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Effect in the Physical and Chemical Properties of Gleysol Soil after an Electro-kinetic Treatment in Presence of Surfactant Triton X - 114 to Remove Hydrocarbon

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The effects of the electro - kinetic treatment in presence of surfactant Triton X – 114 on the physical and chemical properties of Gleysol soil were investigated. With the characterization of polluted Gleysol soil, the results showed the highest concentration of greases and oils related with hydrocarbon content in the fraction of soil between 50 and 100 μm, which is the smallest group of particle size with 4 452 mg kg^{-1} of light and medium petroleum fraction. This sand fraction of polluted soil showed a decrease of real density with an increase of organic matter content, because they have low densities than saturated fractions and are more easily oxidized by the Walkley - Black method. However, the electric conductivity and the cation exchange capacity did not have any effect with the presence of the pollutant, because by scanning electron microscopy was observed the heterogeneous hydrocarbon distribution and the presence of laminate structures in some areas. This effect was evaluated using X - ray diffraction, mineral morphology by petrography light microscope, vibrations of the functional groups by infrared spectroscopy and hydrocarbon presence by photoluminescence. This characterization of polluted Gleysol soil using sand fraction was evident that the type and concentration of the pollutant play an important role in different groups of particles in the bulk soil. Once the polluted soil samples were physical and chemical characterized, electroremediation treatment was applied in presence of the nonionic surfactant Triton X -114. Parameters assessed in soil cleaning were the variations of Triton X -114 concentration, while for the electrochemical treatment were the potential. With the best conditions of the electrochemical treatment in presence of surfactant, the percentage of remotion of hydrocarbon was of 49 % after 6 h and 66 % after 24 h, than the individual chemical treatment and the electro-kinetic treatment, both of them after 6 h of treatment with 1.5 mL min^{-1}, which was of 12 % and 35 % of removal respectively. Furthermore, this coupled system was very successful; the inconvenient was the permanency of Triton X-114 in the soil after the remediation.

Keywords: Gleysol soil, hydrocarbon, electro – kinetic treatment, Triton X – 114

1. INTRODUCTION

Soil polluted with organic compounds such as hydrocarbon (HC) products is an important environmental problem around the world [1]. The term hydrocarbon has been used to petroleum complex mixtures in which there are hundreds of organic compounds ranging from light, volatile and short - chained compounds to heavy, long - chained and branched compounds [2].

Some researchers have been interested in studying how HC presence affects soil matrix in its physical and chemical properties [3-4]. Studied properties include texture, moisture content, density, soil organic matter, pH, electrical conductivity and cation exchange capacity, among others.

However, at interfacial level physical and chemical interactions between soil and hydrocarbon have not been well understood, because in any remedial treatment are involved several external factors such as simultaneous reactions, electrolysis, acidification and adsorption. External factors influence strongly depends on site location, exposed environment and pollutant concentration [5]. Consequently, these phenomena must be considered before making any choice for remediation or fertility treatment [6]. Published works point to soil texture as the most important factor that determines physical and chemical soil performance in an HC polluted media, stronger interactions become evident when particle size is in the range from 2 000 μm to less than 2 μm [7].

Clayey soil has been studied more than any other soil type for interactions between soil and pollutants. The main difference between clays and other soils is that clay has a large specific surface area, a high number of available active sites and a dynamic crystalline structure which makes it different in bulk physical properties in respect of sand or silt soils [8]. For the last two are characterized by their larger pore size and gritty texture, as well as low specific surface, and low holding capacity for water and nutrients [9].

Sand and silt textures are mainly composed of quartz with some fragments of feldespat, mica and traces of other heavy minerals [10], their composition evidences colloidal properties absence, and so far the physical, chemical and electrokinetic properties of soils composed mainly of these particles cannot be modified as it happens for clayey soils [11-12].

Although some researchers have observed that major HC concentrations take place in clays, there are some studies mentioning that hydrocarbons are mainly concentrated in coarser size fractions, like sand, rather than clay or silt [13-14]. In this sense, few investigations have been carried out to clarify the role of hydrocarbons on chemical and physical soil affectation as a function of particle sizes, as well as their subsequent impact on others bulk soil properties.

On other hand, during recent years several remediation techniques have been studied in an effort to clean soil that has been polluted with petroleum hydrocarbon (HC) [15]. Recently, the usage of electro-kinetic techniques as a mean to clean soil has called the attention and the interest of many people due to its convenient application on low permeability soils [16], since soil properties can be present and non-soluble pollutants can be removed.

It is of great importance to compare this option against other existing treatments – such as cleaning with surfactant - to evaluate the efficiency of the electrochemical treatment [17], according to the following parameters: strategy, place of application and kind of treatment in order of Environmental Protection Agency, 2001.

Treatment classification includes soil cleaning and physicochemical treatment, which consists of water or surfactant solutions injection through soil. Water allows pollutants to move being then extracted and depurated. This method is considered a convenient one for water soluble pollutants (with solubility of > 1 000 mg L^{-1}). It is necessary to add surfactants for hydrophobic or non-water soluble compounds, such as hydrocarbons.

Soil flushing is a method consisting in dragging the contaminants using the groundwater streams. For this purpose, surfactants are added to achieve desorption of the hydrophobic pollutants from soil. This treatment can be performed in situ when applied by means of water with surfactant incorporation, or ex situ, when soil is take up and then treated with a tanked water solution with a previous separation of sample (sand, clay and lime) [18]. Therefore, this technique is useful for a wide variety of pollutants such as heavy metals, metallic cyanide, organic solvents, aromatic hydrocarbons, gas, mineral oils, PBC (organochloride products such as polychlorobiphenyls), etc. Surfactants or tensoactive products belong to the chemical species which have both: an hydrophobic and an hydrophilic part, which can be either aliphatic or aromatic with neutral or loaded functional groups, negatively (anionic) or positively (cationic) groups [19].

When surfactants are dissolved in water, after reaching certain concentration identified as micelar critical concentration (CMC), added micelles are formed [20]. A typical micelle consists of 50 to 120 monomers. In addition, one of the most important properties of these organized structures is its high capacity of associating or dissolving different kind of solutes. These solute particles can interact in different ways such as electrostatically, hydrophobically or a combination of both. Solubility is then increased by this association, reaching several levels of interaction [21-26].

Electro-kinetic (EK) remediation or electroremediation is a technology, which takes advantage of conductive properties of the soil, being its purpose to separate and extract organic and inorganic pollutants (metals) from soil, mud and sediments through an electric field which allows the extraction of loaded ions, due to low intensity direct current applied between a positive and a negative electrode [27-30].

Metallic ions such as ammonium and / or positive - loaded organic compounds migrate towards the cathode; while anions such as chloride, cyanide, fluoride, nitrates and negative - loaded organic compounds migrate towards the anode. The electrolyte enhance allows pollutants transportation to the wells from which they will be removed. Differently from fluids flows, this technique makes it possible to establish a controlled migration, preventing pollutants dispersion from the treated area. Transportation mechanisms through which the electric field drives pollutants to the electrodes are:

electro - migration, electro - osmosis and electro - phoresis [23-26]. The first two options are the ones mostly used in pollutants transportation.

