hydrometer. This technique is based on measurements of sedimentation speed of suspended soil in water in order of the different fractions of clay, silt and sand, and then the results are compared with a soil texture triangle, used to classify the texture class of a soil.

### *2.1.3. Color determination.*

The color of soil is determined with the Munsell table in accordance with the method AS-07-1997, verifying the clarity, matiz and purity.

### *2.1.4. Moisture content and pH determination.*

These parameters were defined according to NOM-147-SEMARNAT / SSA1-2004 and AS-11-1997 with water.

### *2.1.5. Density and porosity determination.*

To define the density the AS-15-2007 was developed using a picnometer. The porosity is the relation between the real density respective to the apparent density.

### *2.1.6. Organic content determination.*

The organic content was defined with the Walkley and Black modified method. This technique involves combustion of the organic matter with a mix of dichromate of potassium ($K_2Cr_2O_7$) and sulfuric acid ($H_2SO_4$) [30].

### *2.1.7. Cation Exchange Capacity (CEC).*

This determination was made with $CaCl_2$ to cation exchange of $Ca^{+2}$, $Mg^{+2}$, $Na^+$ and $K^+$ with sucesive extractions determined by volumetric measurements.

### *2.1.8. Metals determination.*

Soil metal contents analysis was made using Inductively Coupled Plasma with a Mass Spectroscopy detector (ICP - MS), where prepared samples were run according to the Mexican Official Norm NOM-147-SEMARNAT/SSA1–2004. To characterize each sample using ICP probes, 50 mL of solution with 5 mL of 2 % $HNO_3$ was used to induce the digestion of the sample. The ICP equipment was a Perkin Elmer, Optima 3300 model with an absorbance of 193.69 nm.

To determine aditional inorganic compounds, Emision Difraction X Ray (EDX) was used to analyze 1 g of soil which was triturate to make compressed homogeneous pills of soil. This analysis was developped with PHILPS XL 30S with low vacum and 20 or 30 kV of aceleration voltage.

### *2.1.6. Fatty and oil content determination.*

Non - volatile hydrocarbon extraction was made by Soxhlet extraction, according to the Mexican Official Norm NMX-AA-005-SCFI-2000 using grade reactive hexane. The resuls were compared with the NOM-138-SEMARNAT/SSA-2003 to define the pollution grade.

### 2.1.7. Organic compounds determination.

Samples extracted by Soxhlet were analyzed by gas chromatography with mass spectrometry.

### 2.1.8. Crystalographic composition determination.

Soil crystallographic composition was determined by X Ray Diffraction (XRD), using SIEMENS D-5000 equipment.

### 2.1.9. Morphological determination of soil.

Scanning Electron Microscopy (SEM) and Emission Diffraction Spectroscopy (EDS) experiments were carried out with a Philips XL 30S scanning electron microscope, with low vacum, using an acceleration voltage of 30 kV with 25 x augmentations. The different samples of soil were put over pines with silver paint and pills were formed with a press of 203 Kg / $cm^3$.

### 2.2. Electroremediation of soil polluted with hydrocarbon.

According to the already determined soil characteristics, electroremediation was applied to polluted soil, in an electrochemical acrilic horizontal tubular cell as reported in the literature [8, 31-32], which was constituted by two compartments for the Ti and $Ti/IrO_2$-$Ta_2O_5$ electrodes as cathode and anode respectively which were separated by the soil compartment to approximately 30 g. The support electrolyte was 0.5 M NaOH.

With the electrochemical reactor different working potentials (5, 10, 15, 20, 25 and 30 V) were tested using a DC power supply model GP-4303DU, keeping hydraulic flow constant with a MASTERFLEX L/S economy drive peristaltic bomb with 2 mL / min, and taking samples at different time intervals.

During the 24 h removal process pH and developed current measurements with UNI-T digital multimeter model UT33B were taken to make sure hydrocarbon removal was being adequately performed. The efficiency of hydrocarbon remotion during the different experiments was determined with UV-Vis spectrophotometry using Ocean Optics equipment with optic fiber and a quartz cell of 3 mL.

### 2.3. Electrochemical impedance determination.

To develop EIS experiments, two electrochemical cells were used, a 10 mL glass cell (Figure 1-B) and 2 mL teflon cell (Figure 1-C) with three electrodes: Ag/AgCl saturated KCl, titanium or platinum wire and soil installed as reference over or not of a platinum plate, auxiliar and work electrode, respectively. The sizes of particles used for this analysis were 0.25, 0.4, 0.65, 1.0 and 1.6 mm, corresponding to fine, medium, gross, and very gross sand respectively.

Clean and polluted soil electrodes were constructed with a plastic syringe of 3 mL using a titanium wire as piston (Figure 1-A). 0.5 g of soil was used because this quantity offered a minimum resistance to the ionic transference detected by EIS in the 10 mL glass cell (Figure 1-B). In this case, in order to have better contact between the particles of soil, nafion was used during the EIS experiments. To decrease the resistance, the soil was analyzed using the 2 mL teflon cell (Figure 1-C) which was put over a platinum plate to provide a better contact.

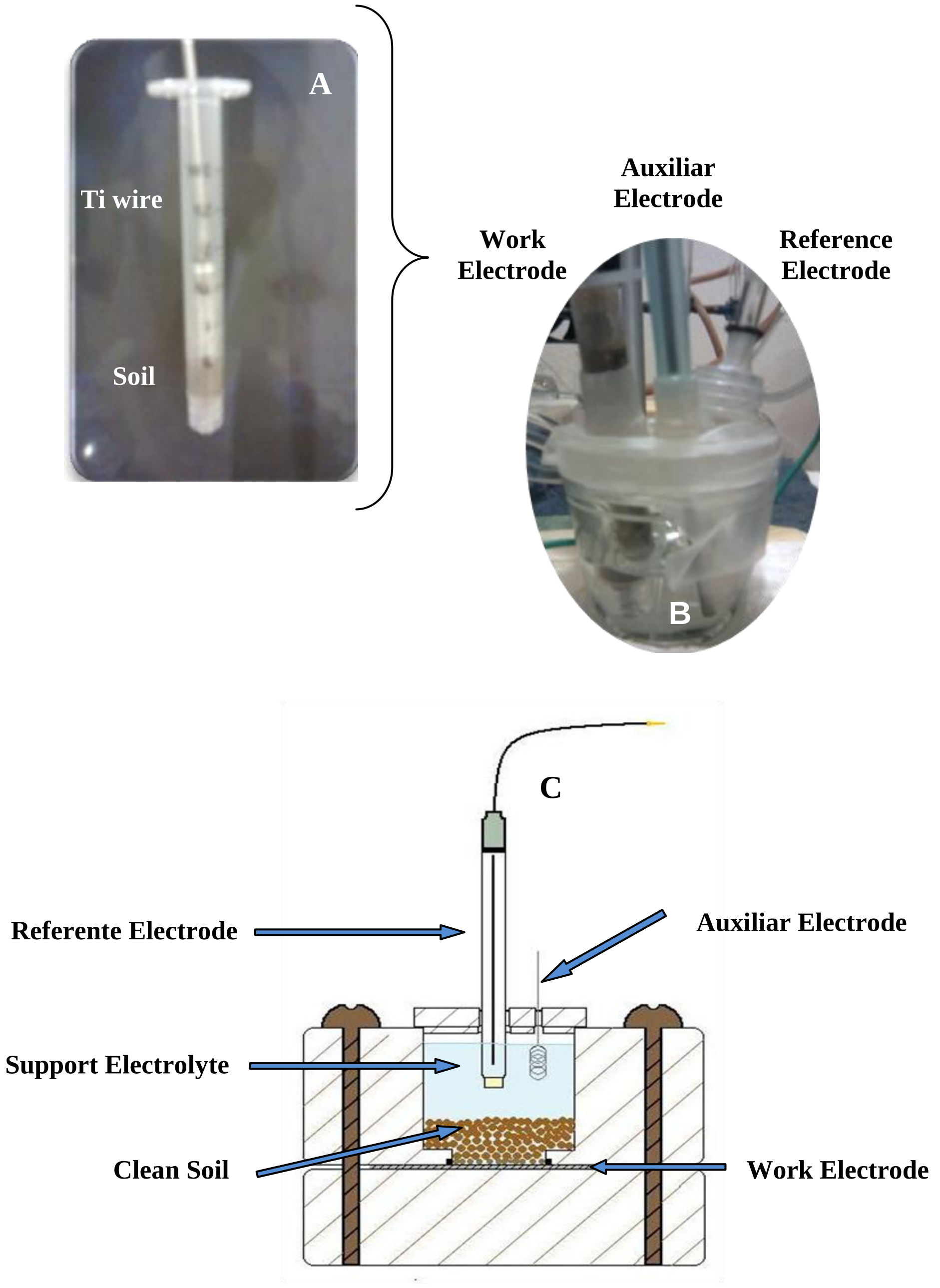

**Figure 1.** Image of the plastic syringe with soil as work electrode (A) which was used in 10 mL glass cell (B) with Ti wire as auxiliar electrode. The 2 mL teflon cell (C) with wire platinum as auxiliar electrode. In both electrochemical cells the Ag / AgCl saturated with KCl was used as reference electrode.

EIS experiments were carried out employing a BAS – Zahner IM68e impedance instrument. Before each electrochemical experiment, the electrolytic solutions were deoxygenated by bubbling ultra-pure nitrogen (PRAXAIR, grade 5.0) for at least 10 min, and during electrochemical experiments $N_2$ was blown gently over the solution surface. They were performed on soil electrodes using a 10 mV amplitude wave around the equilibrium potential. The range of frequencies applied was from 5 mHz to 5 MHz with an amplitude of 10 mV with 10 measurements by logaritmic decade.

The resistance of ionic transference ($R_t$) and the total capacitance ($C_t$), which is approximately equal to the capacitance of the particles in the soil ($C_s$) plus that of the double - layer ($C_{dl}$), were obtained by fitting the experimental impedance data to the Randles equivalent – circuit model included in the Z-plot software. The Randles equivalent circuit, while not the only model possible, has frequently been employed to represent modified electrochemical interfaces and in the present case provided an excellent fit to the data [33].

## 3. RESULTS AND DISCUSSION.

### *3.1. Physicochemical characterization of soil.*

Physicochemical properties of clean and polluted soils by hydrocarbon were examined, where the polluted soil presented additional compounds and different properties than the clean soil.

On table 1 it can be observed that the soil sample being studied shows an abundance of sand particles from coarse to fine sand, with size particles between 12.5 to 1 mm, respectively.

**Table 1.** Particle size separation according to USDA system.

| Size of Particle (mm) | Soil without Hydrocarbon (g) | Soil with Hydrocarbon (g) |
|---|---|---|
| > 12.5 | 427 | 211 |
| 12.5-1 | 405 | 409 |
| 1 | 19 | 90 |
| 0.63 | 24.53 | 154.72 |
| 0.315 | 23 | 18 |
| 0.1 | 9 | 0 |

Different physicochemical parameters were evaluated in the CS and PS (Table 2). The pH of the CS and PS was around of 6.64 and 4.66, respectively. The decrease of the pH of the polluted soil was caused by the presence of HC, which agregated the particles of soil and decreased the protons exposed to the solution.

**Table 2.** Some physical and chemical characteristics of clean and polluted soil used in this study.

| Parameter | Clean Soil | Polluted Soil |
|---|---|---|
| Soil solution pH | 6.64 | 4.66 |
| Clay (%, < 0.002 mm) | 52.54 | 19.18 |
| Silt (%, 0.05 – 0.002 mm) | 22.16 | 16.85 |
| Sand (%, > 0.05 mm) | 25.30 | 63.97 |
| Texture | Clay | Franc - Sand |
| Color | Dark gray | Black |
| Moisure (%) | 13.14 | 20.24 |
| Aparent Density (g / cm$^3$) | 1.7 | 1.7 |
| Real Density (g / cm$^3$) | 2.5 | 1.99 |
| Pore (%) | 32 | 14.57 |
| Organic Content (%) | 2.68 | 18.46 |
| Cation Exchange Capacity (meq / Kg soil) | 38.2 | 15.68 |
| Mineral species | $SiO_2$, $Na_3(PO_4)$-$Al(PO_4)$, MgO-MnO | $SiO_2$, $Na_3(PO_4)$-$Al(PO_4)$, MgO-MnO, $Ga(PO_4)$, $AlSi_4$, FeO |
| Fatty and Oils (mg fatty and oil / kg dry soil) | 5 500 | 118 300 |

The texture of soil was measured with the Bouyoucos hydrometer. In the case of CS, it had 52.54, 22.16 and 25.30 % of clay, silt and sand respectively because this soil is Vertisol Pelic class with clay predominating, while the PS had 19.18, 16.85 and 63.97 % respectively, and it is franc - sand by the presence of HC which agglomerates the clay and forms major particles similar to sand.

With the Munsell table of color, the CS showed a dark gray probably because of the presence of reduced iron ($Fe^{2+}$) caused by the intensive rain in that area and different minerals like filosilicates such as caolinita ($Al_2Si_2O_5(OH)_4$) and talc ($Mg_3Si_4O_{10}(OH)_2$), and tectosilicates such as quarz $(SiO_2)_n$ detected with XRD. The PS showed a black color because of the hydrocarbons which increase the organic matter (18.46 %) compared to the CS (2.68 %) obtained with the Walkley and Black modified method [30].

The real density in table 2 was different for the two soils in the study, where the PS had a lesser density than CS (1.99 and 2.5 g / cm$^3$ respectively) by the presence of HC, which weight of organic compounds less than the volume of minerals present in the CS [30]. In the same manner, the percentage of pores was higher in the CS than the PS, which is indicative that HC occupied approximately a quarter of the empty spaces of the pores. This result was verified with the CEC measured, where the CS had 38.2 meq / Kg soil and the PS had 15.68 meq / Kg soil.

The chemical composition of soil was of Fe, Ca, V, Mg, K, Na, Ni, Ti, Mn, As and Tl verified with ICP and O, Si, C and Al by EDX. The ICP analysis performed on hydrocarbon contaminated soil shows lead, evidenced by the presence of 142.56 mg / Kg Ni in the soil polluted with hydrocarbons (Table 3) just as was expected by the catalyzers in hydrocarbon even when the clean sample did not show it [34].

**Table 3.** ICP analysis performed of soil with and without hydrocarbon.

| Element | Soil without Hydrocarbon (mg / kg) | Soil with Hydrocarbon (mg / kg) |
|---|---|---|
| Fe | 23 562.89 | 12 447.84 |
| Al | 37 184.59 | 18 115.44 |
| Mn | 299.75 | 146.04 |
| K | 5 236.20 | 2 433.94 |
| Ni | 0.00 | 142.56 |
| Cu | 0.00 | 0.00 |
| As | 147.98 | 0.00 |
| Si | 24 928.86 | 20 653.69 |
| Ca | 8 081.96 | 6 954.10 |
| Mg | 6 450.39 | 3 424.90 |
| Na | 13 856.95 | 3 473.57 |

Likewise, the percentage of moisture was determined in the sample of the soil studied, which was of 13.14 %, having 7.1 % of volatile hydrocarbon. Soil with hydrocarbon showed double the moisture percentage (20.24 %) compared to clean soil.

It was also determined that the clean soil contained 5 500 mg / Kg of oil, compounds of natural origin in the soil. On the other hand, the polluted soil showed 118 300 mg / Kg of oil, that is to say, 112 800 mg of oil with an anthropogenic origin / Kg of soil which was over the permissible limits for industrial soil (6 000 mg / Kg soil dry base).

Once the oil had been extracted from the polluted soil, the organic compounds were identified using gas chromatography coupled to a mass spectrometer according to the norm NOM-138-SEMARNAT-SS-2003. With this analysis, met- aromatic (naphthalene and phenanthrene) and aliphatic hidrocarbons with chains of 20 to 32 carbons that according to this norm, are classified as hydrocarbons of hard fraction, among which are identified Gasoil, Diesel, Turbosine, Kerosene and Creosote, that are not lubricant oils (chains with > 18 C, Table 4).