Electro - migration is the movement of ionic species, and the electro - phoresis is a phenomenon where electric-loaded colloids are moved. Both processes are present in solution towards the electrode with opposite charge under the influence of an electric field. Electro - osmosis is a transportation phenomenon where solvent along with substances hanging from it (colloids with and without electric load) flow toward one of the electrodes (cathode, mainly to organic compounds).

In this way, the main objective of this research is contributed to elucidate how the physical and chemical properties of Gleysol Soil (GS) are affected by the EK treatment in presence of surfactant polyoxiethylen – 7, 5 – octifenil (Triton X – 114) non ionic ether to remove HC.

2. MATERIALS AND METHODS

The sampling was conducted in an industrial zone at southern Mexico named Moloacan (18º04' N and 94º20'W, see Figure 1). Applied procedures are those established in both the Mexican norm NMX2 – 12 / 1 – 1987b and SW82 - EPA series Chapter 9. Samples of HC polluted soil (PS) were collected at depth between 0 and 2 m with respect the natural ground level. Samples were transported in sterilized glass containers and kept at 277 K until used.

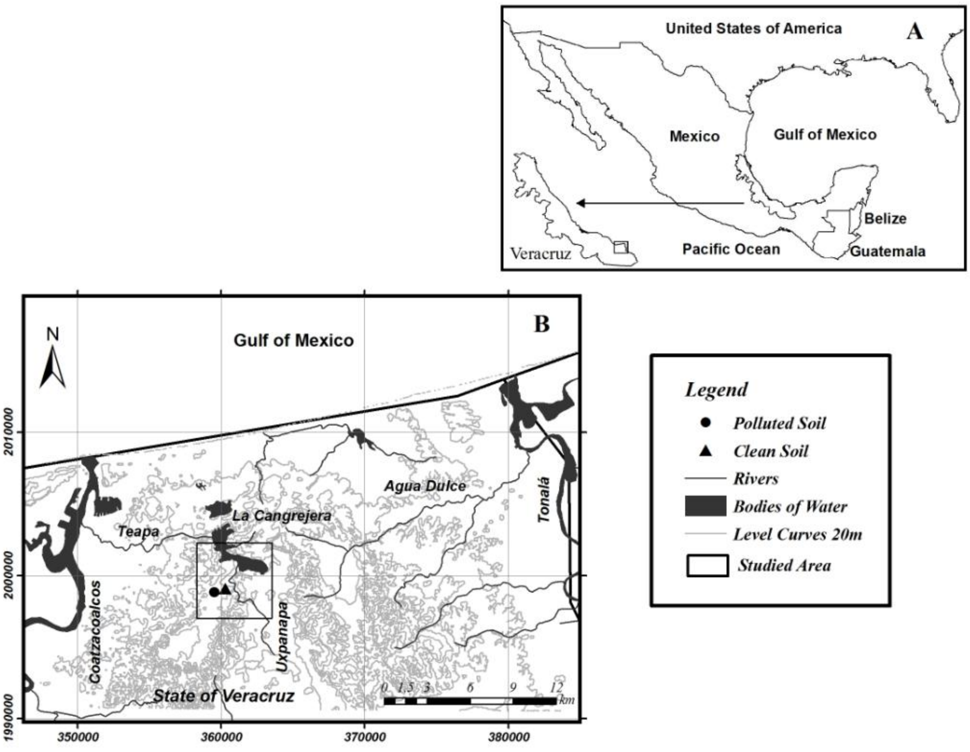

Figure 1. Geographical location of sampling area in Mexico (A) showing the site where polluted soil was taken (B).

Prior to experimentation, collected samples were put to dry at room temperature and darkness conditions during two weeks; this step allowed eliminating moisture, without volatilization of semi - volatile compounds contained in the soil. With the purpose to eliminate interference during each analysis, dried samples were sieved through a 2 mm mesh. By doing so, those fractions that, by size, were not considered part of the soil (roots, gravel and non - soil components) were removed. All analytical determinations were done by triplicate, in order to assure that experimental error was less than 5 %.

Global properties assayed for the PS include: (a) color determined using the Munsell system under the AS – 07 - 1997 method; (b) soil pH measured with a glass pH electrode (BECKMAN); (c) electric conductivity measured with an ORION conductimeter; (d) texture determined by the hydrometer method based in a sedimentation cylinder using calgon as the dispersing agent. Last property was measured based on the guide AS – 09 - 2007, in which it is required to apply hydrogen peroxide (H_2O_2) for organic matter removal.

In order to evaluate some physical and chemical properties of the sandy fraction, a 100 g PS sample was fractionated on a mechanical shaker (ROTAP Vibratory Shaker) using stainless - steel testing sieves of numbers 10, 18, 35, 60, 120 and 230. To calculate the contribution of each particle size to the total sand fraction, after 15 minutes shaking, each group of particles was collected and weighted. The five groups of particles according to the USDA method [10] correspond to: very coarse (2 000 – 1 000 μm), coarse (1 000 – 500 μm), medium (500 - 250 μm), fine (250 - 100 μm) and very fine sand (100 - 50 μm).

Each particles group was evaluated for organic matter content (SOM), real density (RD) and electric conductivity (EC); by established techniques under the Mexican standard NOM – 021 – SEMARNAT – 2 000 [30]. The cation exchange capacity (CEC) was determined by EDTA titration method using 1 g of soil, which was washed two times with 5 mL of 0.2 N $CaCl_2$, two times with ethylic alcohol and one time with 0.1 N NaCl. Supernatants from the first four washings with $CaCl_2$ and ethylic alcohol were discarded, and the last supernatant with NaCl was kept for titration with EDTA. Greases and oils were recovered from the soil by Soxhlet extraction after 4 h of reflux with hexane (Karal brand, reactive grade), according to procedures reported in NMX – AA – 008 - SCFI – 2000. The corresponding determination of semi – volatile compounds was made by gas chromatography coupled to mass spectrometry (Hewlett-Packard GC - MS) in accord to NMX – AA – 146 – SCFI - 2008.

Morphology of the very coarse and very fine sand particles was obtained by a scanning electron microscope (PHILIPS XL 30 SEM) under vacuum using 20 kW of power and a GSED detector (Gaseous Secondary Electron Detector). For mineralogical characterization unaltered materials were mounted on a two - sided adhesive carbon paper and then analyzed by X - Ray Diffraction (XRD) patterns using a RIGAKU MINIFLEX X - ray diffractometer with CuKα (λ =1.54 Å) radiation in an interval of 5° to 80° of 2θ with a scanning rate of 2º 2θ per minute. In this case, samples were pulverized before analysis.

In the smallest particle group, additional information of mineral morphology was identified through polished and transparent thin glass slides using a petrography light microscope (32 - 0040C - 210 Evolution MP 5.0) with natural light and a 5x objective.

Fourier Transform - Infrared Spectroscopy (FT – IR) was used to determine chemical bonds and functional groups vibration in soil. For analysis of each group of particles, a set of tablets were prepared with approximately 12 mg of dry soil and 204 mg of KBr, these were placed in a PERKIN ELMER FT - IR.

Presence of hydrocarbon onto soil particles was verified by photoluminescence technique, measurements on different surface points were done in a DILOR LABRAM II using a green excitation line (argon lamp at 514.5 nm).

To wash PS with Triton X-114, a horizontally - cylindrical cell of acrylic was used of 6 x 3 cm inner diameter, with a capacity of 30 g approximately. During the experiments filter paper with small porous (Crisol brand) was used to contain the soil in the middle of the reactor.