**Table 4.** Semi-volatile compounds determinate with GC-MS of the oil extracted of polluted soil.

| Compound | Molecular Weight (g / mol) | Retention Time (min) | Area (a.u. / min) |
|---|---|---|---|
| Dotriacontane | 452 | 38.27 | 0.32 |
| Triacontane | 422 | 33.69 | 0.27 |
| Nonacosane | 408 | 32.88 | 0.62 |
| Heptacosane | 380 | 31.24 | 0.59 |
| Hexacosane | 366 | 30.38 | 0.55 |
| Pentacosane | 352 | 29.48 | 0.63 |
| Tetracosane | 338 | 28.56 | 0.32 |
| Tricosane | 324 | 27.61 | 0.77 |
| Docosane | 310 | 26.64 | 0.68 |
| Heneicosane | 296 | 25.63 | 1.04 |
| Eicosane | 282 | 24.65 | 1.98 |
| Nonadecane | 268 | 32.07 | 0.5 |
| Octadecane | 254 | 27.21 | 0.21 |
| Heptadecane | 240 | 26.97 | 0.4 |
| Dodecane | 170 | 13.1 | 0.28 |
| 3-Methyl-dibenzotiophiene | 294 | 23.52 | 1.79 |
| 2,5-Dimethyl-phenantreno | 210 | 25.32 | 0.76 |
| 9-Methyl-phenantreno | 196 | 23.85 | 2.1 |
| 7-Ethyl-1,4-dimethyl-azulene | 194 | 20.6 | 2.63 |
| 1,4,6-Trimethyl-phtalene | 170 | 18.41 | 9.25 |
| 2,3,6-Trimethyl-naphtalene | 170 | 19.26 | 3.36 |
| 2,3,5-Trimethyl-phenantrene | 170 | 26.35 | 0.35 |
| 1,5- Dimethyl-naphtalene | 156 | 17.59 | 8.75 |
| 1,4-Dimethyl-naphtalene | 156 | 17.37 | 2.15 |
| 1-Piperidineacetonitrile | 153 | 25..83 | 0.63 |
| 1-Methyl-naphtalene | 142 | 15.41 | 1.86 |
| 2-Etenil-1,4-dimethyl-bencene | 128 | 12.19 | 0.04 |
| Indane | 124 | 11.96 | 0.01 |
| 1,3-Dimethyl-bencene | 112 | 13.33 | 0.19 |
| Bencenamine | 99 | 28.35 | 0.24 |

The SEM analysis of polluted soil with hydrocarbons showed large aggregates because of the presence of pollutants which agglomerated the particles of smaller size (size particle of 0.25 mm,

Figure 2 B-1). For the other two sizes of particles (0.63 mm in Figure 2 B-2 and 1 mm in Figure 2 B-3) there was not an evident change in their form or a joining of particles.

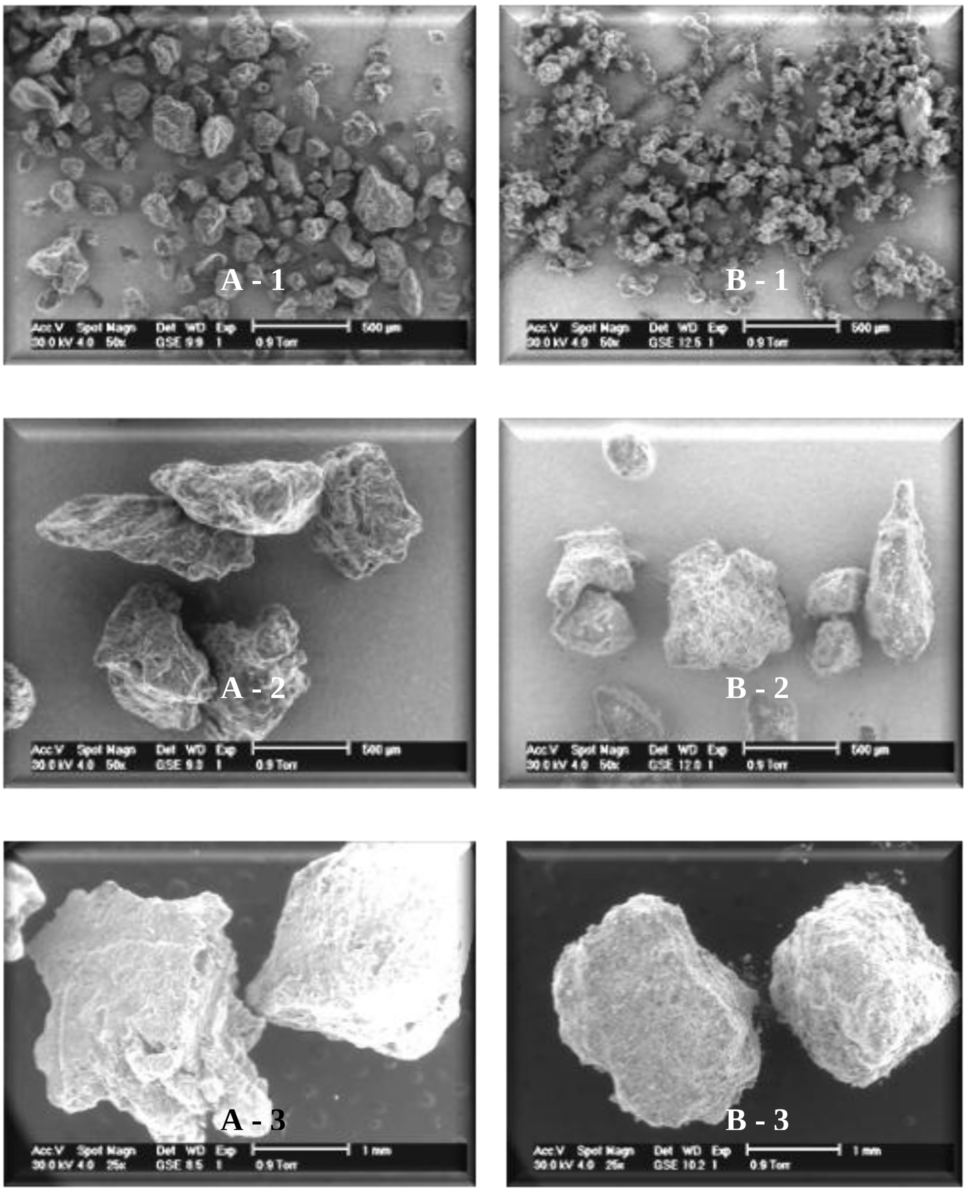

**Figure 2.** Scanning emision microscopy of the different size of particle to clean (A) and polluted soil (B) of 0.32 (1), 0.65 (2) and 1.0 mm (3).

### *3.2. Electroremediation of soil polluted with hydrocarbon.*

With the characterized soil, the electroremediation was done in the soil using a constant potential and taking samples each hour during 7 h of treatment, with the purpose of determining the percentage of relative remotion using UV - Visible spectroscopy following the signal at 276.45 nm, which generated an absorbance signal by the electronic transitions n - $\pi^*$ of free couple of electrons and double links presents in the hydrocarbon molecules. In figure 3 the biggest percentage observed in the relative remotion percentage (% Remotion = ($Abs_{max}$ - Abs) / $Abs_{max}$)*100) was of 61.86 %, which was obtained when using 20 V during 270 min of treatment (Figure 3).

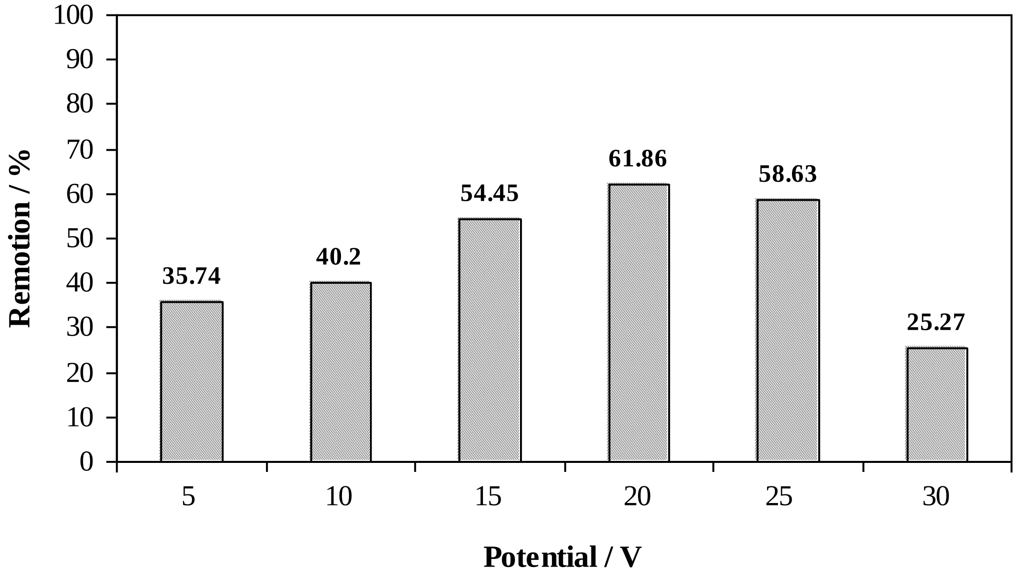

**Figure 3.** Graph with the percentage of hydrocarbon removal and the time with the major remotion across the different potential constant applied in the electro-kinetic cell.