Once the system was mounted, water containing 1, 2, 3, 4 and 5 % Triton X-114 (Sigma - Aldrich, 99 % reactive grade) was though across the soil considering the presence of micelles in solution with these concentration values (CMC > 0.35 mM). Every solution was pumped by a peristaltic pump (Cole Parmer, Masterflex L / S Economy Drive, Model 7554 - 85) and a feeding flow of 1.5 mL min^{-1} was kept constant.

During the tests, different samples in the came out of reactor were taken every 30 min during 5 h, measuring pH and UV - Vis spectra was obtained. This measure was made following the absorbance pick at 232 nm by the $\pi \rightarrow \pi^*$ electronic transitions of the electron resonance in the aromatic rings present in the pollutant in study [28].

On other hand, in order to perform electroremediation of polluted soil, a horizontal electro-kinetic cell with an approximate capacity of 30 g was used with a cathode and anode of Ti (7.5 cm^2) with 6.5 cm of gap between them during the electro - kinetic process. For electro - kinetic tests, working potential varied from 5, 10, 15, 20, 25 and 30 V applied with a power supply (PC Power Supply, GP - 430BDO model). During each experiment the current generated in the electrochemical reactor was monitored as the pH variations to understand the behavior of the system.

Using the experimental conditions where the electroremediation showed the highest percentage of remotion, the treatment was developed in presence of Triton X-114 with the corresponding concentration that removed more HC. The efficiency of the remediated soil (RS) was calculated in base to Soxhlet extraction results. At last, the RS was characterized with the global properties assayed for the PS as color, pH, electric conductivity, texture and organic matter described before.

3. RESULTS AND DISCUSSION

Obtained results for bulk polluted soil characteristics correspond to color, texture, pH, and electric conductivity (Table 1). In respect to color, samples were categorized as 2.5Y, a typical color for subtropical and sub - humid regions soil, sites where water bodies are present [30]. This kind of soil shows neutral pH and relative low EC values; the ones obtained in this analysis were 6.59 and 0.3 dS m^{-1}, respectively.

Table 1. General characteristics defined to polluted and electro-remediated soil in presence of Triton X - 114 surfactant, as: pH, soil organic matter, color, real density and cationic exchange capacity.

Parameter	Polluted Soil	Electro-remediated Soil in Presence of Triton X-114
pH H_2O	6.59	6.74
Soil Organic Matter (%)	1.94	3.89
Color (dry soil)	2.5Y, 5/4	2.5, 6/4
Color (humid soil)	2.5Y, 3/2	2.5, 3/2
Real Density (g cm^{-3})	2.60	2.45
Cationic Exchange Capacity (cmol Kg^{-1})	6.8	7.03

PS textural analysis showed a sandy clay loam texture containing 55.40 % sand, 24.21 % silt and 20.39 % clay. Based on these percentages, the sand fraction provides the highest contribution to the total soil mass, a typical characteristic of Gleysol soil [31-32].

Considering the high contribution of the sand fraction to the total soil mass, and to get an insight on how hydrocarbons behave in different particle size media, specifically in sandy fraction, some physical and chemical parameters were evaluated as function of particle size before the electro-kinetic treatment. Figure 2, shows the retained weight or mass percentage contribution of the different group of particles in the sand fraction for very coarse (A), coarse (B), medium (C), fine (D) and very fine (E) groups of particles of PS, where the A group of particles had the highest value (35 %), followed by the C group with 30 % of the total sand fraction.

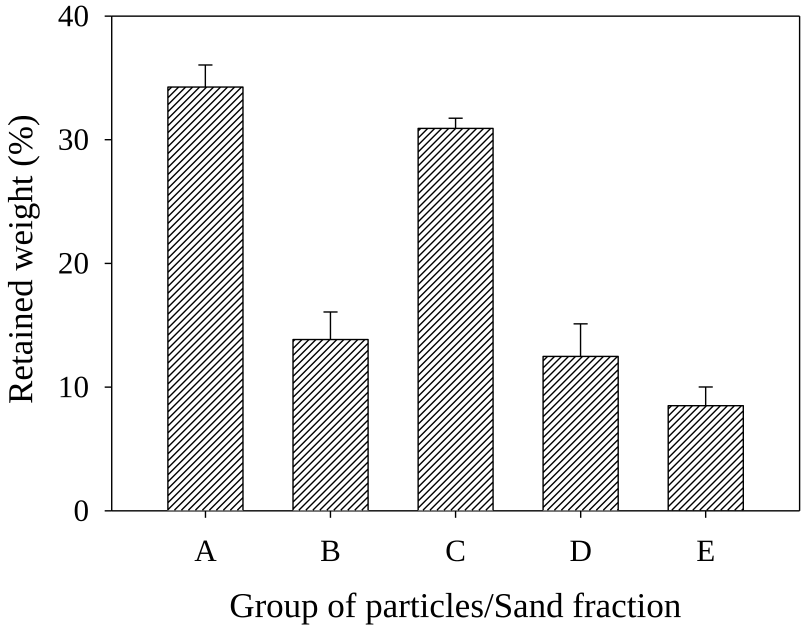

Figure 2. Retained weight or mass contribution to the sand fraction according to group of particles of the sand fraction for very coarse (A), coarse (B), medium (C), fine (D) and very fine (E) sand in polluted soil (PS).

Organic matter content is one of soil properties which plays a strong role defining different chemical interactions between the organic pollutant and soil [5]. In consequence, based on the NOM – 021 – SEMARNAT – 2 000 methods, the organic carbon was quantified as soil organic matter content (SOM). Obtained values were approximately 2 % higher than those reported in the literature [33] for a soil. Results are shown in Figure 3, it can be observed that SOM increases as the particle size decreased, which suggest that hydrocarbon pollutants are mainly retained by the smallest particle group.

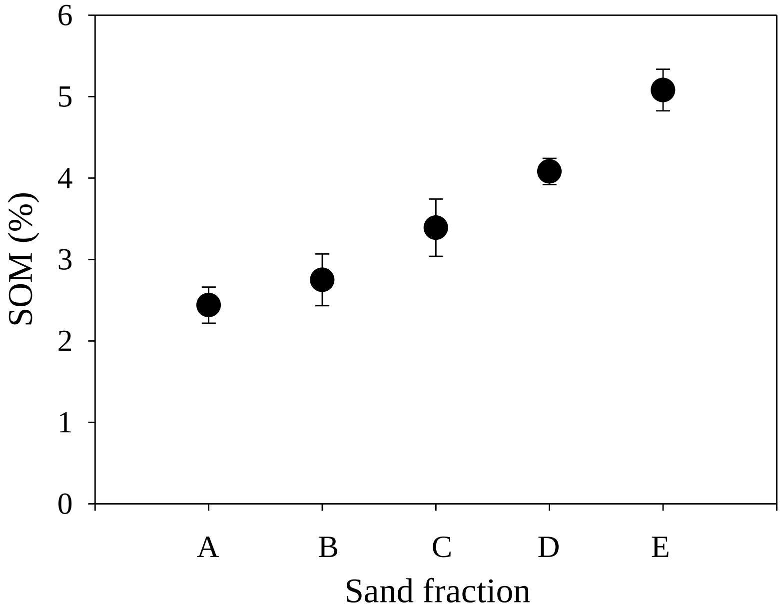

Figure 3. Soil organic matter content (SOM) easily oxidized by the Walkey and Black method in polluted soil, divided by groups of particles in very coarse (A), coarse (B), medium (C), fine (D) and very fine (E) sand fraction.