Following the electroremediation under the previous conditions after 24 h, the remotion of hydrocarbon was evident by the disappearance of the brown color of the initial sample (Figure 4). During this experiment the current achieved its highest value at 200 min, and then it decreased to just 900 min. After 200 min of electrochemical treatment, the electrical conductivity was constant due to the re-arrangment of charges originating from the metallic ions or salts between the particles of soil which migrated to the electrodes over time.

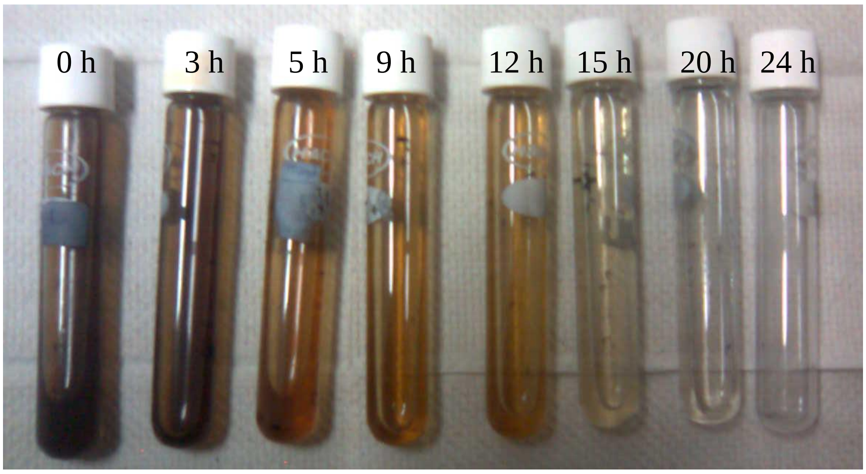

**Figure 4.** Image of the different solutions obtained after the electrochemical treatment during 24 h of reaction applying 20 V, where the remotion of HC was evident by the disappearing of the brown color of initial sample.

To verify the efficiency of hydrocarbon remotion after the electroremediation, the pollutants closest to the anode, to the middle of the cell and closest to the cathode were measured with Soxhlet extractions, which were 40.46, 24.46 and 33.99 % respectively after 24 hours of electrochemical treatment. The extracts obtained were analyzed with GC-MS and the electroremediated soil eliminated some chemical compounds such as dotriacontane, triacontene, heptacosane, 2,3,5-trimethylphenantrene, indane and methyl-naphtalene.

As different organic pollutants were removed by applying an electric field, this situation suggested the electrical relation between hydrocarbon – soil and led to electrochemical impedance spectroscopy as a test for evaluating the hydrocarbon – type pollutants contained in soil, taking ionic transference as the comparison parameter.

### *3.3. Electrochemical impedance determination with clean and polluted soil using different sizes of particles to determine the ionic transference.*

In figure 5, Nyquist diagrams of clean soil obtained using a 10 mL glass cell (Figure 1-B) showed that ionic transference ($R_t$) related to the loop diameter, changed with the size of the particle, where the largest size of particle showed the highest $R_t$. Thus, $R_t$ changes with size in the sequence: 1.00 >> 0.63 ≈ 0.25 mm. In contrast, in the polluted soil (Figure 6) the smallest size of particle showed the highest $R_t$: 0.25 >> 0.63 > 1.00mm.

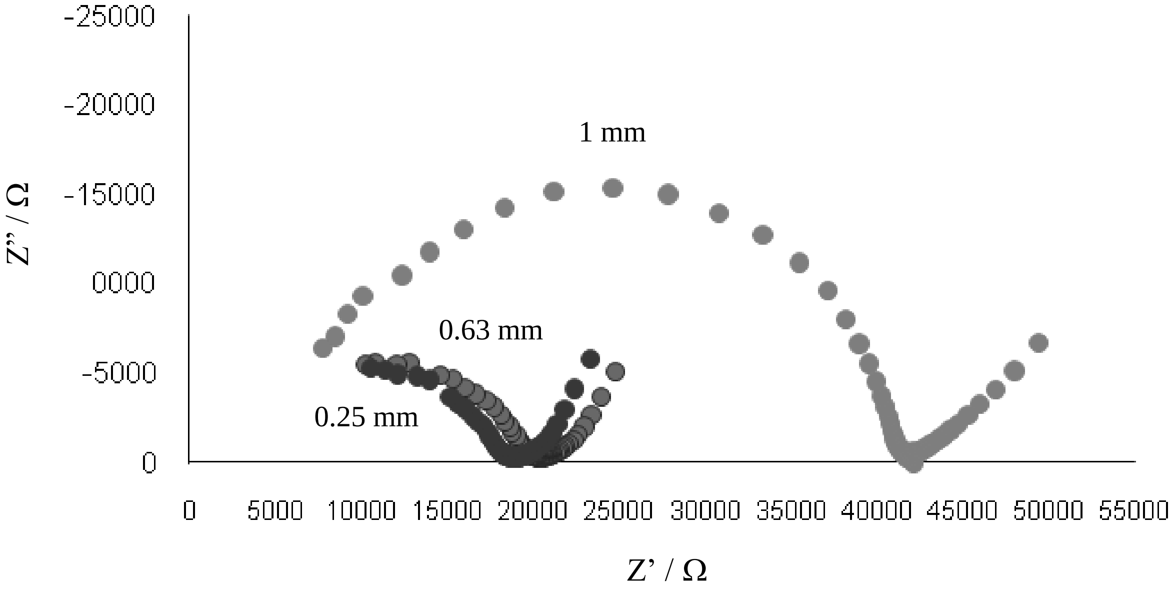

**Figure 5.** Nyquist diagram of clean soil with different size of particle: 0.315, 0.65 and 1 mm.

To obtain the value of the different electrochemical parameters, the Nyquist diagrams of figure 5 and 6 were ajusted using Z-plot program and modified Randles Circuit, where total electrode capacitance ($C_T$) and Warburg element (W) were changed by a Constant Phase Element (CPE) and Warburg element for porous electrodes ($W_o$), respectively (Figure 7-C).

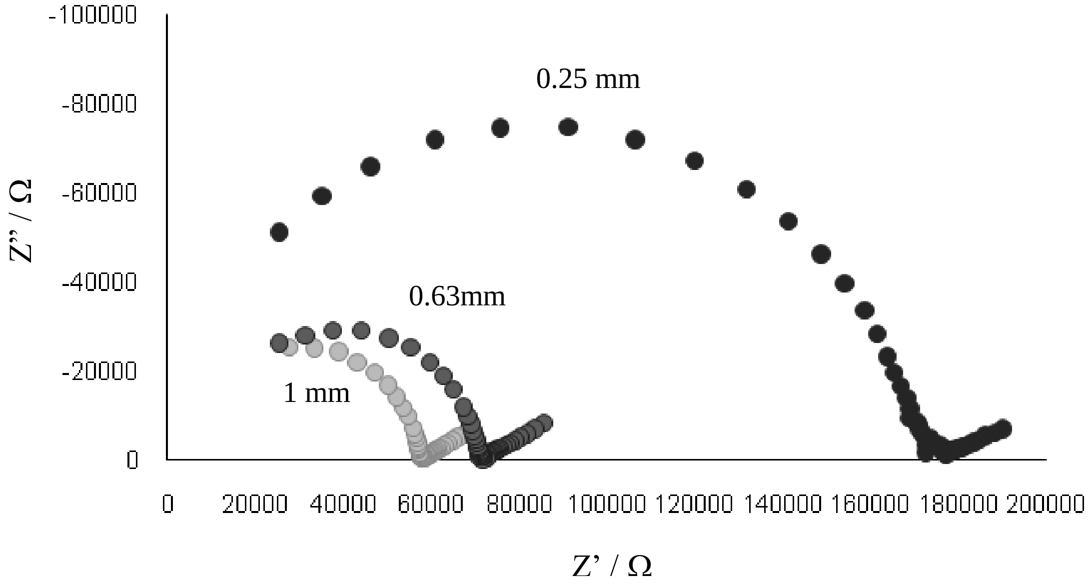

**Figure 6.** Nyquist diagram of polluted soil with different size of particle: 0.315, 0.65 and 1 mm.

Making a graph of the simulation results (Table 5), clean soil showed that $R_t$ decreased (Figure 7-A), and in the polluted soil increased (Figure 7-B), both in an exponential way related to the increase in the size of particles.

**Table 5.** Comparison of electrochemical parameters of EIS: resistance of solution ($R_s$), resistance of ionic transference ($R_t$), double layer capacitance ($C_{dl}$), constant phase coefficient (n), resistance to sonde molecule diffusion ($W_o$-$_R$), effective diffusion coefficient of sonde molecule across the particle ($W_o$-$_T$) and slope of the line diffusion ($W_o$-$_P$).

| Size of Particle (mm) | $R_s$ (Ω) | $R_t$ (Ω) | $C_{dl}$ ($F*10^{-11}$) | n | $W_{o-R}$ | $W_{o-T}$ | $W_{o-P}$ |
|---|---|---|---|---|---|---|---|
| **CLEAN SOIL** | | | | | | | |
| 1.00 | 3 174 | 15 096 | 45.1 | 0.92 | 6 769 | 3.65 | 0.35 |
| 0.65 | 3 751 | 15 944 | 52.2 | 0.88 | 7 011 | 4.44 | 0.33 |
| 0.32 | 5 489 | 35 903 | 12.9 | 0.97 | 4 192 | 0.69 | 0.23 |
| **POLLUTED SOIL WITH HYDROCARBON** | | | | | | | |
| 1.00 | 1 761 | 169 510 | 7.72 | 0.93 | 45 686 | 330.10 | 0.10 |
| 0.65 | 9 209 | 61 623 | 6.57 | 0.97 | 38 658 | 47.60 | 0.30 |
| 0.32 | 3 985 | 53 601 | 6.31 | 0.97 | 95 888 | 714.50 | 0.33 |

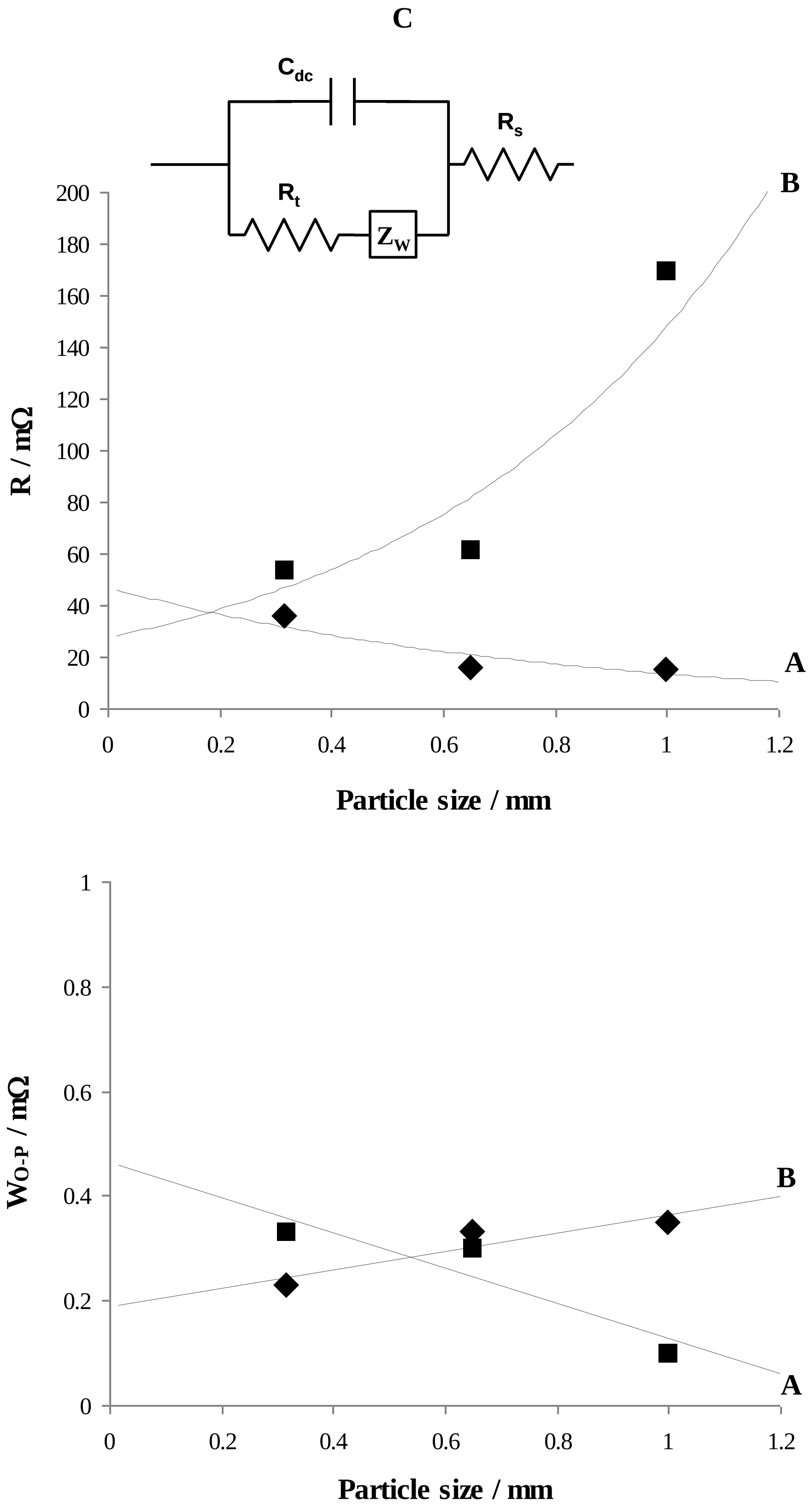

**Figure 7.** Variation of the $R_t$ and $W_o$-P with the size of particle in clean (A) and polluted soil (B). Randles Circuit (C): $R_t$ = resistence of the charge transference, $Z_w$ = Warburg diffusion, $C_{dl}$ = capacitance of the double layer, $R_s$ = resistance of the solution.

This behavior is probably because when there is non hydrocarbon, the larger particles contain more salts which are favorable to a transport charge, but when the pollutant is present over the surface of the material, the conjunction of particles is observed as Figure 7 shows decreasing the $R_t$ in an exponential relationship with the augmentation of the size of particles.

Others parameters showed in table 5 are related to the Warburg element,: $W_0$-R, $W_o$-T, $W_o$-P, where $W_o$-R represents the resistance to diffusion of sonde molecules, $W_o$-P represents the slope of the line diffusion, with a value between 0 and 1, and $W_o$-T is related to the effective diffusion coefficient of sonde molecules across the particle (D) and the effective diffusion thickness (L), as $W_o\text{-T} = L^2 / D$ [35-36].

In the case of polluted soil, this showed a higher resistance to diffusion of sonde molecule ($W_o$-P, Figure 7-B) than clean soil (Figure 7-A), decreasing with the increasing of particle size (Table 5). But, the effective diffusion coefficient was the same with the particle size of 0.65 mm in clean and polluted soil, with the behavior contrary to 0.25 and 1 mm of particle size, as figure 7 shows, probably because of the effective thickness diffusion.

Observing the difference of ionic transference when the hydrocarbon is present in the particles of soil studied, EIS was developed with clean soil using an organic solvent to verify the non - covalent interaction of organic pollutant and soil, and the same study was developed using an inorganic solvent to validate the interaction HC – soil as a reference system.

### *3.4. Electrochemical impedance determination with clean soil using an organic and inorganic solvent to verify the non – covalent interaction of hydrocarbon and soil.*

EIS experiments were developed to evaluate the interaction hydrocarbon – soil. To test this proposal, an inorganic (0.1 M $Na_2SO_4$ in deionized water, Figure 8) and organic (0.1 M $KClO_4$ in 0.1 M carbonate of propylene, Figure 9) solvents were evaluated in the presence of different sizes of particles of soil using the electrochemical cell of Figure 1-C.

In the Figure 8-A the Bode-phase spectra are shown using inorganic medium, which were obtained for each size of particle where one observes that the spectrum corresponding to the target and that obtained making the measurement without adding soil, presented a decrease of around 10 Hz of frequency, which indicated that a transfer of protons exists [37].

However, this decrease disappeared when adding the soil and any spectra reached a phase displacement of 90°. For this reason, a non ideal capacitor was considered in the equivalent circuit. In the Nyquist diagrams (Figure 8-B) the obtained answer shows a slanted line, reason enough for considering the resistance to the transference of ions in the solution, or the resistance ($R_t$).

An important behavior observed was the variation of $R_t$ in order of the size of particles of soil evaluated, because in Figure 8-B the $R_t$ increased with the decrease in the size of particles. This result demonstrated that the soil has less likeness to an inorganic medium.