An explanation for this behavior has been proposed in order to in a soil containing saturated polyaromatic compounds, those compounds between C_{23} - C_{35} were difficult to oxidize by the Walkley - Black method, while compounds between C_{10} - C_{23} were easily oxidized. Furthermore, the percentage of SOM was considered as consequence of materials being introduced from animal and plant residues decomposition [34]. Moreover, it has been reported in the literature [35-36] that sequestration of an organic pollutant can take place on organic matter, which is the most important soil adsorbent of hydrophobic organic compounds.

In order of the FT - IR spectrum for each sand fraction obtained before, the FT - IR spectrum from 3 250 to 3 600 cm^{-1} exhibit some bands attributed to hydroxyl groups (-OH), which are associated with narrow water vibrations. Otherwise, signals close to the 1 640 cm^{-1} were attributed to amide (-NH-) or ketone groups (-C=O); also presence of asymmetric and symmetric stretching of alkyl groups (-C-H) become evident at 2 931 and 2 851 cm^{-1}, respectively. The last molecular vibrations were associated with aliphatic groups of $-CH_3$ and $-CH_2-$, respectively. However In the literature signals between 2 900 to 3 000 cm^{-1} have also been related to (–C–H) bonds in aromatic compounds [35].

Furthermore, weak signals around 1 600, 1 514 and 1 424 cm^{-1} were assigned to the aromatic rings (-C=C-). Finally, in the region known as the fingerprint, Si-O bonds were found at 1 034 cm^{-1} and 787 cm^{-1}, these are associated to silica and another one related to quartz is found at 694 cm^{-1}. The –Si-O bonds were found between 789 and 470 cm^{-1}, and the Al-OH deformation was at 918 cm^{-1} [38]. Following the signal of the alkyl region, it was evaluated the area under the curve of these bands for each particle group. Results shown in Figure 4 make evident that the highest area value corresponds to the smallest particle size, that is the E group.

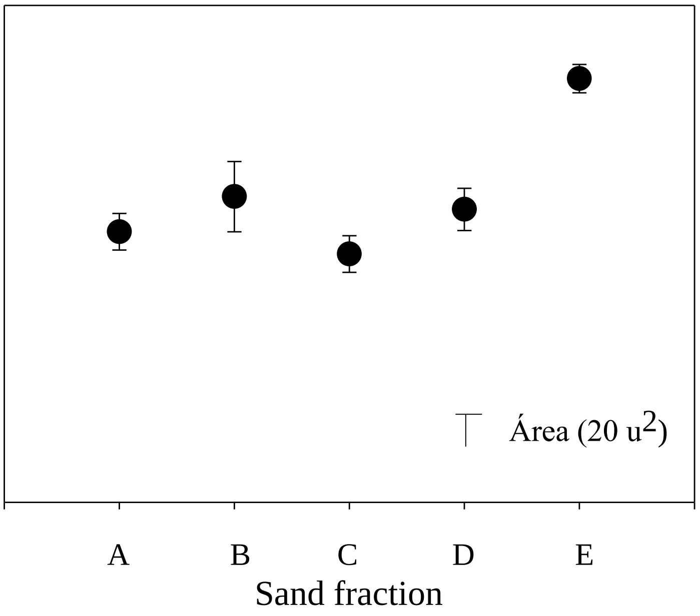

Figure 4. Areas under the 3 000 to 2 800 cm^{-1} tension vibration alkyl curve with each sand fraction of PS obtained with FT - IR spectrum for each group of particles: very coarse (A), coarse (B), medium (C), fine (D) and very fine (E) sand fraction.

Also, the real density (RD) was evaluated in all fractions, however, as fraction size decrease a slight negative variation of the RD is observed, results are shown in Figure 5. According to the literature [39], the obtained average RD value is lower than the reported RD value of 2.60 and 2.75 g cm^{-3} which corresponds to soil formed by quartz (2.65 g cm^{-3}), feldespat and colloidal silicates [40]; the real density of a mineral should be constant even though the size and the arrangement of the particles change.

To verify the mineral soil content, X - Ray Diffraction (XRD) analysis were obtained, results indicate there is quartz presence (ICPDS 99-000-3084) as the main crystalline phase. The XRD spectra of A and E particles were analyzed, where the clay signal was not observed, even in the smallest group (E) around 13º of 2θ.

Therefore, the lower RD value should be related to the presence of another soft material in the soil. Considering that HC have lower density than the composite minerals, plus organic matter and mineral surface could influence the retention of hydrophobic organic contaminants (HOCs) under certain conditions. This assumption is reinforced if results of SOM (Figure 3) are related with RD (Figure 5) since the group with the lower RD corresponds to the highest SOM content.

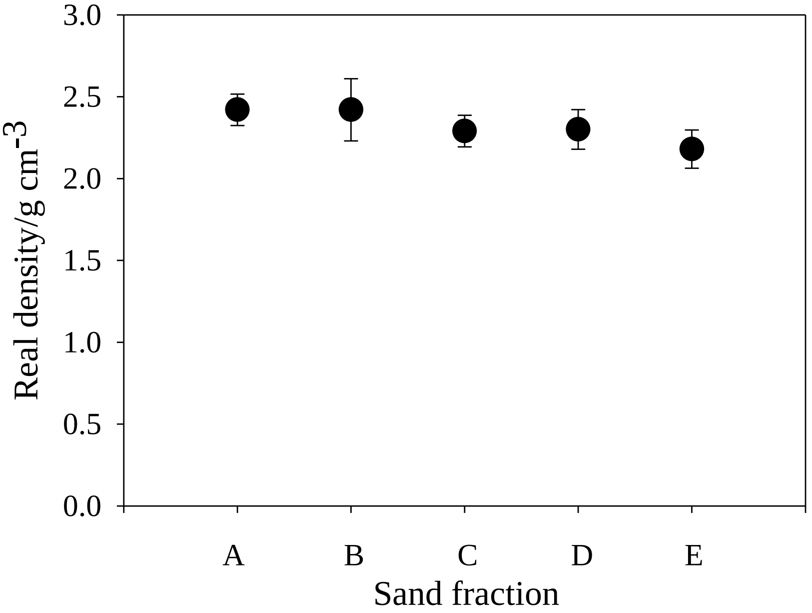

Figure 5. Behavior of real density in a sand fraction of polluted soil in different groups of particles: very coarse (A), coarse (B), medium (C), fine (D) and very fine (E) sand fraction.

To verify the above assumption, a petrography light microscope analysis was run for the smallest group of particles. Results provide evidence of a wide range of quartz morphologies with light color and some angular fragments without polyhedral faces (Figures 6 A and 6 C). In addition, in Figure 6 A and 6 D it was observed that grains had dirty surfaces, marked edges and typical conchoid fractures with parallel and arcuate steps (Figure 6 A), the last suggested that they had different origins, that could be an inheritance from gravel or dissolved bedrock, but the exact source was unknown.

Figure 6 B and 6 C show the presence of aggregates with small fractions of minerals inside, there is evidence of mechanical action effects such as smooth surfaces and various irregular quartz fractures, factors evidencing a complex soil matrix. Also, HC presence was observed between channels, this could be caused by agglomeration of soil particles between minerals, which suggested that the HCs were mostly dependent on the amount of clay and organic matter in a soil (Figure 6 D) [40].

In consequence, observed differences in chemical and physical properties of the smallest sandy fraction particles, evidence the ability to interact with organic pollutants as HC. The relationship between hydrocarbons and each group of particles was relatively easy to verify by grease and oil extracted by Soxhlet technique. The results indicated that the grease and oil content was inversely proportional to the particle size (Figure 7), these findings are in agreement with results from literature [41-43].

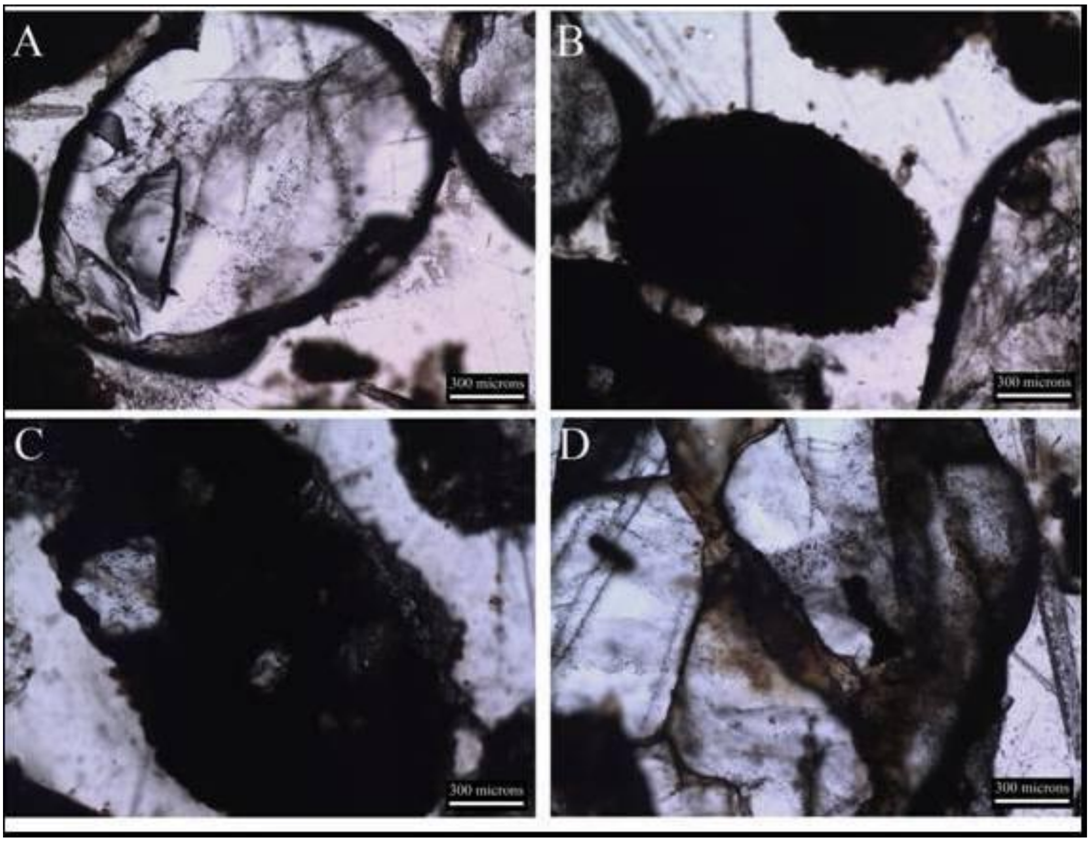

Figure 6. Petrographic images of the smallest group of particles showing the mineral morphology (A), aggregate groups with (B) and without (C) quartz fragments, and hydrocarbon presence between some minerals within the organic matter (D).

However, it was observed that pollutant presence affect the electrical response of the smallest particle group, in both parameters CEC and EC, these values increased with the decreased of particle size (Figure 8). In addition, detected water - soluble cation concentrations by EC measurement showed that EC increased as particle size decreased, effect which could be explained considering that small particles possess higher superficial area than big particles, so the majority of the ions would consequently be easily release in solution [37]. In addition, there is a report mentioning that CEC depends on the pH value, the content of SOM and the clay in the soil to retain ions on the surface [44].

SEM images can highlight on the assumed role of particle size for HC retention. This effect could be explained by observing the possible HC distribution on particles; in this approach SEM images are a source of information. Figure 9 shows the images for the biggest (Figure 9 A and B) and smallest (Figure 9 C and D) groups of particles. The images revealed that the HC was not present homogeneously on surface (Figure 9 B and D as semicontinued circules) suggesting that the HC can be found also in the pores, and the only difference between both groups of particles is that in some areas of the smallest particle (Figure 9 C) it is observed some smaller films of 0.5 μm in thickness which could retain the ions onto the soil surface [44]. This finding confirms that particle size influence particle arrangement as well as some changes in the physical and chemical properties, as those evaluated in this work.

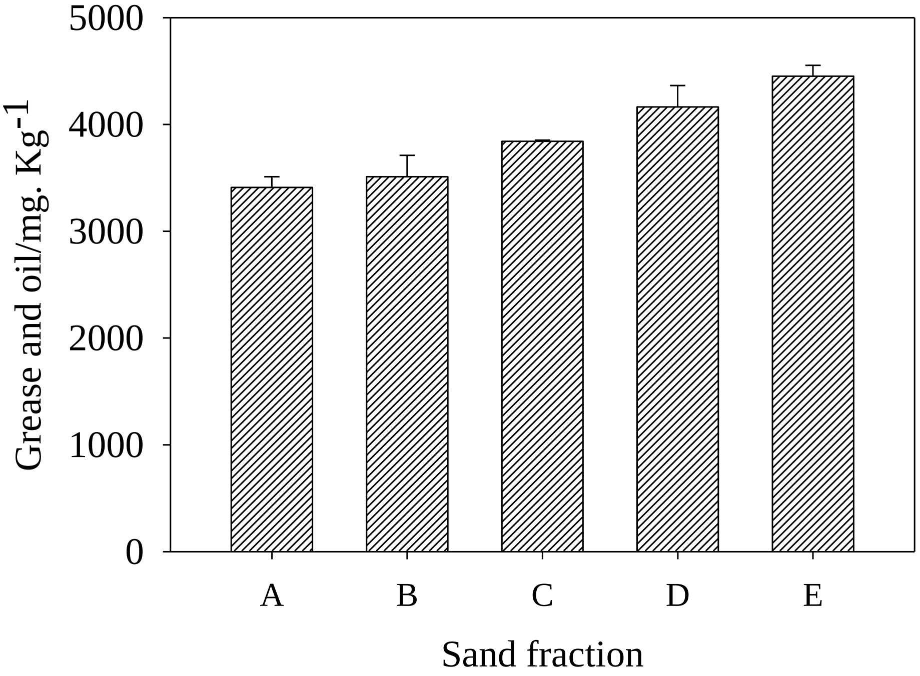

Figure 7. Grease and oil extracted by Soxhlet technique, in different groups of particles in a sand fraction of the polluted soil: very coarse (A), coarse (B), medium (C), fine (D) and very fine (E).