It may be due to the organic matter present which gives the soil a non-polar behaviour. This situation indicates that the inorganic pollutants have greater mobility in soil because of the smallest adsorption that they have, especially with soil with a small particle size such as in clays.

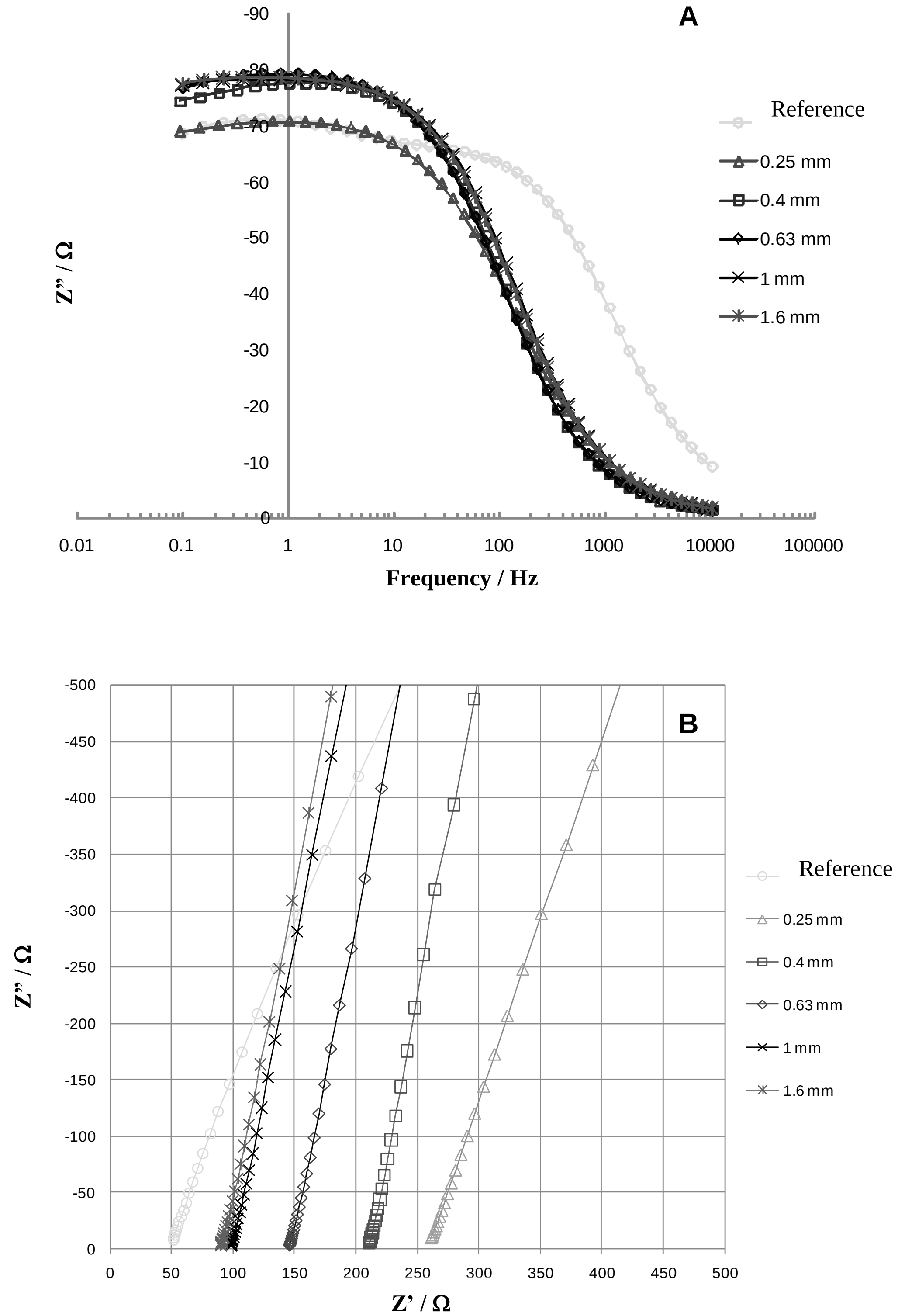

**Figure 8.** Bode-Phase (A) and Nyquist (B) diagrams to each size particle of clean soil in inorganic medium.

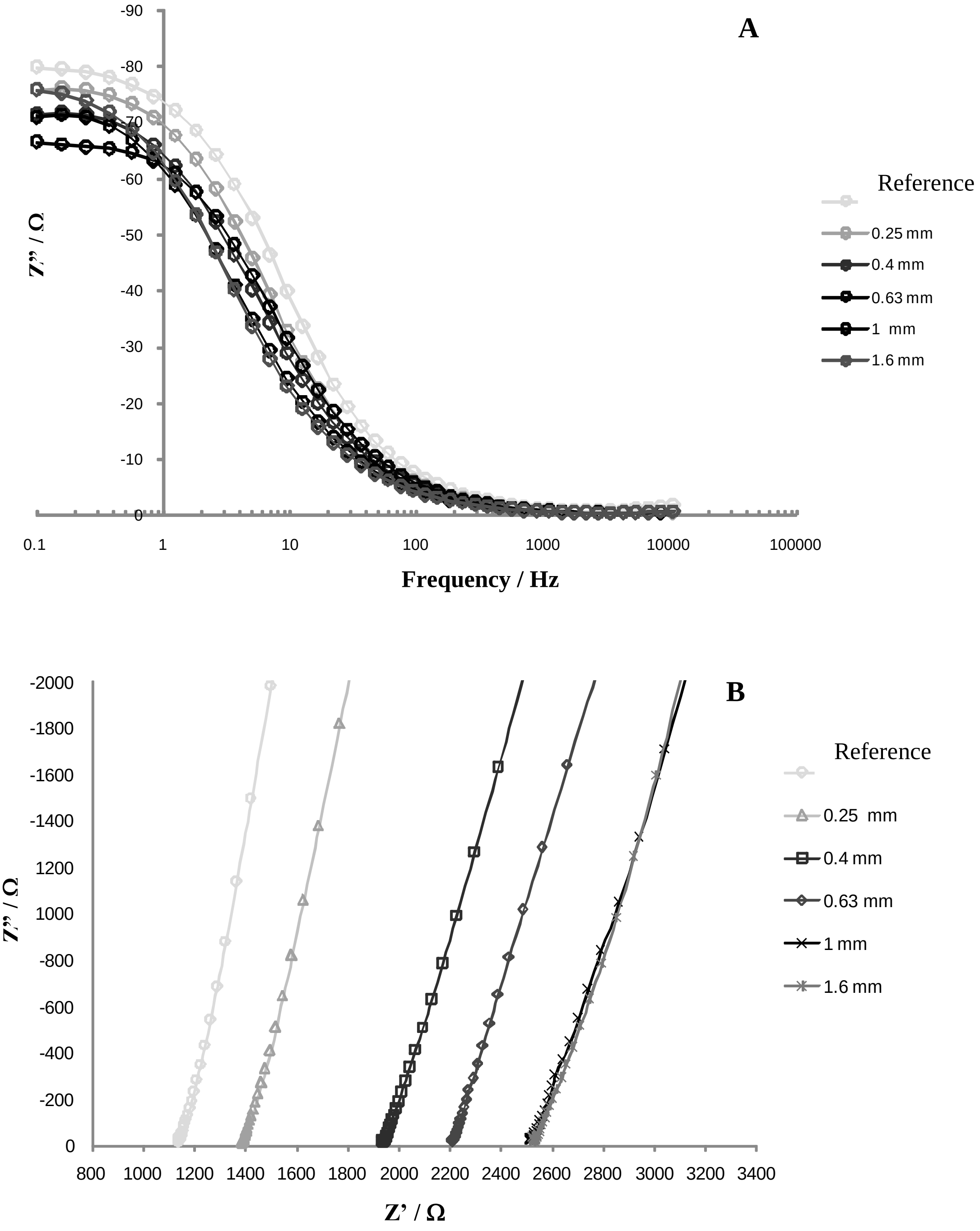

**Figure 9.** Bode-Phase (A) and Nyquist (B) diagrams to each size particle of clean soil in organic medium.

On other hand, in the diagrams of Bode-phase using organic mediums (Figure 9-A), the behavior was similar to that obtained in the presence of inorganic mediums (Figure 8-A). In the Nyquist diagrams (Figure 9-B) the $R_t$ increased in the same manner as particle size. In this sense, the behaviour of $R_t$ in respect to the size of particles in the organic medium was inverse to that observed in the presence of inorganic mediums.