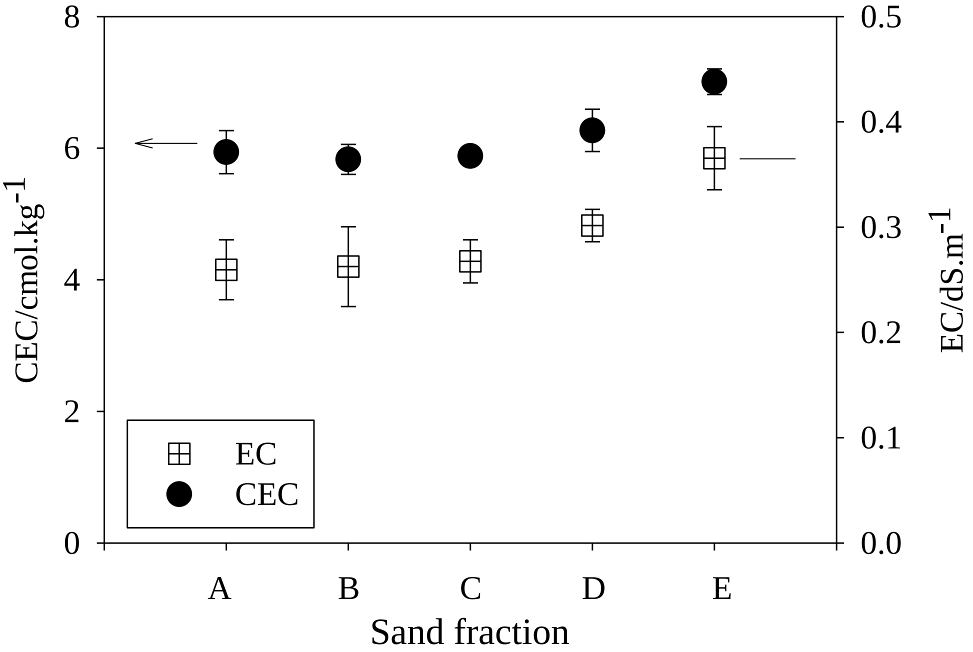

Figure 8. Behavior of cation exchange capacity (CEC ●) and electric conductivity (EC □) of a sand fraction of polluted soil in different groups of particles.

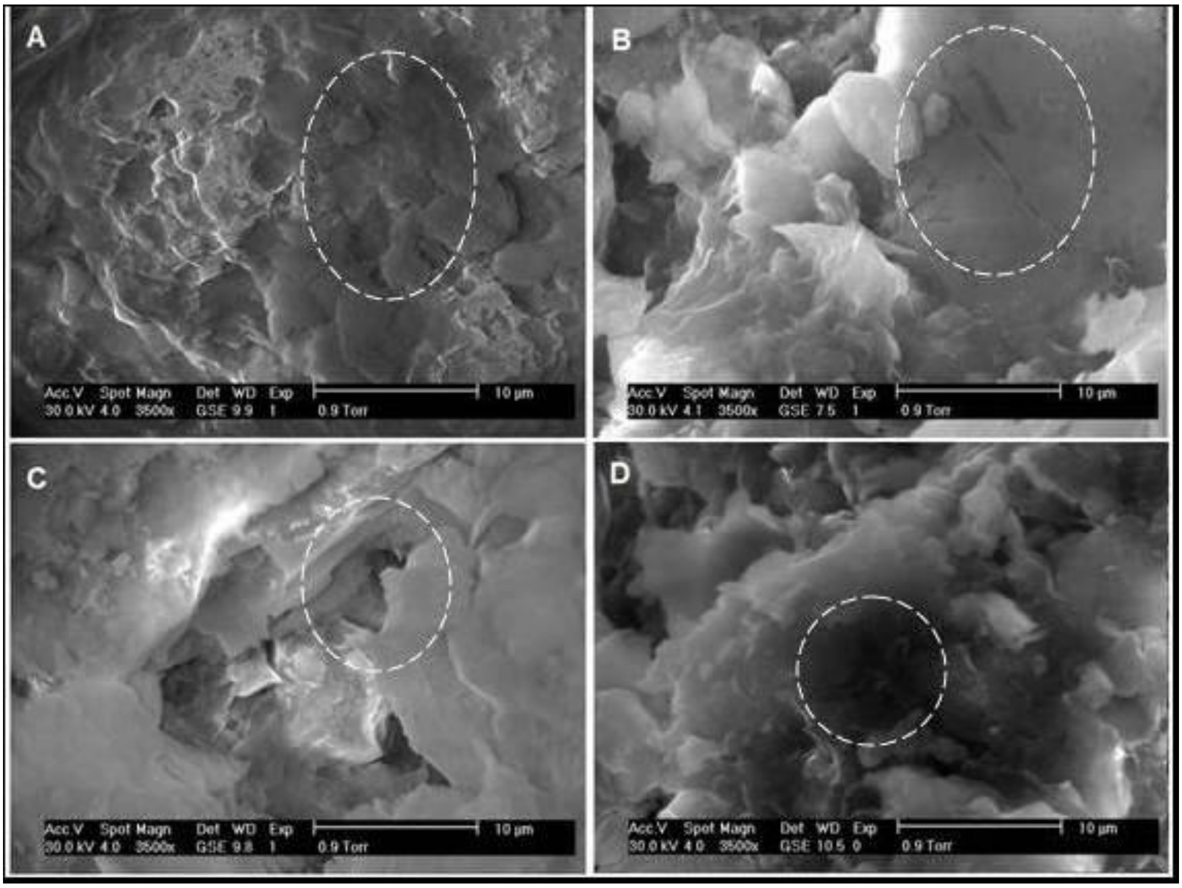

Figure 9. Scanning electron microscopy images from two groups of particles: the biggest (A and B) and the smallest particles (C and D) taken in different particle surface. The white semicontinued circules show the hydrocarbon presence in the soil.

On other hand, many researchers have observed fluorescence of aromatic rings present in water or sediments due to delocalized electrons within the aromatic ring, which can be easily excited. These excited electrons can not easily undergo vibrational relaxation due to the rigid structure [45-46], leading to luminescence.

For this reason, in order to identify the chromophore compounds. An alternative photoluminescence technique was developed for each group of particles. In this sense, to evaluate the photoluminescence response in the sand fraction, diverse measurements were taken on many particles surfaces in order to obtain the area under the curve. In this case, the area of the signal increased until the third particle group and then decreased in a linear fashion. Furthermore, there was not a significant difference in signal intensity between them, only the A group of particles had differences with respect of the rest. However, A and B groups had major differences with respect to values observed for the C, D and F groups.

Once the interaction HC – GS was undestood, the remediation of PS was made with surfactant Triton. In this case, during the washing experiments the initial flow was 1.5 mL min^{-1} and in the end of treatment after 7 h, the solution with a concentration of 1 and 2 % of Triton X - 114 originated a final flow of 2 mL min^{-1}, which afterward it diminished to 0.2, 0.1 and 0.125 mL m^{-1} for the 3, 4, and 5

% of Triton solutions, respectively. This situation could be arose from the fact that when the concentration of surfactant was increased, also increasing Triton X - 114 micelar concentration originating slow flow coming out from the reactor, being visually confirmed due to a more turbid solution.