These results indicate that the organic material has a greater likelihood to be adsorbed on the surface of particles of bigger size such as sand in polluted soil, and the smaller size of particles as in clay is aggregated by HC.

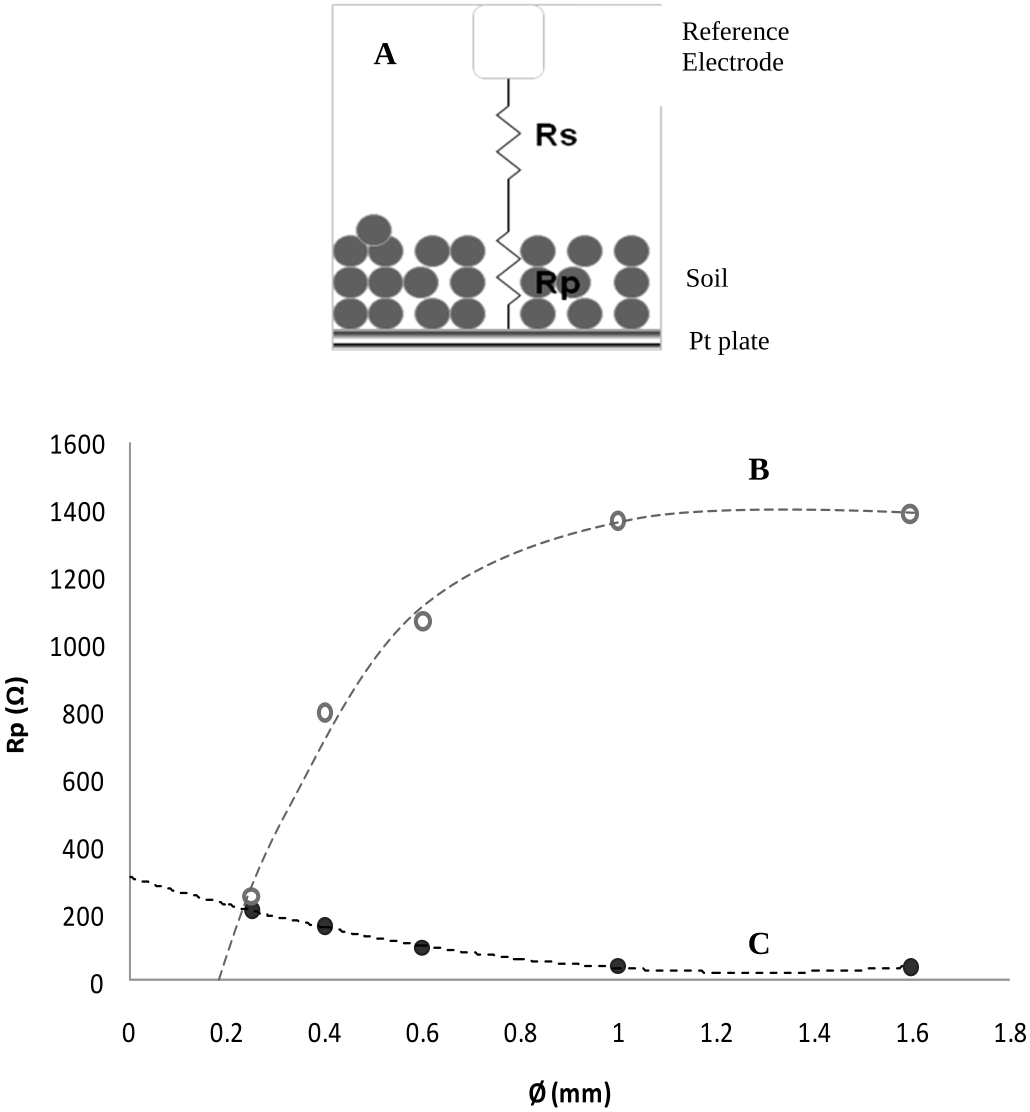

**Figure 10.** Representation of the variation of resistance to the transference of ions in the solution (A, $R_t = R_S + R_P$) with respect of the size particle in organic (B) and inorganic (C) medium.

The $R_t$ is not more than the result of the resistance to the transfer in solution Rs, to which is added the resistance to transfer of ions through the pores of soil ($R_p$) (Figures 10-A).

The above-mentioned can be represented by means of the equation 1:

$$R_t = R_s + R_p \qquad \text{Equation 1}$$

Where $R_s$ is similar to the resistance obtained with the target (impedance measured with the cell without soil), $R_t$ is the obtained resistance of the mesurements and $R_{pore}$ is the resistence to the transfer of ions through the pores in soil. In this way, in equation 2 the $R_p$ can clear up, therefore:

$$R_p = R_t - R_s \qquad \text{Equation 2}$$

Concerning Equation 2, in Figures 10-B and 10-C are shown the $R_p$ related to both systems (organic and inorganic) with regard to the size of particles in soil. As $R_p$ is related with $R_t$, then the $R_t$ increases with the size of particle in organic medium (Figure 10-B) and it decreases in inorganic medium with the increase of the size of particles in soil (Figure 10-C).

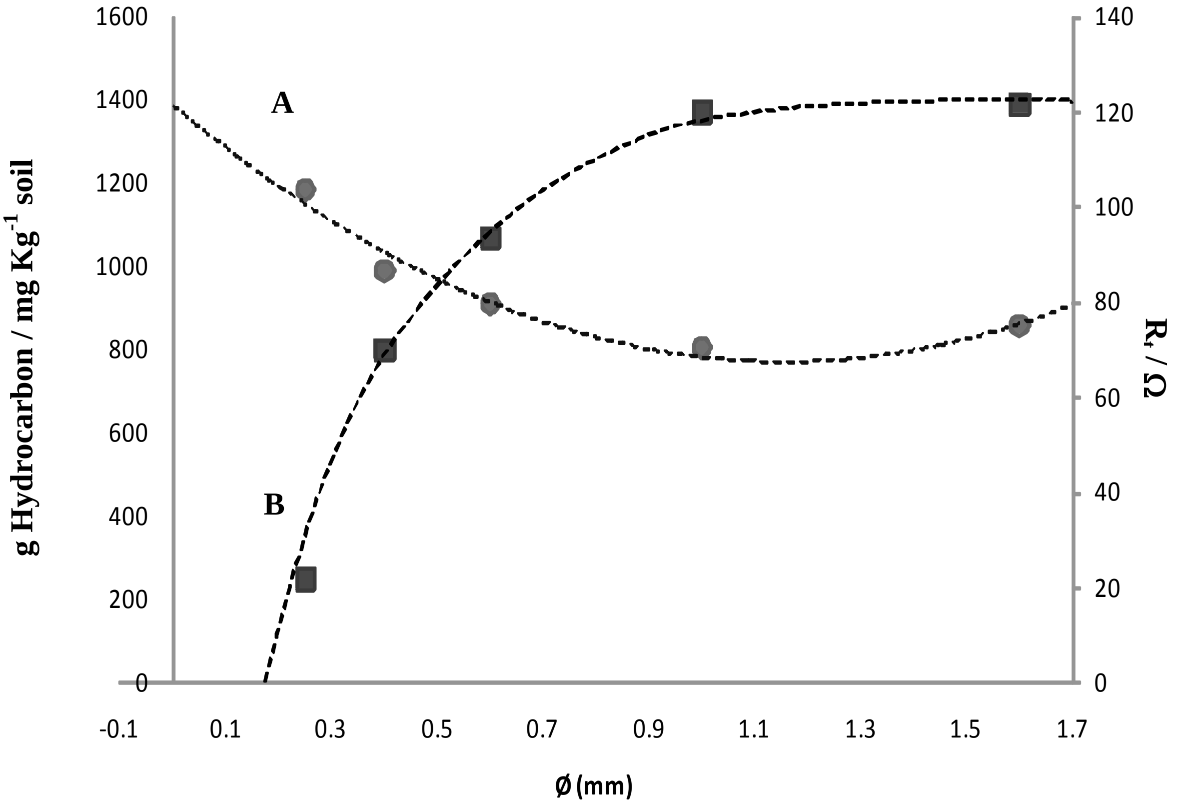

**Figure 11.** Comparison of the results of fatty and oils content by Soxhlet extraction (A) and EIS (B).

To confirm the above-mentioned, it would be expected that the hydrocarbon was in greater quantity in the smallest soil particles, and the reason why, a Soxhlet extraction was done of soil electro-remediated during 24 h, separating the soil by the different sizes of particles (Figure 11). In this sense, the extraction of hydrocarbon for Soxhlet indicates that hydrocarbon is in greater concentration in the smallest particles (Figure 11-A) with the lowest $R_t$ (Figure 11-B) which indicates that for this type of soil the organic compounds have a greater likeness, and therefore, they present the greatest sorption in the smallest particles (Figure 11-A).