On the other hand, while treatment was being followed and right from analysis performed on each UV - Vis sample, the signal observed was in 322 nm, evidencing electronic transition π - π* due to double - linked compounds and un - located pairs of electrons [28]. Following this signal with respect to the variation of surfactant concentration (Figure 10) showing that when using 4 % Triton X - 114 the time of major removal of HC was obtained in 360 minutes after cleaning had started. In this way, when PS was washed with 4 % Triton X - 114, the percentage HC removal was of 12 % after 6 h of treatment, considering the reteined surfactant in the soil without pollutant and using the Soxhlet extraction.

The HC extracted of the washed soil with Triton X - 114 was analyzed by GC - MS. In this sense, compounds as n - hexadecane, pyrene, n - methyl acetamide, toluene, phenanthrene and tetrachloro - ethene, they appeared in the PS but not in the surfactant washed soil (Table 2).

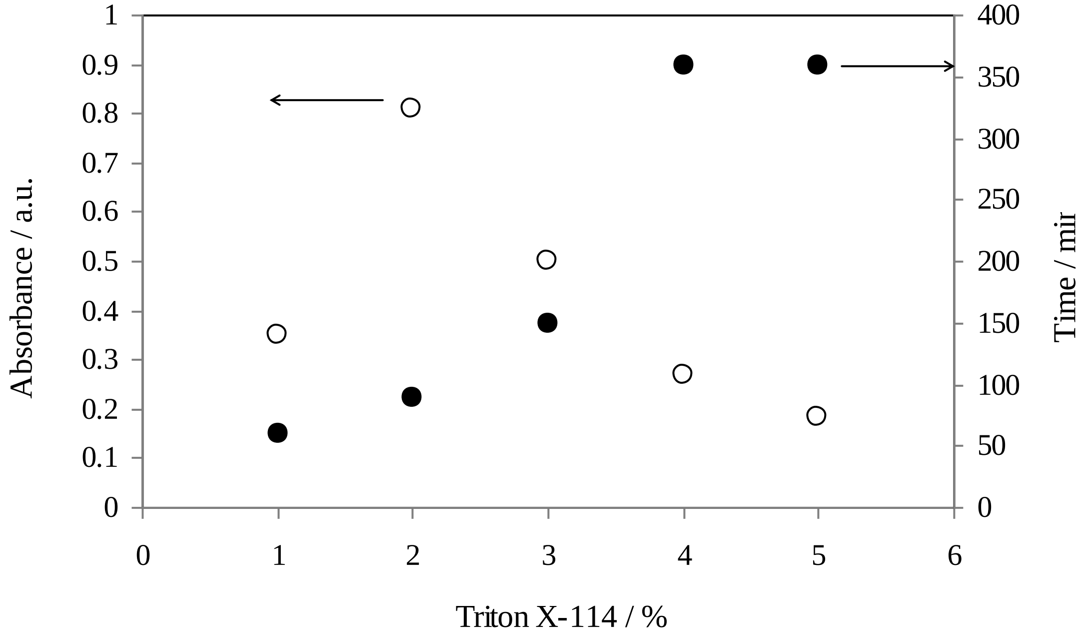

Figure 10. Graph of absorbance and the time of electrolysis to remove hydrocarbon in presence of different concentrations of Triton X - 114 following the 232 nm signal by UV - Vis spectrophotometry.

On other hand, the flouranthene was reduced after the washing process, but other compounds appared after the treatment as, dimethyl - naphtalene, tetramethyl - phenol and tetra - ethanol which probably are originated by the interaction between the Triton X - 114 and the HC present in soil (Table 2). This situation could be explained by the retention of the surfactant once concluded the washing of soil.

Table 2. Chemical compounds present in the polluted soil, washed soil with 4% Triton X - 114 and electro-remediated soil in presence of Triotn X - 114.

Compound	Polluted Soil	Washed Soil with 4% Triton X-114	Electro-remediated Soil in Presence of Triton X-114
Benzenedicarboxylic acid	3.21	4.12	3.32
Flouranthene	2.13	0.14	0
n – Hexadecane	3.6	0	0
Pyrene	2.17	0	0
n – Methyl acetamide	1.85	0	0
Toluene	1.39	0	0
Phenantrene	1.22	0	0
Tetrachloro ethene	0.75	0	0
Dimethyl naphtalene	0	0.44	0.21
Tetramethyl phenol	0	0.41	0.82
Tetra ethanol	0	7.87	8.59
Pentadecane	0	0	0.16
Nonadecane	0	0	0.17

During the electro-remediation of PS, in order of UV-Vis signals and checking the time of major remotion of HC, it was removed after 180 minutes of treatment, when a constant potential of 17 V was managed (Figure 11). On this way, there was a difference between the electroremediation and washing method; the electrochemical treatment was carried out in the half of the time needed for surfactant washing (180 and 360 min, respectively). This is why it is so interesting to couple both techniques.

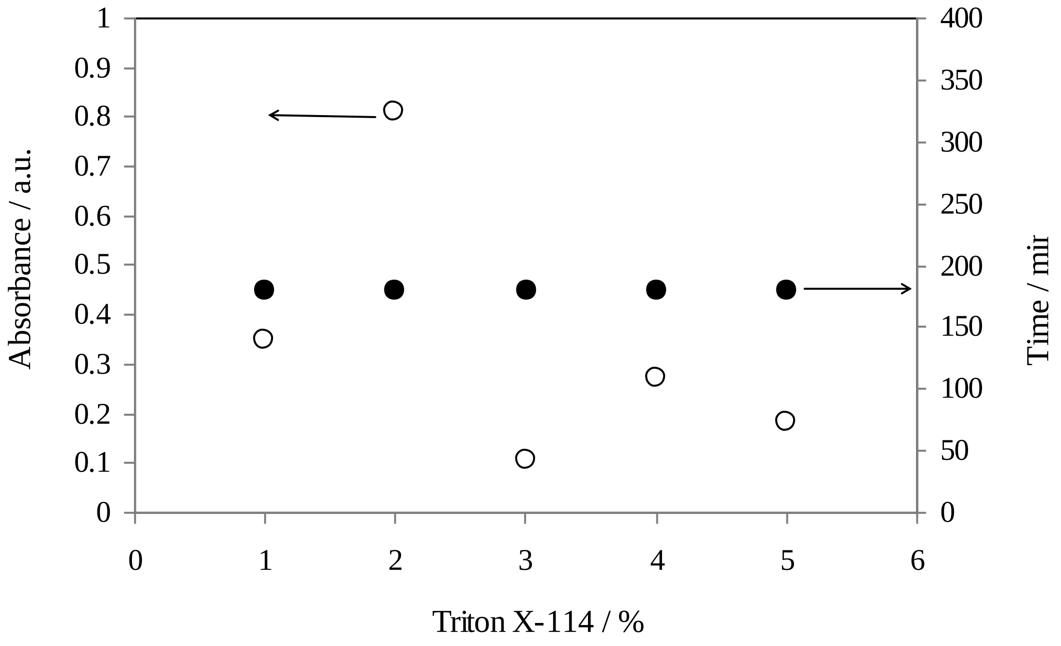

Figure 11. Graph of absorbance and treatment time at the different potential evaluated considering the answer of sample at 232 nm by UV-Vis spectrophotometry.

About the time necessary to make each treatment process, while the washing time increased with the increase of the concentration of surfactant, the electroremediation time was constant at the different potential applied in the system. During electroremediation of PS in presence of 4 % Triton X - 114, there were several differences in pH of the flow out of reactor during the different applied constant potential and the time of electrolysis, originating higher values of pH as a major potential was applied, around pH 10 (Figure 12).

The basic pH values observed in the flow out of the system [21-24] could be due by two possible reasons, one of them was because the hydraulic flow had a direction from, the anode to cathode, and the characteristic basic frontier comes out immediately of the electrochemical cell. The second reason could be in consequence of using a Ti anode, and in high overpotentials this material is commonly passivated, situation which originated a decreasing of current in the cell (Figure 13), of 2.387 to 1.788 mA after 6 h of treatment and the increase of hydroxiles species over the cathode electrode.

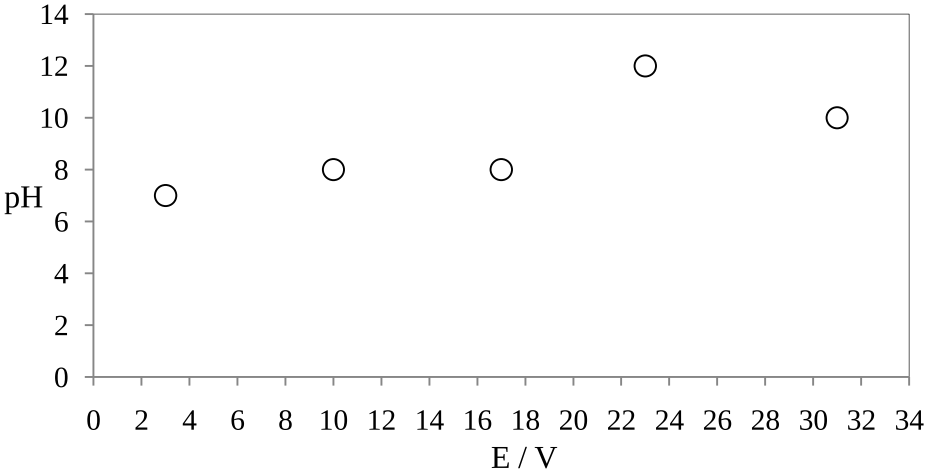

Figure 12. Graph of pH versus the different potential applied during the electro-remediation treatment.

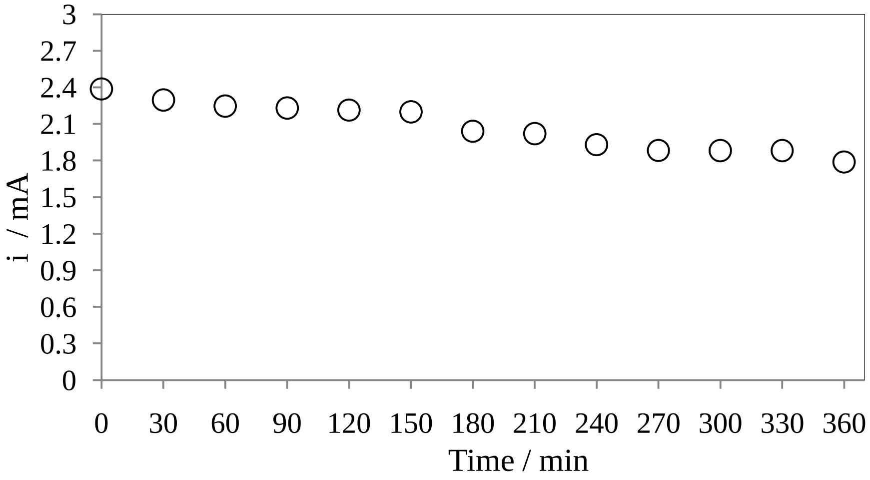

Figure 13. Graph of current versus the electrolysis time applying 17 V by 360 min.

In this way, UV - Vis spectra every 30 min of collected samples decreased the absorbance without a clear pick at 232 nm. The pH (Table 1) of the RS was close to a neutral value (6.74) as the PS (6.59) by the surfactant presence. This behaviour indicated that remediation process did not affect the natural condition of a healty soil with a neutral pH.

In addition, the SOM (Table 1) in the RS had a major value (3.89 %) than the PS (1.94 %) by the retention of the surfactant probed by GC - MS before. In contrast, the texture of the RS was not defined by the complex determination of the quick sedimention of particles in a period of 24 h, it was consequence of the high density of the agglomerates in presence of surfactant, than the PS (Franc Clay).

The color and real density values were the same for two different soil compared (PS and RS), clear yellow with 2.5 Y and around 2.5 (Table 1). The few increment in CEC for RS (7.03 cmol Kg^{-1}) with respect to the PS (6.8 cmol Kg^{-1}) was evident by the elimination of hydrocarbon which was blocking this exchange, mainly in the smallest size of particle (D and E fraction).

Quantifying the percentage of removal of the HC with this coupled method considering 11.87 g kg^{-1} of the RS after 5 h and 10.54 g kg^{-1} after 25 h. This system removed aromatic compounds such as flouranthene (Table 2), which was present after the washed soil with the surfactant, and it reduced other compounds as benzenedicarboxylic acid and dimethyl-naphtalene, but it produced other compounds such as tetramethyl - phenol, tetra - ethanol, pentadecane and nonadedane.

4. CONCLUSIONS

In general, observed changes in all the physical and chemical parameters evaluated in this study could be related not only to the concentration of HC but also to the type and location of the pollutant present in each group of particle size mainly in organic matter and real density. The results showed that the major effects of HC were observed in the smallest group of particles (100 - 50 μm) where the grease and oil extracted was the highest in respect of other groups of particles (4 452 mg kg^{-1} of dry soil from Soxhlet technique).

However, in the smallest group of particle, hydrocarbon presence did not affect soluble ions and salts mobility because it was observed an increase in EC and CEC values. This response was attributed to the heterogeneous pollutant concentration on particles surface, this assumption was verified by photoluminescence signal, and by SEM images which evidence the presence of laminated structures capable to retain ions onto surface, in a similar way as clays do.

After the chemical and physical characterization of PS, it was treated with two assessments, one consisting in electroremediation and the other was a soil washing with surfactant Triton X - 114. The electrochemical treatment was obtained in half the time when applying electroremediation (180 minutes) than when using surfactant cleaning (360 minutes). The PS was washed with 4 % Triton X - 114 obtaining 12 % of removal after 6 h of treatment with 1.5 mL min^{-1} of washing flow in and neutral pH in all experiments. Although, the electro - kinetic treatment showed a 35 % of removal using 17 V during 6 h of treatment at the same flow in, decreasing the current of cell with the time.

Finally, the electroremediation of the PS in presence of 1.5 mL min^{-1} of 4 % Triton X - 114 with 17 V of applied constant potential originated 49 % of HC removal after 6 h, and 66 % after 24 h of treatment. Furthermore, this coupled system was very successful; the inconvenient was the permanency of Triton X - 114 in the soil after the remediation. Although, the increment of SOM, the stability of CEC and the neutral pH of the RS, without difference in the real density and color.

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