## 4. CONCLUSIONS

In the ordering of the physico and chemical characterization of clean and polluted soil, the sample of particles of soil presents, coarse sand, medium sand and something resembling fine sand. Also, with the analysis of ICP the presence of hydrocarbon was evident with the nickel contained in the sample of polluted soil. Likewise, it was observed that the pH of polluted soil was acid (pH = 4.59), which evidences the presence of hydrocarbons with some acid groups. The percentage of moisture in the studied soil was 13.14%, having 7.1% by the volatile hydrocarbon.

The characterization of hydrocarbon removed from the polluted soil was verified with chromatography of gases with mass spectrometry, where hydrocarbon of heavy fraction were found, and the heavy fraction by the lubricant oils was not present. This hydrocarbon aglomerated the particles of smallest size (0.25 mm), and in the case of the other two sizes of particles studied (0.65 and 1mm) the hydrocarbon was observed by the change in the bordering particles verified with SEM analysis.

On other hand, when doing the electroremediation of the polluted soil, Vertisol Pelic, the best percentage of electro-remotion using 20V during 270 min, showed a decrease of pH, possibly because of the generation of secondary reactions during electrolysis. Therefore, a loss of existing transference of mass, achieving with it alone 62 % of remotion of hydrocarbon according to measurements in UV-Vis by absorbance. Comparing the concentration of hydrocarbon in the soil before and after electrochemical treatment, the remotion of pollutant was around 40.46 % close to the anode, 24.46 % in the middle of the cell and 33.99 % close to the cathode after 24 h of treatment.

To verify the presence of hydrocarbon in the polluted soil, EIS was used to characterize it comparing the change in the resistance by ionic transference and Warburg elements originated by the hydrocarbon present in the polluted soil. While clean soil showed decreased ionic transference in a logarithmic manner with the increase in particle size, polluted soil showed increased ionic transference in an exponential relationship with the increase in particle size.

The resistance to the transference of ions through the soil increases when there are organic compounds, however for this case the $R_t$ decreases considerably when the size of particles is smaller in an organic medium. On other hand, in the tests with inorganic mediums the $R_t$ increased when the size of particle diminished. This behavior confirms that the pollutant is confined in greater quantity in particles with smaller size due to their larger superficial surface area, which was observed in the same way with the results of Soxhlet, because when the $R_t$ is bigger the quantity of hydrocarbon in soil decreases.

With this study we demonstrate that EIS can be used as an electrochemical test to verify the content of an organic pollutant in waste soils, which is a promising avenue to follow for some remediation techniques or to define the trail of a pollutant in industrial waste soils.

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## References

1. M. Juárez, J. Sánchez and A. Sánchez, *Química del Suelo y Medio Ambiente,* Universidad de Alicante, San Vicente (2006).
2. Dickerson, United States Patent. *Process and Material for Bioremediation of Hydrocarbon Contaminated Soils.* Patent Number 5,609,667 (1997).
3. S. Gan, E. V. Lau and H. K. Ng, *J. of Hazard. Mat.*, 172 (2009) 2-3, 532 – 549.
4. D. Li, X. Quan, Y. Zhang and Y. Zhao, *Soil & Sediment Contamination,* 17 (2008) 486 – 496.
5. K. Popov, A. Kolosov, V. G. Yachmenev, N. Shabanova, A. Artemyeva, A. Frid, B. Kogut, S. Vesnovskii and V. Sukharenko, *Separation Sci. and Tech.,* 36 (2001) 13, 2971 - 2982.
6. D. De la Rosa-Pérez, M. Teutli and M. Ramírez, *Int. Contam. Ambient.,* 23 (2007) 3, 129 - 138.
7. M. Prasad, K. Sajwan and R. Naidu, *Trace elements in the environment, biogeochemistry, biotechnology and bioremediation.* Taylor & Francis, Florida (2006).
8. C. Ruíz, J. M. Anaya, V. Ramírez, G. I. Alba, M. G. García, A. Carrillo – Chávez, M. M. Teutli and E. Bustos. *Int. J. Electrochem. Sci.,* 6 (2011) 548 – 560.
9. X. Doménech, *Química del suelo el impacto de los contaminantes.* Miraguano, Barcelona (1995).
10. W. L. Choo and M. I. Jeffrey, *Proceedings of the 9th Asian Pacific Confederation of Chemical Engineering.* Christchurch, New Zeland (2002).
11. A.Mas, P. Patrier, D. Beaufort and A. Genter, *J. of Volcan and Geother. Res.,* 124 (2003) 195 – 218.
12. L. M. Döppers, Ch. Breen and Ch. Sammon, *Vibrat. Spectro.,* 35 (2004) 27 - 32.
13. D. N. Gabov, V. A. Beznosikov and B. M. Kondratenok, *Euras. Soil Sci.,* 40 (2007) 3, 256 – 264.
14. H. Richter, V. Risoul, A. L. Lafleur, E. F. Plummer, J. B. Howard and W. A. Peters, *Environ. Health. Perspec.,* 108 (2000) 8, 709 – 717.
15. M. Sh. Akhlaq, *Environ. Sci. & Pollut. Res.,* 4 (1997) 4, 217 – 222.
16. E. Saari, P. Peramaki and J. Jalonen, *Anal. Bioanal. Chem.,* 392 (2008) 1231 – 1240.
17. A.A. Olajire, A. O. Alade, A. A. Adeniyi and O. M. Olabemiwo, *J. of Environ. Sci. & Health Part A*, 42 (2007) 1043 – 1049.
18. M. A. Trancoso, M. M. Correia dos Santos and M. I. Simöes Gonçalves, *Accred. Qual. Assur.,* 8 (2003) 323 - 333.
19. A. Khan, M. Ishaq and M. A. Khan, *Environ. Monit. Assess.,* 137 (2008) 363 - 369.
20. J. B. Sirven, B. Bousquet, L. Canioni, L. Sarger, S. Tellier, M. Potin – Gautier and I. Le Hecho, *Anal. Bioanal. Chem.,* 385 (2006) 256 – 262.
21. M. Alostaz, K. Biggar, R. Donahue and G. Hall, *J. Environ. Eng. Sci.,* 7 (2008) 661 – 675.
22. P. A. Gerin, M. J. Genet, A. J. Herbillon and B. Delvaux, *Euro. J. of Soil Sci.* 54 (2003) 589 - 603.

23. M. Sayito, *J. of Engin. Mechan.* (2007) 1101 – 1114.
24. N. G. Bukun and A. E. Ukshe, *Russ. J. of Electrochem.* 45 (2009) 1, 11 – 24.
25. T. W. Hegarty and Sh. M. Royle, *J. of Appl. Ecol.*, 15 (1978) 897 – 904.
26. V. A. Rinaldi and F. M. Francisca, *J. of Geotech. and Geoenviron. Engin.* (1999) 111 – 121.
27. Y. C. Han and G. C. W. Sabin, *J. of Engin. Mechan.* (1995) 939–947.
28. C. Brett and A. Oliveira, *Electrochemistry Principles, Methods, and Applications.* Oxford University Press Inc. New York (1993).
29. J. Zang, H. Wang, H. Huang and W. Liu, *J. Appl. Electrochem.* DOI: 10.1007/s10800-009-9838-x (2009).
30. S. Pérez, *Análisis Físico - Químico de Suelos y Sedimentos.* Escuela Nacional de Antropología e Historia, México, D. F. (2005).
31. B. Haran, B. Popov, G. Zheng and R. White, *J. of Hazard. Mat.*, 55 (1997) 1 - 3, 93 - 108.
32. S. Trasatti, *Electrochem. Acta*, 45 (2000) 2377 - 2385.
33. J. Newman, *Electrochemical Systems*, 2nd edition. Prentice – Hall, Englewood Cliffs, New York (1991).
34. PEMEX. *El Petróleo, Gerencia de Información y Relaciones Públicas.* México (1988).
35. *Guía de usuarios del programa Z-plot and Z-view for Windows*, Software de medición de EIE (2010).
36. D. Becker and K. Jüttner, *J. Appl. Electrochem.*, 33 (2003) 959 – 967.
37. J. Manríquez and L. A. Godínez, *Thin Solid Films*, 515 (2007) 2402 - 3413.